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Studies on Titania and Zirconia Supported Transition Metal Catalysts for Reforming of Methane and Biomass Derived Oxygenates

メタン及びバイオマス由来の含酸素化合物改質用
チタニアまたはジルコニア担持遷移金属触媒に関する研究

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Chapter 1

General Introduction

1.1 Natural gas

Crude oil is one of the most important commodities for the economy of every country, due to its wide use as a fuel and in the chemical industry. However, because its reserves are limited, it is desired to substitute it with other resources. It is generally accepted that natural gas is one promising alternative source of energy and carbon-based chemicals since there is an abundance of natural gas on earth. Since the mid-1970s, new findings have been achieved each year, resulting in increase of world natural gas reserves. As of January 1, 2005, proved world natural gas reserves, as reported by *Oil & Gas Journal*, reaches 171 trillion cubic meters (tcm) while around 2 tcm is consumed every year. Currently, it is used for home and industrial heating as well as for the generation of electrical power.

The geographical distribution of natural gas is given in Fig. 1.1 [1]. More than 70% of the known resources are in remote areas. Therefore it has to be transported to the prospective markets. It is commonly transported under pressure as liquefied natural gas (LNG) or in pipelines. However, transport of LNG is about three times more expensive than that of methanol, normalized to the energy transported [2], and pipelines may not be available for transporting the whole remote gas, especially in medium or smaller scale of gas field. Approximately 11% of the gas originated from natural gas fields is re-injected, and unfortunately, another 4% is flared off or vented [3], which is a waste of energy and a contribution to green house gas emission.

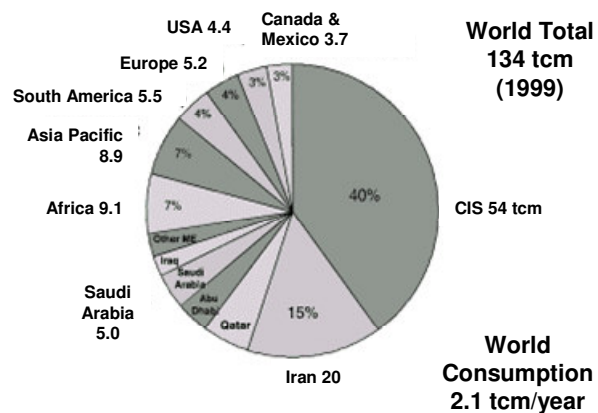


Fig. 1.1. The geographical distribution of world proven natural gas reserve [1].

The main component of natural gas is methane, of which the drawback is its low reactivity. Methane has the highest C-H bond strength of all alkanes ($\Delta(\text{C-H}) = 438.8 \text{ kJ mol}^{-1}$), high ionization potential (12.5 eV), low proton affinity (4.4 eV) and low acidity ($\text{pK}_a = 42$). In general, if methane should react, highly reactive species or harsh conditions are necessary [5]. On the other hand, the stability of methane is probably the reason why it is found in such huge resources under the earth. The enormous amounts of reserves of natural gas could serve as a feedstock for the production of chemicals and as a source of energy well into the 21st century.

A number of strategies are being explored at levels that range from fundamental science to engineering technology. The realistic ways of methane conversion to useful primary products can be compiled below: (a) steam and carbon dioxide reforming or partial oxidation of methane to form carbon monoxide and hydrogen (synthesis gas), (b) the direct oxidation of methane to methanol and formaldehyde, (c) oxidative coupling of methane to ethylene, and (d) direct conversion to aromatics and hydrogen in the absence of oxygen [6,7]. Fig. 1.2 shows the main scheme of the natural gas conversions. Among these processes, indirect route with synthesis gas production has been of interest in industrial application and utilization from practical and economical points of view.

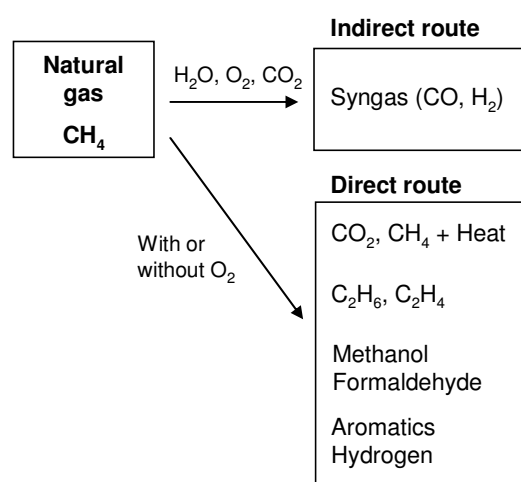


Fig. 1.2. Direct and indirect routes for the production of chemicals from natural gas.

1.2 Biomass and biomass derived oxygenates (bio-oil)

1.2.1 Biomass and biomass conversion technology

Driving the global energy system into a sustainable way is progressively becoming a major concern and policy objective [8]. Biomass, a substantial renewable resource, may play an important role with respect to energy supply. The term “biomass” means any plant derived organic matter available on a renewable or recurring basis (excluding old-growth timber), including dedicated energy crops and trees, agricultural food and feed crop residues, wood and wood wastes and residues, aquatic plants, grasses, residues, fibers, and animal wastes, municipal wastes, and other waste materials,

according to US department of energy (DOE). The energy supplied by the sun comes available as 1250 Exajoule: 1.25×10^{21} J *via* biosynthesis, in contrast to an annual consumption of energy, which accounts for 400 Exajoule: 4×10^{20} J [9]. Therefore, it is demanded to develop technology making it possible to compensate significant parts of fossil fuels.

Biomass contains varying amounts of cellulose, hemicellulose, lignin and a small amount of other extractives, which are produced from CO_2 and water by photosynthesis, thereby capturing solar energy in living plants. This energy in biomass can be harvested and stored for subsequent release. Although energy production from biomass releases CO_2 into atmosphere, the CO_2 will be absorbed in growing plants, making carbon supply neutral in an energy cycle. In contrast to other renewables, such as wind, solar, geothermal, and wave etc. that give heat and power, biomass represents the only source of liquid, solid and gaseous fuels: Biomass is the only renewable source of ‘carbon’.

Biomass can be treated in a number of different ways to provide power and fuels. In general, biomass conversion technologies are divided into two methods, thermo-chemical and biological. Fig. 1.3 shows an overview of the candidate primary conversion technologies of biomass, ranked according to water content [10]. A dominant method largely used in industry is ‘combustion’ of materials such as timber industry scrap or municipal solid waste to generate electricity [11]. Recently, use of liquid transportation fuels, so-called biofuels, is increasing dramatically. “Biofuels” is a term used to describe a more convenient form originated from raw biomass to be used as a fuel. Three biofuels account for almost all consumption in the transport sector at present: bioethanol, biodiesel, and biogas [12], which is made by ‘fermentation’ of sugars and starch, by the chemical

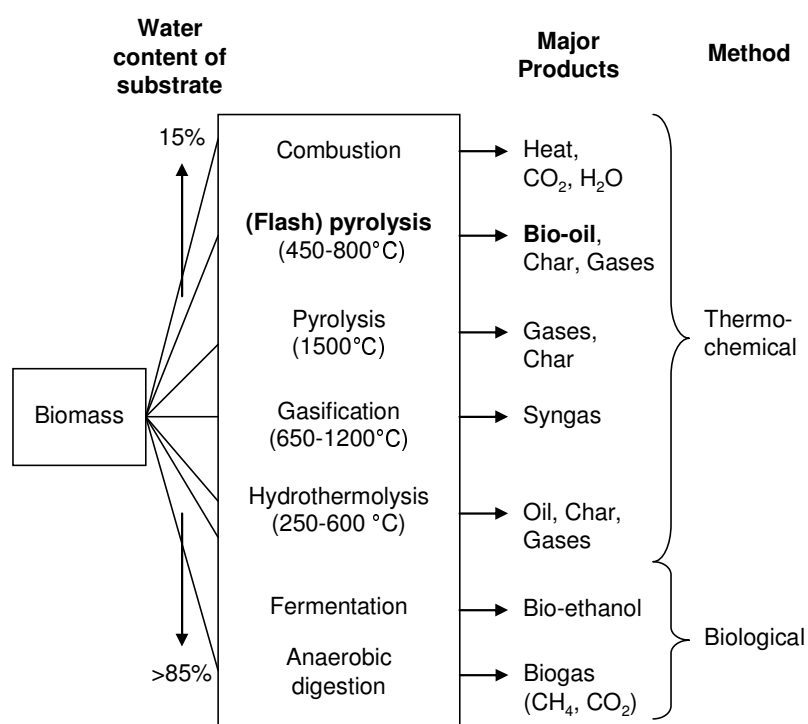


Fig. 1.3. Primary conversion technologies of biomass [10].

esterification of oils with methanol, by the ‘anaerobic digestion’ of organic material, respectively. The bioethanol and biodiesel can be blended with or directly substitute for gasoline and diesel, respectively, and the biogas is compressed and used in vehicles equipped for natural gas. Biofuels cannot replace crude oil completely because sufficient agricultural area is unavailable [13]. In addition, a drawback of these processes is that types of biomass are limited to those mentioned above. Therefore, it is still required to develop highly efficient technology which can operate in total independence of types of biomass.

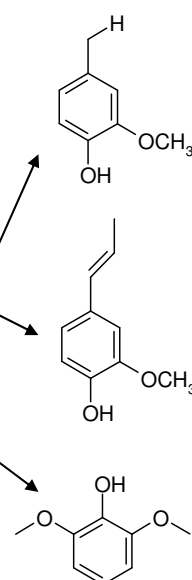
1.2.2 Flash pyrolysis oil: “Bio-oil”

Recent developed ‘flash pyrolysis’ technology can provide a liquid mixture of oxygenated compounds, so-called bio-oil or bio-crude, with high efficiency [14]. The flash pyrolysis is operated at a very high heating rates and short vapor residence times of typically less than 1 s in the absence of air at typically 500°C. Since the bio-oil can be readily stored and transported, production of it is beneficial when biomass resources are remote from where the energy is needed. It has been reported that up to 80% yields on dry feed can be achieved, together with by-product char and gas which is used within the process so there are no waste streams [15]. This technology makes it possible to convert also lignocellulosic biomass which is difficult to convert efficiently to a useful fuel.

Bio-oil contains a complex mixture of oxygenated compounds, such as acid, aldehyde, alcohol, and ketones, and this complexity provides both the potential and challenge for utilization. Table 1.1 shows some important chemicals identified in the bio-oil [16]. The average composition of

Table 1.1 Composition of wet bio-oil [16]

Chemical	
acids	
Formic acid	.3-20
Acetic acid	.5-32
sugars	
Levogluconan	.4-3.9
phenols	
Phenol	.3-3.8
guaiacols	
Eugenol	.1-2.3
Isoeugenol	2.4-7.2
Pyrolytic lignin, water insoluble	21-47
syringols	
Syringol	.7-4.8
furans	
Furfural alcohol	5.2
mixed oxygenates	
Glyoxal (ethandiol)	2.8
Hydroxyacetaldehyde	12.9
1-hydroxy-2-propanone	1.5-7.4



bio-oil is $C_6H_8O_4$ [14]. A heating value is about 17 MJ kg^{-1} , as compared to around $42\text{--}44 \text{ MJ kg}^{-1}$ for conventional fuel oil. As produced water content is about 25 wt % that cannot be separated. Water is miscible with the bio-oil up to around 30–45% and not miscible with fossil fuels. The degradation products from cellulose include organic acids such as formic and acetic acids which give the bio-oil its low pH. The density of pyrolysis liquid is very high at around 1.2 kg l^{-1} .

Bio-oil can directly be burned to generate electricity. Upgrading of bio-oil (*via* e.g. hydrotreating) is also under development [14]. Alternatively, it can be separated to directly provide higher value chemicals for biobased products, such as phenolic resins [17]. The aqueous fraction of bio-oil is a potential source of hydrogen, especially *via* steam reforming that can utilize high content of water in bio-oil. Steam reforming combined with separating valuable chemicals makes the process economically more realistic. Fig. 1.4 shows scheme of the hydrogen production from bio-oil, of which the concept is applied also in this study.

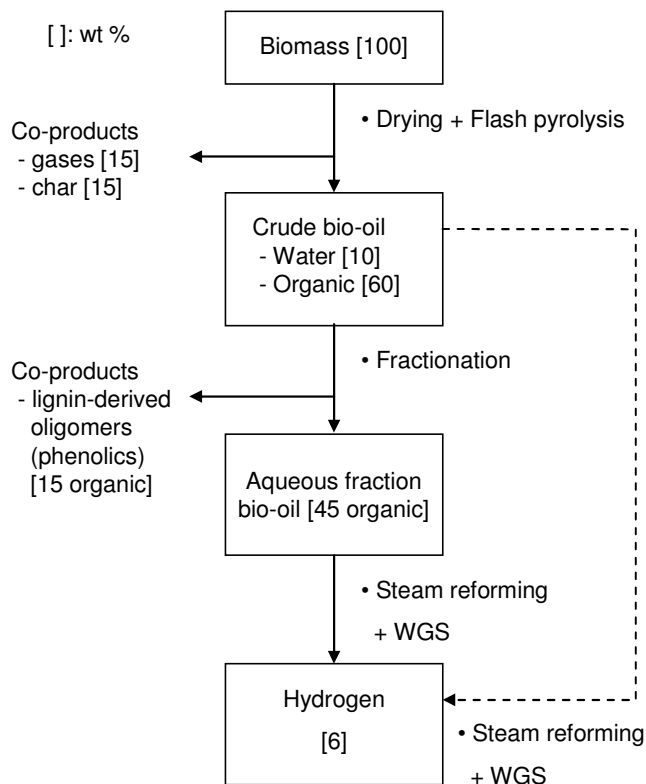
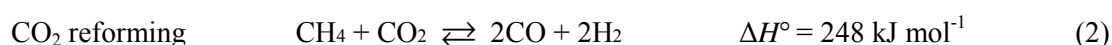
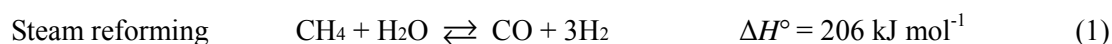


Fig. 1.4. A schematic process diagram proposed for the production of hydrogen from biomass *via* flash pyrolysis and steam reforming.

1.3 Synthesis gas production for synfuel and hydrogen

1.3.1 Synthesis gas (syngas)

Synthesis gas (syngas) is composed of two diatomic molecules, carbon monoxide and hydrogen, which provide various products covering an entire field of fuel science and technology as shown in Fig. 1.5. Syngas can be produced by chemical reactions of hydrocarbons with steam, CO_2 , or oxygen (followings are example for methane as a reactant):



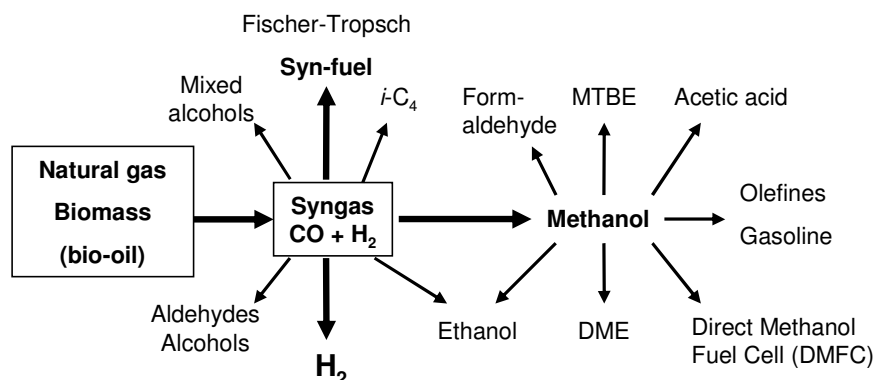
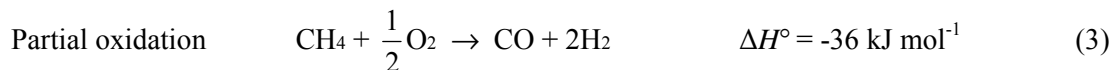


Fig. 1.5. Diagram of syngas conversion processes [30].

Alternatively, ‘gasification’ of biomass can also produce syngas, when biomass is heated with limited oxygen. Recently, Tomishige et al. have developed catalytic gasification process to convert biomass with high efficiency in laboratory scale [18]; however, using noble metal catalysts still necessitates improvement for application.

The applications of syngas are broad. An adequate H₂/CO ratio in syngas is required to be adjusted according to the desired products as drawn in Fig. 1.6. Syngas is used in fuel cells or ammonia synthesis (only H₂), for manufacturing hydrocarbons in the Fischer-Tropsch (F-T) synthesis to make syn-fuel (H₂/CO = 2), and oxygenates such as methanol (H₂/CO = 2) (Fig. 1.5 and 1.6).

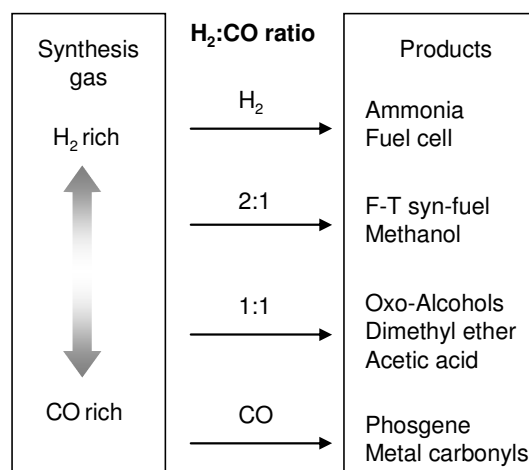


Fig. 1.6. Desired H₂/CO ratio in syngas for following conversion to various chemical products.

1.3.2 Gas To Liquid: Fischer-Tropsch synfuel and methanol

In practice, steam reforming of methane together with WGS provides H₂/CO > 3, and CO₂ reforming of methane along with RWGS gives H₂/CO < 1. For F-T synfuel production or methanol synthesis, a H₂/CO ratio of 2 is required, and thus, combining steam and CO₂ reforming is applicable. Partial oxidation reaction by itself gives a ratio of H₂/CO equivalent to 2. However, pure oxygen is necessary to convert CH₄ in this process and the cost of making pure oxygen makes it difficult economically to be a real process. The overheating hazard at hot spots caused by combustion reaction

of methane should also be overcome [19]. Although build-up catalysts for direct conversion to syngas without the combustion has been investigated (e.g. [20]), it seems far from practical use yet due to fairly low activities. Nevertheless, the utilization of heat of exothermal partial oxidation is also being investigated to apply auto-thermal reforming combined with other endothermic reforming reaction (no additional heat supply necessary), optimizing a ratio of H_2/CO .

It should be mentioned that a new method for transporting natural gas, so-called “Gas To Liquid (GTL)” technology, is being developed. The most important point for improving economics of a GTL process is how to produce syngas at the H_2/CO ratio desired in the following reaction in a single stage reactor. In some natural gas fields, high content of carbon dioxide has been found. CO_2 reforming of methane, therefore, must be the suitable process to be developed. Since methane is preserved at high pressures in natural gas fields and most of F-T synthesis and methanol synthesis from synthesis gas (H_2/CO) are performed at high pressures in the GTL process, the CH_4/CO_2 reaction should also be carried out under high pressures (≥ 1 MPa), from an economical point of view. It is well known that higher pressure favors coking thermodynamically as well as kinetically [21-23], and thus the build-up of catalysts which possess high resistance for coking is essential. Because the products of this process contain no pollution materials such as sulfur and aromatic hydrocarbons, the GTL process combined with this syngas process has a clear advantage over other processes in marginal gas fields with small reserves and there is ample scope for improvements.

1.3.3 Hydrogen

Although many alternative sustainable energy pathways may emerge, “hydrogen economy” has received particular attention [24]. A hydrogen-based energy system is regarded as a viable and advantageous option for delivering high-quality energy services in a wide range of applications in an efficient, clean and safe manner while meeting sustainable goals [25]. Fuel cells [26,27] and related technologies are well developed, mature and have become ubiquitous [24]. Thus, developing methods for efficient and sustainable hydrogen production is desired.

Hydrogen production is the largest use of syngas. Combination of steam reforming and WGS can maximize hydrogen yields from feedstock. At present, hydrogen is mainly consumed for ammonia production, followed by refining and methanol production. Generally, as the feedstock goes from

natural gas to light hydrocarbons to heavy hydrocarbons (77% petrochemicals) and then to solid feedstocks (18% from coal), there is an increase in processing difficulty and capital costs [28]. Also, there is tremendous interest when hydrogen originates from renewable resources, such as biomass. The most significant step in a process of hydrogen production is again steam reforming in terms of cost and scale.

For large volume users, pipeline delivery is the most economical followed by bulk liquid hydrogen delivery; however, pipeline cannot be applied to anywhere energy is required, due to its high cost for infrastructure. Therefore, it is considered that making fuels which can be easily transported is the primary step and subsequently converted to hydrogen on site in which it is required. Choice of the fuels is under debate, F-T synfuel and methanol from natural gas and bio-oil can be their candidates.

1.4 Steam reforming and carbon dioxide reforming: Background and state of the art

1.4.1 Background

At present, syngas is produced by steam reforming. In 1888, steam reforming was reported as a homogeneous reaction of methane and steam for the first time [29]. In industry, BASF was the first company to develop steam methane reforming in the early 1900s [30]. Steam reforming of natural gas was developed in United States because of its availability, whereas steam reforming of naphtha produced superfluously on petrochemical process was developed by ICI in 1962. The process is well established, and the aspects of chemistry, catalysts, reactor engineering and other details can be found in an excellent review by Rostrup-Nielsen [21]. Steam reforming is an endothermic reaction, favored thermodynamically at elevated temperatures (700 - 830°C). In practice, operation has been carried out under high pressure 15 - 40 bar, which allows the system to be compact and is economically feasible. Steam reforming of hydrocarbon can be represented as follows;



The reaction is followed by water gas shift (WGS) reaction and methanation (reverse reaction for steam reforming of methane Eq. 1):



With regard to thermodynamic equilibrium, Eq. 5 and 6 determine gas composition solely regardless of types of hydrocarbon; when temperature, pressure and steam to carbon ratio are given. For kinetics, the quasi-equilibrium of the WGS reaction (or reverse WGS: RWGS) results in the H_2/CO ratio to be a function of feed conversions [31].

In contrast to “steam” reforming, CO_2 reforming is called “dry” reforming. The first report of methane reforming with carbon dioxide dates back to Fischer and Tropsch [32] in 1928. Then, severe catalyst deactivation due to coking was identified to be major obstacles for successful industrial applications. There are two major technologies for industrial processes based on methane carbon dioxide reforming: the SPARG process [33] and the CALCOR process [34,35]. SPARG process achieved the low H_2/CO from 2.7 to 1.8 with carbon-free operation by introducing a partially sulfur-passivated nickel catalyst. CALCOR process is aimed to produce very pure CO, and the prevention of carbon formation is claimed to be achieved by using catalysts with different activities and shape and by their specific arrangement throughout the reformer tube. Both the processes are operated at high temperatures ($> 900^\circ C$) where carbon formation is thermodynamically less favorable [36].

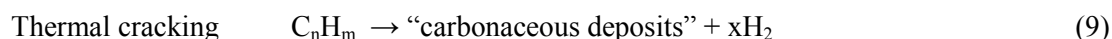
1.4.2 Coke formation

One of the most difficult issues to be solved to develop the effective catalysts for steam/ CO_2 reforming of methane is how to avoid coke formation during reaction. Coking or the formation of carbonaceous deposits is an important side reaction in many industrial processes [37]. General route to coke is catalyzed by metals. Some metal catalysts (nickel, cobalt and iron) may form whisker carbon in a process where the hydrocarbon or carbon monoxide is dissociated into carbon atoms on one side of the metal crystal and a carbon fiber nucleates from the opposite side [21,38-40]. Although the carbon whisker can grow without deactivation of the active site, the accumulation of whisker carbon may result in destroying the catalyst particle [21]. Metal catalyst may form carbonaceous deposits encapsulating the metal particle in other conditions (generally at lower temperature), resulting in catalyst deactivation [21,41,42]. In tubular reforming, no carbon is accepted because the break-down of the catalyst will result in build-up of pressure drop with uneven flow distribution and hot spots, etc. [21]. To prevent coking in the reformer tubes, excess of steam (molar steam to carbon ratio between 2

and 6) is used, depending on the feedstock and process conditions. However, use of excess steam causes additional energy expenditure.

Also, acid site on the catalyst is active for both the catalytic cracking reaction and coke formation [43]. Coke formation via pyrolysis of the hydrocarbons also occurs if the temperature is above approximately 650°C. Carbon formation may cause not only encapsulating the catalytic active sites but also blockage of the pore mouth [44,45]. The formation of bulk phase carbides may also be related to the carbon formation, which is essential for the iron-based Fischer-Tropsch catalyst [46].

It is generally accepted that in hydrocarbon reforming reaction, coke formation occurs via following reactions [21]:



From thermodynamic point of view, it is clear that the lower reaction temperature and higher reaction pressure induces less CH₄ decomposition and more CO disproportionation.

1.4.3 Catalysts for steam/ carbon dioxide reforming of methane: State of the art

Conventional steam reforming catalysts are 10-33 wt % NiO on a mineral support such as alumina, cement, or magnesia [30]. In addition to the review by Rostrup-Nielsen [21], several reviews were established since 1970s [47-50] and catalysts for steam reforming and their difficulties in realization have been well discussed. Nevertheless, the catalysts for steam reforming often cannot be applied directly for CO₂ reforming where severe carbon deposition occurs. After a number of studies on CO₂ reforming of methane several elaborative reviews have been published since 1990s [6,51-58]. The deactivation of catalyst is caused in general by encapsulating coke, sintering of metal, oxidation of metal and the blockage of metal by the carrier. For the CH₄/CO₂ reforming thermodynamics predict coke to form under all usual conditions of CO₂ reforming [59]. It can be slightly improved by adding water or oxygen to the feed gas stream [60]. However efforts are required to acquire the knowledge for design of the catalysts that lower the rate of methane decomposition and/or CO disproportionation, which lead to carbon formation [59].

Most of the Group VIII metals are more or less catalytically active for the steam and dry

reforming. It is revealed that noble metal catalysts (e.g., Rh [61-63], Ru [64], Pt [65], Pd [66] and Ir [67]) can give operation without coke formation even in stoichiometric feed of CO₂ and CH₄. This can be due to the different mechanism of carbon formation and stability of surface carbide on noble metals from that for nickel.

Long-life operations with little coke formation over Pt/ZrO₂ were reported and the catalytic functions were discussed profoundly [68-77]. Bitter et al. [75] suggested that Pt-based catalysts with fine-tuning the particle size of the metal and the acid-base properties can provide high stability toward this reaction. Nagaoka et al. reported that high capability to avoid coke deposition on Pt/ZrO₂ was attributed to less possibility of coking on both Pt and ZrO₂ and the high ability to activate CO₂ to remove the intermediate carbon species which is a source of coke deposition [76].

Due to high cost and limited availability of the noble metals, Ni based catalysts are available in the large-scale commercial applications. However, Ni based catalysts are reported to be more prone to coking than catalysts based on noble metals [60]. Nevertheless, the use of sulfur passivation of Ni based catalysts [78,79] show excellent stability of catalysts for steam reforming. It was proposed that “ensemble control” on a partly sulfur-poisoned nickel catalyst might minimize carbon formation; i.e., with sulfur coverage, the rate of carbon formation decreases more intensively than the rate of reforming does, showing that the ensemble for the reforming reaction is smaller than that required for the nucleation of the carbon whisker. On contrary, Bengaard *et al.* [80] claimed that the nucleation of graphite is initiated at defect (step) sites of Ni and blocking of the stepsites with additives like potassium, sulfur, and gold gives higher tolerance against graphite formation and not significantly against reforming. There still remains the alternative explanation that “alloy formation” with nickel could interfere the formation of the carbide and hence the dissolution of carbon into the nickel crystallite [81]. In addition, quantum mechanical calculations and electrostatic calculations using medium theory proposed adsorbed alkali atoms would influence the electronic properties of surface nickel atoms [82] and promote the adsorption of steam on nickel [83], respectively. The importance of the geometric factor and of electronic factor with the advent of the band theory of the electronic states of solid are still controversial, both of these being likely to be reasonable.

It is well known that the supports strongly affect the catalytic behavior and coke formation. Firstly, it has been suggested that carbon deposition during CH₄/CO₂ reforming is suppressed when the metal

is supported on a metal oxide with strong Lewis basicity [84-86], which increases the ability of the catalyst to chemisorb CO_2 [87]. Accordingly, alkaline earth metal oxide, such as MgO and CaO are often components in commercial reforming catalysts [88,89]. Particularly, a well-known Ni-Mg-O solid solution catalyst shows unique characteristics [90-100]. A synergistic effect between high Ni dispersion and basicity of support surface is suggested to produce very high resistance to carbon formation [100]. It should be mentioned that the reactions of metallic nickel with MgO or Al_2O_3 to form NiMgO_2 or NiAl_2O_4 lead to the deactivation [21]. Promotion with trace amount of noble metals successfully stabilized the Ni-Mg-O catalyst [101,102] by probably improving the reducibility of base metal [103].

Alternatively, strong interaction between metal and support influences the catalytic behavior significantly, as discussed previously. Many studies suggested that the carbon formation is suppressed when TiO_2 is used as a support [22,62,64-66,67,92,93,104-109]. During reduction, the partially reduced TiO_2 , so-called TiO_x ($x < 2$) species, can migrate over the surface of metal particles, leading to a decrease of the surface free energy of the catalyst. This phenomenon is called “strong metal support interactions (SMSI)” [110-112]. For CH_4/CO_2 reforming, it is proposed that the TiO_x species decorate the exposed metal surfaces and preferentially eliminate large ensembles of metal atoms necessary for carbon deposition. In addition, the dramatic increases in specific reaction rates were observed, which is attributed to the creation of new sites in the metal-support interfacial region which promote both CH_4 and CO_2 dissociation [65,107]. Similarly, Ni/ La_2O_3 catalyst is reported to show the remarkable stability for CH_4/CO_2 reaction [105,113,114]. It was suggested that strong chemisorption of CO_2 on La_2O_3 to form $\text{La}_2\text{O}_2\text{CO}_3$ observed may lead to the high durability [105]. For hydrocarbon steam reforming, ceria, which is known as car exhaust catalyst component to show excellent oxygen redox, was found to slightly enhance steam reforming and dramatically enhance coke gasification [115].

Secondary-metals and additive effects were also reported to improve the catalytic performances and prevent the carbon formation [116]. For instance, additive effects of Co to Ni catalysts have been revealed to show beneficial effects by eliminating or significantly reducing the formation of filamentous carbon on the catalyst [116,117]. The doping of small amount of Sn [23], Cr [116,118], La [119], and Mn [120,121] to Ni catalysts lead to the alloy formation which produce a dilution effect of Ni crystal, modify the basicity of the support, and presumably form a number of cationic vacancies

which enhance the mobility of the active lattice oxygen anions, O^{2-} .

In spite of thermodynamically favorable coke formation, up to now, there have been a number of suggestions and innovations. In order to avoid the carbon formation on the catalyst, the catalysts should be constructed considering the mechanism of carbon formation. Options to minimize the carbon formation can be summarized as follows [122];

- to restrain the surface carbide species or control the concentration of it,
- to restrain the carbon dissolution and dispersion into the metal crystal,
- to restrain the reaction of carbon species to form the whisker carbon.

Relating mainly to the first and the second points, Alstrup *et al.* [123] proposed how to avoid carbon formation as follows:

- to enhance the adsorption of CO_2 ,
- to enhance the rate of the surface reaction,
- to decrease the rate and degree of methane activation and dissociation.

It is a challenge to suppress carbon formation kinetically with thoroughly understanding the reaction mechanism.

1.4.4 Reaction mechanism for steam/ carbon dioxide reforming of methane and higher hydrocarbons

There have been considerable proposals of reaction sequence, as more effective catalysts have been developed. It should be noted before going into details that Rostrup-Nielsen and Hansen [124] concluded that replacing steam by CO_2 induces no significant difference on reaction mechanism.

Regarding the active sites for steam reforming, it is generally accepted that hydrocarbon is adsorbed, activated and decomposed on the metal [21]. In terms of water activation, Rostrup-Nielsen suggested that water is adsorbed and activated on the support over Ni based catalysts [21,125], i.e., “bifunctional mechanism”. The study by Ross *et al.* [126] in comparison of Ni/ Al_2O_3 catalyst with Ni foil revealed that the aluminium ions of surface nickel aluminate species (or related species) participate in the reaction by adsorbing the water molecules. Alternatively, the bifunctional mechanism was also proposed for steam dealkylation of toluene to produce benzene and syngas over supported noble metal catalysts by Grenoble [127,128] and Duprez *et al.* [129,130], where carbon-carbon bond splitting occurs on the metal, and surface hydroxyls derived from H_2O on the oxide support participate

in the reaction. It should also be mentioned that the concept of the bifunctional mechanism was extended to the WGS reaction, where CO adsorbs on the metal, and the water on the support [131].

As for CO₂ reforming, although the study using Rh/MgO by Qin et al. suggested that CO₂ dissociates on the metal as CO-M and O-M [132], most reports commented the importance of the interfacial region between metal and support for reforming reaction (“bifunctional mechanism”). Nakamura et al. [67] reported that the mechanically mixture of TiO₂, MgO, and Al₂O₃ with Rh/SiO₂ catalysts enhanced catalytic activities, proposing that the metal oxide as carrier enhance CO₂ activation. The stable Pt/ZrO₂ catalysts were investigated by van Keulen et al. [69] showing that both methane and carbon dioxide dissociate independently of one another. In addition, Bitter et al. suggested that on Pt/ZrO₂ catalyst carbonate derived from CO₂ on ZrO₂ at the metal-support boundary is reduced to formate by carbon on the metal to yield CO, and subsequently the formate decomposes rapidly to CO and a surface OH group [74]. On the other hand, O’Connor et al. also studied Pt/ZrO₂ catalyst and suggested that the resultant carbon species on the metal react with lattice oxygen species from ZrO₂ [72]. Furthermore, Slagtern et al. [133] observed lanthanum carbonates on Ni/La₂O₃ catalyst which are suggested to remove adsorbed carbon species from nickel surface at the Ni-La₂O₃ interface.

Further in details of mechanism for CO₂ reforming of methane, Erdöhelyi et al. [62,66] and Rostrup-Nielsen and Hansen [124] proposed as follows. The initial step of methane decomposition is to generate CH₃ species and adsorbed H atom, followed by additional decomposition to form CH_x and adsorbed H atoms. Subsequently, adsorbed H atoms promote CO₂ dissociation, i.e., $\text{CO}_2 + \text{H(a)} \rightleftharpoons \text{CO} + \text{OH(a)}$. Then, adsorbed OH species combine themselves to produce H₂O and adsorbed O. The final step is adsorbed O atom reacts with CH_x species to generate CO and H₂. Osaki et al. proposed that the initial step is CH₄ dissociation to produce adsorbed CH_x species and gas-phase H₂ directly [133]. With regard to the final step, Walter et al. suggested that adsorbed OH groups rather than adsorbed O atoms react with CH_x [134]. Alternatively, Bradford and Vannice suggested that in the study of Ni/MgO and Ni/TiO₂ catalysts a formate-type intermediate, CH_xO, was generated through the reaction of adsorbed CH_x with surface OH group at the metal-support interface, which subsequently decompose to yield H₂ and CO [93]. In the case of steam reforming, Grenoble [127,128] and Duprez et al. [129,130] suggested that surface hydroxyl groups on the support participate in the reaction. For

both CO₂ and steam reforming, it is still under discussion whether the adsorbed CH_x species react with adsorbed O or OH.

Moreover, rate determining step of reforming is also controversial. The results of Wang et al. [113], Zhang et al. [135] and Wei and Iglesia [136] showed methane decomposition is the rate determining step, whereas Bradford and Vannice [93] and Osaki et al. [137] suggested the CH_xO decomposition is such for CH₄/CO₂ reforming. Further investigations to clear up the precise mechanism are necessary.

1.4.5 Steam reforming of biomass derived oxygenates: State of the art

Not so many studies on steam reforming of oxygenates in literature can be found as those on methane reforming [138]. The most studied oxygenates are simple alcohols; methanol and ethanol. Additionally steam reforming of bio-oil has been recently focused as a new route to lead to sustainable hydrogen.

Methanol can be easily steam reformed at lower temperatures (<300°C) than methane without inducing carbon formation. Mostly copper supported catalysts [139-141] were investigated, followed by Pd catalysts [141-143]. The advantage of using copper catalysts is that, unlike nickel, copper does not catalyze methanation (where chopping of carbon-oxygen bond in CO is necessary) and therefore, “ideal” reaction can be achieved that forms only H₂ and CO₂ without forming CO. There are two major mechanisms proposed. Jiang et al. [140] proposed that the decomposition-shift mechanism, where chemisorbed methanol is totally dehydrogenated on the metal surface to form CO, followed by WGS reaction to form CO₂ and H₂. On the other hand, Takahashi et al. [141] proposed that the formate mechanism, which proceed via methyl formate which further decompose to form formate and methanol, and formate then decompose directly to CO₂ and H₂ without forming CO.

One of the most attractive methods to produce renewable hydrogen at present is use of bioethanol as a feedstock [144]. However, stable operations are impeded by coke/oligomer deposition, awaiting improvement of the catalysts. It has been proposed that acetaldehyde is the key intermediate, subsequently decomposed to CO and CH_x over Rh catalysts [145] and Ni catalysts [146]. It has also been claimed that acidic support, such as Al₂O₃ assists dehydration of ethanol to form ethylene, leading to carbon formation [145]. Unlike steam reforming of methanol, copper metal alone cannot

achieve complete reforming of ethanol; only dehydrogenating ethanol to form predominantly acetaldehyde at low temperatures (e.g. 300°C) [147]. Mariño et al. have shown that adding nickel to copper catalysts significantly accelerates gasification of ethanol, catalyzing decomposition of intermediate acetaldehyde produced where C-C bond splitting is required. Co based catalysts [148] have also been reported to show high activities. Nevertheless, reaction mechanism as well as catalyst durability for steam reforming of ethanol has not been investigated sufficiently.

As mentioned earlier, bio-oil is the potential candidate for sustainable source of hydrogen. The initiative for steam reforming of flash pyrolysis oil is NREL (National Renewable Energy Laboratory) [149]. They have given insight for steam reforming of bio-oil by primarily investigating model compounds present in bio-oil, such as acetic acid and hydroxyacetaldehyde [138,150] and sugars [151] etc. over commercial nickel based catalysts. Although the catalysts appear to be more stable at higher temperatures, attempts to convert bio-oil to syngas using commercial steam reforming catalysts have been severely hindered by rapid catalyst deactivation due to coke/oligomer deposition on the catalysts. In order to avoid the deposition, Garcia et al. [152] reported that the modified Ni/Al₂O₃ catalyst, namely Ni-Co/MgO-La₂O₃-Al₂O₃ catalyst, greatly improved catalyst stability; however, the deposition cannot be suppressed completely. The almost none of mechanistic aspects have been described. Improvement of the catalysts is essential for advancing the technology, with acquiring knowledge based on reaction mechanism.

Simple but important question is whether reaction mechanism is the same or similar to steam reforming of hydrocarbon. It is important to mention that in the case of oxygenates, studies so far have few and based on non optimized catalysts. Severe deactivation observed during steam reforming of e.g. ethanol or bio-oil is needed to be diminished. Understanding mechanism certainly helps to achieve this.

1.5 Objective and structure of the thesis

The first target of this study focuses on how to eliminate carbon formation during carbon dioxide reforming of methane using the metal catalysts available for the industry. In this context, cobalt has been chosen as a primary metal for the catalyst since cobalt is applicable for industrial application due to its availability and low price comparable with nickel catalysts. Cobalt catalysts have not been

extensively focused due to lower catalytic activities than nickel catalysts [32,153,154]. High endothermic reaction requires low space velocity for sufficient heat supply and high temperature for high conversions. Therefore, the issue to be solved is prevention of coke formation rather than improvement of catalytic activity. Recently, cobalt catalysts have been claimed to show sufficiently high activities for carbon dioxide reforming of methane [155-158], and, therefore, have great possibilities to be improved. In addition, only few studies have been carried out for the reactions under high pressure. Prior investigation by Nagaoka et al. [22] revealed that TiO₂ supported Ru catalyst provides stable catalytic performance with no carbon deposition even at 2.0 MPa. As mentioned previously, reducible supports, like TiO₂, can play an important role to inhibit the coke formation. Hence, the combination of cobalt and TiO₂ has been thoroughly applied to investigate in this study. The cause of catalyst deactivation observed has been pointed out. Further modification of Co/TiO₂ catalysts with Ni or noble metals have been tried out in order to inhibit the deactivation and improve the catalyst activity and stability. When the condition is set properly, the (modified) Co/TiO₂ catalysts demonstrate excellent performance as a promising catalyst for carbon-free CO₂ reforming of CH₄.

The second objective is to give insight over reaction mechanism for steam reforming of acetic acid as a model compound present in bio-oil. Progresses in process for steam reforming of bio-oil will give significant impact to assist sustainable development of energy matter. Attempts to convert bio-oil have been impeded by severe coke/oligomer deposition on the catalysts. There are only few studies have been reported on steam reforming of bio-oil and bio-oil derived oxygenates [149-152]; none of them deals with mechanistic aspects. Noble metal catalysts show promise over conventional Ni based catalysts for conversion of biomass [18]. In this study, the Pt/ZrO₂ catalysts, active and stable catalysts for CO₂ reforming of CH₄, have been selected and thoroughly investigated for steam reforming of acetic acid. The purpose of this study is to elucidate the reaction and deactivation mechanisms and to provide a knowledge base for the design of active and stable catalysts.

The dissertation consists of the following eight chapters: In **chapter 1**, the state of the art in syn-gas/hydrogen production from natural gas and biomass is briefly described. Therein, the background of the reactions including the catalysts studied and the reaction mechanism proposed in literature available, is summarized together with the objective of this study. In **chapter 2**, an investigation of Co/TiO₂ catalysts for the CH₄/CO₂ reaction under ambient pressure is presented.

Effects of pre-treatment for the reaction (reduction temperature etc.) are discussed. The results obtained gives understanding a basic concept to develop the promising catalysts for the reaction. Based on the considerations after chapter 2, the Co-Ni bimetallic catalysts have been investigated and shown in **chapter 3**. In order to suppress carbon deposition on the catalysts perfectly, the catalysts with various Co/Ni ratio have been prepared and tested. The nature of the catalysts has also been clarified by several characterizations. In **chapter 4**, an application for high pressure CH_4/CO_2 reforming has been demonstrated. The promoting effects of Pt, Ru, and Ni on the Co/ TiO_2 catalysts have been investigated. From **chapter 5**, steam reforming of acetic acid as a model compound derived from biomass has been investigated over supported Pt catalysts. The reaction mechanism is elucidated. **Chapter 6** further focuses on steam reforming of acetic acid over Pt/ ZrO_2 catalysts. The reaction pathway is further studied. Discussion focuses on the site requirements and the active species on the catalysts. In **chapter 7** the deactivation during steam reforming of acetic acid is focused. Understanding pathway for deposits which deactivate catalysts helps to clarify the requirement for development of efficient catalysts for the reaction. Finally the results of this study are summarized in **chapter 8**.

1.6 References

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Chapter 2

Influence of Reduction Temperature on the Catalytic Behavior of Co/TiO₂ Catalysts for CH₄/CO₂ Reforming and its Relation with Titania Bulk Crystal Structure

Abstract

The influence of reduction temperature on the catalytic behavior of 10 wt% Co/TiO₂ catalysts, for CO₂ reforming of methane to synthesis gas under atmospheric pressure, was investigated. The Co/TiO₂-anatase catalysts reduced at lower temperatures (≤ 1073 K) showed stable activities. On the other hand, the catalyst reduced at higher temperatures (≥ 1123 K), where the crystal phase of TiO₂ is transformed from anatase to rutile during the reduction, provided almost no activity. In addition, Co/TiO₂-rutile also showed very low activity, regardless of the reduction temperature. For all of the Co/TiO₂ catalysts after the reaction, no carbon deposits (< 0.01 wt%) were observed. XPS and XRD analysis revealed that the main cause of low activity and deactivation of the catalyst was due to the oxidation of metallic cobalt. Experimental observations suggest that the large difference in initial activity corresponds to the different crystal structure of TiO₂ after reduction.

2.1 Introduction

CO₂ reforming of methane to synthesis gas ($\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$) has been a topic of considerable interest for natural gas conversion. It is well known that deposition of carbonaceous species on catalysts is a serious issue for the reaction, causing catalyst deactivation and pressure drop due to plugging of the reactor [1]. Carbon originates mainly from two reactions; CH₄ decomposition ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and CO disproportionation ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) [2]. One of the mechanisms proposed for the reforming of hydrocarbons suggests that the hydrocarbon is dissociatively adsorbed on metallic sites, whereas CO₂ is adsorbed on the support and the adsorbed oxygen species derived from CO₂ on the support reacts with the adsorbed carbon species derived from hydrocarbon on the metal [3,4]. In order to minimize the deposition of carbon on the catalyst, it has been suggested that the catalyst should be designed to avoid large ensembles of the metal species that facilitates carbon formation [2], and to enhance sorption of oxidants (i.e., CO₂ and H₂O) on the support which can remove the deposited carbon formed on the metal [5,6].

In general, supported noble metals, such as Rh, Ru, Pd, Pt and Ir, can lead to lower carbon deposition in the CH₄/CO₂ reaction [2]. However, from a practical point of view, noble metals are unsuitable for industrial use considering their high cost and restricted availability. Supported Ni catalysts are commonly studied due to their low cost; however, nickel can easily induce carbon deposition. Although cobalt catalysts have not been a focus of attention until recently, it has been revealed that Co/MgO [7] and Co/Al₂O₃ [8] showed considerable activity for the CH₄/CO₂ reaction, which suggests that cobalt could be a potentially suitable metal.

In agreement with the mechanism mentioned above, a number of contributors have suggested that the nature of the support strongly affects the catalytic behavior and carbon deposition in the CH₄/CO₂ reaction [2]. Among oxide supports, TiO₂ [3,9-14] and ZrO₂ [4,15-19], which are known to show strong interaction with the catalytic metal [20-22], effectively suppress carbon deposition. The proposed mechanism [3,4,18] suggests that, by H₂ reduction, partially reduced oxide species, such as TiO_x and ZrO_x, migrate onto the metal particles to destroy large ensembles of the metal and enhance the extent of the active interfacial region between the metal and support. In this respect, pretreatment of TiO₂ or ZrO₂ supported catalysts with H₂ can directly change the nature of the support at the perimeter of the metal particles, which is claimed to be the active site for CH₄/CO₂ reforming.

It should also be mentioned that TiO_2 has two kinds of stable crystal structures; anatase and rutile. The anatase-phase is irreversibly transformed to rutile at high temperature. Studies of adsorption and reaction of CO [23-25] and alcohol [26,27] on TiO_2 suggested that the different bulk crystal structures of TiO_2 influence the adsorption properties and catalytic activities for the reactions. However, little is known about the influence of the structural phase of TiO_2 in the CH_4/CO_2 reaction. In this chapter, the catalytic behavior and nature of Co/TiO_2 catalysts for CH_4/CO_2 reforming at atmospheric pressure will be discussed thoroughly. Prior to kinetic measurements, catalysts prepared with TiO_2 , having only the anatase or rutile phase, have been reduced in H_2 at different temperatures. In order to determine the parameters that influence catalytic behavior and deactivation, extensive characterization has been performed.

2.2 Methods

2.2.1 Catalyst preparation

Two types of TiO_2 were obtained by calcination of TiO_2 (Ishihara Sangyo, A-100) at 773 K (anatase phase, denoted as $\text{TiO}_2(\text{a})$), and at 1373 K (rutile phase, denoted as $\text{TiO}_2(\text{r})$). The phase compositions were confirmed by X-ray diffraction (XRD) analysis. The BET surface areas of $\text{TiO}_2(\text{a})$ and $\text{TiO}_2(\text{r})$ were 11 and 2 $\text{m}^2 \text{g}^{-1}$, respectively.

$\text{Co}/\text{TiO}_2(\text{a})$ and $\text{Co}/\text{TiO}_2(\text{r})$ were prepared by incipient wetness impregnation using either $\text{TiO}_2(\text{a})$ or $\text{TiO}_2(\text{r})$ and an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Cobalt loading was set to 10 wt%. The catalysts were dried at room temperature and then at 373 K overnight, followed by calcination at 673 K for 4 h in order to remove ligands from the cobalt precursor. The powder-form catalysts were pressed into pellets, crushed and sieved to obtain grains with diameters between 600 and 900 μm .

2.2.2 CH_4/CO_2 reaction

All catalysts were tested at atmospheric pressure. Typically, 0.1-1.0 g of the catalyst was loaded into a fixed-bed tubular inconel reactor (ID 6 mm) which was passivated with alumina. The reactor was operated in an up-flow mode with the catalyst bed held between quartz wool plugs. Before the reaction, the catalysts were reduced *in situ* with a H_2 flow (25 ml min^{-1}) at various temperatures in the range of 973-1223 K. The required temperature was reached at a rate of 10 K min^{-1} and maintained for

1 h. After the reduction, H₂ was purged with He and the reactor was then set to a reaction temperature of 1023 K. CH₄/CO₂ gases were passed through a bypass of the reactor to measure the exact feed composition, and subsequently introduced into the catalyst bed to give space velocity (SV) = 1200-60000 ml g-cat⁻¹ h⁻¹. An ice cold-trap was set between the reactor exit and a gas chromatograph (GC), to remove water formed during the reaction. The reactants and products were analyzed with an on-line GC (Aera, M-200) equipped with a Porapak Q column, Molecular Sieve 5A column, and two thermal conductivity detectors (TCD). After the reaction, the catalysts were purged with He at reaction temperature and cooled down to room temperature for subsequent characterization. A blank test in the absence of the catalyst revealed no yield of CO and H₂. The schematic drawing of the setup is shown in Fig. 2.1.

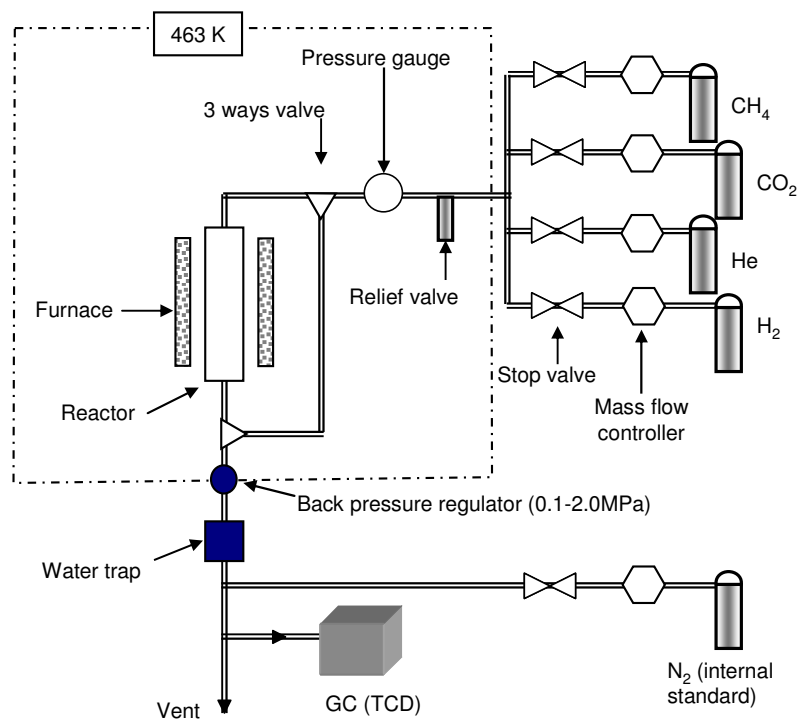


Fig. 2.1. Schematic representation of the setup for activity test.

The exit composition of the gases, at the initial stage of the reaction was continuously monitored by a quadrupole mass spectrometer (Q-MS), M-QA200TS from ANELVA. The m/e values of 2 (H₂), 16 (CH₄), 28 (CO) and 44 (CO₂) were used. The intensities for all gases were calibrated with the GC after stable catalytic activities were obtained. The contribution of CO₂ fragmentation to CO ($m/e = 28$) was appropriately taken into account.

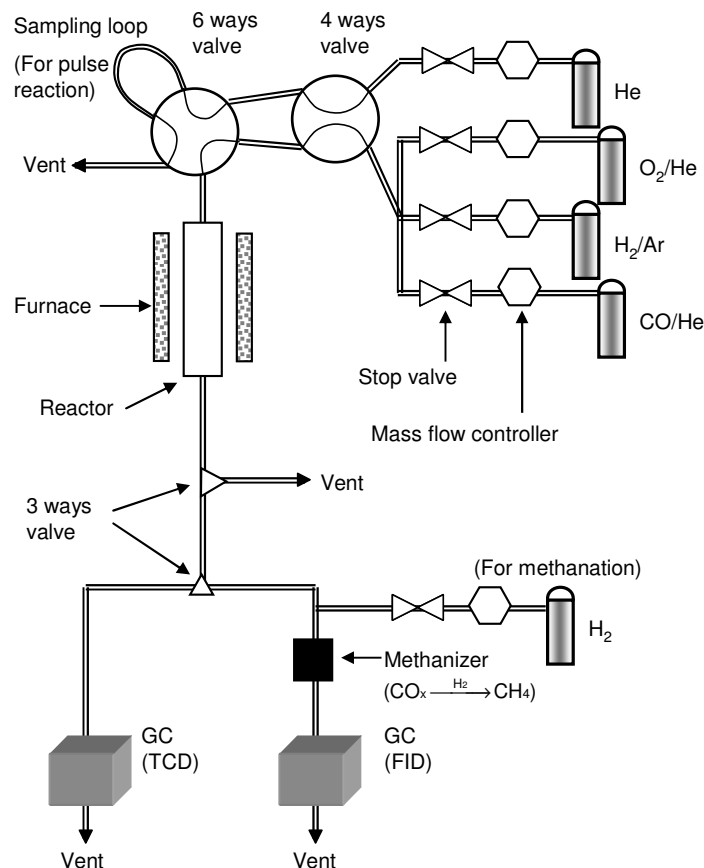


Fig. 2.2. Schematic drawing of multi setup for TPO, TPR, and CO pulse, etc.

2.2.3 Catalyst characterization

X-ray photoelectron spectroscopy (XPS) was performed with an ULVAC-PHI Model 3057 ESCA system using monochromated Al K_{α} (1486.7 eV, 200 W) under a pressure of approximately 10^{-7} Pa. Samples were pressed into pellets and treated in the desired gas atmosphere and temperature. After each treatment, the pellets were purged in Ar and closed in glass capsules, then transferred into the spectrometer system without exposure to the ambient air. The measurements were carried out under approximately 1.0×10^{-6} Pa, using the C1s peak at 284.8 eV as a reference. In order to compensate for the loss of electrons during the measurements, a pass energy of 23.5 eV was used for all samples.

XRD analyses were performed with a Rigaku MULTIFLUX X-ray diffractometer with monochromatized CuK_{α} . Metal crystallite sizes were calculated from line broadening using the Scherrer's equation [28].

The schematic drawing of the set up for temperature-programmed oxidation (TPO), temperature-programmed reduction (TPR), and CO pulse chemisorption etc. is represented in Fig. 2.2.

Quantification of deposited carbon was achieved by a TPO method. After the reaction, the catalyst was heated to 1273 K, at a heating rate of 10 K min⁻¹, in an O₂/He mixture (5/95 vol/vol with a total flow of 50 ml min⁻¹). CO_x gases derived from deposited carbon were monitored using a methanator and a flame ionization detector (FID).

The specific surface area of the catalysts after H₂ reduction was determined by the BET method. The amounts of chemisorbed CO were determined by a pulse injection method. Typically, 0.1 g of catalyst was reduced *in situ* at the required temperatures for 1 h in a H₂ flow, and flushed with He (> 99.999% purity) for 15 min at each temperature. Pulses of 1.08 ml containing 1% CO in He were injected over the catalysts at room temperature until no further adsorption of CO was detected using a TCD. Dispersion of the metal was calculated assuming a 1/1 Co:CO stoichiometry.

TPR measurements were carried out over 0.1 g of calcined catalyst from room temperature to 1223 K, at a rate of 10 K min⁻¹ in flowing H₂/Ar gas mixture (5/95 vol/vol with a total flow of 30 ml min⁻¹). The hydrogen consumption was monitored with a TCD. A water-trap column was placed after the reactor to remove the water formed during the TPR.

TPO of the reduced catalyst was carried out using CO₂, to investigate oxidation behavior. The temperature was increased from room temperature to 1223 K, at a rate of 10 K min⁻¹. The increase in the catalyst weight during oxidation of the reduced catalyst in flowing CO₂ was monitored using differential thermogravimetry (SSC/5200, SII).

2.3 Results

2.3.1 Catalytic behavior of the Co/TiO₂ catalysts

Fig. 2.3 shows CH₄ conversions vs. time on stream over the Co/TiO₂(a) catalysts reduced at different temperatures at SV of 6000 ml g-cat⁻¹ h⁻¹.

Conversions of CH₄ and CO₂ for the Co/TiO₂(a) and Co/TiO₂(r) are listed in Table 2.1. From Fig. 2.3, it is obvious

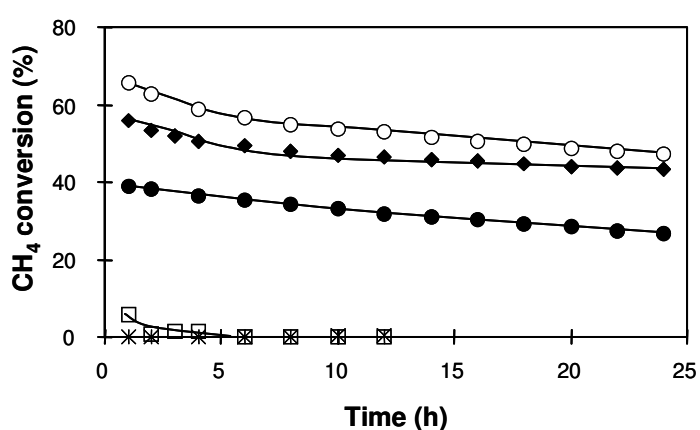


Fig. 2.3. CH₄ conversion vs. time on stream for Co/TiO₂(a) reduced at various temperatures. Reduction temperature: (○) 973 K; (◆) 1023 K; (●) 1073 K; (□) 1123 K; (×) 1173 K; (+) 1223 K. (reaction condition: CH₄/CO₂=1; 1023 K; 0.1 MPa; SV=6000 ml h⁻¹ g-cat⁻¹)

that the activities of Co/TiO₂(a) decreased with increasing reduction temperature. The catalysts reduced at 973-1073 K showed relatively high CH₄ conversions and became only slightly deactivated with prolonged usage. On the other hand, the catalysts reduced at 1123-1223 K showed fairly low activity from the beginning of the reaction. The activities for the Co/TiO₂(r) catalysts reduced within the temperature range of 973-1123 K were all very low from the initial stage of the reaction (Table 2.1).

Table 2.1
Conversions, yields and coke amounts for Co/TiO₂(a) and Co/TiO₂(r) reduced at various temperatures

Catalyst	Reduction temperature (K)	Space velocity (ml g-cat ⁻¹ h ⁻¹)	Time (h)	Conversion (%)		Coke amount (wt%)
				CH ₄	CO ₂	
Co/TiO ₂ (a)	973	6000	1	65.5	71.7	
			24	47.1	58.4	n.d. ^a
	1023	1200	1	80.2	81.9	
			50	59.8	66.6	n.d. ^a
		6000	1	55.7	64.3	
			24	43.4	54.7	n.d. ^a
		60000	1	20.5	33.1	
			24	n.d.	n.d.	0.02
	1073	6000	1	39.0	51.2	
			24	26.5	38.9	n.d. ^a
	1123	6000	1	5.6	9.2	
			12	n.d.	n.d.	n.d. ^a
	1173	6000	1	0.1	2.0	
			12	n.d.	n.d.	n.d. ^a
	1223	6000	1	n.d.	0.2	
			12	n.d.	n.d.	n.d. ^a
Co/TiO ₂ (r)	973	6000	1	2.4	5.4	
			12	n.d.	n.d.	n.d. ^a
	1023	6000	1	0.8	2.0	
			12	n.d.	n.d.	n.d. ^a
	1123	6000	1	n.d.	n.d.	
			12	n.d.	n.d.	n.d. ^a

^an.d. (not detected) is below 0.01 wt%.

Fig. 2.4 shows the relative gas compositions for exit gases monitored by Q-MS as a function of time, focusing on the initial time on stream (< 60 sec). For the Co/TiO₂(a) catalyst reduced at 1023 K (I), after the reactant gases were introduced to the reactor, concentrations for all the gas components including reforming products, CO and H₂, increased and remained stable during the measurements, indicating consistency with the reforming shown in Fig. 2.3. On the other hand, for the Co/TiO₂(a) catalyst reduced at 1173 K (II) and the Co/TiO₂(r) catalyst reduced at 1023 K (III), the concentrations of the reforming products, CO and H₂, increased only initially and decreased rapidly to a very low level (20-40 sec in Fig. 2.4 (II) and (III)). The decreases in CO and H₂ occurred simultaneously with increases in CH₄ and CO₂. These phenomena indicate that reforming proceeded only slightly at the beginning of the reaction, and almost all catalytic activity was lost immediately. The concentration of CH₄ increased more rapidly than that of CO₂, indicating greater CO₂ consumption than CH₄. It should be noted that CO and H₂ were still produced after deactivation of the catalyst. This suggests that the reaction proceeds, however, only in small quantity.

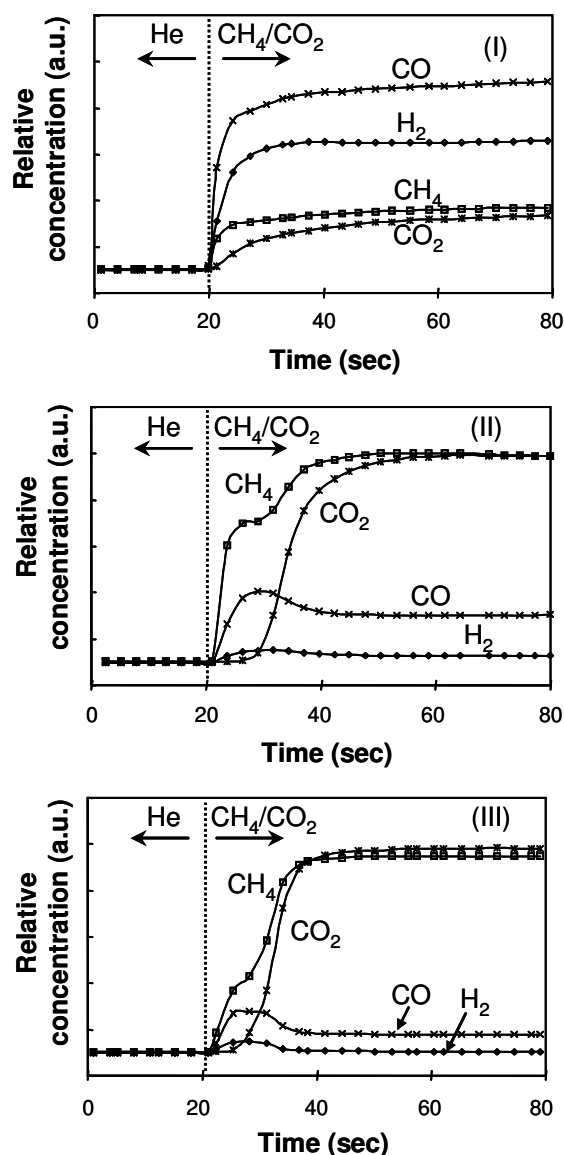


Fig. 2.4. Relative concentration of the exit gases at the initial stage of the reaction. (I) Co/TiO₂(a) reduced at 1023 K; (II) Co/TiO₂(a) reduced at 1173 K; (III) Co/TiO₂(r) reduced at 1023 K.

The Co/TiO₂(a) catalysts reduced at 973-1073 K showed relatively stable activities (Fig. 2.3). Therefore, activity tests for the Co/TiO₂(a) catalyst reduced at 1023 K were performed over a wide range of SV (1200-60000 ml g-cat⁻¹ h⁻¹). Fig. 2.5 shows CH₄ conversions vs. time on stream at SV of 1200, 6000, and 60000 ml g-cat⁻¹ h⁻¹. The conversion percentages are listed in Table 2.1. The CH₄

conversion increased with decreasing SV as expected. However, the equilibrium values for conversions (83.5% for CH₄) and yields were not obtained even at the lowest SV of 1200 ml g-cat⁻¹ h⁻¹. At this SV, deactivation was pronounced at the beginning of the reaction (within 6 h), but suppressed with time. At a SV of 60000 ml g-cat⁻¹ h⁻¹, the catalyst initially showed reforming activity (CH₄ conversion: 20.5%). However, the catalyst gradually lost activity with time and completely within 20 h.

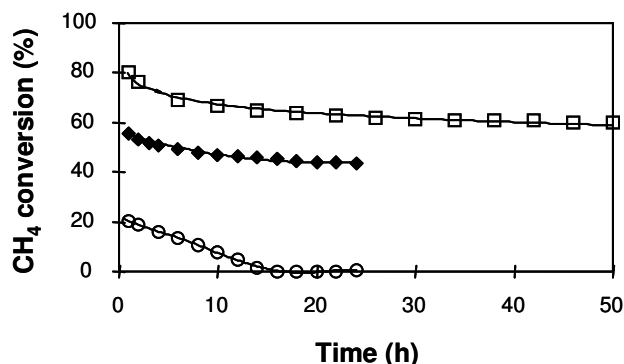


Fig. 2.5. CH₄ conversion vs. time on stream for Co/TiO₂(a) reduced at 1023 K with different SVs. SV: (□) 1200 ml h⁻¹ g-cat⁻¹; (♦) 6000 ml h⁻¹ g-cat⁻¹; (○) 60000 ml h⁻¹ g-cat⁻¹. (reaction condition: CH₄/CO₂=1; 1023 K; 0.1 MPa)

2.3.2 Characterization of the Co/TiO₂ catalysts

Firstly, the TPO results revealed that no carbon was detected (< 0.01 wt%) for all the Co/TiO₂ catalysts after the CH₄/CO₂ reaction (see Table 2.1).

The Co 2p XP spectra for the Co/TiO₂(a) catalysts reduced at 1023 and 1123 K, before and after reaction (1 h), are shown in Fig. 2.6. Peaks located at 777.4 and 777.5 eV, characteristic for metallic cobalt, appeared for the catalysts reduced at 1023 and 1123 K, respectively. For the catalyst reduced at 1023 K, peaks in the 779.5-781 eV region, attributed to an oxide phase of cobalt, were also observed with smaller intensity. A peak at 777.2 eV, which can be assigned to metallic cobalt, remained after the reaction. However, a large shift of this peak to 780.1 eV was observed for the catalyst reduced at 1123 K. This indicates that

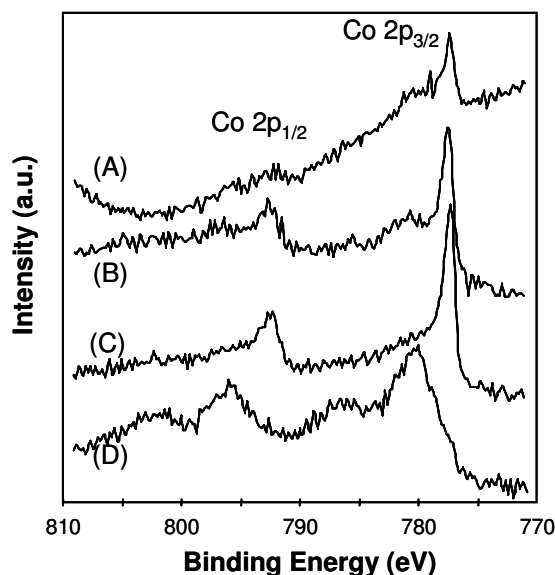


Fig. 2.6. XP spectra of (A) Co/TiO₂(a) reduced at 1023 K before reaction, (B) Co/TiO₂(a) reduced at 1023 K after reaction, (C) Co/TiO₂(a) reduced at 1123 K before reaction, and (D) Co/TiO₂(a) reduced at 1123 K after reaction. (reaction condition: CH₄/CO₂=1; 1023 K; 0.1 MPa, 1 h).

metallic cobalt was oxidized during the CH_4/CO_2 reaction.

Fig. 2.7 shows the XRD patterns of the $\text{Co}/\text{TiO}_2(\text{a})$ catalysts (I) reduced at 1023-1173 K, before the CH_4/CO_2 reaction, and (II) after the CH_4/CO_2 reaction, respectively. Prior to the CH_4/CO_2 reaction (see Fig. 2.7 (I)), the metallic cobalt phase was observed for all the catalysts (see the expanded scale on the right of Fig. 2.7). In addition, a slight phase transfer of TiO_2 from anatase to rutile was observed at 1073 K and predominantly so at 1123-1223 K. After the reaction (see Fig. 2.7 (II)), the metallic cobalt phase remained in the catalysts reduced at 973-1073 K, with higher intensities than those before the reaction. However, for the catalysts reduced at 1123-1223 K, the peak intensities for Co^0 decreased slightly during the reaction and, instead, a CoTiO_3 phase was formed. Similarly, in the XRD pattern of the $\text{Co}/\text{TiO}_2(\text{a})$ catalyst after the reaction at a SV of 60000 $\text{ml g-cat}^{-1} \text{ h}^{-1}$, the CoTiO_3 phase was

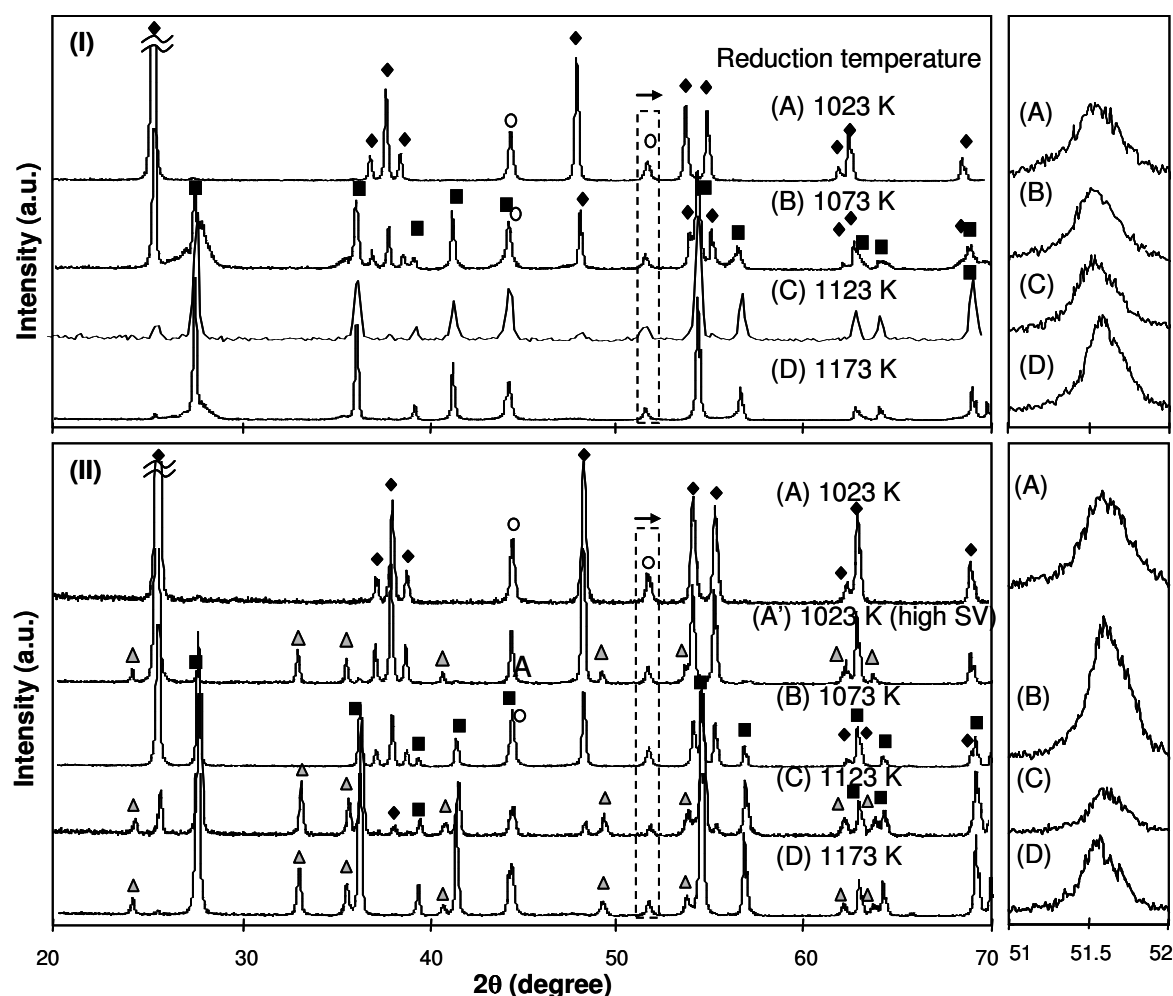


Fig. 2.7. XRD patterns for $\text{Co}/\text{TiO}_2(\text{a})$ reduced at different temperatures. (I) after the reduction, (II) after the reaction. Right box shows narrow scanning diffraction peaks for $\text{Co}(200)$. Reduction temperature: (A), (A') 1023 K; (B) 1073 K; (C) 1123 K; (D) 1173 K. (○) Co^0 ; (▲) CoTiO_3 ; (◆) TiO_2 -anatase; (■) TiO_2 -rutile. (reaction condition: $\text{CH}_4/\text{CO}_2=1$; 1023 K; 0.1 MPa; SV 6000 $\text{ml h}^{-1} \text{ g-cat}^{-1}$, except (A') 60000 $\text{ml h}^{-1} \text{ g-cat}^{-1}$).

observed with small intensity, as shown in Fig. 2.7 (II), (A'). On the other hand, for the XRD pattern of the catalyst after reaction at a SV of 1200 ml g-cat⁻¹ h⁻¹ (not shown), the CoTiO₃ phase was not observed as it was for a SV of 6000 ml g-cat⁻¹ h⁻¹ (Fig. 2.7 (II)). The XRD patterns of the Co/TiO₂(a) catalysts reduced at 973 and 1223 K, before and after the reaction, were similar to those of the catalysts reduced at 1023 K, (A), and 1173 K, (D), respectively (hence, excluded from the figures). With respect to Co/TiO₂(r), the XRD results displayed a similar tendency to that of the Co/TiO₂(a) catalyst reduced at 1173 K before and after the reaction (not shown).

Table 2.2

Specific surface area, metal surface area, and Co⁰ crystallite size for Co/TiO₂(a) and Co/TiO₂(r) reduced at various temperatures

Reduction temperature (K)	Specific surface area ^a (m ² g-cat ⁻¹)	CO adsorption ^a (μmol g-cat ⁻¹)	Cobalt dispersion (%)	Space velocity (ml g-cat ⁻¹ h ⁻¹)	Co crystallite size ^b (nm)	
					before ^a	after ^c
Co/TiO ₂ (a)						
973	11	6.07	0.36	6000	30	32
1023	10	5.07	0.30	1200	26	39
				6000	26	28
				60000	26	38 ^d
1073	9	1.80	0.11	6000	30	35
1123	5	1.08	0.06	6000	33	41 ^d
1173	5	1.48	0.09	6000	34	37 ^d
1223	3	2.00	0.12	6000	33	43 ^d
Co/TiO ₂ (r)						
973	2	3.70	0.22	6000	29	— ^d
1023	2	3.16	0.19	6000	29	— ^d
1123	2	1.44	0.08	6000	35	— ^d

^aBefore CH₄/CO₂ reaction (after reduction).

^bCalculated from line broadening applying the Scherrer's equation [28].

^cAfter CH₄/CO₂ reaction.

^dCoTiO₃ phase was formed.

Physico-chemical properties of the catalysts are compiled in Table 2.2. For Co/TiO₂(a), the specific surface area decreased with increasing reduction temperature. The specific surface area decreased drastically with the reduction at 1123 K, which corresponds to the predominant phase

transition of TiO_2 from anatase to rutile. For $\text{Co/TiO}_2(\text{r})$, the specific surface areas were the same for catalysts reduced at 973-1123 K, due to the strongly sintered structure of $\text{TiO}_2(\text{r})$ after calcination at 1373 K.

Dispersion of cobalt was evaluated by CO pulse chemisorption measurements. For $\text{Co/TiO}_2(\text{a})$, the dispersion of cobalt decreased with increasing reduction temperature up to 1073 K (0.36 to 0.11%), and then remained comparable above 1073 K (between 0.06 and 0.12%). For $\text{Co/TiO}_2(\text{r})$, dispersion of cobalt decreased gradually with increasing reduction temperature from 973 to 1123 K. It should be mentioned that the dispersions for $\text{Co/TiO}_2(\text{r})$ catalysts reduced at 973 (0.22%) and 1023 K (0.19%) were lower than those for the $\text{Co/TiO}_2(\text{a})$ catalysts reduced at 973 (0.36%) and 1023 K (0.30%), but higher than those for the $\text{Co/TiO}_2(\text{a})$ catalyst reduced at 1073-1223 K ($\leq 0.12\%$).

The cobalt metal crystallite sizes for the reduced catalysts were evaluated from XRD line broadening. Comparable values (26-35 nm) were obtained for all the catalysts, regardless of the support phase composition. For all catalysts, the cobalt crystallite sizes increased slightly during the reaction at $6000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$, indicating that the cobalt particles experienced moderate sintering. It should be noted that the peak intensities for metallic cobalt, in $\text{Co/TiO}_2(\text{a})$ reduced at 1123 K-1223 K and $\text{Co/TiO}_2(\text{r})$, decreased after the reaction and formation of CoTiO_3 was observed for these catalysts. For the $\text{Co/TiO}_2(\text{a})$ catalysts reduced at 1023 K, the crystallite size after the reaction (39 nm) at a SV of $1200 \text{ ml g-cat}^{-1} \text{ h}^{-1}$ was distinguishably larger than before the reaction (26 nm), indicating that the catalyst experienced sintering. For the catalyst after the reaction at a SV of $60000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$, the formation of the CoTiO_3 phase was accompanied by a decrease in the intensity of the Co metallic phase.

In order to follow the changes in the catalyst structure during the reduction, XRD analyses and TPR measurements were carried out. Fig. 2.8 (A) and (C) show the XRD patterns of $\text{Co/TiO}_2(\text{a})$ and $\text{Co/TiO}_2(\text{r})$ calcined at 673 K (before reduction). These patterns indicate that cobalt was present as an oxide, Co_3O_4 , after calcination at 673 K for both anatase and rutile phases. Fig. 2.9 (A) and (B) show TPR profiles of the calcined $\text{Co/TiO}_2(\text{a})$ and $\text{Co/TiO}_2(\text{r})$. Both catalysts had two main peaks with maxima at 590-650 K, and the H_2 uptake ended below 850 K. These results indicate that Co_3O_4 was first reduced to CoO , and subsequently to metallic Co, as discussed in an earlier report [29]. Since cobalt oxide was reduced completely below 850 K, the lowest reduction temperature of 973 K in this

study was sufficiently higher than the temperature required to reduce the cobalt oxides completely.

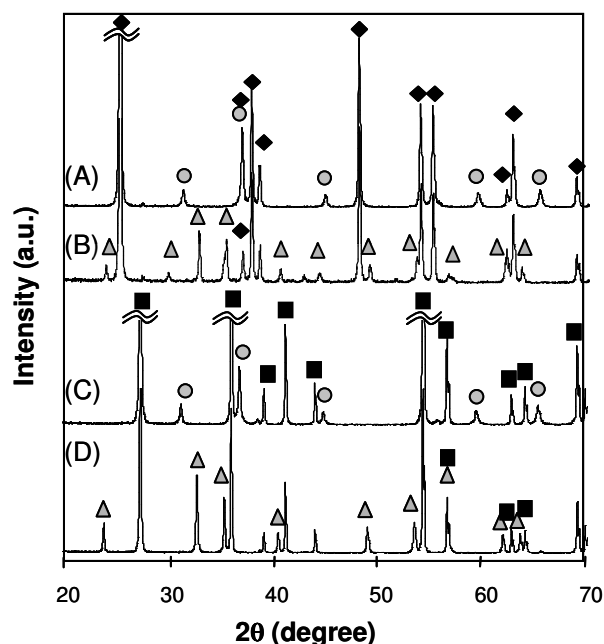


Fig. 2.8. XRD patterns for Co/TiO₂(a) and Co/TiO₂(r) after different treatments. (A) Co/TiO₂(a) after calcination at 673 K (before reduction); (B) Co/TiO₂(a) after CO₂/He treatment at 1023 K following the reduction at 1023 K; (C) Co/TiO₂(r) after calcination at 673 K (before reduction); (D) Co/TiO₂(r) after CO₂/He treatment at 1023 K following reduction at 1023 K. (●) Co₃O₄; (▲) CoTiO₃; (◆) TiO₂-anatase; (■) TiO₂-rutile.

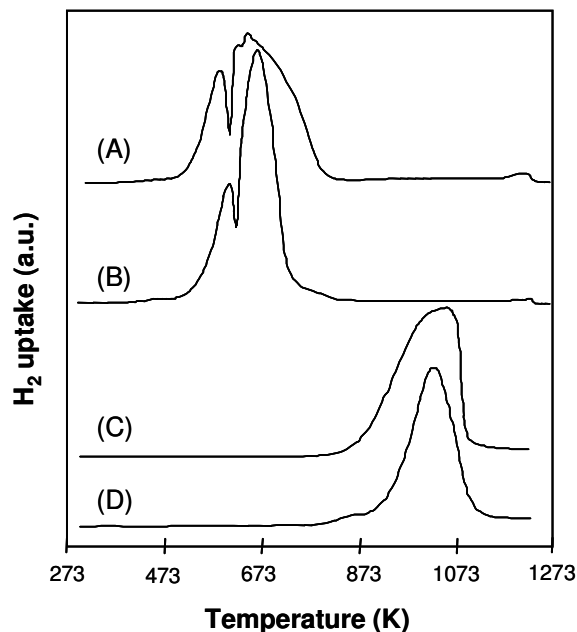


Fig. 2.9. TPR profiles for (A) Co/TiO₂(a) calcined at 673 K, (B) Co/TiO₂(r) calcined at 673 K, (C) Co/TiO₂(a) oxidized in CO₂/He at 1023 K, and (D) Co/TiO₂(r) oxidized in CO₂/He at 1023 K.

The XP spectra and the XRD patterns suggested formation of an oxidized phase of cobalt in some catalysts investigated during the reaction; therefore, the oxidation behavior of the reduced catalyst in CO₂ was investigated. After Co/TiO₂(a) and Co/TiO₂(r) were reduced at 1023 K, the catalysts were treated in a CO₂/He (1:1) mixture at 1023 K. The XRD patterns after this treatment are shown in Fig. 2.8 (B) and (D) for Co/TiO₂(a) and Co/TiO₂(r), respectively. It was found that the metallic cobalt in Co/TiO₂ was oxidized at 1023 K by CO₂ to form CoTiO₃, regardless of the TiO₂ phase composition. After this treatment, TPR measurements were carried out and the profiles are shown in Fig. 2.9 (C) for Co/TiO₂(a) and (D) for Co/TiO₂(r). Each profile had one peak at approximately 1000 K, indicating that reduction of CoTiO₃ took place for both Co/TiO₂(a) and Co/TiO₂(r). It should be noted that the reduction temperature of CoTiO₃ was much higher than that of Co₃O₄ (< 850 K). This implies that once CoTiO₃ is formed it is difficult to reduce under the reaction conditions.

2.4 Discussion

2.4.1 Catalytic behavior and causes of deactivation for the Co/TiO₂ catalysts

There is general agreement that catalytic deactivation during the CH₄/CO₂ reaction is caused by carbon deposition on active sites, sintering of metal particles, and oxidation of the metal [2]. In the present study, no carbon was detected (< 0.01 wt%) for all the Co/TiO₂ catalysts. The cause of the deactivation for the Co/TiO₂ catalysts in this study is, therefore, metal oxidation and/or sintering of metal.

The reduction temperature had a strong influence on the catalytic behavior of Co/TiO₂(a) (Fig. 2.3). It was clearly shown that the Co/TiO₂(a) catalysts, reduced at 1123-1223 K, showed low activities for the reforming reaction (Fig. 2.3). At the beginning of the CH₄/CO₂ reaction (Fig. 2.4), CO₂ consumption for the Co/TiO₂(a) catalyst reduced at 1173 K (II) was much larger (complete CO₂ consumption within 10 sec) than that of the Co/TiO₂(a) catalyst reduced at 1023 K (I). The reforming did not occur significantly over the Co/TiO₂(a) reduced at 1173 K, as seen by a small production of hydrogen and its complete loss within one minute. It should be noted that the higher concentration of CH₄ compared to CO₂ (or higher concentration of CO to H₂), for all the catalysts, are ascribed to a preferential reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) over reforming. However in this case, the large CO₂ consumption is not due mainly to reforming, but to oxidation of the catalyst surface. It is considered that the oxidation of the surface metal and the reforming reaction occur simultaneously. For the Co/TiO₂(a) catalyst reduced at 1023 K, reforming was faster than the oxidation, showing constant activity for reforming, and for the Co/TiO₂(a) catalyst reduced at 1173 K and Co/TiO₂(r) reduced at 1023 K, the oxidation of the metal was faster, resulting in a low activity for reforming.

XPS and XRD results give direct information about the surface state and the bulk state of the catalysts. In the Co 2p XP spectra (Fig. 2.6 (C), (D)) of Co/TiO₂(a) reduced at 1123 K, which showed fairly low activity towards the reaction, the metallic cobalt (777.4 eV) was oxidized during the reaction (broad peak at approximately 780.1 eV). It was reported that CoO, Co₃O₄ and CoTiO₃ have binding energy of cobalt at 780.0-780.5, 779.5-780.2, and 781.2 eV, respectively [30-33]. Although it is not clear to identify the exact species of cobalt, the results obviously revealed that surface Co atoms in the catalysts were oxidized to Co²⁺ and/or Co³⁺ during the CH₄/CO₂ reaction. In addition, XRD

patterns show the formation of a CoTiO_3 phase (Fig. 2.7 (II)). The XRD patterns still indicate the presence of metallic cobalt, even if the catalyst had lost all activity. However, sharp peaks of metallic cobalt were not observed and peak intensities were lowered during the reaction, which confirms that the degree of sintering of metal was not significant. Therefore, it was considered that the oxidation of metallic cobalt would occur at the surface of Co particles, as was confirmed by XPS, and that a CoTiO_3 phase crystallization would proceed in the periphery between the metal and TiO_2 . It is also considered that Co in the core of the particles still remains metallic, as detected by XRD. Similar results for the $\text{Co/TiO}_2(\text{r})$ catalysts reduced at 973-1123 K were obtained by XRD analysis. Therefore, it was concluded from the kinetic measurements and the XPS and XRD results, that low activities of $\text{Co/TiO}_2(\text{a})$ reduced at higher temperatures (≥ 1123 K) and $\text{Co/TiO}_2(\text{r})$ are attributed to rapid oxidation of the surface cobalt.

On the contrary, the $\text{Co/TiO}_2(\text{a})$ catalysts reduced at 973-1073 K showed relatively high and stable activities (Fig. 2.3). However, a moderate decrease in catalytic activity was observed during the reaction. Metal sintering during the reaction was not significant compared to the decrease in activity (Table 2.2). Therefore, it is speculated that deactivation for these catalysts is due to both metal sintering and oxidation. The surface of metal particles can be oxidized slowly, and therefore the catalysts showed mild deactivation.

To confirm this idea, the $\text{Co/TiO}_2(\text{a})$ catalyst reduced at 1023 K was tested at different space velocities. The CH_4 conversion of the catalyst at a SV of $1200 \text{ ml g-cat}^{-1} \text{ h}^{-1}$ was higher than that at $6000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$, as expected (Fig. 2.5). Deactivation was observed especially at the beginning of the reaction and then gradually reduced over time. XRD patterns of the catalyst after reaction indicate the metallic cobalt phase was retained during the reaction, but cobalt sintering occurred during the reaction, as was seen from a change in crystallite size from 26 to 38 nm. This degree of sintering and increase in crystallite size was much greater than that which occurred at a SV of $6000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$ (26 to 32 nm). Therefore, the sintering of metal causes deactivation in this case. Although there are no additional data to reveal the causes and the incidental effects of sintering, it is suggested that the gas atmosphere of the latter part of the catalyst bed, where there are more products and less reactants, might have some influence on the catalyst, thereby accelerating sintering of the metal.

With regard to the reaction at a SV of $60000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$, $\text{Co/TiO}_2(\text{a})$ reduced at 1023 K initially

showed a 20% CH₄ conversion, but was deactivated with time and completely lost catalytic activity within 20 h (Fig. 2.5). Formation of the CoTiO₃ phase after the reaction (Fig. 2.7 (II)(A')) suggested that the metallic cobalt on TiO₂(a) was gradually oxidized with time. The degree of sintering was not significant (Table 2.2). Therefore, the main cause of complete deactivation would be oxidation of the metal. It can be considered that higher SV provide the catalyst with more contact of the reactants (CO₂, CH₄). In this context, the inlet part of the catalyst in the reactor could be oxidized more easily due to a higher concentration of CO₂. On the other hand, metallic Co in the latter part in the catalyst bed is exposed to reductive products and could be sintered (as observed for the catalyst after the reaction at a SV of 1200 ml g-cat⁻¹ h⁻¹). From this point, the cause of deactivation of the catalyst, reduced at 973-1073 K during reaction at a SV of 6000 ml g-cat⁻¹ h⁻¹, would be attributed to slow oxidation of metal from the front part of the catalyst bed, and sintering of metal at the latter part of the catalyst bed.

2.4.2 Key parameters for the differences in catalytic behavior of the Co/TiO₂ catalysts

After calcination at 673 K (before reduction), Co₃O₄ was the only cobalt phase identified by XRD in the catalysts (Fig. 2.8 (A), (C)). In Fig. 2.9, the TPR spectra of Co/TiO₂(a) and Co/TiO₂(r) suggest that the lowest reduction temperature, i.e., 973 K, must be high enough to reduce all cobalt oxides in the catalysts. However, the Co 2p XP spectrum for Co/TiO₂(a) reduced at 1023 K showed a rather small peak attributed to an oxide phase of cobalt. Note that the TPR gave evidence that CoTiO₃ was less reducible than Co₃O₄ (Fig. 2.9). These results indicate that trace amounts of CoTiO₃ can be formed by calcination at 673 K, and are not reduced by a reduction at 1023 K, although the amounts were too small to be detected by TPR and XRD analysis. This is in agreement with the report by Ho et al. [30] that surface CoTiO₃-like species, relatively less reducible, were formed in Co/TiO₂ by calcination at 673 K. However, due to the fact that the catalyst reduced at lower temperature (<1123 K) showed much higher activity than the catalyst reduced at higher temperature (≥1123 K), it is concluded that the difference in the reduction degree of cobalt is not a crucial factor regarding catalytic behavior.

For the Co/TiO₂(a) catalysts reduced at 973-1073 K, which showed relatively high activity, and only moderate deactivation during the reaction, catalytic activities decreased with increasing reduction temperature (Fig. 2.3). Among these catalysts the cobalt crystallite size, phase composition of TiO₂,

and the specific surface areas were very similar, and therefore the differences in activity would be attributed to the amounts of cobalt available on the surface, which decreases with increasing reduction temperature (Table 2.2). The Co/TiO₂ catalysts have been reported as Strong Metal Support Interactions (SMSI) catalysts [34]. It has been reported for TiO₂ supported catalysts that the surface oxygen of TiO₂ could be removed in the range of the temperatures investigated (≥ 773 K), and TiO_x species would be generated and cover the metal surface so that less CO chemisorption is detected. It has also been discussed [3,12] that TiO_x species could block a large ensemble of metal particles that facilitate CH₄ decomposition and the resultant coke deposition. In addition, the generation of those TiO_x species would have a number of oxygen defect sites that enhance CO₂ dissociation to supply oxygen to the metal particles, and therefore remove the surface carbon species. Synergistic effects of creating new active sites toward CH₄/CO₂ reaction in the metal-support interfacial region will lead to an increase of turn-over frequency (TOF, s⁻¹) [12,13]. In this study, the dispersion was roughly estimated from the crystallite size using the following equation [34],

$$\%D = 96.2 / d$$

where %D is the dispersion percentage of cobalt, and d is the particle size of cobalt, assuming an fcc structure for Co. This calculation resulted in approximately 3% dispersion for all the catalysts studied, which is more than 10 times larger than the values calculated from CO adsorption measurements (the highest dispersion is 0.36% for Co/TiO₂(a) reduced at 973 K) (Table 2.2). Therefore, it is confirmed that a higher reduction temperature increased the TiO_x coverage on metallic cobalt for the Co/TiO₂ catalysts, without increasing the metal crystallite size significantly. Strong resistance to coke deposition would be due to a small exposure of the cobalt surface, which destroys the large ensemble of metallic cobalt (coke deposition site), and creates active sites for reforming, especially CO₂ activation in the periphery of metal particles. In the current work, the TOF increased with increasing reduction temperature; e.g., TOFs for CH₄ conversions after 1 h were estimated to be 4.0, 4.1, and 8.1 s⁻¹ for the Co/TiO₂(a) catalysts reduced at 973, 1023, and 1073 K, respectively (TOFs were calculated from the molar flow rate of converted CH₄ divided by mole of CO adsorbed on the metal). However, TiO_x species may also block active metallic sites for reforming, and therefore the net value for conversions decreased with increasing reduction temperature (Fig. 2.3, Table 2.1).

Compared to Co/TiO₂(a) reduced at 973-1073 K, the Co/TiO₂(a) catalyst reduced at 1123-1223 K and the Co/TiO₂(r) catalyst reduced at 973-1123 K showed low activities from the beginning of the reaction (Figs. 1, 2). The metal crystallite sizes of Co/TiO₂(a) and Co/TiO₂(r) before the reaction (after reduction) were almost the same for these catalysts (Table 2.2). According to these results, the differences in the catalytic activity at the initial stage of the reaction

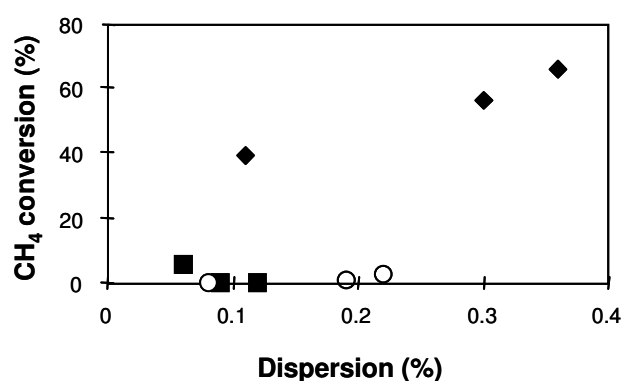


Fig. 2.10. CH₄ conversion at 1 h vs. dispersion of cobalt for the Co/TiO₂ catalysts reduced at different temperatures. (◆) Co/TiO₂(a) reduced at 973-1073 K; (■) Co/TiO₂(a) reduced at 1123-1223 K; (○) Co/TiO₂(r) reduced at 973-1123 K.

were *not* attributed to the metal crystallite size. The relationship between CH₄ conversion and cobalt dispersion for the Co/TiO₂ catalyst is collected in Fig. 2.10. As shown in this figure, low activities observed at the beginning of the reaction are *not* related to cobalt dispersion. The phase transfer from anatase to rutile was observed for the Co/TiO₂(a) catalyst at a reduction temperature of 1123 K (Fig. 2.7), and therefore the catalytic behavior seems to depend on the main TiO₂ structures, i.e., anatase or rutile. In other words, it is possible to say that the Co/TiO₂(a) catalyst, which retained the anatase phase, showed relatively high activity, whereas both Co/TiO₂(a), which obtained the rutile phase during reduction and Co/TiO₂(r), originally supported on rutile phase, showed fairly low activity due to rapid oxidation of metallic Co to CoTiO₃.

Interestingly, the large differences in catalytic behavior are in accordance with different TiO₂ phase compositions, i.e., formation of CoTiO₃ is more favored on rutile than anatase phase in CH₄/CO₂ reaction. Hence, the CoTiO₃ formation rate under CO₂ treatment was compared for Co/TiO₂(a) reduced at 1023 K, and Co/TiO₂(r) using TPO with CO₂ (Fig. 2.11). Oxygen uptake was observed above 773 K for both catalysts. Co/TiO₂(a) gave a maximum at 1030 K and Co/TiO₂(r) had a maximum at 1100 K. The O/Co ratio, calculated from the net amount of oxygen uptake, was approximately in the range from 1.0 to 1.1. In addition, CoTiO₃ was the only cobalt species observed with XRD after these measurements (Fig. 2.8 (B), (D)). Therefore, the oxygen uptake would mainly correspond to the formation of CoTiO₃ (Co + TiO₂ + CO₂ → CoTiO₃ + CO). Since Co/TiO₂(a) had a

lower temperature onset of the peak and peak maximum compared to Co/TiO₂(r), it can be suggested that Co/TiO₂(a) was more reactive with CO₂ than Co/TiO₂(r) to form CoTiO₃. This tendency for forming CoTiO₃ in CO₂ was different from that in the CH₄/CO₂ reaction, because the CoTiO₃ phase was formed more easily in Co/TiO₂(r) during the CH₄/CO₂ reaction than in Co/TiO₂(a). In other words, the tendency to form CoTiO₃ in CH₄/CO₂ can

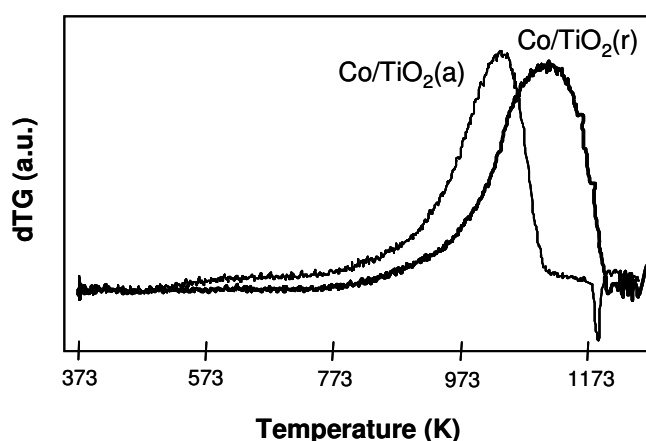


Fig. 2.11. Differential weight increase of Co/TiO₂(a) and Co/TiO₂(r) reduced at 1023 K flowing CO₂. Ramping rate: 10 K min⁻¹.

not be predicted from the reactivity of Co supported on TiO₂ with only CO₂. Therefore, the difference in catalytic activities would correlate with the state of active sites (both metal and support participate) [3,4,16,18] on the catalyst surface and with the kinetics of the reactions with CH₄/CO₂ on those sites, where reductive (CH₄, H₂, CO) and oxidative (CO₂, H₂O) species co-exist. When the reaction between these reductive and oxidative species keeps balance on the catalyst surface, no carbon deposition or oxidation of metal occurs, and accordingly the catalyst exhibits an extended life. For the Co/TiO₂ catalysts, the CoTiO₃ phase is formed by oxidative species when the CH₄/CO₂ reaction is not balanced. Once formed, the CoTiO₃ phase is difficult to be reduced, and the catalyst becomes inactive toward the reforming reaction.

Anatase and rutile structures are different in the surface structures and chemical properties such as facets of the surface, acid-base properties, and the degree of oxygen vacancies, etc. Such factors can directly affect the reaction between reductive and oxidative species in the reforming. As a result, anatase-type TiO₂ comparatively keeps the surface cobalt in the metal state and gives the catalyst relatively stable activity, whereas rutile-type TiO₂ induces rapid oxidation of cobalt and provides very low activities from the beginning of the reaction.

2.5 Conclusions

Influence of the reduction temperature for Co/TiO₂ catalysts for the CO₂ reforming of CH₄ was

investigated. Differences in the reduction temperature significantly affect the catalytic behavior for Co/TiO₂. Remarkably, all the Co/TiO₂ catalysts showed strong resistance for coke deposition (< 0.01 wt%) in the CH₄/CO₂ reaction at 1023 K. The catalysts reduced at relatively lower temperatures (973-1073 K), where TiO₂ retained the anatase phase, had relatively high and stable activities. On the other hand, for the Co/TiO₂ catalysts, where anatase phase was mainly transformed to the rutile phase by reduction at higher temperatures (1123-1223 K) or where the cobalt was supported on the rutile phase, showed fairly low activities from the beginning of the reaction. Both kinetic measurements and characterization with XPS and XRD techniques revealed that low activities are ascribed to rapid oxidation of metallic cobalt. Since the differences in catalytic activity can not be correlated with the differences in Co dispersion and Co crystallite sizes, it is suggested that the large difference in the initial activities could be ascribed to the differences in the TiO₂ bulk crystal structure. As a result, oxidation of cobalt supported on rutile is more favored than that of cobalt supported on anatase during CH₄/CO₂ reforming. This indicates that TiO₂, together with Co, strongly participate in the reaction and is of importance to optimize a balance of the reactions between CH₄ and CO₂. Such knowledge obtained from this study, for example, the influence of reduction temperature and TiO₂ phase composition on the catalytic behavior of TiO₂ supported catalysts, can be judiciously applied for further improvement.

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Chapter 3

Titania Supported Cobalt and Nickel Bimetallic Catalysts for Carbon Dioxide Reforming of Methane

Abstract

The titania supported cobalt and nickel bi-metallic catalysts were investigated for CO₂ reforming of methane to synthesis gas at 1023 K under ambient pressure. The bimetallic Co-Ni/TiO₂ catalysts with appropriate Co/Ni ratio showed highly stable activities without carbon deposition. While the mono-metallic Co/TiO₂ catalyst deactivated rapidly due to oxidation of metal, 10 mol% substitution of cobalt with nickel suppress the oxidation of metal, providing a high catalytic stability. However, the catalysts with excess nickel content (>80 mol%) experienced the carbon formation. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses revealed that homogeneous alloy of cobalt and nickel was formed from bulk to surface by the H₂ reduction and the alloy was stable during the reforming. The advantages of the bi-metallic catalysts are high resistance to the undesirable metal oxidation and coking, by controlling balance of reactions between CH₄ and CO₂.

3.1 Introduction

Carbon dioxide reforming of methane to synthesis gas ($\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$) has been of great interest for technology of natural gas conversion since the reaction can optimize the H_2/CO ratio by combining with, for instance, steam reforming of methane. In general, carbon formation on the catalysts is the serious issue for the reaction. Supported Ni catalysts are commonly applied due to their low cost [1]. The nickel catalysts are known to show high catalytic activity; however, nickel catalysts easily induce formation of graphitic carbon, causing catalyst deactivation and plugging of a reactor tube [1,2].

There have been a number of discussion on how to avoid the carbon formation [3,4]. Many contributions have claimed that the nature of the supports strongly affects the catalytic behavior and carbon deposition for the CH_4/CO_2 reaction [5-10]. Among oxides titania is reported an excellent support to suppress carbon deposition [5-7,10-12]. It is proposed that during H_2 reduction, the partially reduced TiO_x species would migrate on the metal particle, so-called strong metal support interaction (SMSI) [13,14], and destroy large ensembles of the metal species and create the highly active sites for the reforming at the boundary between metal and support, resulting in reduction of the amount of carbon deposits [7,11].

Another idea to minimize carbon deposits is preventing the carbide formation on the metal particles because the carbide formation is suggested to be the essential intermediate for carbon formation [4]. It has been reported that doping to the Ni catalysts with other metal, such as tin [15], chromium [16,17], and manganese [18,19], has significant effects to suppress carbide formation. Some elaborative works [20,21] have shown that additives like potassium, sulfur, and gold preferentially bind to the step sites working as the coking sites, and hence, suppress the graphite formation, without significantly influencing the catalytic activity for the reforming.

It has also been reported that the addition of cobalt to nickel catalysts reduce coke formation during reactions, such as CO methanation [22], partial oxidation of methane to synthesis gas [23,24], and steam or CO_2 reforming of methane [25]. Bartholomew et al. suggested that the suppressing coke formation by adding cobalt to the nickel catalyst for CO methanation would be due to enhancement of hydrogenation of atomic carbon and/or inhibition of the formation of carbide species in the metal crystal [22]. However, the beneficial effects as well as the nature/state of the bimetallic catalysts

remain unclear and are needed to be investigated.

In the previous chapter, 10 wt% Co/TiO₂ was investigated thoroughly. It is proposed that, during the CH₄/CO₂ reforming, the reactions between CH₄ and CO₂ should be balanced appropriately [26]; i.e., the coke species formed by decomposition of CH₄ on the metal has to be removed by the activated oxygen species derived from CO₂. The cobalt catalysts tended to be deactivated by oxidation of the metal, implying that the oxygen species derived from CO₂ reacts more preferentially than the coke-species derived from CH₄.

This chapter pertains to the carbon dioxide reforming of methane over the bimetallic Co-Ni/TiO₂ catalysts (metal loading: 10 wt% in total) at atmospheric pressure. The motivation of this work is to combine the nature of cobalt (stronger affinity with oxygen species) and nickel (stronger affinity with carbon species) and to suppress both the metal oxidation and carbon formation. The catalysts with various Co/Ni ratio have been prepared and tested for CO₂ reforming of CH₄. In order to clarify the beneficial effects of the bimetallic catalysts, the state and nature of the Co-Ni/TiO₂ catalysts have been extensively characterized.

3.2 Methods

3.2.1 Catalyst preparation

Co-Ni/TiO₂ catalysts were prepared by incipient wetness co-impregnation of an aqueous solution of Co(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O (Wako Pure Chemical Industries Ltd.) with TiO₂ (Ishihara Sangyo, A-100, anatase phase), which is pre-calcined at 773 K for 15 h. The metal loading was set to 10 wt% for Co/TiO₂ and cobalt was substituted with the same moles of nickel. The catalysts were dried at room temperature and then 373 K overnight, followed by calcination at 673 K for 4 h in flowing air in order to remove ligands from the cobalt and nickel precursors. The powder-form catalysts were pressed into pellets, crushed and sieved to obtain grains with diameters between 600 and 900 μm. The catalyst with the ratio (Co:Ni=m:n) is denoted as CoNi(m:n)/TiO₂.

3.2.2 Catalyst characterization

CH₄ pulse reaction was operated to investigate the reactivity of the catalysts to CH₄. After *in situ* reduction, high purity CH₄ pulses (99.999%, pulse size: 44.1 μmol) were injected at 1023 K in Ar

carrier (flow rate: 30 ml min⁻¹) over 100 mg of the catalyst. The reactant and product gases were separated by active carbon column and detected by a TCD. In addition to the expected product (H₂ and C remaining on the catalyst surface), CO was observed in a small quantity, which is probably derived from the reaction between CH₄ and the impurity in Ar carrier. However, the amount produced was small (< 2 μmol) and therefore the total amounts of the converted CH₄ was used to discuss the catalytic activity.

The methods for other characterizations are described in the previous chapter.

3.2.3 CH₄/CO₂ reaction

All catalysts were tested at atmospheric pressure. Typically 0.5 g of the catalyst was loaded into a fixed-bed tubular inconel reactor (ID 6 mm). The axial temperature profile was measured for the furnace without the catalyst bed. Subsequently, the catalyst was placed in the isothermal zone of the furnace. The catalysts were reduced *in situ* in a H₂ flow at 1123 K for 1 h. The reaction temperature was set to 1023 K. CH₄/CO₂ gases were introduced into the catalyst bed at a total flow rate of 50 ml min⁻¹ (space velocity (SV) 6000 ml g-cat⁻¹ h⁻¹). During the reaction, temperature at the inlet of the catalyst bed was measured (where the reaction was expected to occur to the largest extent). Throughout the series of experiments, the temperature decrease in the catalyst bed due to the reaction was very small (1-2 K). Further details of procedure and apparatus were described in the previous chapter.

3.3 Results

3.3.1 The state of the reduced Co-Ni/TiO₂ catalysts

For the CoNi(50:50)/TiO₂ calcined at 673 K (before reduction) Co₃O₄ and NiO were observed in the separate phases, confirmed by XRD analysis (not shown). shows TPR profiles of the Ni/TiO₂, CoNi(50:50)/TiO₂, Co/TiO₂ catalysts

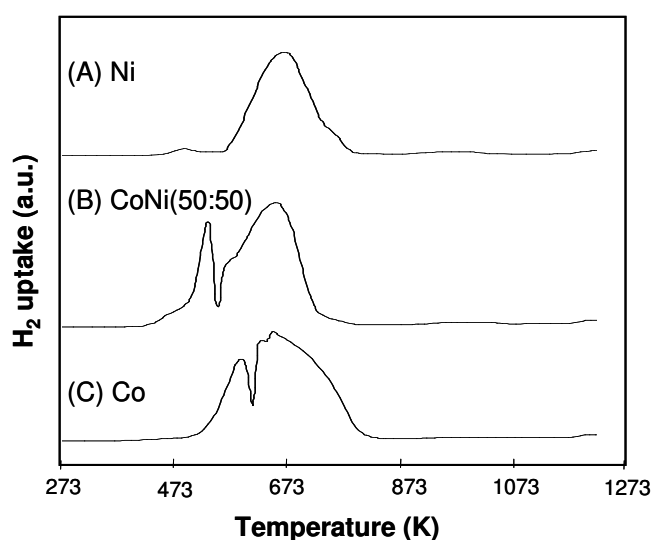


Fig. 3.1. TPR profiles for (A) Ni/TiO₂, (B) CoNi(50:50)/TiO₂ and (C) Co/TiO₂.

calcined at 673 K. For Ni/TiO₂ one peak was observed starting from around 600 K till around 800 K with the maximum at 690 K, corresponding to the reduction of NiO to Ni⁰. For Co/TiO₂ two continuous peaks were observed; one was observed at 490-650 K and the other ended below 850 K. These results indicate that the reduction of Co₃O₄ to CoO occurred first, subsequently to metallic Co [27]. For the bimetallic catalyst the peaks were observed starting at lower temperature of 460 K and ending at 700 K. Two or more overlapped peaks were observed, which can be assigned to simultaneous reduction of Co₃O₄ and NiO. Note that all nickel and cobalt oxides were reduced completely at the reduction temperature of 1123 K in this study.

Table 3.1

CO chemisorption capacity, metal crystallite size, turn over frequency and the amount of deposited carbon for Co-Ni/TiO₂ with different Co/Ni ratio (Reaction conditions: 1023 K; CH₄/CO₂=1; 0.1 MPa)

Co:Ni	The amount of CO chemisorbed (μmol g-cat ⁻¹)	Metal crystallite size ^a (nm)		Turn over frequency for CH ₄ at 1 h (s ⁻¹)	Carbon amount (wt%)
		Before reaction ^a	After reaction		
0:100	2.20	34	36	4.7	0.93
10:90	1.91	37	33	4.9	1.05
20:80	1.79	37	36	4.1	0.25
50:50	1.83	33	34	4.0	0.07
80:20	1.44	37	38	4.2	n.d. ^c
90:10	1.48	34	37	4.2	n.d. ^c
100:0	1.08	33	41 ^b	1.0	n.d. ^c

^aCalculated from line broadening using the Scherrer's equation [33].

^bCoTiO₃ phase was formed after the CH₄/CO₂ reaction.

^cn.d. (not detected) represents below 0.01 wt%.

Table 3.1 shows the amounts of CO chemisorbed on the reduced Co-Ni/TiO₂ with different Co/Ni ratio. The amounts of chemisorbed CO increased with increasing Ni content (Co/TiO₂: 1.08 μmol g⁻¹, Ni/TiO₂: 2.20 μmol g⁻¹). It should be noted that the values were fairly small for all catalysts (0.06-0.13% dispersion assuming CO/metal = 1 stoichiometry). This may be partly ascribed to the strong metal support interaction phenomena of TiO₂ [13,14] taking place during high temperature reduction (1123 K), discussed in the previous chapter. Alternatively, the specific surface area of the catalysts did not vary among the catalysts (for Co/TiO₂ was 5 m² g-cat⁻¹ and Ni/TiO₂, 3 m² g-cat⁻¹),

strongly depending on the structure of support TiO_2 after the reduction at 1123 K (rutile phase).

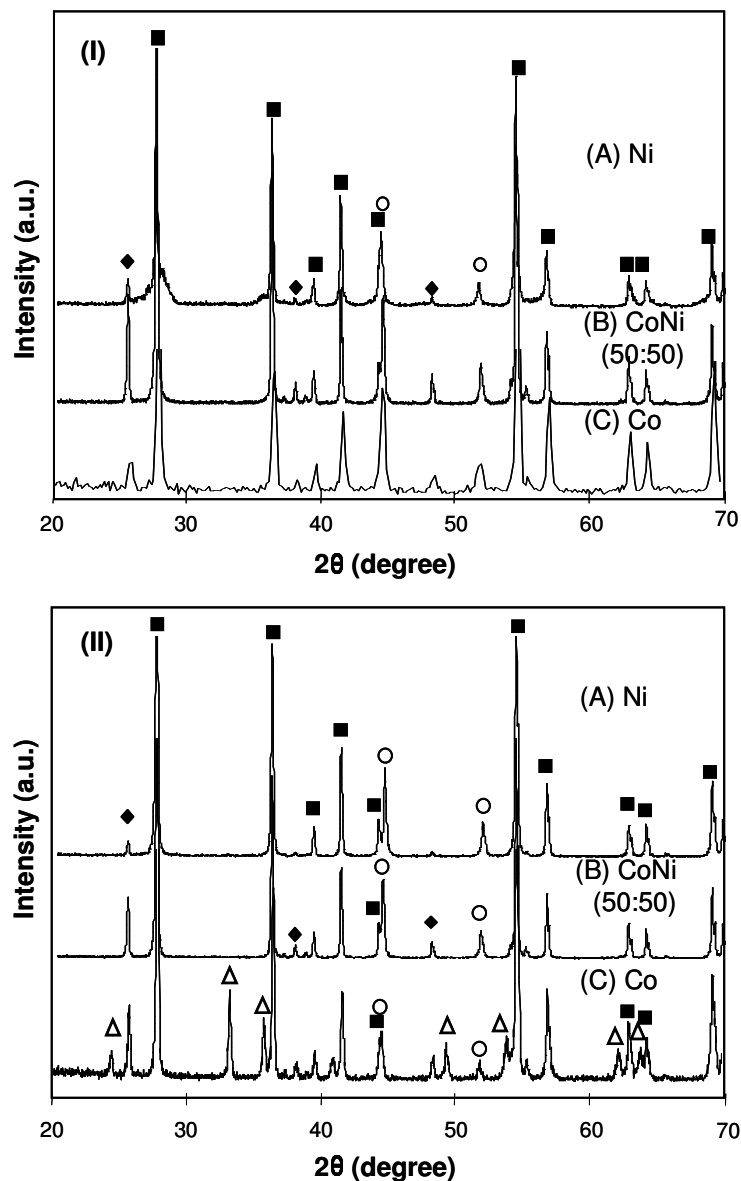


Fig. 3.2. XRD patterns for (A) Ni/TiO_2 , (B) CoNi(50:50)/TiO_2 and (C) Co/TiO_2 (I) before and (II) after the reaction. (○) Co^0 or Ni^0 ; (◆) TiO_2 -anatase; (■) TiO_2 -rutile; (Δ) CoTiO_3 .

Fig. 3.2 (I) shows the XRD patterns for Co/TiO_2 , CoNi(50:50)/TiO_2 , Ni/TiO_2 after the reduction at 1123 K. After the reduction, the metallic phase of cobalt and nickel was observed. A phase transfer of TiO_2 from anatase phase to rutile was also observed. There is hardly any difference in TiO_2 structure among these three catalysts after the reduction. In order to investigate the metallic cobalt and nickel more intensely, the narrow scanning on the metallic phase was carried out. Fig. 3.3 (I) shows the XRD

diffraction lines for the reduced catalysts. The line assigned to TiO₂ rutile (44.05°) was used as the internal standard to obtain reliable shifts of the peaks of the metals. The XRD pattern in physically mixed sample of the reduced catalysts (shown on the top of Fig. 3.3 (I)) showed two separate peaks for the metals assigned to cobalt (44.22°) and nickel (44.51°). On contrary, only one peak for the metals was observed for all the Co-Ni/TiO₂ catalysts. Fig. 3.3 (II) shows the Ni content in mol% vs. 2 θ value of the peak. It is clearly seen from Fig. 3.3 (II) that the maxima of the metallic peak were shifted in proportion to Co/Ni ratio. This reveals the formation of homogeneous alloy of Co and Ni during the reduction for all the bimetallic catalysts. On the basis of assumption that all of the cobalt and nickel formed alloy by the reduction, the crystallite sizes of the metal were estimated from XRD line broadening and are listed in Table 3.1. The crystallite sizes were comparable for all the reduced catalysts (33-37 nm).

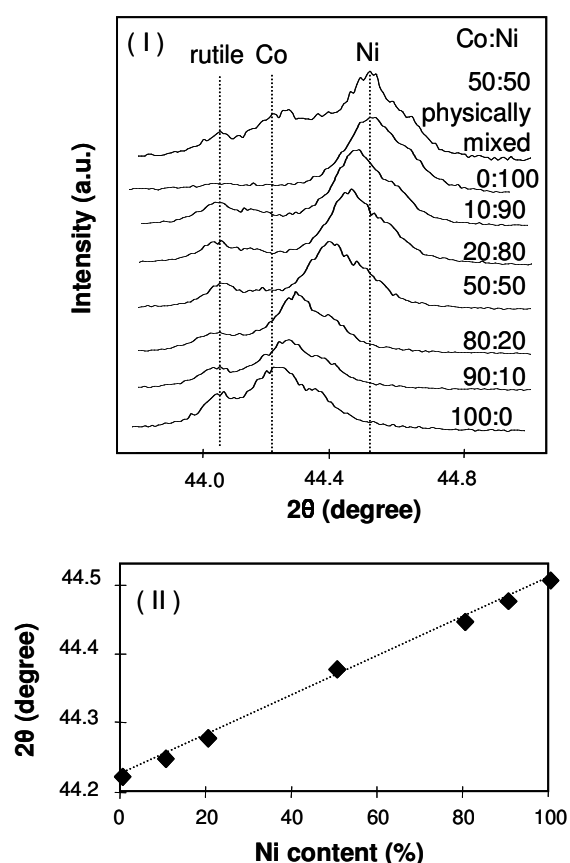


Fig. 3.3. (I) XRD patterns for the reduced Co-Ni/TiO₂ with different Co/Ni ratio and (II) Co/Ni ratio vs. peak maximum for the facet (111) of Co and/or Ni.

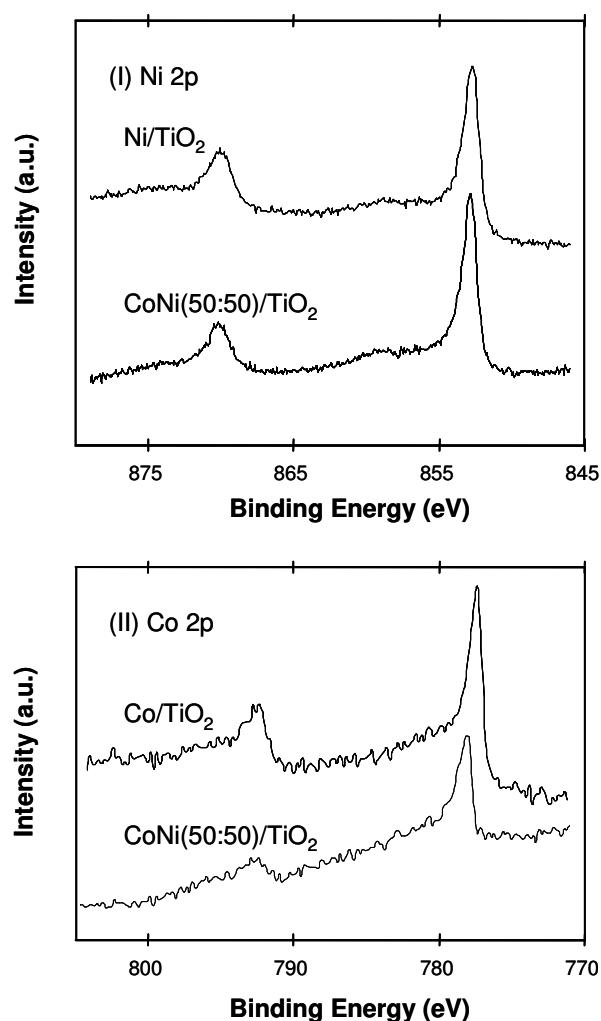


Fig. 3.4. XP spectra for reduced Ni/TiO₂, CoNi(50:50)/TiO₂ and Co/TiO₂. (I) Ni 2p. (II) Co 2p.

The XRD results indicated the formation of alloy of Co and Ni in the bulk of the catalysts. To obtain the information of surface state of the alloy, XPS analysis was carried out. Fig. 3.4 (I) shows XP spectra for Ni 2*p*. For the Ni/TiO₂ catalyst the spectrum exhibited the peak at 852.7 eV and for CoNi(50:50)/TiO₂ the peak was observed at 852.8 eV, assigned to characteristic of metallic nickel. Fig. 3.4 (II) for Co 2*p* showed the peak at 777.5 eV for Co/TiO₂ and 777.4 eV for CoNi(50:50)/TiO₂, assigned to characteristic of metallic cobalt. It is confirmed that all the metal oxides were reduced on all the catalysts. In addition, the Co/Ni ratio for CoNi(50:50)/TiO₂ was 45/55, indicating that the nearly stoichiometric surface composition of cobalt and nickel was also obtained as the bulk composition of the metals for CoNi(50:50)/TiO₂. No evidence of electronic effects by alloying cobalt and nickel, such as transfer of d-electrons between metals [28], was observed for the CoNi(50:50)/TiO₂.

3.3.2 Catalytic performance over Co-Ni/TiO₂ and the state of the used catalysts

Fig. 3.5 shows CH₄ conversion vs. time on stream over Co-Ni/TiO₂ with different Co/Ni ratio. Table 3 shows turn over frequency calculated using the CO chemisorption capacity, assuming that the surface state remains unchanged during the reaction. It can be seen from Fig. 3.5 that, while the Co/TiO₂ catalyst lost its activity during initial stage of the reaction, the CoNi(90:10)/TiO₂ showed much higher and more stable activity (CH₄ conversion: 34%). The catalytic activity increased gradually with increasing Ni content (CH₄ conversion: 50.6% for Ni/TiO₂). Remarkably, the deactivation was not observed for 24 h for all the Co-Ni/TiO₂ and Ni/TiO₂ catalysts. In terms of turn over frequency, the CoNi(90:10)/TiO₂ improved dramatically. Among the catalysts with the Co/Ni ratio of 90:10 to 20:80, the values are very similar (4.0-4.2 s⁻¹). It can be interpreted that the cobalt and nickel catalyze

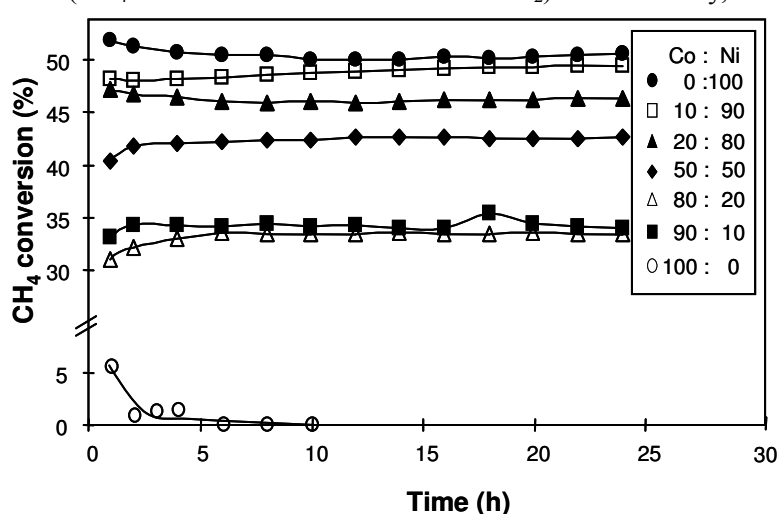


Fig. 3.5. Time on stream vs. CH₄ conversion for Co-Ni/TiO₂ with different Co/Ni ratio (Reaction conditions: CH₄/CO₂=1; 1023 K; 0.1 MPa; SV= 6000 ml g-cat⁻¹ h⁻¹).

the reaction equivalently for the reforming. The CoNi(10:90)/TiO₂ and Ni/TiO₂ catalysts showed slightly higher TOFs (4.9 and 4.7 s⁻¹, respectively). Thermodynamic equilibrium for CH₄ conversion at 1023 K is 83.4%, which is far above the observed values. In order to check whether the mass transfer limitations existed, following measurements were also carried out. First, changing catalyst weight and reactant space velocity simultaneously, so as to keep the contact time the same, did not affect conversion values. Subsequently, the same experiment conducted with smaller grain size of the catalyst did not show significant difference in conversions. It is therefore concluded that external and internal mass transfer limitations can be neglected and the measurements have been carried out under the kinetic domain.

Table 3.1 also lists the amounts of carbon deposited on the catalysts after the reaction for 24 h. The Co/TiO₂ catalyst which showed fairly low activity did not experience any carbon formation. The amounts of carbon increased with increasing Ni content in the catalyst slightly. The more carbon was formed especially over the catalysts with high nickel content, i.e., CoNi(90:10)/TiO₂ (1.05 wt%) and Ni/TiO₂ (0.93 wt%). It should be noted that yield of carbon is still negligible compared to yield of CO; for e.g., for Ni/TiO₂ the yield of carbon is approximately 0.01% whereas the yield of CO is 56.6%.

The XRD patterns for the catalysts after the catalytic tests for 24 h are shown in Fig. 3.2 (II). It can be seen for all the catalysts that TiO₂ rutile phase remained nearly the same. For Co/TiO₂, the CoTiO₃ phase was observed and the intensity of metallic cobalt phase decreased during the reaction, indicating the oxidation of cobalt took place. The metallic phases in XRD patterns after the reaction for all the bimetallic catalysts and nickel catalyst were still observed and the 2 θ values of peak maxima remained unchanged before and after the reaction (not shown), suggesting the state of the alloy was sustained during the reaction. The crystallite sizes remained constant during the reaction regardless of the Co/Ni ratio (see Table 3.1), suggesting that the degree of sintering was not significant for all the catalysts.

Long-term catalytic tests (100 h) were carried out over the CoNi(50:50)/TiO₂ and CoNi(80:20)/TiO₂ catalysts at 1023 K and at low SV of 1200 ml g-cat⁻¹ h⁻¹. Fig. 3.6 shows time on stream vs. CH₄ conversions for those catalysts. Conversions of CH₄ reached 73.6 and 68.1% for the CoNi(50:50)/TiO₂ and CoNi(80:20)/TiO₂ catalysts, respectively. The catalysts showed highly stable activities during the period of study for 100 h. The amounts of carbon deposited on the

CoNi(50:50)/TiO₂ and CoNi(80:20)/TiO₂ were very small even after 100 h test; 0.19 and 0.01 wt%, respectively. It should be noted that the amounts observed were lower than that observed on Ni/TiO₂ catalyst after 24 h-test (0.93 wt%), showing lower conversions and yields (see Fig. 3.5).

Oxidation of the metal can be a cause of deactivation, as observed in the case of

Co/TiO₂ (chapter 2). To investigate the oxidation behavior of the reduced catalysts, TPO was carried out using CO₂ and the profiles are shown in Fig. 3.7. CoNi(50:50)/TiO₂ showed a peak at around 1060 K and the peak ended below 1180 K. Compared to Co/TiO₂ catalyst (the peak at 1030 K), the temperature of the oxidation peak was 30 K higher, indicating higher tolerance to oxidation of metal. For Ni/TiO₂, oxidation temperature of nickel is much higher than that of Co/TiO₂ and CoNi(50:50)/TiO₂ (the peak at 1180 K). After the measurements, it was confirmed by XRD analysis that titanate phases were formed in all the catalysts, i.e., CoTiO₃ and NiTiO₃ (not shown).

Activation of CH₄ is considered to be the very initial and important step for the reforming [2]. Hence, CH₄ pulse reaction (in the absence of CO₂) was carried out over Ni/TiO₂, CoNi(50:50)/TiO₂ and Co/TiO₂. The results are compiled in Table 3.2. It can be seen that the activity to CH₄ decomposition (both net conversion and TON) is in the order, Ni/TiO₂ > CoNi(50:50)/TiO₂ > Co/TiO₂, indicating that the CH₄ decomposition is more facile over the catalysts with higher Ni content.

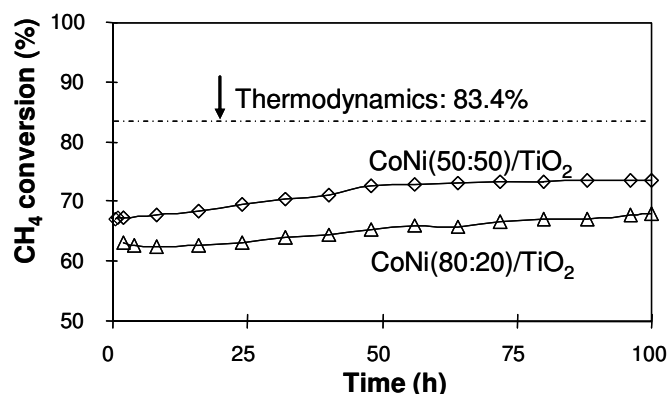


Fig. 3.6. Time on stream vs. CH₄ conversions for CoNi/TiO₂ (Reaction conditions: CH₄/CO₂=1; 1023 K; 0.1 MPa; SV= 1200 ml g-cat⁻¹ h⁻¹).

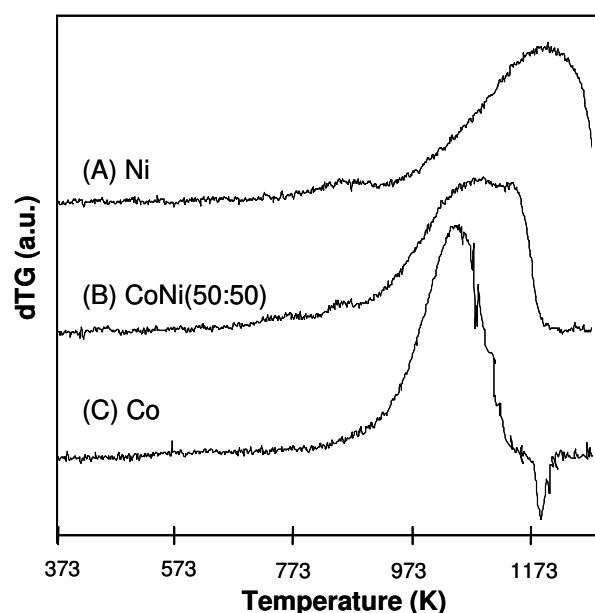


Fig. 3.7. dTG profiles of TPO in CO₂ for (A) Ni/TiO₂, (B) CoNi(50:50)/TiO₂ (C) Co/TiO₂.

3.4 Discussion

3.4.1 The state and catalytic behavior of the bimetallic Co-Ni/TiO₂ catalysts

First of all, state of the metal in the bimetallic catalysts will be discussed. The XRD analysis showed the only one peak for metallic phase for the Co-Ni/TiO₂ catalysts (Fig. 3.3 (I)). As seen in Fig. 3.3 (II), the shift of metallic peak from cobalt to nickel was observed in proportion to the Co/Ni ratio, indicating the formation of alloy in bulk of the catalysts. The surface Co/Ni composition for CoNi(50:50)/TiO₂ had a almost stoichiometric value (Co/Ni=45/55), confirmed by the XPS analysis. The formation of uniform alloy from bulk to surface can be achieved during the reduction starting from the separate NiO and Co₃O₄ phases. It was also confirmed that the state of alloy remained unchanged during the CH₄/CO₂ reforming.

The Co-Ni alloy catalysts showed highly stable activities for CH₄/CO₂ reforming. It can be seen from Fig. 3.5 that the mono-metallic Co/TiO₂ catalyst deactivated rapidly. Since no carbon formation was observed (Table 3.1) and the XRD analysis indicated the formation of the titanate phase after the reaction (Fig. 3.2 (II)(C)), the low activity and deactivation of Co/TiO₂

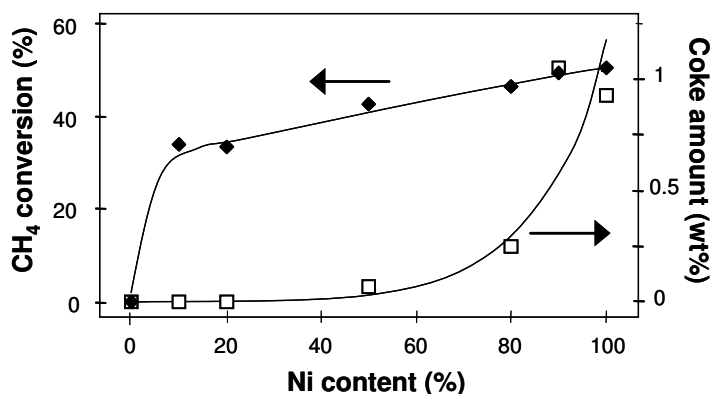


Fig. 3.8. Co/Ni ratio vs. CH₄ conversion and coke amount for Co-Ni/TiO₂ (Reaction conditions: CH₄/CO₂=1; 1023 K; 0.1 MPa; SV=6000 ml g-cat⁻¹ h⁻¹).

are attributed to the oxidation of metal, which was discussed thoroughly in the previous chapter. The small amount of substitution (10 mol%) of cobalt by nickel improved the catalytic activity and stability dramatically, suppressing the oxidation of metallic cobalt. The CH₄ conversion increased gradually with increasing Ni content (see Fig. 3.5). The carbon amount drastically increased with introducing higher Ni content (>80%). Although the carbon formed during the reaction did not cause the deactivation in this study, the accumulation of deposited carbon on the catalyst may cause the undesirable pressure drop or blockage of the reactor [1,2]. The correlation between conversions and coke amounts as a function of Ni content is shown in Fig. 3.8. It can be seen that an inhibition of oxidation observed over mono-metallic Co/TiO₂ is achieved by adding small amounts of Ni in the

catalyst, and a suppression of carbon formation which occurred over the catalyst with high Ni content is achieved by adding appropriate amounts of Co in the catalyst, i.e., there seems the ideal Co/Ni ratio which can provide the ideal operation without metal oxidation and carbon formation.

3.4.2 Nature of the Co-Ni/TiO₂ catalysts for CH₄/CO₂ reforming

Now, the parameters/ nature of the catalyst that affect the catalytic activity, stability and the carbon deposition will be discussed. From TPR spectra of the Co-Ni/TiO₂ (Fig. 3.1), the reduction of metal oxide would be complete below 800 K. The crystallite sizes of the metal before and after the reaction (Table 3.1) and BET surface areas were similar among all the catalysts. CO chemisorption capacity is the only parameter that varied for the reduced catalysts, which increased with increasing Ni content. Hence, turn over frequency (TOF) was calculated using the amounts of CO chemisorbed and compared among the catalysts. In fact, 10 mol% nickel substitution with the cobalt catalyst improved the TOF (4.2 s⁻¹), and the values remained constant even when more nickel was added up to 80 mol%. The excess of nickel in the catalyst (90-100 mol%) led to the higher TOF (4.7-4.9 s⁻¹) but also carbon formation. As can be seen in Fig. 3.8, there is no proportional relationship between the catalytic activity and Co/Ni ratio. It is more likely that the metal property was changed by forming alloy with different Co/Ni ratio, to exhibit the synergistic effects of cobalt and nickel in terms of the reactivity for the reforming.

It is generally known that CH₄ can decompose only on the metal surface, not on the support, whereas CO₂ can be activated also on the support [7,8,29]. In the current study, all Co-Ni/TiO₂ catalysts consist of the same support and same treatment, implying that the support effects should be comparable among the catalysts. Therefore, the reaction with only methane was investigated because it should reflect the metal properties directly. CH₄ pulse reaction

Table 3.2
CH₄ pulse reaction^a over Co/TiO₂, CoNi(50:50)/TiO₂ and Ni/TiO₂ (Reaction conditions: 1023 K; 0.1 MPa)

Catalyst (metal)	The amount of CH ₄ converted (μmol)	TON _{CH₄} ^b
Ni	19.37	88.1
CoNi(50:50)	12.87	70.3
Co	4.68	43.3

^a44.1 μmol of CH₄ was pulsed

^bTurn over number (TON) was calculated from the mole of the reacted CH₄ divided by the mole of the chemisorbed CO

results (Table 3.2) indicate that the CoNi(50:50)/TiO₂ catalyst showed the moderate activity between the Ni catalyst and the Co catalyst. Turn over number (TON) of CH₄ converted over the CoNi(50:50)/TiO₂ catalyst was much higher than that over the Co catalyst. It is considered that the decomposition of methane provides hydrogen to the catalyst ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$). Therefore, it is concluded that the improvement of CH₄ decomposition activity observed for the bi-metallic catalyst suppresses the oxidation of metal during the reforming. On the other hand, the Ni/TiO₂ catalyst showed even higher activity to CH₄ than CoNi(50:50)/TiO₂. Higher activity for CH₄ decomposition leaves the larger amount of coke species on the metal surface, which becomes inactive carbon and therefore, has to be removed to proceed the reforming. This control of CH₄ decomposition activity explains why the Co-Ni/TiO₂ catalyst showed higher tolerance to carbon formation than Ni/TiO₂. To conclude, the catalyst with appropriate Co/Ni ratio could inhibit both metal oxidation and carbon formation *kinetically* during CH₄/CO₂ reforming.

Furthermore, the oxidation of the Co-Ni metal alloy for CoNi(50:50)/TiO₂ took place at higher temperature than the oxidation of mono-metallic Co catalyst (see Fig. 3.7). It is suggested that the Co-Ni alloy on TiO₂ was more reluctant to be oxidized to titanate phase than mono-metallic cobalt. The formation of alloy enhances the resistance to the unfavorable oxidation of the metal, giving more stable activity for the reforming.

It is possible to control the rate of reactions between oxidative (CO₂, H₂O) and the reductive (CH₄, CO, H₂) species on the catalyst surface [26]. The results suggest that, together with the strong interaction of TiO₂ with metal, the metal surface on the catalysts with appropriate activity be designed by adjusting the appropriate composite of cobalt and nickel to avoid any deactivation of the catalyst. The beneficial effects of alloying Ni to Co for CH₄/CO₂ reforming are 1) promoting the catalytic reactivity, especially CH₄ activation on the metallic surface, and 2) improving the tolerance to the undesirable metal oxidation. The knowledge obtained through this study can be applied further to develop highly efficient catalysts for the CH₄/CO₂ reforming.

3.5 Conclusions

The long-life Co-Ni/TiO₂ catalysts without inducing carbon formation as well as metal oxidation have been developed for the CH₄/CO₂ reforming. XRD and XPS analyses revealed that homogeneous

alloy of cobalt and nickel was formed after the H₂ reduction and remained after the reaction. The monometallic Co/TiO₂ catalyst deactivated rapidly due to the oxidation of metal during the reaction. The small nickel substitution of cobalt (10 mol%) dramatically improved the catalytic activity and stability. Compared to the mono-metallic cobalt catalyst, the bimetallic catalysts improved the resistance to oxidation to form titanate and the reactivity toward CH₄ decomposition on the metal, giving the more reductive atmosphere over the catalyst (e.g., H₂ as a product). With the excess of nickel content (> 80 mol%), the catalyst showed higher activity to the CH₄ decomposition and the reforming, but also caused more carbon formation. By adjusting the ratio of cobalt and nickel loading appropriately, the catalyst provides the optimum balance between the reactions of CH₄ and CO₂.

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Chapter 4

Development of Titania Supported Cobalt Based Catalysts for High Pressure CH₄/CO₂ Reforming with High Resistance against Carbon Formation

Abstract

The 0.5 wt% Co/TiO₂ catalysts were tested for high pressure CH₄/CO₂ reaction (2.0 MPa). It was found that reduction temperature significantly affected the catalytic activity. The Co/TiO₂ reduced below 1123 K lost its activity completely at the beginning of the reaction, due to rapid accumulation of the carbon deposit which blocked the active sites. On the other hand, the Co/TiO₂ reduced at and above 1123 K kept relatively stable activity for 24 h with little amount of carbon deposit. However, the catalysts showed slow deactivation in time due to the oxidation of metallic cobalt during the CH₄/CO₂ reaction. The catalytic stability for the Co/TiO₂ was dramatically improved when trace amount of noble metal (Pt or Ru) were added into the catalysts. The strong resistant nature of Co/TiO₂ to coke deposition was also retained. It was considered that noble metals improved the reducibility of cobalt oxide. Similarly, the replacement of Co by a small amount of Ni also enhanced the catalytic stability of Co/TiO₂ although replacement by an excess of Ni resulted in the more rapid deactivation because of carbon deposit. The catalysts developed in this study exhibit high stability without forming considerable amount of carbon deposit under 2.0 MPa, where coke deposition is highly favorable.

4.1 Introduction

The dry reforming of methane to synthesis gas ($\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$) has attracted academic and industrial interests since the reaction is associated with the utilization of the natural gas fields containing CO_2 *via* gas to liquid (GTL) technology. Methane is preserved at high pressures in natural gas fields, and most of Fischer-Tropsch synthesis and methanol synthesis from synthesis gas (H_2/CO) are performed at high pressures in the GTL process. Hence, the CH_4/CO_2 reaction should also be carried out under high pressures (≥ 1.0 MPa) in such processes from an economical point of view. However, most of the researches performed the experiments with atmospheric pressure, and only a few studies were done with high pressures [1-4]. Since it is well known that higher pressure favors coking which is the major drawback for the reaction [1,2], real effectiveness of the catalysts should be discussed based on the results under high pressures.

It was found that 2 wt% Ru/ TiO_2 showed high tolerance against carbon formation even at 2.0 MPa [1]. However, ruthenium may not be suitable for an industrial use because of its limited supply. In this context, cobalt has been chosen as an active metal. As shown in chapter 2, the 10 wt% Co/ TiO_2 catalysts show strong resistance to coking for the reaction at 0.1 MPa. Thus, this catalyst was applied for the reaction at 2.0 MPa, which is a practical condition for the reforming of methane in GTL system [1]. At 2.0 MPa, however, the coking on 10 wt% Co/ TiO_2 was favored and the reactor was shortly plugged out by carbon formed, indicating that severe coking is more feasible at higher pressure, which was consistent with the earlier observation [1,2]. Hence, the loading of the cobalt was reduced to 0.5 wt% to avoid large cobalt particles to be made on which carbon deposition was considered to be feasible.

In this chapter, the catalytic behavior of the 0.5 wt% Co/ TiO_2 catalysts for CH_4/CO_2 reaction at 2.0 MPa is discussed thoroughly. Firstly, influence of reduction temperature was investigated because it can affect the catalytic activity of Co/ TiO_2 significantly as observed for the reaction at 0.1 MPa shown in chapter 2. Further, attempts to inhibit oxidation of metallic cobalt during the reaction, which was found as a cause of deactivation, were performed with two approaches; trace amounts of noble metal (Pt or Ru) were added to Co/ TiO_2 , and the cobalt was partly replaced by Ni. It is known that the addition of the noble metals and nickel can promote the reducibility of the base metals and stabilize their degree of reduction during the catalytic process [5,6].

4.2 Experimental

4.2.1 Catalyst preparation

TiO₂ (Ishihara Sangyo, A-100, 100% anatase form) was pre-calcined for 15 h at 773 K in flowing air before impregnation. The Co/TiO₂ catalysts were prepared by incipient wetness impregnation with calcined TiO₂ and an aqueous solution of Co(NO₃)₂·6H₂O (Wako Pure Chemical Industries, Ltd.) (0.005 g-Co ml⁻¹). The cobalt loading was set to 0.5 wt%. The samples were dried at room temperature for 24 h and 373 K for overnight, followed by calcination at 673 K for 4 h in flowing air to remove the nitrate from the cobalt precursor. The obtained catalyst powders were pressed into pellets at 200 bar for 5 min. The pellets were crushed and sieved to obtain grains with diameters between 0.6 and 0.9 mm. The 0.5 wt% Co/TiO₂ catalyst is denoted simply as Co/TiO₂. The Co/TiO₂ catalyst with a loading of 2 wt% was also prepared with the same procedure for X-ray diffraction (XRD) analysis.

To prepare Co/TiO₂ with additives, the calcined titania was co-impregnated in aqueous solutions of Co(NO₃)₂·6H₂O with H₂PtCl₆·6H₂O (Wako Pure Chemical Industries Ltd.), RuCl₃·nH₂O (Wako Pure Chemical Industries Ltd.), or Ni(NO₃)₂·6H₂O (Wako Pure Chemical Industries Ltd.). The Co loading was set to 0.5 wt% for Co-Pt/TiO₂ (Pt/Co = 0.005, 0.01, or 0.05 in molar ratio) and Co-Ru/TiO₂ (Ru/Co = 0.01 or 0.05 in molar ratio). For Co-Ni/TiO₂, total loading of Co and Ni was set to 0.5 wt% (Co:Ni = 1:99 to 50:50). The catalyst with the ratio (Co:Ni = m:n) is denoted as CoNi(m:n)/TiO₂. In addition, 0.5 wt% Ni/TiO₂, denoted simply as Ni/TiO₂, was also prepared in the same manner. The drying and calcination methods were the same as for Co/TiO₂.

The crystal structure of the TiO₂ in all catalysts after calcination was confirmed to be 100% anatase form by XRD analysis.

4.2.2 Activity test

The catalytic activity tests were carried out using the same setup described in chapter 2. After the catalysts were reduced *in situ* in H₂ flow at various temperatures between 973 and 1223 K for 1 h under atmospheric pressure, the temperature was adjusted in He to 1023 K. Subsequently, the pressure was increased to the reaction pressure (2.0 MPa). The reaction mixture (CH₄/CO₂ = 1, total flow rate of 50 ml min⁻¹) was introduced to the reactor to achieve space velocity (SV) of 3,000-12,000 ml g-cat⁻¹ h⁻¹. After the reaction, the catalysts were purged with He at the reaction temperature, cooled down to

room temperature, and used for the subsequent characterization.

4.2.3 Catalyst characterization

TPR measurements were carried out using 0.4 g of the calcined catalysts. TEM images were observed with a (JEOL) JEM-2010F with a 200 kV accelerating voltage. Other experimental details are described in chapter 2.

4.3 Results

4.3.1 Influence of reduction temperature on catalytic behavior of Co/TiO₂

Fig. 4.1 shows CH₄ conversions vs. time on stream for the Co/TiO₂ reduced at different temperatures. The results are summarized with specific surface areas measured after the reduction in Table 4.1. The ratio of hydrogen to carbon monoxide produced was less than 1 (= stoichiometric value for the CH₄/CO₂ reaction), indicating the occurrence of reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$). The tendencies of catalytic activities for the Co/TiO₂ were completely divided into two groups depending on the reduction temperatures. The catalysts reduced below 1123 K showed very low activity, whereas the catalysts reduced at and above 1123 K kept relatively high and stable activities for 24 h.

Fig. 4.2 shows CH₄ conversion for the Co/TiO₂ reduced at 1023 K vs. initial time on stream (within 50 min) with that for the Co/TiO₂ reduced at 1123 K (the hidden part of Fig. 4.1).

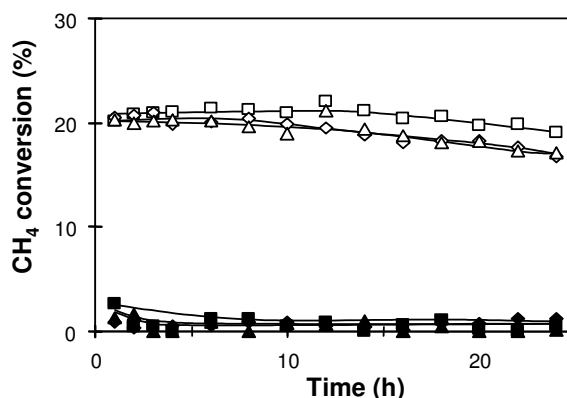


Fig. 4.1. CH₄ conversion vs. time on stream for 0.5 wt% Co/TiO₂ reduced at various temperatures (Reaction conditions: CH₄/CO₂ = 1; 1023 K; 2.0 MPa; SV = 6000 ml g-cat⁻¹ h⁻¹). Reduction temperature: (▲) 973 K; (◆) 1023 K; (■) 1073 K; (△) 1123 K, (◇) 1173 K, (□) 1223 K.

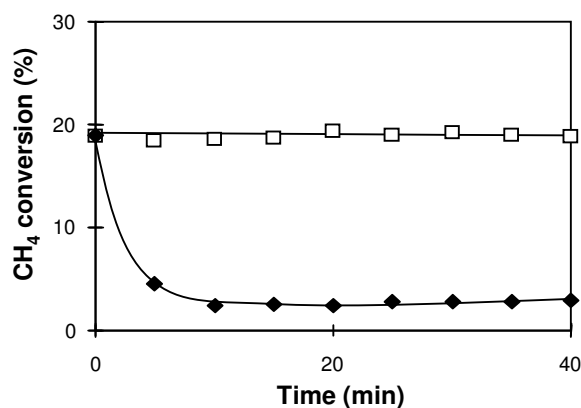


Fig. 4.2. CH₄ conversions vs. initial time on stream for 0.5 wt% Co/TiO₂ reduced at (◆) 1023 K and (□) 1123 K (Reaction conditions: CH₄/CO₂ = 1; 1023 K; 2.0 MPa; SV = 6000 ml g-cat⁻¹ h⁻¹).

Although the initial activities of the two catalysts were similar, it was found that the Co/TiO₂ reduced at 1023 K lost its activity rapidly at the beginning of the reaction. The result indicates that the rapid deactivation resulted in the very low activities for the Co/TiO₂ reduced below 1123 K in Fig. 4.1.

Table 4.1

Specific surface areas^a, and CH₄ and CO₂ conversions for 0.5 wt% Co/TiO₂ reduced at various temperatures (Reaction conditions: CH₄/CO₂ = 1; 1023 K; 2.0 MPa; SV = 6000 ml g-cat⁻¹ h⁻¹)

Reaction temperature (K)	Specific surface area (m ² g-cat ⁻¹)	Time (h)	Conversion (%)		Yield (%)	
			CH ₄	CO ₂	CO	H ₂
973	10	1	1.3	3.9	2.6	0.2
		24	0.1	1.5	0.8	0.1
1023	11	1	0.9	3.9	2.4	0.4
		24	0.2	1.2	0.7	0.1
1073	9	1	0.4	2.7	1.6	0.1
		24	0.8	0.5	2.7	0.1
1123	5	1	20.3	35.1	27.9	8.6
		24	17.1	29.5	23.5	6.5
1173	4	1	20.5	35.3	28.0	8.8
		24	16.7	30.1	23.6	6.8
1223	3	1	20.2	34.8	27.6	8.3
		24	19.1	32.1	25.7	7.4

^ameasured after the reduction

The amounts of coke were measured after the reaction for 24 h and are shown in Table 4.2. The tendencies of coking for the Co/TiO₂ catalysts were also divided into two groups. Large amounts of coke (2.9 wt% carbon) were detected on the Co/TiO₂ reduced below 1123 K. On the other hand, the amount of coke on the Co/TiO₂ reduced at and above 1123 K was not significant and much lower (0.25 wt% carbon) than on the Co/TiO₂ reduced below 1123 K. Especially, the catalyst reduced at 1123 K experienced only a slight amount of coke (0.02 wt% carbon).

TEM observation was performed to investigate the natures of the coke on the Co/TiO₂ reduced below 1123 K (Fig. 4.3). Electron micrographs of Co/TiO₂ after the CH₄/CO₂ reaction for 24 h

following to the reduction at 1023 K showed the formation of whisker and encapsulating carbons on the surface of the catalyst (formation of carbon was confirmed by an energy dispersive spectroscopy (EDS) analysis). On the other hand, coke was not visible in the TEM image and not detected by EDS on the Co/TiO₂ after the reaction for 24 h following to the reduction at 1123 K, which was in agreement with the slight amount of coke on the catalyst (Table 4.2).

Table 4.2

Coke amount for 0.5 wt% Co/TiO₂ reduced at various temperatures (Reaction conditions: CH₄/CO₂ = 1; 1023 K; 2.0 MPa; SV = 6000 ml g-cat⁻¹ h⁻¹)

Reduction temperature (K)	Coke amount (wt%)
973	2.90
1023	3.41
1073	4.26
1123	0.02
1173	0.25
1223	0.21

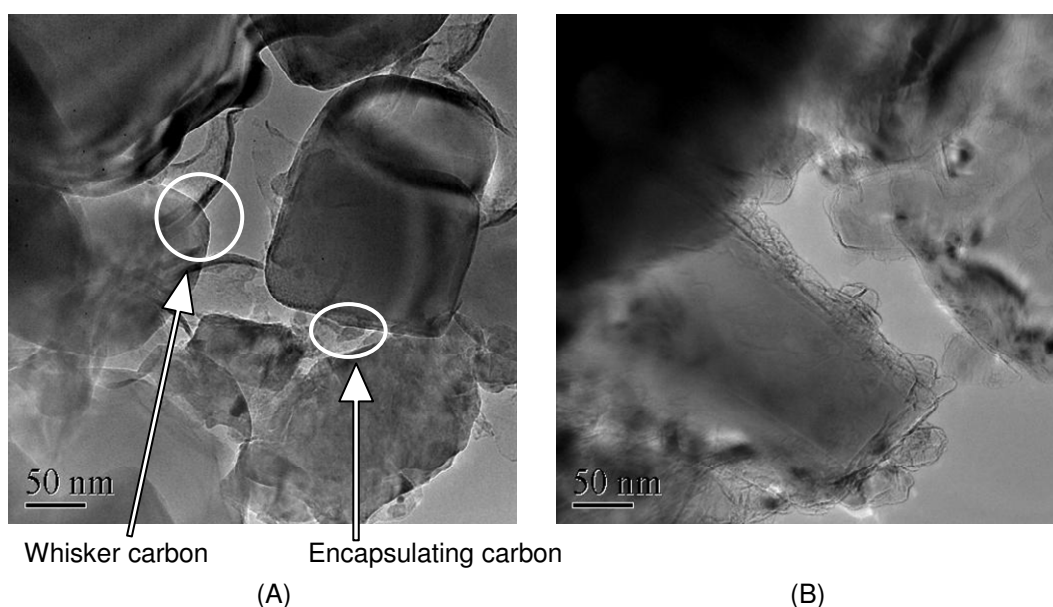


Fig. 4.3. TEM photographs for 0.5 wt% Co/TiO₂ after the reaction for 24 h following to the reduction at 1023 K (A) and 1123 K (B) (Reaction conditions: CH₄/CO₂ = 1; 1023 K; 2.0 MPa; SV = 6000 ml g-cat⁻¹ h⁻¹).

TPR profiles for the TiO₂ calcined at 773 K and the Co/TiO₂ calcined at 673 K are shown in Fig. 4.4. A small uptake of H₂ was observable for TiO₂ without metal, which indicates the reduction of the TiO₂ as follows; TiO₂ + xH₂ → TiO_{2-x} + xH₂O. Four peaks were visible for the Co/TiO₂ (589, 660, 747, and 1030 K) and the ratio of O/Co calculated from the net amount of H₂ uptake for the first three

peaks and all the peaks were approximately 1.4 and 3.6, respectively. These results suggest that H_2 uptake observed below 873 K would be ascribed to reduction of cobalt species (Co_3O_4 , CoO , and $CoTiO_3$ -like species) [7] and cobalt exist mainly as Co_3O_4 on 0.5 wt% Co/TiO_2 after the calcination at 673 K. A large uptake of H_2 above 873 K can be ascribed to the reduction of the TiO_2 . The amount of TiO_2 reduced on the Co/TiO_2

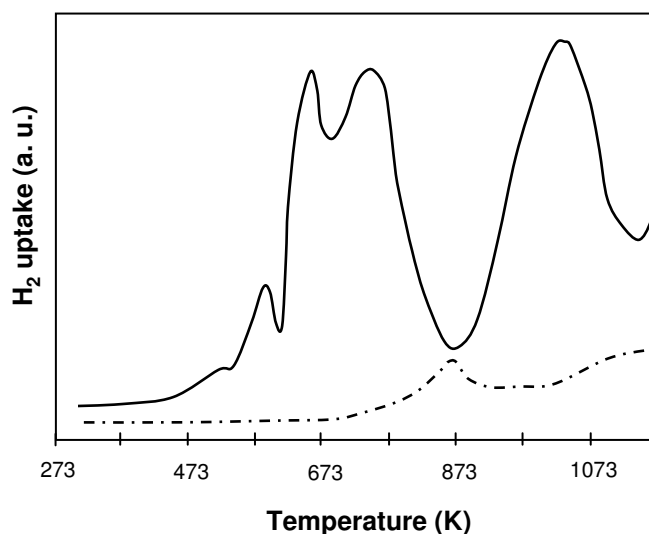


Fig. 4.4. TPR profiles of TiO_2 (broken line) and 0.5 wt% Co/TiO_2 (solid line).

was much higher than on the TiO_2 without metal, and this could be due to the spilt-over hydrogen originated from metallic cobalt [8]. The TPR results showed that all cobalt oxide species supported on TiO_2 were reduced to the metallic state by the reduction at 873 K, indicating that all cobalt in the catalysts was present as reduced metal before the reaction, regardless of the reduction temperature.

XRD patterns for the Co/TiO_2 after the reduction and after the subsequent reaction are shown in Fig. 4.5. The cobalt loading in the catalysts was so low that cobalt species were not detected by XRD on any samples. The initial phase of TiO_2 , i.e. anatase-type, was retained after reduction below 1123 K, whereas it was mostly transformed to rutile-type by reduction at and above 1123 K. The phase transition was followed by a decrease of specific surface area (Table 4.1). The TiO_2 phase after the reduction was mostly maintained during the CH_4/CO_2 reaction for most of the catalysts, except for the catalyst reduced at 1073 K.

4.3.2 Influence of SV on catalytic behavior for Co/TiO_2

Fig. 4.6 shows CH_4 conversions vs. time on stream at different SVs for the Co/TiO_2 reduced at 1123 K. Table 4.3 summarizes the catalytic results and the amounts of coke during the CH_4/CO_2 reaction. In order to compare the degree of catalytic stability, Table 4.3 includes the stability ratio, which is defined as the difference between the initial and final CH_4 conversion with respect to the initial one (i.e., the value increases with increasing stability). The initial activity decreased with

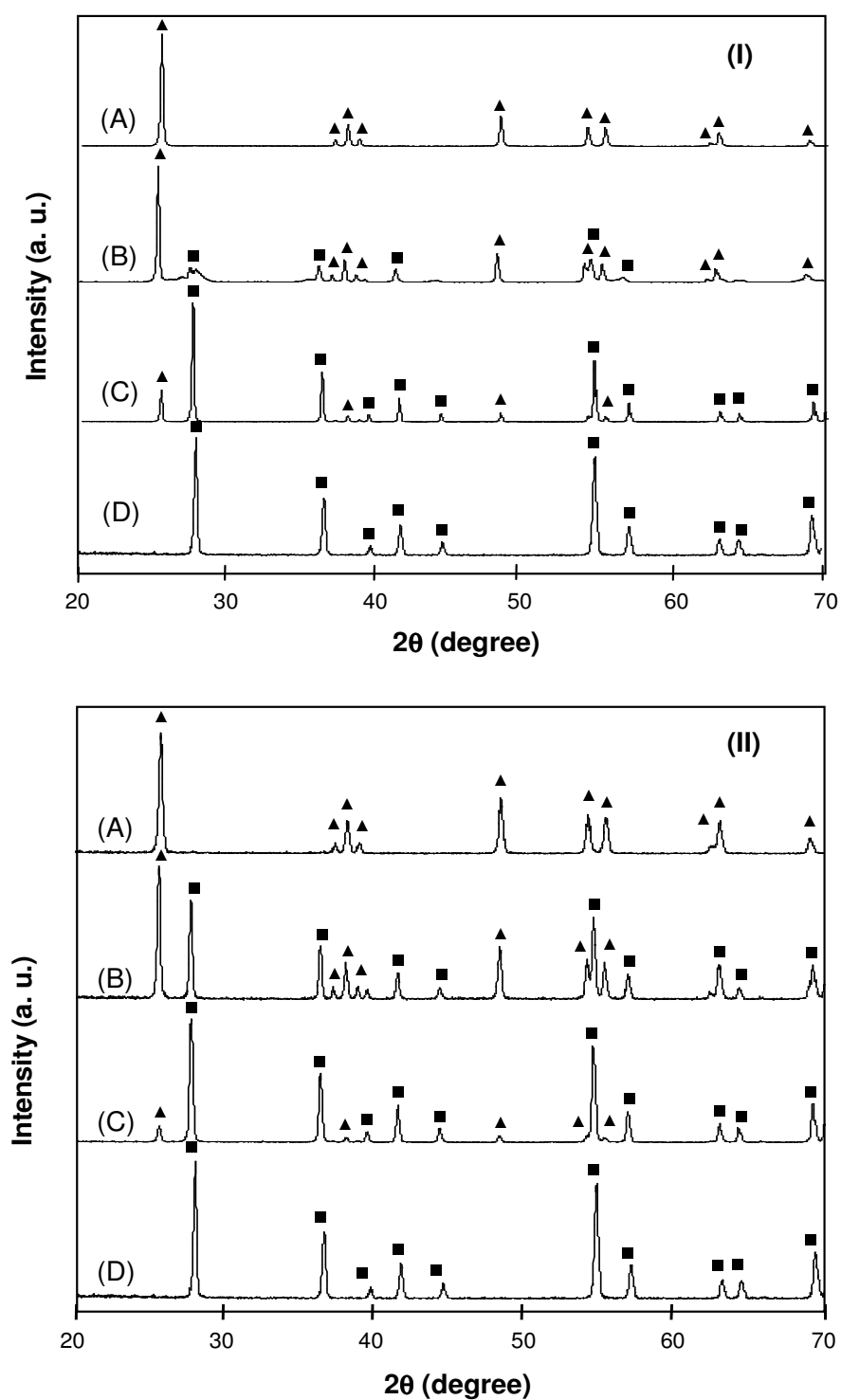


Fig. 4.5. XRD patterns for 0.5 wt% Co/TiO₂ (I) after reduction at various temperatures and (II) after reaction following to the reduction at various temperatures. Reduction temperature: (A) 1023 K; (B) 1073 K; (C) 1123 K; (D) 1173 K. (▲) TiO₂-anatase; (■) TiO₂-rutile.

increasing SV. However, initial CH_4 conversion at the SV of 3000 ml $\text{g-cat}^{-1} \text{h}^{-1}$ was 23.0% (34.6% at equilibrium) and was not so much different from that at the SV of 6000 ml $\text{g-cat}^{-1} \text{h}^{-1}$. There are several possible factors causing this phenomenon, e.g., inhabitation by accelerated reverse reforming ($2\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{CO}_2$), or mass transfer limitation. On the other hand, at a SV of 12,000 ml $\text{g-cat}^{-1} \text{h}^{-1}$, the

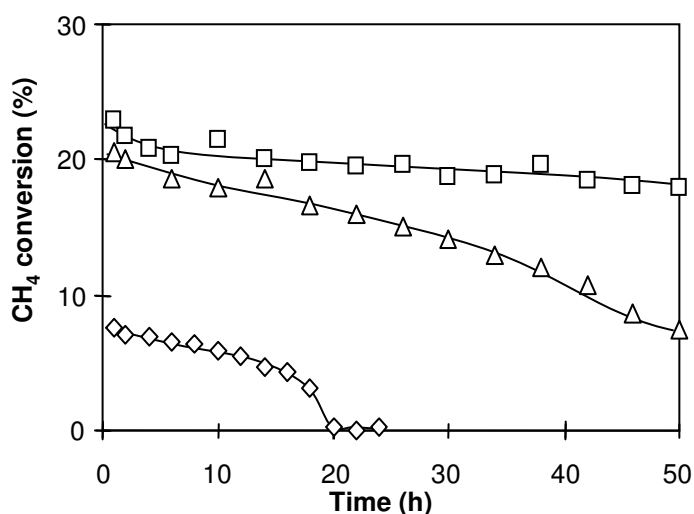


Fig. 4.6. CH_4 conversion at different SV vs. time on stream for 0.5 wt% Co/TiO₂ reduced at 1123 K (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1$; 1023 K; 2.0 MPa). SV: (□) 3000 ml $\text{g-cat}^{-1} \text{h}^{-1}$; (△) 6000 ml $\text{g-cat}^{-1} \text{h}^{-1}$; (◇) 12000 ml $\text{g-cat}^{-1} \text{h}^{-1}$.

deactivation of the catalyst became observable more clearly and the activity was lost completely after the reaction for 20 h. It was found that the amounts of carbon deposit were very small (<0.1 wt%) after the reaction for 24 h regardless of SV, indicating that the deactivation in time was not due to the carbon deposition. Based on the knowledge obtained in the study (chapter 2), the oxidation of metallic cobalt may be a main cause of the deactivation.

It should be noted that, after the treatment of the catalyst reduced at 1123 K with CO_2 ($\text{CO}_2/\text{He} = 1$, 2.0

MPa, 1023 K, 1 h, SV=12 000 ml $\text{g-cat}^{-1} \text{h}^{-1}$), the catalyst did

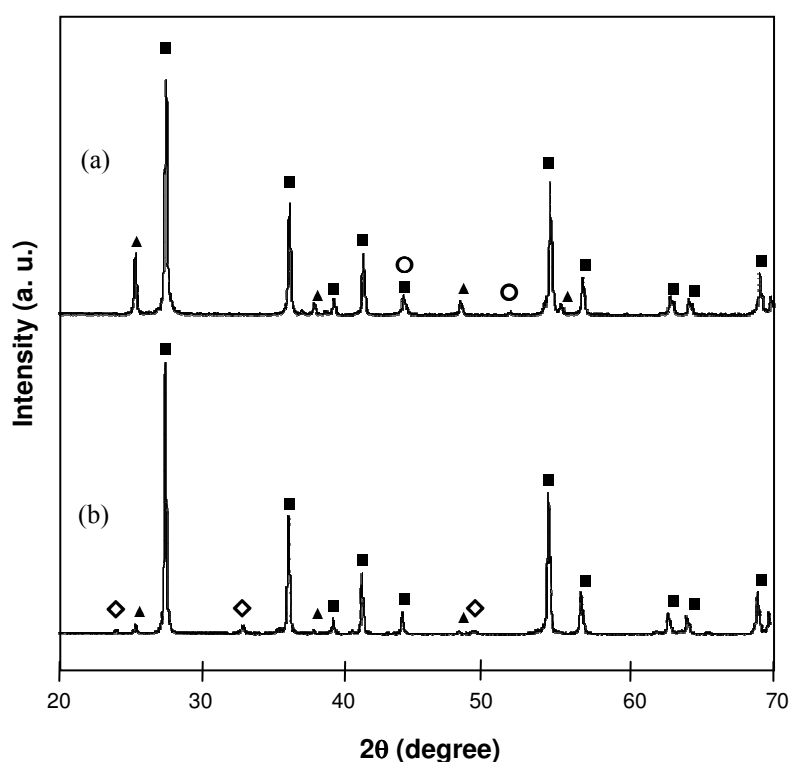


Fig. 4.7. XRD patterns for 2 wt% Co/TiO₂ (a) after reduction at 1123 K and (b) after the subsequent exposure to CO_2/He at 1023 K for 1 h. (▲) TiO₂-anatase; (■) TiO₂-rutile; (○) metallic Co; (◇) CoTiO₃.

not show any catalytic activity for CH_4/CO_2 reforming, indicating that metallic Co was oxidized by CO_2 and that the oxidized Co was inactive for the CH_4/CO_2 reaction. In this context, the crystal structure of the oxidized Co was attempted to assign with XRD measurements. However, the XRD patterns for Co/TiO_2 did not show peaks of the Co species, probably due to the small loading of Co (0.5 wt%). Therefore, 2 wt% Co/TiO_2 was prepared and XRD measurements were performed after the H_2 reduction and after the subsequent CO_2 treatment at 1023 K (Fig. 4.7). After the CO_2 treatment the metallic Co, which was observable after the H_2 reduction, was not detected and a phase of complex oxide, CoTiO_3 , was observed. This implies that the metallic cobalt in Co/TiO_2 is oxidized to CoTiO_3 by CO_2 . Further details regarding oxidation of cobalt will be discussed later in discussion section.

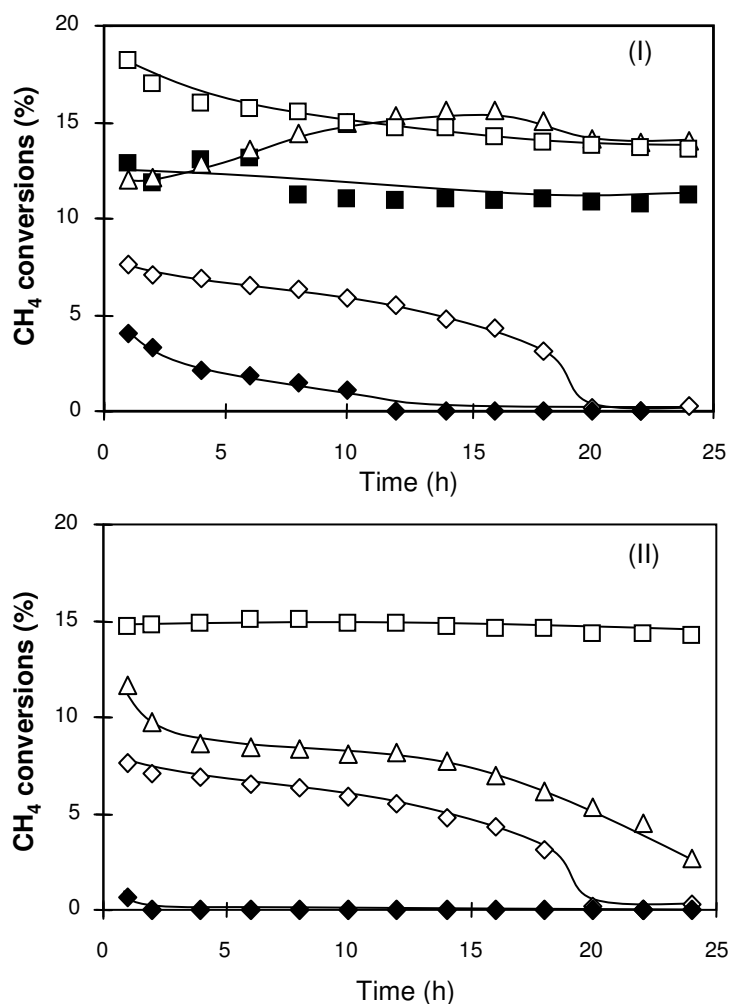


Fig. 4.8. CH_4 conversion vs. time on stream for (I) $\text{Co-Pt}/\text{TiO}_2$ and (II) $\text{Co-Ru}/\text{TiO}_2$ (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1$; 1023 K; 2.0 MPa; $\text{SV} = 12000 \text{ ml g}^{-1} \text{ h}^{-1}$ except for Pt/TiO_2 and Ru/TiO_2 of $6000 \text{ ml g}^{-1} \text{ h}^{-1}$). Additive/Co: ($\diamond$) only Co; ($\blacksquare$) 0.005; ($\triangle$) 0.01; ($\square$) 0.05; ($\blacklozenge$) only noble metal (loading of noble metals is identical to that of $\text{Co-(Pt or Ru)}/\text{TiO}_2$ (additive/Co = 0.05)).

4.3.3 Effects of addition of noble metals to Co/TiO_2

Small amounts of Pt or Ru were added to Co/TiO_2 and their influence on the catalytic activity and stability was studied. Fig. 4.8 and Table 4.3 show the results of catalytic tests at the SV of $12000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$. The stability of Co/TiO_2 was improved drastically by a trace amount of Pt ($\text{Pt}/\text{Co}=0.005$)

and all Co-Pt/TiO₂ showed stable activities for 24 h (Fig. 4.8 (I)). The stability of Co-Ru/TiO₂ was improved with increasing the amount of Ru and Co-Ru/TiO₂ (Ru/Co=0.05) showed high stability for 24 h (Fig. 4.8 (II)). Comparing the effectiveness of Pt and Ru as additives, it can be said that Pt was superior to Ru since a trace amount of Pt (Pt/Co=0.005) improved the catalytic stability more efficiently than the double amount of Ru (Ru/Co=0.01). The activities of TiO₂-supported noble metal catalysts were rather low even at the lower SV of 6000 ml g-cat⁻¹ h⁻¹. In addition, the amounts of coke deposited on the catalysts were not significant (≤ 0.25 wt%) after the reaction. Such results demonstrate that the strong resistance of Co/TiO₂ to coking was retained after the addition of noble metals.

Fig. 4.9 shows TPR profile for noble metal-promoted Co/TiO₂. For all Co/TiO₂ with noble metals presented three peaks observed below 873 K, which can be attributed to the reduction of Co oxides (Co₃O₄, CoO and/or CoTiO₃-like species) [7,9], which were based on the amount of H₂ consumption during the TPR measurement. It is surmised that the third peaks should be ascribed to very small Co oxide clusters which have strong interactions with TiO₂ or small surface Co species which include support atoms in the structure [10], i.e., CoTiO₃-like species [7]. On the other hand, H₂ uptake above 873 K was

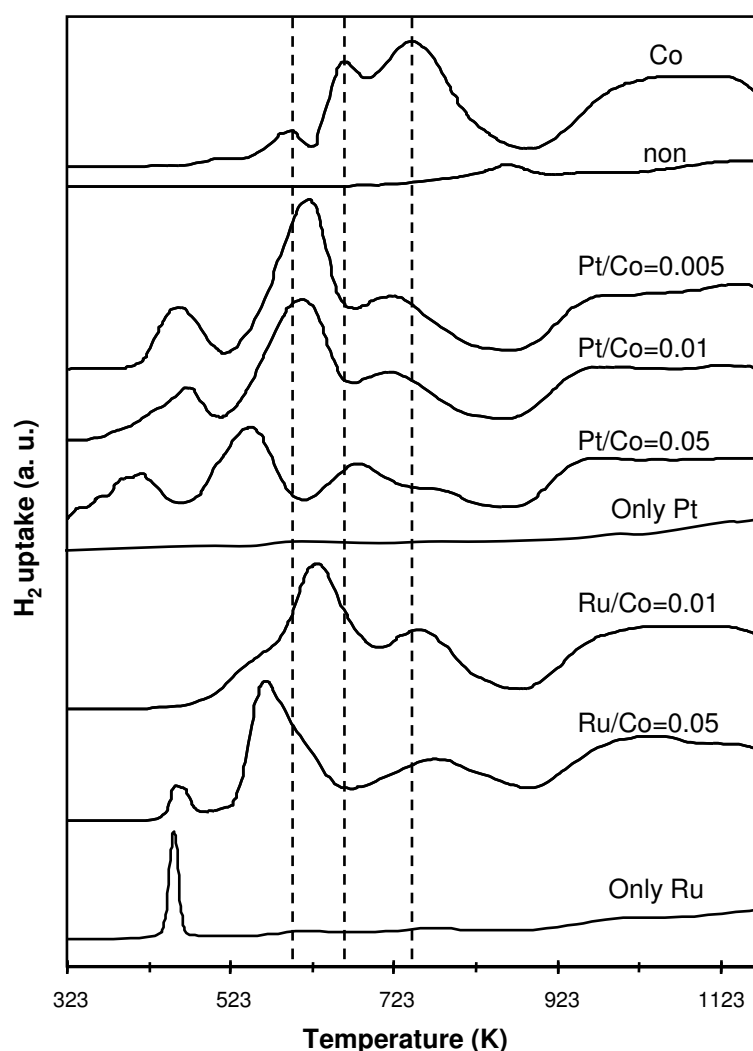


Fig. 4.9. TPR profiles of Co/TiO₂, TiO₂ (denoted as none), Co-Pt/TiO₂, Pt/TiO₂ where loading of Pt is identical to that of Co-Pt/TiO₂ (Pt/Co = 0.05), Co-Ru/TiO₂, and Ru/TiO₂ where loading of Ru is identical to that of Co-Ru/TiO₂ (Ru/Co = 0.05).

attributed to the reduction of TiO_2 . No peaks were observable for Pt/TiO_2 , implying that platinum might already be reduced before starting TPR measurement, whereas a single peak assigned to the formation of metallic Ru was viewable at 373 K for Ru/TiO_2 .

4.3.4 Effects of replacement of Co by Ni in Co/TiO_2

A part of Co in Co/TiO_2 was replaced by Ni and the activity tests were carried out at the SV of $12000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$. The results are shown in Fig. 4.10 and Table 4.3. Although $\text{CoNi}(95:5)/\text{TiO}_2$ showed complete deactivation after the reaction for 24 h, the addition of a higher amount of Ni ($\text{CoNi}(90:10)/\text{TiO}_2$) enhanced the catalytic stability greatly and the amount of deposited coke was also insignificant. It must be mentioned that the activity of Co/TiO_2 was improved with the replacement of Co by Ni. However, it can also be said that noble metals were more effective in retarding the oxidation of metallic Co than that of Ni because Co/TiO_2 with noble metals (noble metal/Co=0.05) showed higher stability than CoNi/TiO_2 (Co:Ni=95:5).

The influence of the Co:Ni ratio was additionally investigated at the lower SV of $6000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$ (Fig. 4.11, Table 4.3). The catalytic stability was initially increased with the increase of the Ni

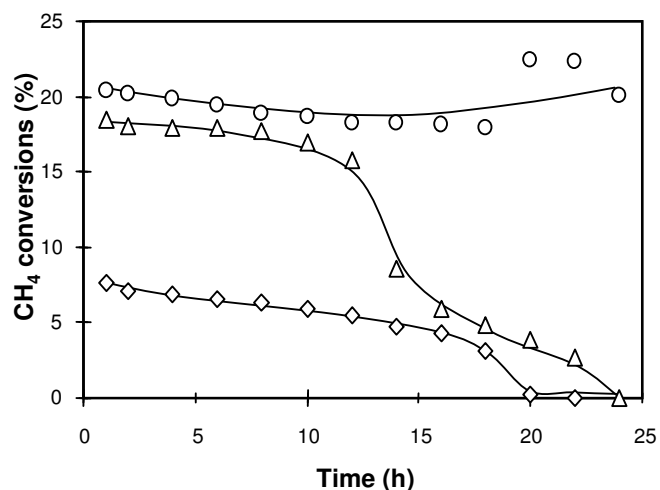


Fig. 4.10. CH_4 conversion vs. time on stream for Co/TiO_2 and CoNi/TiO_2 (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1$; 1023 K; 2.0 MPa; SV = $12000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$). Co:Ni: ($\diamond$) 100:0; ($\triangle$) 95:5; ($\circ$) 90:10.

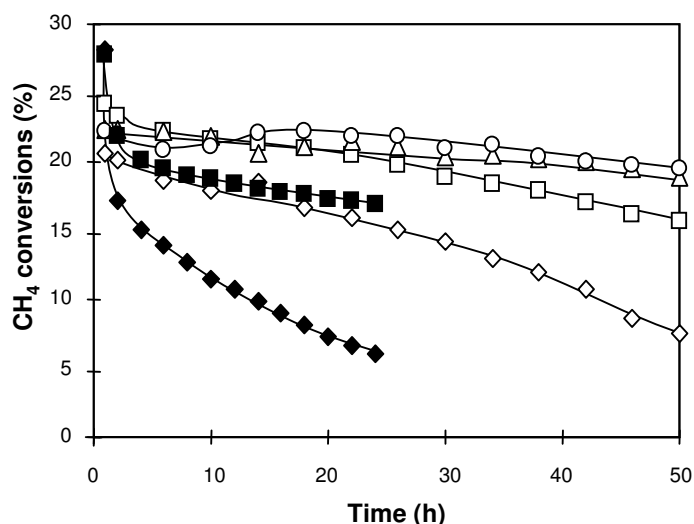


Fig. 4.11. CH_4 conversion vs. time on stream for Co/TiO_2 , CoNi/TiO_2 , and Ni/TiO_2 (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1$; 1023 K; 2.0 MPa; SV = $6000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$). Co:Ni: ($\diamond$) 100:0; ($\square$) 99:1 ($\triangle$) 95:5; ($\circ$) 90:10; ($\blacksquare$) 50:50; ($\blacklozenge$) 0:100.

loading up to the Co:Ni ratio of 90:10, but decreased with further replacement by Ni. On the other hand, the amount of deposited coke was increased by the addition of Ni and more than 7 wt% of coke was accumulated over CoNi/TiO₂ (Co:Ni=50:50) and Ni/TiO₂ after the reaction continued for 24 h.

Table 4.3
Conversions, coke amount, and stability ratio for TiO₂ supported mono- and bi-metallic catalysts
(Reaction conditions: CH₄/CO₂ = 1; 1023 K; 2.0 MPa)

Metal	Specific surface area ^a (m ² g-cat ⁻¹)	SV (ml g-cat ⁻¹ h ⁻¹)	Time (h)	Conversion (%)		Coke amount (wt%)	Stability ratio ^b (%)
				CH ₄	CO ₂		
Co	4.4	12000	1	7.6	18.1		
			24	0.0	0.0	0.01	0
		6000	1	20.6	34.0		
			50	7.5	14.5	0.1	36
		3000	1	23.0	35.9		
Co-Pt (Pt/Co=0.005)	°	12000	1	12.9	24.1		
			24	11.2	21.9	0.08	87
		12000	1	12.0	22.9		
			24	14.0	26.3	0.21	117
		12000	1	18.1	30.4		
Co-Pt (Pt/Co=0.05)	°	12000	1	18.1	30.4		
			24	13.6	24.9	0.08	75
		6000	1	2.5	4.1		
			24	0.0	0.0	0.18	0
		12000	1	11.6	20.3		
Co-Ru (Ru/Co=0.01)	°	12000	1	11.6	20.3		
			24	2.7	6.3	0.25	23
		12000	1	14.7	28.8		
			24	14.2	28.6	n.d.	97
		6000	1	0.6	3.8		
CoNi(99:1)	°	6000	1	0.6	3.8		
			24	0.0	0.0	0.04	0
		6000	1	24.1	38.1		
			50	15.7	27.1	0.67	65
		12000	1	18.4	30.9		
CoNi(95:5)	°	12000	1	18.4	30.9		
			24	0.0	0.0	0.36	0
		6000	1	22.4	36.2		
			50	18.9	30.4	1.02	84
		12000	1	20.3	33.8		
CoNi(90:10)	°	12000	1	20.3	33.8		
			24	20.1	32.8	0.15	99
		6000	1	22.3	36.5		
			50	19.5	33.2	0.67	87
		4.4	1	27.7	39.3		
CoNi(50:50)	4.4	6000	1	27.7	39.3		
			24	16.9	29.3	7.74	61
		6000	1	28.2	35.1		
			24	6.1	12.4	18.11	22
		6.2	1	28.2	35.1		
Ni	6.2	6000	1	28.2	35.1		
			24	6.1	12.4	18.11	22

^aMeasured after the reduction

^bDefined as the difference between the initial (after 1 h) and final CH₄ conversions with respect to the initial one and multiplied by 100.

^cNot measured

Fig. 4.12 shows TPR profiles of Co/TiO₂, CoNi/TiO₂ and Ni/TiO₂. Two peaks were observed for Ni/TiO₂, with peak maxima at approximately 650 and 853 K. By calculating the H₂ consumption during the TPR measurement, the former and latter peaks were ascribed to the reduction of NiO and TiO₂, respectively. The peak attributed to the reduction of NiO was in the middle of the first and the second peaks for Co/TiO₂. CoNi/TiO₂ exhibited

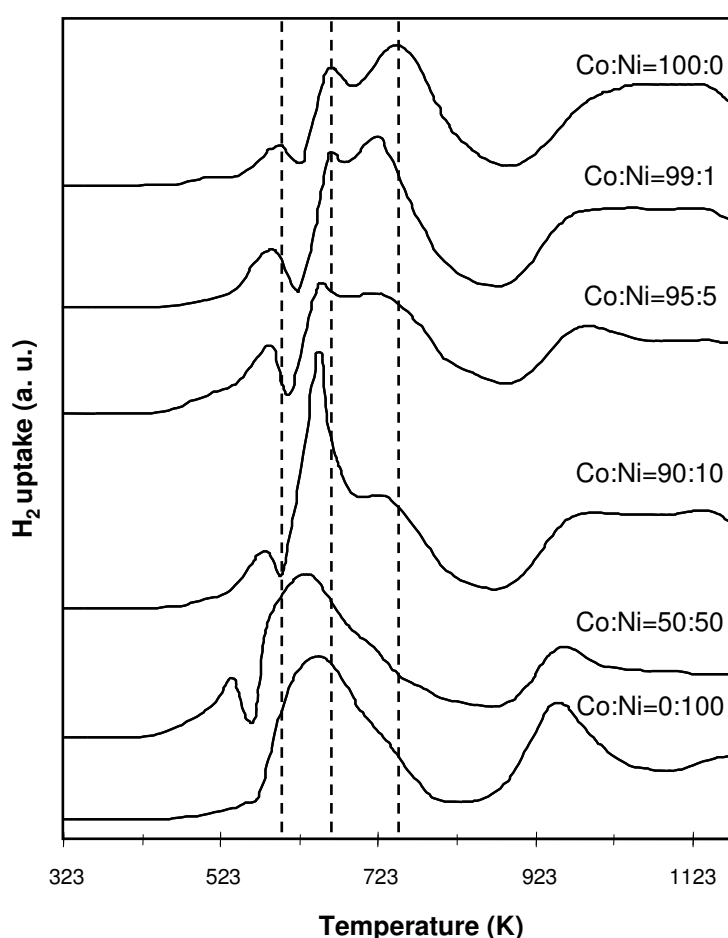


Fig. 4.12. TPR profiles of CoNi/TiO₂ with different Co/Ni ratios.

overlapping reduction peaks for Co and Ni oxides in the TPR profiles. For CoNi/TiO₂ peak

maxima ascribed to the Co oxides were slightly shifted to lower temperatures and the peak maximum for the reduction of metal oxide for CoNi/TiO₂ (Co:Ni=50:50) is lower than that of Ni/TiO₂ and Co/TiO₂.

4.4 Discussion

4.4.1 Influence of reduction temperature on catalytic behavior of Co/TiO₂

The Co/TiO₂ reduced below 1123 K and the Co/TiO₂ reduced at and above 1123 K showed different tendencies of the catalytic activities (Fig. 4.1) and the amount of coke deposit (Table 4.2). Although the initial activities of the catalysts reduced at 1023 and 1123 K were similar, the Co/TiO₂ reduced at 1023 K lost its activity rapidly at the beginning of the reaction (Fig. 4.2) and experienced a marked coking (Table 4.2). TEM of the catalyst after the CH₄/CO₂ reaction revealed the formation of

whisker and encapsulating carbons on the surface of the catalyst (Fig. 4.3). Hence, it seems that catalyst deactivation was associated with the carbon deposition. In chapter 2, it was reported that higher temperature reduction (≥ 1123 K) resulted in oxidation of metallic cobalt more easily during CH_4/CO_2 reaction at 0.1 MPa than lower temperature reduction (≤ 1073 K). In the current work, the Co/TiO_2 reduced at and above 1123 K showed relatively stable activity at the same conditions (Fig. 4.1). Therefore, it is reasonable to consider that the rapid deactivation of the Co/TiO_2 reduced at 1023 K would not be due to the oxidation of the metallic cobalt. Although the cause of the rapid deactivation of the Co/TiO_2 reduced below 1123 K is still not clear, it would be either coking on active sites or sintering of metallic cobalt and the results suggested that the deactivation would be related, at least, to the blockage of the active sites by carbon deposit.

4.4.2 Influence of reduction temperature on the nature of Co/TiO_2

The results of TPR showed that all cobalt in Co/TiO_2 was reduced below 873 K (Fig. 4.4) and, thus, the reduction degree of cobalt after the reduction was 100% and identical among the all catalysts. To compare the particle size of metallic cobalt after the reduction, TEM observations (Fig. 4.3) and XRD measurements (Fig. 4.5) were carried out. However, metallic cobalt was not observable probably due to a lack of contrast between cobalt and titania for TEM observation and due to the very low loading of cobalt in the catalysts for TEM observation and XRD analysis. The higher reduction temperature possibly causes the sintering of metallic cobalt, so that the particle of metallic cobalt might be smaller on the Co/TiO_2 reduced below 1123 K than on the Co/TiO_2 reduced at and above 1123 K. In addition, smaller particles are well known to contribute to the inhibition of the coking [11-14]. However, the results in the current work showed the opposite tendency, i.e., larger amounts of coke were deposited on the catalysts reduced at higher temperatures, which might possess smaller particles of metallic cobalt (Table 4.2). Therefore, the catalytic behavior caused by the different reduction temperature would not be related to the reduction degree of the cobalt and particle size of metallic cobalt.

The results of XRD indicated that the phase transition of TiO_2 from anatase- to rutile-type occurred during the reduction between 1073 and 1123 K for the Co/TiO_2 (Fig. 4.5). Hence, the reduction temperature which deduced large differences in catalytic behavior would correspond to that

of the phase transition from anatase- to rutile-type of the TiO_2 , i.e. the ‘transition’ might contribute to the inhibition of the rapid deactivation and coking. It has been addressed that the interaction between metal and support affects strongly the catalytic behavior of the catalysts for the CH_4/CO_2 reaction [1,15-25]. It has been reported that TiO_2 supported metal catalysts exhibit suppressed coke formation during CH_4/CO_2 reaction [1, 15-22], probably due to the presence of mobile TiO_x species on the metal particles (strong metal support interaction) [26,27], which destroy large ensembles of the metal atoms that are active for coke deposition and due to the promotion of the CO_2 activation at the metal/ TiO_x boundary [16,17,22]. In addition, Bradford and Vannice have reported that the activity of TiO_x/Pt increased with increasing TiO_x coverage [20]. As the reduction temperature increased, the amounts of the decoration of cobalt by TiO_x would increase and its nature can be drastically changed. The changes of the cobalt/ TiO_x boundary, which were brought about by the reduction at and above 1123 K, might be critical to the catalytic behavior of the Co/TiO_2 and correlate with the phase transition of TiO_2 from anatase- to rutile-type.

4.4.3 Oxidation of metallic cobalt causing deactivation during CH_4/CO_2 reforming

Co/TiO_2 reduced at 1123 K showed relatively high activity with little amount of carbon deposit. However, the catalyst showed mild deactivation in time, observable at higher SV. The amount of deposited carbon on the catalyst was very small, indicating that the deactivation was not due to carbon deposition. Thus it would be mainly due to the oxidation of metallic cobalt or sintering of the Co particles. To investigate the cause of the deactivation, the initial activities were measured over Co/TiO_2 after different treatments (Fig.

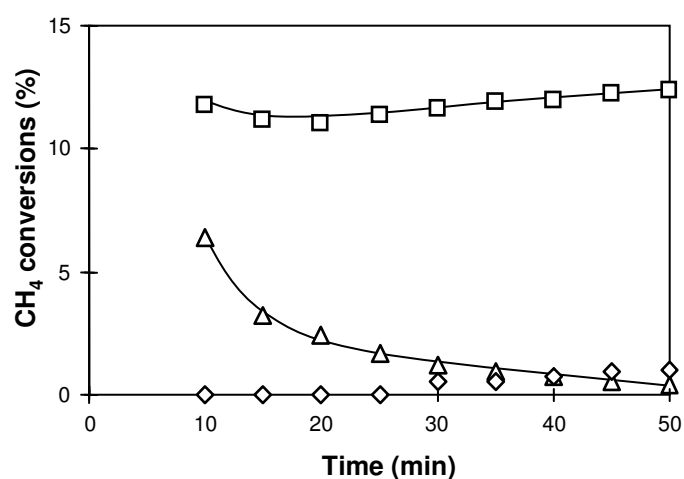


Fig. 4.13. CH_4 conversion vs. time on stream for Co/TiO_2 after different treatments following the H_2 reduction at 1123 K (Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1$; 1023 K; 2.0 MPa; $\text{SV} = 12000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$). Treatments: (Δ) $\text{CH}_4/\text{CO}_2 = 1$, 1023 K, 2.0 MPa, 24 h $\rightarrow \text{H}_2$, 1123 K, 0.1 MPa, 1 h; ($\square$) $\text{CO}_2/\text{He} = 1$, 1023 K, 2.0 MPa, 1 h $\rightarrow \text{H}_2$, 1123 K, 0.1 MPa, 1 h; ($\diamond$) $\text{CO}_2/\text{He} = 1$, 1023 K, 2.0 MPa, 1 h $\rightarrow \text{He}$, 1023 K, 2.0 MPa, 23 h $\rightarrow \text{H}_2$, 1123 K, 0.1 MPa, 1 h.

4.13). Note that CH₄ conversion at 10 min in the figure can be regarded as the initial activities for these catalysts, because it took approximately 10 min for the gases to be detected in the system after introducing the CH₄/CO₂ gas to the reactor.

If the deactivation of freshly reduced Co/TiO₂ during the CH₄/CO₂ reaction is due to the oxidation of the metallic Co, the catalyst can be regenerated by H₂ reduction. After Co/TiO₂ lost its activity completely due to the CH₄/CO₂ reaction (SV = 12000 ml g-cat⁻¹ h⁻¹) for 24 h (Fig. 4.6), the catalyst was re-reduced at 1123 K and then the initial activity (SV = 12000 ml g-cat⁻¹ h⁻¹) was measured. Since the initial CH₄ conversion for the freshly reduced catalyst was 8.5%, approximately 75% of the initial conversion for the catalyst was recovered by the regeneration (Fig. 4.13). This observation suggests that the slow deactivation of the freshly reduced Co/TiO₂ can be ascribed to oxidation of the metallic Co. However, the regenerated catalyst showed deactivation immediately and lost most of its activity within 1 h. To understand the nature of the regenerated catalyst, the initial activity was measured for Co/TiO₂ after H₂ reduction at 1123 K, following the CO₂ treatment for 1 h. The initial activity of freshly reduced Co/TiO₂ was completely recovered or rather improved when the catalyst was reduced immediately after the CO₂ treatment (Fig. 4.13). It has been reported that nickel dissolved in crystalline mixed oxide structure, such as perovskite, is reduced to well-dispersed Ni particles, and that the catalyst shows high and stable activity for the methane reforming reactions (reviewed by Takehira [28]). He mentioned that the formation of the well-dispersed Ni particles is due to the thermal evolution of nickel species from the corresponding cations homogeneously distributed in the inert perovskite matrix, where interaction between the Ni species and support material is so strong that it can inhibit the aggregation of the Ni species. According to this, it can be considered that immediate re-reduction following oxidation by CO₂ over reduced Co/TiO₂ may cause the formation of CoTiO₃ and subsequent reduction would possibly give better-dispersed Co particles, which resulted in the enhanced initial activity of Co/TiO₂. On the contrary, when reduced Co/TiO₂ had been kept ('aging') for 23 h in He after the CO₂ treatment, the activity was hardly recovered by re-reduction, indicating that the aging process in He induced very low activity to Co/TiO₂. Two kinds of possibilities can be considered to describe this phenomenon. First, it can be deduced that the CoTiO₃ formed was not reduced by the re-reduction. It is generally known that it is difficult for the metal cations in crystalline mixed metal compounds to reduce to the metal state, due to the strong interaction with the support

material [28]. The interaction may be somewhat increased by reconstruction of Co cations in TiO_2 during the aging process. Alternatively, it can be speculated that the Co particles formed by the re-reduction were too small to maintain their activity and the Co particles were rapidly oxidized. This may also be caused by reconstruction of Co cations during the aging process. Although any additional data to elucidate the assumptions at the present stage was not obtained, at least the results showed that the aging process brought about reconstruction of the catalyst and were accounted for deducing the large differences in catalytic behavior. In addition, this observation may suggest that the reconstruction of active sites by oxidation-reduction process is critical to the catalytic behavior and that optimization of this process can lead to enhanced catalytic behavior. Due to the aging effects, only 75% of the activity for the freshly reduced catalyst was restored by the re-reduction, after the catalyst lost its activity completely due to the CH_4/CO_2 reaction. The rapid deactivation of the catalyst may be due to the formation of small Co particles which were easily oxidized to CoTiO_3 during the CH_4/CO_2 reaction.

4.4.4 Effects of noble metal addition to Co/TiO₂

Co/TiO_2 reduced at 1123 K showed slow deactivation in time (Fig. 4.6), probably due to the oxidation of metallic cobalt. By adding small amount of noble metal into Co/TiO_2 , the catalytic stability was drastically improved (Fig. 4.8). From TPR profiles (Fig. 4.9), the peak maxima were shifted to much lower temperatures as the amount of noble metals increased. In addition, the temperature for the reduction of TiO_2 also decreased by the addition of noble metals. This effect was independent of the sorts and amounts of noble metals. Furthermore, the ratios of the second to the third peaks were much higher for promoted Co/TiO_2 than those for unpromoted Co/TiO_2 . Hence, the results suggest that the number of Co oxides interacting strongly with TiO_2 were reduced by the addition of noble metals. These observations suggest that the addition of both noble metals results in the decrease of the reduction temperature of Co oxides and titania, presumably due to hydrogen spilt-over from the noble metal surface [29,30]. It is well known that small amounts of noble metals can promote the reducibility of the base metal, such as Ni, and also stabilize the reduced state during the catalytic reaction [5,6]. For instance, the oxidation of Ni for the Ni-MgO catalyst in the CH_4/CO_2 reaction was diminished by addition of small amounts of noble metals [13]. Thus, it can be considered

that under the CH₄/CO₂ reaction, noble metal addition to Co/TiO₂ should maintain the catalyst surface reduced, promoting the activation of hydrogen produced and the spilt-over of it, and therefore, the catalyst would show stable activity.

For Pt-promoted catalysts, all peaks for Co oxides were shifted to lower temperatures. For Ru-promoted catalysts, the third peaks were not affected by the addition of Ru and only the other two peaks were shifted to lower temperatures. However, it must be noted that the peak for Co oxides interacting strongly with TiO₂ was shifted only by the addition of Pt. It can be mentioned that Pt promoted the reduction of Co oxides more effectively than Ru, resulting in well-enhanced catalytic stability for Co-Pt/TiO₂.

Further, it should be noted that the catalytic activity was also enhanced by adding promoters. This can be because generated metal particles for bi-metal catalysts are probably improved compared to those for mono-metal catalysts, and/or because formation of alloys in bi-metal catalysts [29-31]. Attempts with XRD measurement, TEM observation and CO chemisorption were also made to measure particle size and dispersion of metal species for the catalysts studied; however, none of them were successful due to the low loadings of the metals. Hence, any information about the influence of noble metals on the geometry of the metallic Co cannot be provided. In spite of this, the fact is that the initial activities of Co/TiO₂ with noble metals (noble metal/Co = 0.05) were higher than the sum of the activities of noble metals supported on TiO₂ (the activities were measured at the lower SV of 6000 ml g-cat⁻¹ h⁻¹) and Co/TiO₂ (Fig. 4.8 and Table 4.1). These results indicate that the improvement of catalytic stability results not only from the nature of noble metals themselves but also from synergistic effects between noble metals and cobalt supported on titania.

To conclude this section, the enhancement of reducibility of the catalysts during the reaction, as well as the possible improvement of metal dispersion by adding noble metal promoters would contribute to improving the catalytic activity and stability of the catalysts for CH₄/CO₂ reforming.

4.4.5 Effects of replacement of Co with Ni in Co/TiO₂

From TPR profile (Fig. 4.12), the reduction peaks were shifted slightly to lower temperatures for the bimetallic CoNi/TiO₂ compared to the mono-metallic catalysts. The results also suggest that reduction of the Co oxides were slightly promoted by the replacement of Co by Ni. The phenomenon

implies that there might be an interaction between Co and Ni in the bi-metal catalysts, which can result in an unusual trend, different from the trend of mono-metals.

The results for catalytic activity (Fig. 4.11) and coke amount (Table 4.3) imply that deactivation would be due to the oxidation of the metals for the Co-dominant catalysts, whereas deactivation would be caused by the coking for the Ni-dominant catalysts. As discussed in chapter 2 and 3, the trend can be interpreted that the rate of activation of oxidative species (CO_2 , H_2O) is more rapid than the rate of activation of reductive species (CH_4 , CO , H_2) on the Co/TiO_2 catalyst, and for Ni/TiO_2 , *visa versa*. The replacement of Co by Ni in Co/TiO_2 brings about an increase in the relative reaction rate of the reductive species against the oxidative species. Hence, replacement by Ni contributes to retarding the oxidation of the metallic Co; however, too much nickel induces coke deposition from the carbon species. The observation is in agreement with the results of Choudhary et al. [32,33], showing that the addition of Co to a supported Ni catalyst causes a drastic reduction in the coke deposition in the CH_4/CO_2 reaction. The reactions between reductive and oxidative reactants are balanced over CoNi/TiO_2 with an optimum Co:Ni ratio (10:90 in this study) and thus the catalyst showed high stability without a significant amount of coke deposit, even under the condition at high pressure of 2.0 MPa where coke formation is highly favorable.

4.5 Conclusions

The catalytic behavior during the CH_4/CO_2 reaction under 2.0 MPa was investigated for the 0.5 wt% Co/TiO_2 . It was found that reduction temperature significantly affected the catalytic activity and the amount of carbon deposit. The Co/TiO_2 reduced below 1123 K showed rapid and complete deactivation at the beginning of the reaction. Since the catalyst experienced a marked coking during the reaction, the deactivation would be correlated to the coking on the active sites. On the other hand, the Co/TiO_2 reduced at and above 1123 K showed relatively stable activity at the same reaction condition. Especially, the catalyst reduced at 1123 K experienced only a slight amount of coke. However, slow deactivation of the catalyst in time during CH_4/CO_2 reforming was observed for Co/TiO_2 . The deactivation was ascribed to the oxidation of metallic Co. The addition of trace amounts of noble metals (Pt or Ru) to Co/TiO_2 improved the catalytic stability drastically. The strong resistant nature of Co/TiO_2 to coke deposition was also retained by the catalysts. Noble metals appeared to

improve the reducibility of cobalt, which may play an important role in preventing the oxidation of metallic Co during the CH₄/CO₂ reaction. The replacement of Co by small amounts of Ni in Co/TiO₂ also enhanced the catalytic stability by inhibiting the oxidation of metallic Co, but replacement by an excess amount of Ni resulted in the decrease of stability due to serious coke deposition. CoNi/TiO₂ with an optimum Co:Ni ratio (10:90 in this study) showed high stability without a significant amount of carbon deposit. It is proposed that the reactions between the reductive and oxidative reactants are balanced kinetically over the catalyst containing proper amounts of Co and Ni, even under the high pressure of 2.0 MPa where coke formation is thermodynamically highly favorable.

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Chapter 5

Hydrogen Production *via* Steam Reforming of Biomass Related Oxygenates over Pt Catalysts: Acetic Acid as a Model Compound

Abstract

Catalytic steam reforming of acetic acid, as a model oxygenate derived from biomass, was studied over supported Pt catalysts. Pt/ZrO₂ catalysts are very active, completely converting acetic acid and give hydrogen yield close to thermodynamic equilibrium. The catalyst deactivated by formation of oligomers which block the active sites. The mechanism of both the reaction and deactivation was studied with kinetic and spectroscopic measurements on Pt/ZrO₂, ZrO₂, and Pt black. It is shown that Pt is essential for steam reforming to proceed. ZrO₂ is needed to activate steam. It is suggested that both Pt and the support are involved in the activation of acetic acid and water, respectively. This manifests in different intrinsic activity for Pt when anchored on different supports. Accordingly, the reforming proceeds most likely at the boundary between the Pt and the support and the number of Pt sites that are in the close proximity of the support determine hydrogen formation rates. On the other hand, ZrO₂ is also active for oligomer-precursor formation under conditions investigated and deactivation occurs for steam reforming when the Pt-support boundary is blocked by oligomers.

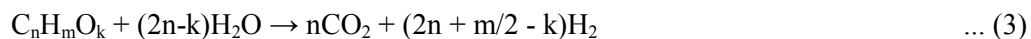
5.1 Introduction

Currently, there is tremendous interest in the use of hydrogen as a clean fuel, especially for power generation with fuel cells. Hydrogen production from sustainable sources, e.g., biomass, is gaining attention for a CO₂ neutral energy supply [1-3]. The main route to the production of hydrogen commercially at present is catalytic steam reforming (SR) of methane (Eq. 1) followed by water gas shift (WGS) reaction (Eq. 2).



The process is well established, and the aspects of chemistry, catalysts, reactor engineering and other details can be found in an excellent review by Rostrup-Nielsen [4]. Steam reforming is an endothermic reaction, favored thermodynamically at elevated temperatures (>820 K) and is catalyzed by metallic Ni supported on high surface area mixed oxides derived from γ -alumina, alkali and alkaline earth oxides.

Biomass, as a source for hydrogen, is a sustainable alternative to fossil hydrocarbons. However, biomass is a complex mixture of organic polymers, made up of ligno-cellulose and has an average chemical composition of CH_{1.47}O_{0.65} [5]. Thus, design of catalysts for its conversion is not straight forward. Recent developments in flash pyrolysis technologies make it possible to convert lignocellulosic biomass efficiently to a bio-oil, which is easier for handling and transport [6]. The bio-oil so generated contains a variety of aliphatic and aromatic oxygenates (aldehydes, ketones, acids, alcohols). The most promising option to generate hydrogen from bio-oil is *via* catalytic steam reforming followed by water gas shift reaction, since these reaction steps maximize hydrogen yield. The reaction can be represented in general as shown below.



Attempts to convert bio-oil to syngas (CO/H₂ mixtures) using commercial steam reforming catalysts have been severely hindered by rapid catalyst deactivation due to coke/oligomer deposition on the catalysts [7] even in the presence of excess of steam (H₂O/C > 5). There is thus a strong incentive at the moment to develop stable and active catalysts for steam reforming of bio-oil.

Bio-oil is a complex mixture of oxygenates. Thus, design of an efficient catalyst requires the use of model oxygenate components to establish structure activity correlations. Acetic acid (CH₃COOH,

AcOH) is one of the major components of bio-oil (up to 32 wt%) [8], and thus, chosen as a model compound in this study.

Supported noble metal (Pt, Rh) catalysts show promise over the conventional Ni based catalysts for conversion of biomass to syngas [9]. Therefore, this study pertains to the steam reforming of AcOH over supported Pt catalysts. Steam reforming and water gas shift reaction (Eq. 2) occur simultaneously and the overall stoichiometry is represented (Eq. 4),



The purpose of this study is to elucidate the reaction and deactivation mechanisms and to provide a knowledge base for the design of active and stable catalysts.

5.2 Methods

5.2.1 Catalyst preparation

ZrO₂ (monoclinic, Daiichi Kigenso Kagaku Kogyo, RC100, calcined at 1125 K), Al₂O₃ (Akzo Novel 000-3AQ, calcined at 925K for γ phase, at 1475K for α phase), MgO (Ube Industries), and SiO₂ (Degussa, Aerosil 380) were used as supports. The calcined support was firstly isostatically pressed into pellets at 400 MPa for 5 min. The pellets were crushed and sieved to give grains having diameters between 0.3 and 0.6 mm. The grains were impregnated with an aqueous solution of H₂PtCl₆·6H₂O (Alfa Aesar, 0.01 g Pt per ml) to yield a catalyst with 0.5 wt% Pt (except for Pt/ZrO₂, four catalysts were prepared in the range, 0.5-2.0 wt% Pt). The catalyst was dried at 325 K for 2 h in a rotating evaporator followed by drying over night at 395 K in static air. Subsequently, the impregnated grains were calcined at 775 K (except for 925 K for Pt/ZrO₂ catalysts) for 15 h (heating rate 5 K min⁻¹). Specific surface areas and hydrogen chemisorption capacities (H/Pt) of the catalysts are compiled in Table 5.1. ZrO₂ has a surface area of 21 m² g⁻¹ after calcination. Pt black powder (Acros Organics, >97.5%(Pt)) was used as received (alkali (K, Na) <0.4%) and has hydrogen chemisorption capacity (H/Pt) of 0.001 after reduction at 925 K.

5.2.2 Catalytic measurements

The setup used is drawn in Fig. 5.1. For continuous flow experiments, 10-50 mg of catalysts were loaded in a fixed bed reactor and held by quartz wool plugs. The catalyst was first reduced in 5% H₂ in

N_2 at 925 K with a total flow rate of 50 ml min^{-1} . Then the gas was purged with Ar at a flow rate of 30 ml min^{-1} . An aqueous solution of AcOH giving a steam to carbon molar ratio (S/C) of 5 was introduced by using a microfeeder (KD Scientific) and a syringe (Hamilton co.). The feed was adjusted in by-pass mode, prior to the experiment, to obtain constant $\text{AcOH}/\text{H}_2\text{O}/\text{N}_2/\text{Ar}$ ($= 3/30/5/82$ or $6/60/5/169 \text{ ml min}^{-1}$, N_2 as an internal standard). This gives weight hourly space velocity (WHSV) for AcOH 9.0 or 90 h^{-1} , and total gas hourly space velocity (GHSV) 160,000 or $1,600,000 \text{ h}^{-1}$. The system was heated at 425 K to avoid condensation of reactants and products. After purging the catalysts with inert gas (Ar), the mixture of reactants was introduced to the reactor. For analysis, a flame ionization detector (FID) and a Hayesep Q column were used for AcOH, acetone (CH_3COCH_3), ketene (CH_2CO), and hydrocarbons; a thermal conductivity detector (TCD) and a Carbosieve column were used for H_2 , N_2 , CO, CH_4 , and CO_2 . The gases were collected in multi-sampling loops drawn in Fig. 5.2 and analyzed later if required.

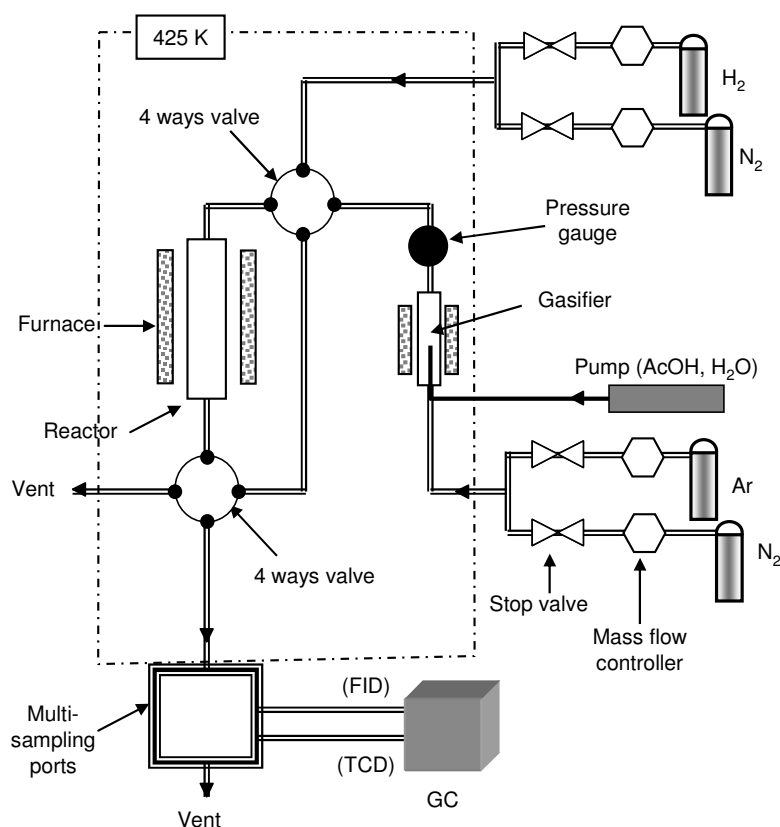


Fig. 5.1. Schematic representation of the setup for activity test.

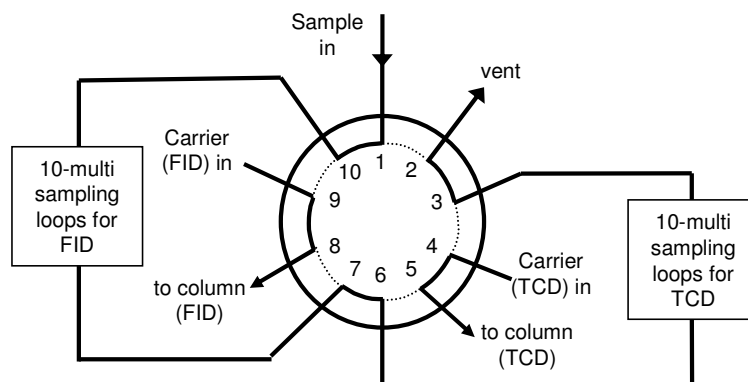


Fig. 5.2. The schematic of multi sampling ports for GC analyses. The gases were collected in multi sampling loops and analyzed later if required.

Pulse experiments were performed with 20 mg of Pt/ZrO₂ or ZrO₂, or 10 mg of Pt black dispersed in quartz wool. After reduction at 925 K, the system was purged in Ar at a flow rate of 37.5 ml min⁻¹. Pulses of 0.2 µl of AcOH or 0.61 µl of AcOH aqueous solution (S/C = 5) at 293 K were introduced. Both type of pulses contained 3.5 µmol of AcOH.

The hydrogen yields were calculated based on Eq. 4. For carbon containing compounds, the yields were calculated based on C₁ equivalent values, e.g., acetone (C₃H₆O) yield was calculated as three times the number of moles produced divided by two times the number moles of AcOH fed.

Thermodynamic equilibrium conversions and yields were calculated using the HSC, Outokump program by specifying reactants and products (H₂O, CH₄, CO, CO₂, H₂ and all possible oxygenates including acetone). However, the only products which had non- zero concentrations at equilibrium at 725 K were H₂O, CH₄, CO, CO₂, and H₂.

5.2.3 Catalyst characterization

H₂ chemisorption measurements were carried out in a volumetric system with 1 g of Pt/ZrO₂ catalyst or 100 mg of Pt black. The sample was reduced at 925 K in H₂ for 1 h. After reduction the sample was degassed at 925 K in vacuum (10⁻⁶ mbar). The sample was cooled to room temperature (293 K) and the H₂ adsorption isotherm was measured by introducing H₂ to the sample. After the first isotherm the sample was again degassed at room temperature, followed by the second H₂ adsorption isotherm. The hydrogen chemisorption capacity was calculated by extrapolation of the hydrogen uptake, which corresponded to the difference of the first and second isotherms, to zero pressure [10].

Thermogravimetry (TG) (Mettler Toledo TGA/SDTA 851E) was used to determine the amount of

deposits in the catalysts. The catalysts used for the reaction were heated from room temperature to 1075 K in 1%O₂/Ar.

IR spectra were recorded *in situ* under vacuum by using a transmission spectrometer (Bruker, Vector 22) with a MCT detector. The schematic drawing of the setup and the cell is shown in Fig. 5.3 and 5.4, respectively. The catalyst reduced *ex situ* at 925 K was pressed into pellet and loaded in a miniature cell, equipped with CaF₂ transparent windows. The cell can be evacuated to pressures below 10⁻⁷ mbar. The catalyst was firstly reduced *in situ* by introducing 0.1 mbar of H₂ at 725 K. After evacuation, oxygenates and steam were introduced into the system with an S/C molar ratio of 5 at a total pressure of 0.1 mbar at 725 K. Each spectrum consists of 32 scans taken at 4 cm⁻¹ resolution. More details will be described wherever necessary.

Transmission electron microscopy (TEM) (Philips CM30) observation was carried out to determine particle sizes and morphology of platinum.

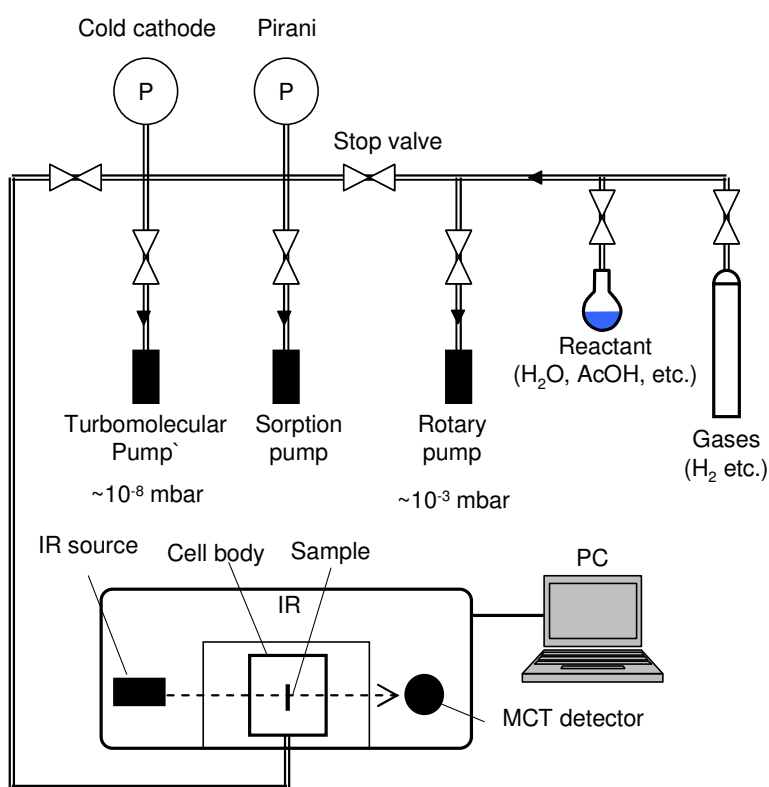


Fig. 5.3. Schematic representation of the IR vacuum setup.

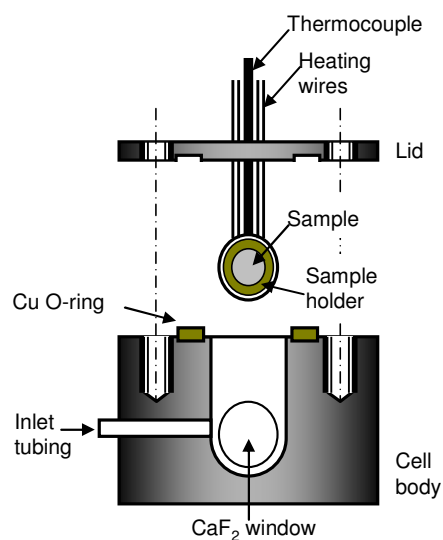


Fig. 5.4. Schematic representation of the high vacuum IR cell.

5.3 Results

5.3.1 Initial activity tests over Pt supported on various oxides

Table 5.1 shows the rates of hydrogen formation over Pt catalysts based on different supports. Steam reforming activity was determined for all the catalysts by following the H₂ formation rate. Initial rates of hydrogen formation (extrapolation to zero time) were used in order to avoid influence of deactivation with time. It can be seen from the Table 5.1 that the turn over frequencies (TOF) were different for catalysts based on different oxides. The Pt/ZrO₂ catalysts showed the highest TOF among the catalysts investigated.

Table 5.1
Influence of supports on the rates of hydrogen formation during steam reforming of AcOH (725K, SV = 1,600,000 h⁻¹, H₂O/C =5)

Catalyst	Specific surface area (m ² g ⁻¹)	H/Pt ^a	TOF (s ⁻¹) ^b	
			per accessible Pt	per Pt on the perimeter
Pt/ZrO ₂	20	0.84	17	39
Pt/γ-Al ₂ O ₃	111	0.99	14	28
Pt/MgO	20	0.18	3	27
Pt/α-Al ₂ O ₃	4	0.58	5	16
Pt/SiO ₂	369	0.41	4	15

^a measured by volumetric hydrogen chemisorption

^b turn-over frequency for H₂ formation

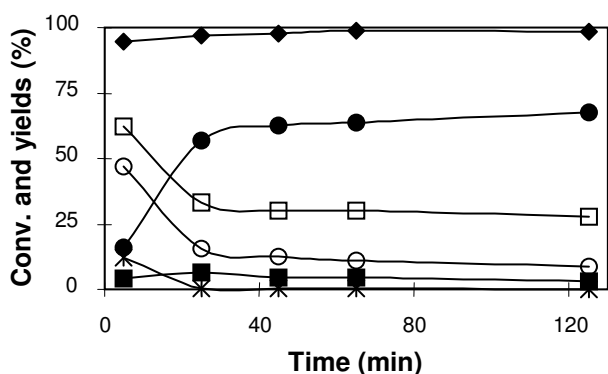


Fig. 5.5. Conversion and yields for steam reforming of AcOH over Pt/ZrO₂ catalyst. (725 K, S/C = 5, GHSV = 160000 h⁻¹) (♦) AcOH convn., yields to (●) acetone, (□) CO₂, (○) H₂, (■) CO, (*) CH₄.

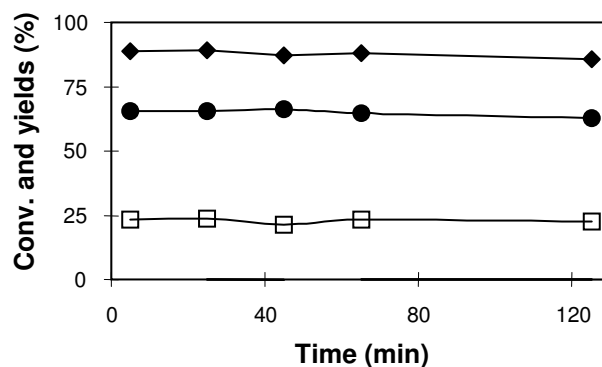


Fig. 5.6. Conversion and yields for steam reforming of AcOH over ZrO₂ catalyst. (725 K, S/C = 5, GHSV = 160000 h⁻¹) (♦) AcOH convn., yields to (●) acetone, (□) CO₂.

5.3.2 Steady state catalytic tests

Firstly, blank experiments (no catalysts) with inert quartz chips did not show any conversion of AcOH. Fig. 5.5 shows AcOH conversion and yields of products during steam reforming of AcOH over Pt/ZrO₂ at 725 K. The AcOH conversion was 100% during the whole experiment. During the test, in addition to steam reforming products (CO, CO₂, H₂), also methane and acetone were observed. Carbon balance throughout the experiment was 100 ± 3%. During initial times on stream, hydrogen yield (47.0%) was lower than that calculated from thermodynamic equilibrium (56.0%). Under thermodynamic equilibrium situation all the possible oxygenates that are formed (including acetone) in this reaction are completely steam reformed at 725 K. In the experimental conditions, acetone is observed, and thus part of the possible hydrogen yield is lost in the acetone that remains unconverted.

It can be seen from Fig. 5.5 that yields of products changed with time. In the beginning (5 min), H₂ and CO₂ were the main products, CH₄ and CO were observed in small quantities. However, after 25 minutes time on stream, H₂ and CO₂ yields decreased drastically, and a corresponding increase in acetone was observed. Acetone is known to form easily from AcOH and the reaction is catalyzed by a variety of oxides [11,12].



Fig. 5.5 also shows that the steam reforming activity of Pt/ZrO₂ catalyst was lost after an initial period of time; however, the route to the formation of acetone was not affected and hence AcOH conversion remained complete.

Fig. 5.6 shows AcOH conversion and yields of products during AcOH/H₂O reaction over ZrO₂ (without Pt). AcOH conversion was close to 90%. However, no steam reforming activity (H₂ and CO) was observed, only acetone and CO₂ were observed as products. Further, no methane was formed in this test. The stoichiometry of the products (acetone and CO₂) corresponded to the ketonization reaction (Eq. 5). The conversion of AcOH and yields of the products were constant for 3 h.

It is seen from Figs. 5.5 and 5.6 that, both Pt/ZrO₂ and ZrO₂ are very active for AcOH conversion. However, H₂ and CO, i.e., steam reforming products were produced only over Pt/ZrO₂ and not over ZrO₂. This implies that presence of Pt is essential for steam reforming. In addition, separate experiments showed that Pt/ZrO₂ catalyst was active for steam reforming of acetone (Eq. 6) and as a result low amounts of acetone were observed in the product in the beginning (Fig. 5.5).



Accordingly, when the catalyst deactivated for steam reforming, acetone was observed in larger quantities (Fig. 5.5). ZrO_2 shows acetone yields similar to those observed over Pt/ZrO_2 after 25 minutes time on stream (Fig. 5.5), indicating that even after the active sites for steam reforming were deactivated, the accessible ZrO_2 sites still provided the activity to form acetone and CO_2 . It is important to recall here that in the Pt/ZrO_2 catalyst, Pt covers only about 5% of the ZrO_2 surface available. For Pt/ZrO_2 and ZrO_2 , TG experiments showed approximately 1.2 and 0.8 wt% deposits, respectively, after 3 hour test. Sintering of Pt particles was excluded as reason for deactivation since oxidative treatment recovers the catalytic activity completely.

5.3.3 Pulse catalytic tests

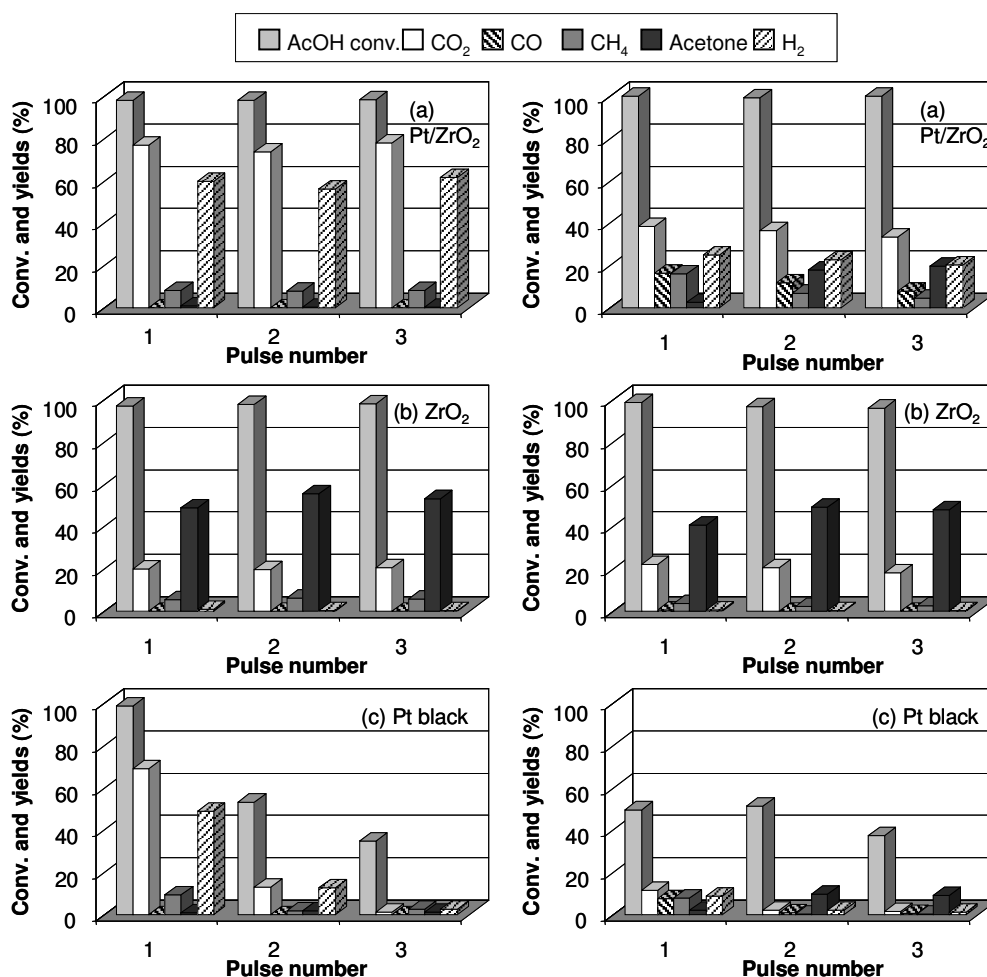


Fig. 5.7. Product distribution during AcOH/H₂O pulsing over (a) Pt/ZrO_2 , (b) ZrO_2 and (c) Pt black at 725 K.

Fig. 5.8. Product distribution during AcOH pulsing over (a) Pt/ZrO_2 , (b) ZrO_2 and (c) Pt black at 725 K.

The results so far indicate an essential catalytic role for Pt during steam reforming; however, if ZrO_2 is required for steam reforming is not evident. In order to establish this, three catalysts, Pt/ZrO_2 , ZrO_2 and Pt black were studied. Experiments were carried out in pulse transient mode since the steam reforming activity of Pt/ZrO_2 catalyst decreased rapidly during steady state experiments. Pulse size of AcOH used ($3.5\ \mu\text{mol}$) is much larger than the amounts of Pt-surface atoms available in Pt/ZrO_2 ($0.43\ \mu\text{mol}$) and Pt black ($0.05\ \mu\text{mol}$). On the basis of amounts of AcOH, the reactant pulse size in these experiments corresponded to the first 2 sec in steady state experiments shown in the previous section.

Fig. 5.7 shows the comparison of conversion/yields obtained by contacting pulses of $\text{AcOH/H}_2\text{O}$ ($\text{S/C} = 5$), at 725 K, over the three catalysts, Pt/ZrO_2 , ZrO_2 and Pt black. Background tests in an empty reactor under these conditions did not show any conversion. As expected from the initial part of the continuous catalytic test (Fig. 5.5), Pt/ZrO_2 showed high AcOH conversion (99%) and main products were CO_2 and H_2 (Fig. 5.7a). CO and acetone was observed only in traces. The catalyst did not show any deactivation even after 5 pulses indicating that the results shown here were in the region where steam reforming activity was high and not yet affected by deactivation. However, carbon balance was around 90%, suggesting that accumulation on the catalysts occurred during these pulses.

Further, over ZrO_2 (Fig. 5.7b), the conversion and product distribution were similar to the steady state tests (Fig. 5.6), i.e., high amounts of acetone and CO_2 , and low amounts of CO and H_2 . Unlike in steady state tests, also methane (12.8 mol%) and ketene (3.3 mol%) were observed here. Conversion and yields did not change during the five pulses, as expected from Fig. 5.6. Carbon balance was approximately 75%, suggesting that accumulation occurred on ZrO_2 .

Over Pt black with $\text{AcOH/H}_2\text{O}$ (Fig. 5.7c), the conversion was high ($\sim 100\%$) only for the first pulse. H_2 and CO_2 were main products and CH_4 was observed in around 10% yield. The distribution of the products was similar to that for Pt/ZrO_2 catalyst (Fig. 5.7a,c). However, Pt black deactivated rapidly as additional pulses were introduced, compared to the other catalysts (Fig. 5.7c). For the second pulse, conversion of AcOH reached only 50%. H_2 and CO_2 yields accordingly decreased. For the third pulse, conversion of AcOH decreased to *ca.* 30% and the catalyst completely deactivated after five pulses.

In order to examine how the absence of steam affects the product yields and catalyst life, experiments with AcOH only over the same catalysts were carried out and the data are shown in Fig.

5.8.

Over Pt/ZrO₂ (Fig. 5.8a), complete conversion was observed during three pulses. For the first pulse, CO₂ and H₂ were the main products and CO and CH₄ were also observed. Acetone was produced only in small amounts. As more pulses were introduced, CO₂, H₂, CO and CH₄ yields decreased gradually and acetone yield increased. It should be noted that CO was clearly observed during pulsing of AcOH only, and not during pulsing of AcOH with steam. This indicates that Pt/ZrO₂ is highly active for the water gas shift reaction (Eq. 2) when steam is present in the feed (Fig. 5.7a). Correspondingly, yields of CO₂ and H₂ for AcOH pulsing were lower than those in the case of AcOH/H₂O pulsing. It can also be seen (Fig. 5.8a) that the acetone yield increased while yields of other products decreased with increasing number of pulses.

Over ZrO₂ (Fig. 5.8b), AcOH conversion was nearly 100%. Acetone and CO₂ were major products; CH₄ (8.0 mol%) and ketene (CH₂CO) (9.3 mol%) were also observed. The distribution of products was similar to that for AcOH/H₂O pulsing. Carbon balance was *ca.* 75%.

Over Pt black (Fig. 5.8c) only 50% conversion was obtained for the first and second pulses. Carbon balance was about 80% in these experiments. The distribution of products was different from that for AcOH/H₂O pulsing. For the first pulse, CO₂, CO, CH₄ and H₂ were obtained (all less than 10% yields) and acetone and ketene were observed only in very small amounts. From the second pulse, acetone was observed more clearly. The catalyst was deactivated almost completely after five pulses.

5.3.4 *In situ* IR measurements

Fig. 5.9 shows *in situ* IR spectra of Pt/ZrO₂ during steam reforming of AcOH at 725 K. Fig. 5.9a shows IR spectrum after the first exposition to AcOH/H₂O (S/C = 5). A peak assigned to linear CO adsorption on Pt was observed at 2060 cm⁻¹. Oxygenate peaks (typical for bidentate acetate and/or carbonates) were observed in the 1300-1500 cm⁻¹ region. After evacuation (not shown), CO on Pt was completely removed, which indicated that CO adsorption was reversible. The oxygenate peaks decreased by about 70% in intensity. The AcOH/H₂O exposure and evacuation cycles were repeated three times. The spectra after each adsorption are shown in Fig. 5.9a-c. CO adsorption peak became gradually weaker as the cycle was repeated. Peaks for oxygenates were almost the same in shape and intensity during the three cycles.

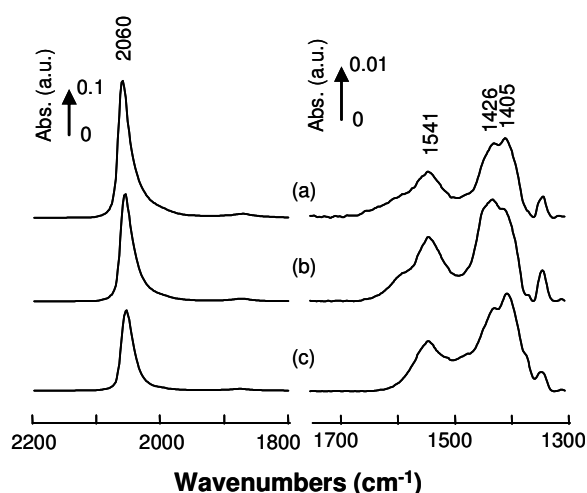


Fig. 5.9. In situ IR spectra over Pt/ZrO₂ at 725 K (S/C = 5, 0.1 mbar). AcOH/H₂O - evacuation cycles. Spectra were collected after AcOH/H₂O was introduced.

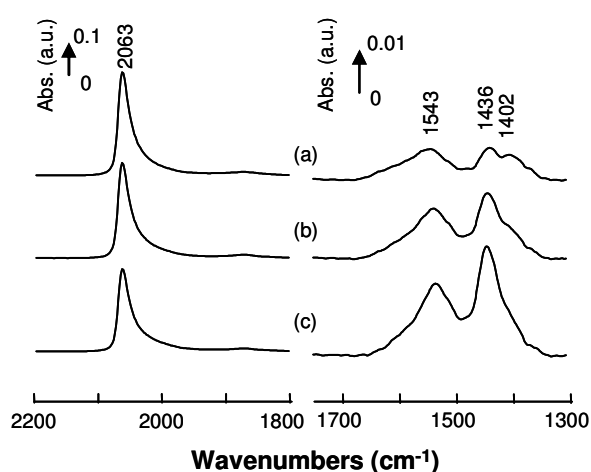


Fig. 5.10. In situ IR spectra over Pt/ZrO₂ at 725 K (S/C = 5, 0.1 mbar). Acetone/H₂O - evacuation cycles. Spectra were collected after Acetone/H₂O was introduced.

Fig. 5.10 shows IR spectra of Pt/ZrO₂ for steam reforming of acetone at 725 K. Similar to the spectra during steam reforming of AcOH, linear CO adsorption on Pt was observed at 2062 cm⁻¹. Oxygenate peaks, similar to those observed with AcOH, were also observed in the 1300-1500 cm⁻¹ region. As in the case of steam reforming of AcOH, CO on Pt was removed and the oxygenate peaks were removed about 50% in intensity during evacuation (not shown). This cycle was repeated three times and spectra are shown in Fig. 5.10a-c. The CO adsorption peak became gradually weaker as the cycle was repeated. Intensities of peaks for oxygenates increased concurrently.

In order to probe catalyst deactivation *in situ* IR measurements have been used. Experiments have been carried out under conditions simulating an accelerated deactivation test. The following text explains the background to these tests.

Acetone is known to undergo aldol type condensation reactions over inorganic oxides [13-15] and give products such as diacetone alcohol ((CH₃)₂C(OH)CH₂COCH₃), mesityl oxide ((CH₃)₂C=CHCOCH₃, MO), etc. MO is known to undergo oligomerization [15,16] and form deposits on the catalysts, which can block active sites. In order to check the effect of MO

Table 5.2

Comparison of AcOH conversion and H₂ yield between fresh Pt/ZrO₂ and MO treated Pt/ZrO₂

Catalyst ^a (Pt/ZrO ₂)	AcOH conv. (%)	H ₂ yield (%)
Fresh	98.2	60.0
MO treated ^b	82.4	29.1

^a20 mg of catalyst was used

^bMO/H₂O pulse (0.32 μmol-MO, S/C = 5) was introduced before a AcOH/H₂O pulse.

on deactivation, Pt/ZrO₂ catalyst was contacted with a MO/H₂O pulse (0.32 μmol-MO, S/C = 5) before a AcOH/H₂O pulse (3.5 μmol-AcOH, S/C = 5). shows AcOH conversions and H₂ yields after this treatment. It was observed that the Pt/ZrO₂ catalyst deactivated for H₂ formation more rapidly when contacted with MO in comparison to AcOH (see Fig. 5.7a). In the case of AcOH the catalyst did not show any deactivation during five AcOH/H₂O pulses (i.e.,

one molecule MO deactivates the catalyst more rapidly than 60 molecules of AcOH).

Fig. 5.11 shows IR spectra of Pt/ZrO₂ during the following procedure. First, MO, in amounts similar to those used in the deactivation experiment in Table 5.2, was introduced with a steam (S/C = 5) (Fig. 5.11a). Linear-CO on Pt peak was observed at 2064 cm⁻¹, indicating that some steam reforming of MO took place. The peaks for oxygenates similar to those obtained from AcOH/H₂O. The catalyst was then evacuated (not shown). Intensities for linear CO peak and almost all of peaks for oxygenates decreased. After evacuation, AcOH/H₂O was introduced (Fig. 5.11b). Spectrum 7b shows that CO adsorption on Pt was significantly suppressed, while the oxygenate peak showed up clearly. At this time, gas phase CO (1% in Ar, 0.1 mbar in total pressure) was introduced into the system without evacuation (Fig. 5.11c). Interestingly, the intensity for CO adsorbed on Pt increases dramatically. The peaks related to oxygenates remained unchanged.

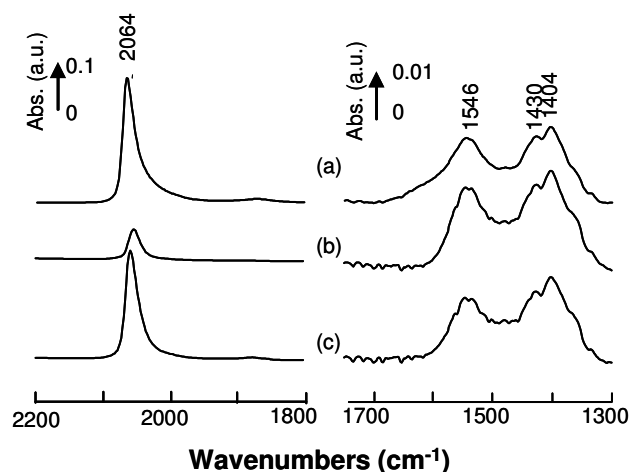


Fig. 5.11. In situ IR spectra over Pt/ZrO₂ at 725 K (S/C = 5, 0.1 mbar). (a) MO/H₂O, (b) AcOH/H₂O (after (a) and evacuation), (c) CO (after (b) without evacuation).

5.4 Discussion

5.4.1 Site requirements for steam reforming of acetic acid

In general, during reaction with oxygenates, e.g., AcOH and acetone, it is reported that a certain extent of homogeneous thermal decomposition is always possible [7]. However, blank experiments demonstrated the absence of significant homogeneous decomposition under reaction conditions used in this study.

In order to understand what happens on Pt, the results over Pt black (Figs. 5.7c, 5.8c) is discussed.

In the absence of steam (Fig. 5.8c), the products observed were H₂, CO₂, CO and CH₄. As this happens in the absence of steam, the products must be formed from decomposition of AcOH on Pt surface. The results are consistent with the observations by Vajo *et al.* [17], that AcOH decomposed to produce CO, CO₂, H₂ and adsorbed C over polycrystalline platinum surface, at the temperatures between 300 and 900 K.

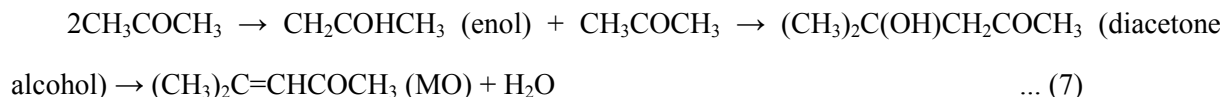
However, the significant observation was that the catalyst deactivated rapidly. After 3 pulses of AcOH were introduced, the amount of deposit on the catalyst, based on C, is about 2.5 μmol. The Pt black catalyst has 0.05 μmol Pt surface available. This indicates that Pt is more or less completely covered by deposits and the resulting deactivation. During this deactivation, CO, CO₂ and CH₄ yields decreased and acetone and ketene yields increased. This could imply that the formation of ketene and acetone could occur on the deposits. This is in agreement with reported information that such oxygenates can be formed on coked Pt catalysts [17,18].

In the presence of steam, typical steam reforming products were also observed over Pt black (Fig. 5.7c). However, CO was not observed and CO₂ and H₂ yields were high. This implies that water-gas shift reaction took place, converting CO to CO₂ (Eq. 2). For both steam reforming and water gas shift, the activation of water is essential. In this case, only Pt sites exist in the Pt black catalysts. It is generally agreed that steam activation would hardly take place on Pt [19]. There is thus the possibility that the steam reforming and water gas shift activity of Pt black observed here is due to the presence of impurities, e.g., alkali (sodium and potassium were present). Alkali metals are known to catalyze steam gasification and the products formed are similar to steam reforming [20].

ZrO₂ by itself is not active for steam reforming (Fig. 5.6, 3b, 4b). However, ZrO₂ is active to convert AcOH to acetone. ZrO₂ is known to be catalytically active for ketonization (Eq. 5) [21,22], and acyl and/or acetate type species are suggested to be involved in the reaction scheme [11,12,23]. IR spectra in the region of 1300-1800 cm⁻¹ at 725 K show oxygenate surface species on ZrO₂, regardless of the treatment with AcOH, acetone or MO (Figs. 5.9-5.11). These bands have been attributed to species such as bidentate acetate [23,24], or carbonates [25]. On the basis of the IR spectra of oxygenate species on ZrO₂, it is not possible to pinpoint the exact nature of the species.

In the pulse experiments with AcOH over ZrO₂, ketene (CH₂CO) and CH₄ were observed in small amounts. Ketene can be formed by dehydration of AcOH (CH₃COOH → CH₂CO + H₂O) [12] or

decomposition of acetone formed from AcOH ($\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_2\text{CO} + \text{CH}_4$) [24]. As excess steam is present during these experiments, the latter seems more likely. Acetone formed on ZrO_2 can also undergo an aldol condensation type reaction scheme, according to;



Both ketene and MO, which can be formed from acetone over ZrO_2 , can undergo oligomerization to form deposits and deactivate the catalyst by blocking active sites. The carbon balance (70-90%) in pulse experiments (Figs. 5.7b, 5.8b) shows formation of these deposits; this is also confirmed by TG analysis of deactivated catalysts. In addition, the molar ratio of acetone to CO_2 formed is significantly lower than one, as expected from the reaction stoichiometry in Eq. 3. Thus, it is reasonable to consider that further transformation of acetone to deposits takes place on the ZrO_2 support.

Over Pt/ZrO_2 and Pt black, typical steam reforming products were observed at initial times on stream (Figs. 5.5, 5.7a,c). As stated earlier, the product over ZrO_2 hardly contained any H_2 (Figs. 5.6, 5.7b, 5.8b). These results clearly show that the presence of Pt is essential to catalyze steam reforming. However, Pt black lost its activity more rapidly (Figs. 5.7c, 5.8c) than Pt/ZrO_2 . This is supported by the results from catalyst testing, where Pt/ZrO_2 catalyst was still active even after at least 1700 TON (Fig. 5.5, after 5 min on stream) (TON = moles of AcOH introduced per moles of available Pt) while Pt black deactivated just after 136 TON (Fig. 5.7c, after 3 pulses). Therefore, ZrO_2 also plays an important role in maintaining steam reforming activity.

5.4.2 Importance of Pt-support boundary sites for steam reforming of acetic acid

The Pt/ZrO_2 showed high activity toward steam reforming of AcOH at initial times on stream; nevertheless, the Pt/ZrO_2 catalysts showed rapid deactivation after certain time on stream (Fig. 5.5). In order to understand this, an accelerated deactivation test has been carried out by contacting the catalyst with MO. As expected, in catalytic experiments, pretreatment with MO caused a strong decrease in steam reforming activity (Table 5.2). IR experiments showed that pretreatment with MO causes decrease in the IR intensity of adsorbed CO (Fig. 5.11b), indicating also a decrease in steam reforming activity. However, the intensity of the CO peak increased when CO was introduced (Fig. 5.11c), indicating that Pt surface was still available in this deactivated catalyst. Thus, when specific parts of Pt

are blocked by deposits, the catalysts seem to lose the activity for steam reforming.

There have been extensive kinetic and mechanistic studies on the steam reforming of methane [4,26] over supported metal (Ni, Pt etc.) catalysts. It is commonly agreed that methane activation occurs on the metal, *via* dehydrogenation and resulting in formation of CH_x type species ($x < 4$). Oxidation of these species by water gives rise to CO and hydrogen. Over supported Ni catalysts (Ni/ γ - Al_2O_3 modified with K, Mg, etc.) activation of water is suggested to occur both on Ni (*via* formation of NiO) and on the support (probably as hydroxyl groups) [4]. However, in the case of supported Pt catalysts, activation of water does not seem feasible on Pt as the resulting PtO_x is not thermodynamically stable at the higher temperatures used here [19]. In that case water activation should occur on the support and both metal and support play a direct role in the activation of the reactants. However, the activation of water on the support may not be kinetically relevant, as was shown by Wei and Iglesia [27] for conditions under which carbon deposition does not occur.

In the case of carbon dioxide reforming of methane over Pt/ ZrO_2 , where CO_2 is the oxidant instead of water, it has been shown that methane activation occurs on Pt and CO_2 activation occurs on ZrO_2 [25,28]. It has been shown further that the active sites are situated at the boundary of Pt particles and ZrO_2 [25,28,29] from the dependence of catalytic activity on the number of Pt sites which are in close proximity of the support.

In order to check the relevance of the above mentioned mechanistic details for the steam reforming of AcOH over Pt/ ZrO_2 , further experiments were designed accordingly and the results are discussed below.

In order to vary the amount of metal-support boundary sites in the catalysts, a series of supported Pt catalysts varying in Pt particle sizes (obtained by sintering) and Pt loading were prepared. Pt dispersions (H/Pt) were measured using hydrogen chemisorption. These values were confirmed by determining particle sizes by EXAFS measurements on the samples [30]. Concentration of Pt atoms on the perimeter (Pt-support boundary) of Pt particles, were calculated based on the assumptions that (i) all Pt particles in a particular catalyst have the same size and hemispherical shape. (ii) Pt site density of $1.25 \cdot 10^{19} \text{ m}^{-2}$, assuming equal proportions of Pt (111), (100) and (110) planes in the crystallites [31]. Transmission electron micrographs (TEM) confirmed that Pt particle sizes were more or less uniform and hemispherical in shape (Fig. 5.12). Calculation of the perimeter after including a

statistical variation of sizes, using about 110 Pt particles from TEM (Fig. 5.12), deviated by not more than 10% from the numbers used.

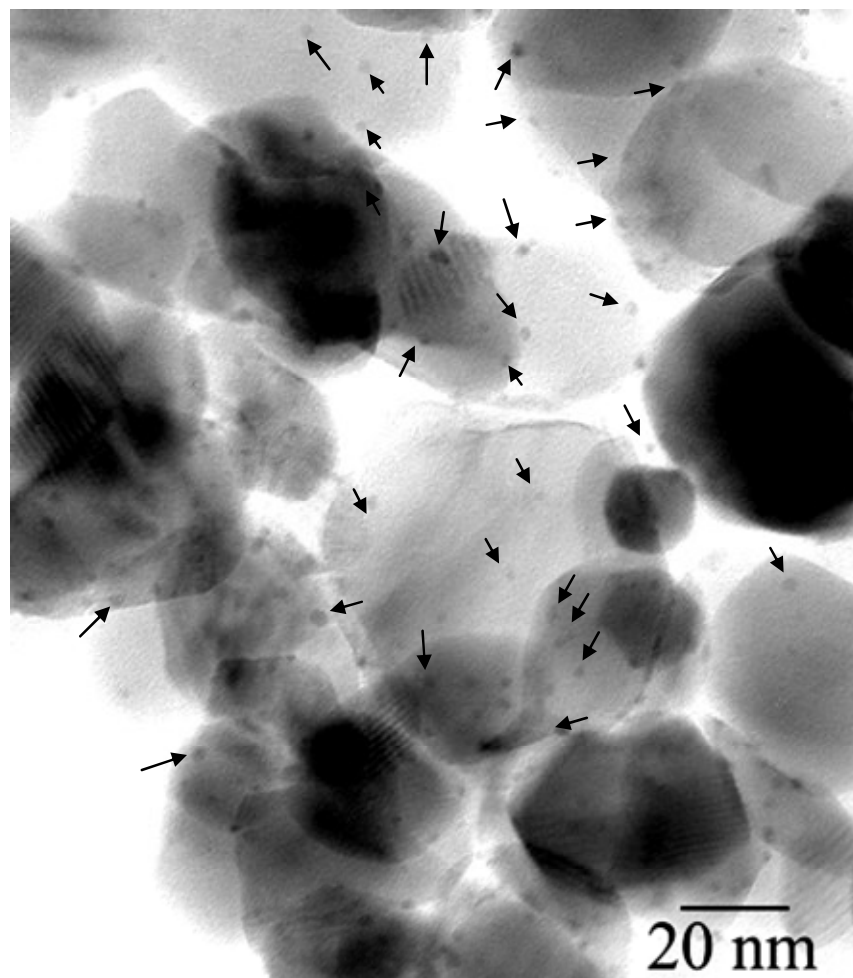


Fig. 5.12. Transmission electron micrograph for 1.0 wt% Pt/ZrO₂ reduced catalyst. The arrows in the figure point at Pt particles (identified by EDX).

Steam reforming activity was determined for all the catalysts by following the H₂ formation rate. Initial rates of hydrogen formation (extrapolation to zero time) were used in order to avoid influence of deactivation with time. In Fig. 5.13, initial hydrogen formation rates are plotted against the concentration of all accessible Pt (I) and the concentration of Pt at the perimeter (II). It is seen that, steam reforming activity correlates better with the concentration of Pt on the perimeter of the Pt particles (II). This can be interpreted that the steam reforming activity is dependent on the number of Pt-ZrO₂ boundary site.

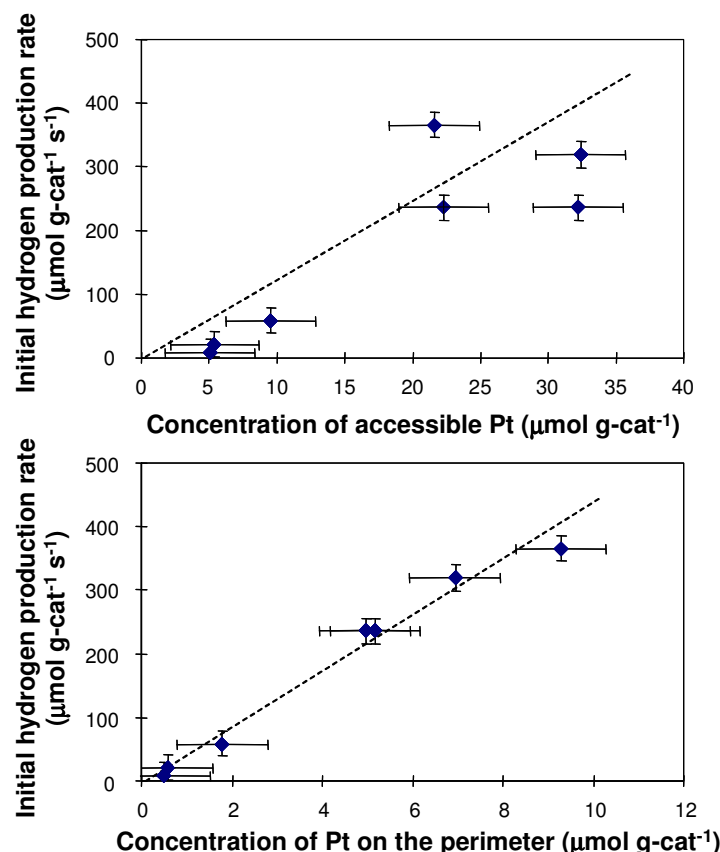


Fig. 5.13. Initial rates of hydrogen formation vs. concentration of (I) accessible Pt atoms and (II) Pt only on the perimeter for the Pt/ZrO₂ catalysts. (725 K, SV = 1,600,000 h⁻¹, H₂O/C = 5)

Table 5.1 shows that the catalysts based on different oxides give not only different TOFs per accessible Pt but also TOFs per Pt on the perimeter. The role of supports could be interpreted as due to (i) an indirect influence of support on the electronic or morphological properties of the metal, or (ii) the supports themselves participate in the activation of water, e.g., forming reactive hydroxyl groups. In order to investigate the role, if any, of Pt particle size on intrinsic catalytic activity, the results of kinetic measurements are compiled again in Table 5.3 for two Pt/ZrO₂ catalysts with different Pt dispersions and a catalyst on different support but having similar Pt dispersion. When supported on ZrO₂, the catalysts gave the same intrinsic activity, thus excluding particle size effects. Comparing ZrO₂ and SiO₂ supported catalysts, with similar Pt sizes, it is seen that the activities are different, demonstrating a significant influence of the support.

Based on these results, it is claimed that steam reforming of AcOH takes place on the Pt sites at the boundary between Pt particles and ZrO₂. Thus, the support also participates in the catalysis of

Table 5.3
Influence of Pt dispersion and the support on the rates of
hydrogen formation during steam reforming of AcOH

Catalyst (0.5 wt% Pt)	H/Pt	H ₂ TOF ^a (s ⁻¹)
Pt/ZrO ₂ ^b	0.84	39
Pt/ZrO ₂ ^c	0.37	33
Pt/SiO ₂	0.41	15

^a per Pt on the perimeter

^b calcined at 925 K

^c calcined at 975 K

steam reforming. At initial time on stream (Figs. 5.5, 5.7a), ZrO₂ effectively activates steam; however, acetone formation as well as further oligomerization also happens on ZrO₂. Deposition of the oligomers at the periphery of the Pt particles is probably responsible for the deactivation of steam reforming.

In order to develop the durable catalysts for steam reforming of AcOH, the condensation reactions on the support, in this case ZrO₂ should be avoided. Acid-base properties of the support are known to play a key role in catalyzing such transformations [15]. Thus, two aspects are to be considered while modifying the support, ZrO₂, (i) enhancing steam activation and (ii) minimize activity towards oligomer formation.

5.5 Conclusions

Steam reforming of acetic acid (AcOH) was investigated over Pt/ZrO₂ catalysts. The Pt/ZrO₂ catalysts showed high activities at initial time on stream, but lost its activity for steam reforming (H₂ production) rapidly. It is revealed that Pt is essential for the steam reforming, and ZrO₂ is needed to extend the catalyst life. Hydrogen formation rates correlated strongly with the number of Pt atoms in the close proximity of the support. Further, the support influenced the intrinsic activity (TOF) per Pt periphery site for hydrogen formation. Results obtained in this study exclude presence of Pt particle size effects on catalytic activity. Thus, a bifunctional mechanism is proposed for steam reforming of AcOH on Pt/ZrO₂, i.e., AcOH activation takes place on Pt and steam activation on ZrO₂, and the active sites for the steam reforming of AcOH are located at the boundary between Pt particles and the

supports. The catalysts deactivate due to blocking of active sites by oligomers derived from AcOH/acetone on ZrO₂. In order to develop efficient catalysts for the steam reforming of biomass derived oxygenates, steam activation on the support may be critical and the oligomerization/condensation reactions which take place on the support need to be minimized.

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Chapter 6

Reaction Sequence and Mechanism for Steam Reforming of Biomass Derived Oxygenates

Abstract

Mechanistic studies on steam reforming of acetic acid over Pt/ZrO₂ catalysts have been performed. It is proposed that a bifunctional mechanism is operative where both Pt and ZrO₂ are participating in the reaction. An overall picture of the bifunctional mechanism for steam reforming of acetic acid is established. On Pt, bond breaking of acetic acid proceeds to form H₂, CO, CH₄, and CO₂ into gas phase, and to form the carbonaceous residue (most probably CH_x species) which can block Pt surface. On the other hand, H₂O can be activated on ZrO₂ to create supplementary surface hydroxyl groups, which reacts to gasify the residue on Pt to give chiefly steam reforming/ water gas shift products (H₂, CO₂), and thus, the catalytic cycles continue. Importance of the Pt-ZrO₂ boundary sites are confirmed by the fact that the removal of the deposits situated on the sites in close proximity of Pt particles should be essential to regenerate the catalysts.

6.1 Introduction

In the previous chapter, it is proposed that a bifunctional mechanism is involved in steam reforming of acetic acid (AcOH) over supported Pt catalysts, where both Pt and the support participate in the reaction. In literature one can find a number of researches elucidating reaction mechanism for steam reforming of hydrocarbons. For instance, a bifunctional mechanism was proposed for methane and higher hydrocarbons by Rostrup-Nielsen for Ni based catalysts. In their proposal, hydrocarbons are adsorbed and primarily activated on the nickel sites while water is adsorbed and activated on the support [1,2]. A similar bifunctional mechanism was also proposed for the dealkylation of toluene with steam, to benzene and syngas, over supported noble metal catalysts by Grenoble [3,4] and Duprez et al. [5,6]. According to them, dissociative chemisorption of hydrocarbon occurs on Pt and surface hydroxyls derived from H₂O on the oxide support help to remove the hydrocarbon residue. Infrared spectroscopy showed that surface hydroxyl groups on the support are consumed by reacting with toluene to produce oxygenated compounds (CO and CO₂) [7]. Importance of the support in activating water has been stressed, especially when the metals, such as Pt, Rh and Pd, were used [4-6]. The concept of the bifunctional mechanism has also been suggested for the WGS reaction, where CO adsorbs on the metal and water on the support [8].

In the case of steam reforming of oxygenates, however, role of support and importance of boundary sites have not been clarified sufficiently. Thus, the aim of this study is to understand the role of the support and to see if a bifunctional mechanism is operative during steam reforming of AcOH. An overall schematic pathway for steam reforming of AcOH is discussed based on sorption and reaction studies of AcOH and H₂O on the Pt/ZrO₂ catalysts.

6.2 Methods

6.2.1. Catalyst preparation

Experimental method for catalyst preparation is described in the previous chapter. Specific surface area of the ZrO₂ and the Pt/ZrO₂ catalysts used were 21 and 20 m² g⁻¹, respectively. Pt dispersion of 0.84 (H/Pt) was determined by hydrogen chemisorption. Pt black (Nilaco Co, 99.98%, 300 mesh) was used as a catalyst without support, without any further purification.

6.2.2. Catalytic measurements

For continuous test, 10 or 50 mg of the catalysts were loaded in a fixed bed reactor. Prior to the reaction, the catalyst was first reduced in 5% H₂ in N₂ at 775 K for 1 h. An aqueous solution of AcOH or acetone giving a steam to carbon molar ratio (S/C) of 5 was introduced by using a microfeeder and a syringe. AcOH and acetone were fed giving a vapor pressure of 2.5 and 1.7 kPa, respectively. Total gas hourly space velocity (GHSV) of 320,000 or 1,600,000 h⁻¹ was achieved with argon as a carrier gas. N₂ was added as an internal standard. After the reaction, the catalysts were purged with Ar at the reaction temperature, cooled down, and used for subsequent characterization. Analyses were carried out by using a gas chromatography (Shimadzu 14B), equipped with a Porapak Q column connected to a flame ionization detector for AcOH, acetone (CH₃COCH₃), and hydrocarbons; and a Active Carbon column connected to a thermal conductivity detector for H₂, N₂, CO, CH₄, and CO₂.

The overall reaction stoichiometry for the conversion of AcOH to hydrogen can be drawn as Eq. 1 (a combination of steam reforming and WGS (Eq. 2)):



Similarly, in the case of acetone reforming, the reaction stoichiometry is (Eq. 3)



The hydrogen yields were calculated based on Eq. 1 or 3. For carbon containing compounds, the yields were calculated based on C₁ equivalent values.

Pulse experiments were performed with 20 mg of Pt/ZrO₂ or ZrO₂. After reduction at 775 K, the system was purged in Ar at a flow rate of 37.5 ml min⁻¹. After cooling down the catalysts to the reaction temperature (625 K), the required pulses of AcOH (3.8 μmol), H₂O (22 μmol) or O₂ (8.9 μmol) were injected. For analyses, a gas chromatography (Shimadzu 8A) was connected in-line to the reactor.

In order to understand the kinetic relevance of secondary reactions that can occur during the conversion of AcOH, the Pt/ZrO₂ catalysts were tested for steam reforming of methane (CH₄/H₂O) and hydrogenation (CO/H₂). For these reactions, carbon partial pressure was kept at 5.1 kPa, and the gas mixture was fed with the ratios of 5 or 3 for H₂O/C or H₂/C, respectively. The GHSV of 1,600,000 h⁻¹ was achieved by dilution with Ar. Products were analyzed as described above.

6.2.3. Catalyst characterization

IR spectra were recorded *in situ* under vacuum by using a transmission spectrometer (JASCO, FTIR620) with a MCT detector. A pellet of 100 mg of the catalyst was loaded in a miniature cell, equipped with CaF₂ transparent windows. The cell can be evacuated to pressures below 10⁻⁶ mbar. The catalyst was firstly reduced *in situ* by introducing 10 mbar of H₂ at 775 K. Then, the catalyst was cooled down to 625 K. Each spectrum, which consists of 128 scans taken at 4 cm⁻¹ resolution, was collected 5 min after the required gas was introduced or evacuated.

Temperature programmed oxidation (TPO) measurements were carried out over the catalysts used for AcOH pulse exposure (3.8 μmol) or the continuous test for 1 h, to investigate nature of carbonaceous deposits. For the measurements after an AcOH pulse, 20 mg of ZrO₂ and Pt/ZrO₂, and 100 mg of Pt black were used. After the required reactions at 625 K, the catalysts were immediately cooled down to 373 K (typically within 120 sec). Then, the gas was switched to 5%O₂/He and the catalysts were heated up to *ca.* 800 K. Carbonaceous deposits were oxidized to CO_x, which passed through a methanator and were finally detected with a flame ionization detector.

6.3. Results and discussion

6.3.1. Steady state catalytic tests

Table 6.1 shows results for steam reforming of AcOH over Pt/ZrO₂ catalyst. The catalyst showed activity for steam reforming, producing H₂, CO₂ and CO, along with CH₄ and acetone. Results on ZrO₂ show that acetone was formed *via* ketonization of AcOH over ZrO₂ (Eq. 4).



The carbon mass balance was at least 25% deficient, suggesting carbonaceous deposits remained on the catalyst. Steam reforming of acetone over Pt/ZrO₂ was also studied under comparable conditions (Table 6.1) because acetone is formed as a product over ZrO₂. The data in Table 6.1 show that acetone indeed can be steam reformed although the level of conversion is about an order of magnitude lower. However, larger carbon loss (<30%) was observed. In the previous chapter, it was suggested that this is due to aldol condensation type reactions of acetone proceeding on the support and forming deposits. In the present study, after 25 min time on stream, formation of hydrogen (as

indication of steam reforming activity) was strongly suppressed (not shown). Since treatment in O₂ of the catalyst regenerates the activity, we suggest the loss of activity is due to blockage of the active sites for steam reforming by deposits.

Table 6.1
Steam reforming of AcOH and acetone over Pt/ZrO₂ catalyst at 5 min time on stream (625 K, H₂O/C = 5, GHSV = 320,000 h⁻¹, AcOH = 2.5 kPa or acetone = 1.7 kPa)

Reactant	Conversion (%)	Yield (%)					
		H ₂	CO ₂	CO	CH ₄	Acetone	C ₁ loss
AcOH	46.2	8.2	7.6	8.7	3.3	6.5	22
Acetone	27.0	1.2	0.8	0.1	<0.1	-	26

6.3.2. Catalytic cycle during steam reforming of acetic acid

A series of pulse reactions with AcOH and/or H₂O were carried out over the Pt/ZrO₂ catalysts. Note that the amount of AcOH in a single pulse corresponds to the amount introduced in the continuous test (section 6.3.1) for less than 2 sec.

Table 6.2 compiles results for products from pulse experiments over fresh Pt/ZrO₂ and ZrO₂. With a pulse of AcOH and H₂O together, AcOH conversion was complete and the products observed were H₂, CO₂, CO, CH₄, and acetone, in agreement with the results in the continuous test (Table 6.1). Carbon loss was around 50%. In the absence of water, the same types of products were observed but different extents. It can be seen from the results that presence of water causes the WGS (Eq. 2).

Table 6.2
Product distributions from AcOH pulse reaction, and conversion of deposits derived from AcOH with H₂O and O₂ (625 K, AcOH 3.8 μmol, H₂O 22 μmol, O₂ 8.9 μmol)

Catalyst	Reactant	Yield (μmol)					Carbon deposit ^a (μmol)	Total C in products (μmol)
		H ₂	CO ₂	CO	CH ₄	Acetone		
Pt/ZrO ₂	AcOH/H ₂ O	1.85	2.01	0.08	1.26	0.14	3.7	-
Pt/ZrO ₂	AcOH	1.32	0.91	1.57	0.75	0.26	3.0	-
ZrO ₂	AcOH	0	0.74	0	0	0.35	3.7	-
Pt/ZrO ₂	(AcOH →) H ₂ O ^b	0.73	0.40	0.04	0.05	0	(2.5) ^c	0.5
Pt/ZrO ₂	(AcOH →) O ₂ ^b	0.06	3.04	0.06	0.01	0	(0) ^c	3.1

^a Based on carbon

^b H₂O or O₂ were injected after 15 sec from AcOH pulse

^c Calculated carbon remaining on the catalysts

Over ZrO_2 , however, ketonization of AcOH to form acetone and CO_2 (Eq. 4) took place, and no H_2 was formed. Less acetone than CO_2 was observed (as would be expected from reaction stoichiometry in Eq. 4), this is due to consecutive conversion of acetone to oligomers. AcOH conversion was 73% while nearly 50% carbon loss was observed. Comparing the results over Pt/ZrO_2 and ZrO_2 , it is confirmed that the presence of Pt is essential for the formation of H_2 . The deposits deactivated the Pt surface as can be seen from the fact that hydrogen formation over Pt/ZrO_2 was strongly suppressed during subsequent AcOH pulses (Fig. 6.1 indicated as ‘without H_2O injection’).

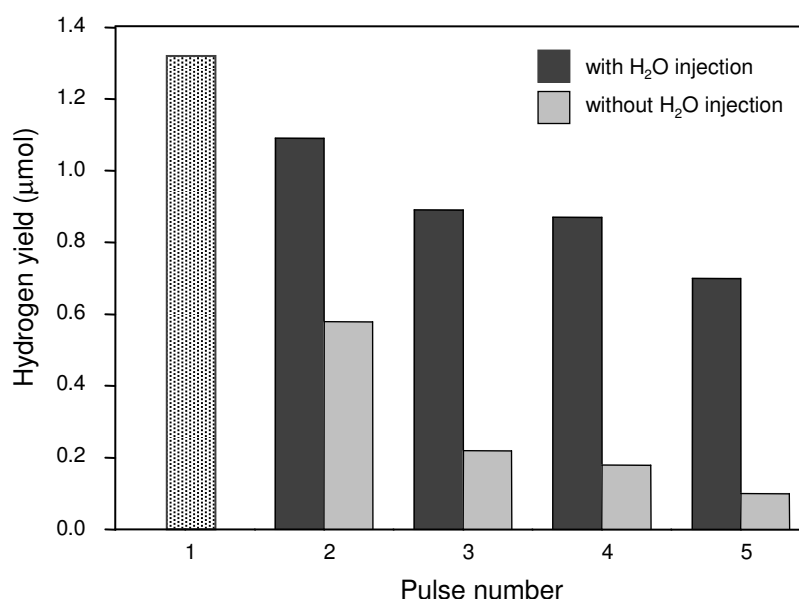


Fig. 6.1. Effects of H_2O injection after AcOH pulse on hydrogen yield over Pt/ZrO_2 . H_2O pulse was injected 15 sec after the AcOH pulse. (625 K, AcOH pulse 3.8 μmol , H_2O pulse 22 μmol)

Thus, water as a co-reactant should play an important role to cleanup deposits on the Pt surface for the subsequent decomposition of AcOH (at least partially). When water pulse was introduced immediately (15 sec) after each AcOH pulse injection, a part of the remaining species on the catalyst derived from AcOH pulse (0.5 out of 3.0 μmol C base) was gasified to form chiefly H_2 and CO_2 as a consequence of steam reforming and WGS (Table 6.2). Indeed, it is seen from Fig. 6.1 (‘with H_2O injection’) that the water treatments greatly improved durability for hydrogen formation. This can be an indication of the catalyst cycle during steam reforming of AcOH ; AcOH decomposes on Pt to give H_2 , CO_x and CH_4 , and some species covering Pt surface, and subsequently, these are gasified by H_2O to make the Pt surface available for the next AcOH turn over (decomposition).

6.3.3. Importance of Pt-support boundary sites for the reforming

All the deposits derived from AcOH on the Pt/ZrO₂ were gasified with oxygen to mainly CO₂ at 625 K (Table 6.2, at the bottom). Fig. 6.2a-c shows temperature programmed oxidation (TPO) profiles of the Pt black, ZrO₂ and Pt/ZrO₂ catalysts exposed to a single AcOH pulse. TPO profile for Pt black exhibits only one peak at 438 K (Fig. 6.2a). TPO profile for ZrO₂ (Fig. 6.2b) has one broad peak with a maximum at 670 K. On contrary, TPO profile for Pt/ZrO₂ (Fig. 6.2c) shows three peaks (maxima at 433, 465, and 575 K, respectively). The presence of Pt in the catalyst considerably lowered the temperature for removal of the deposits with O₂ (compare Figs. 6.2b and c) as expected from the well known fact that Pt is a good combustion catalyst.

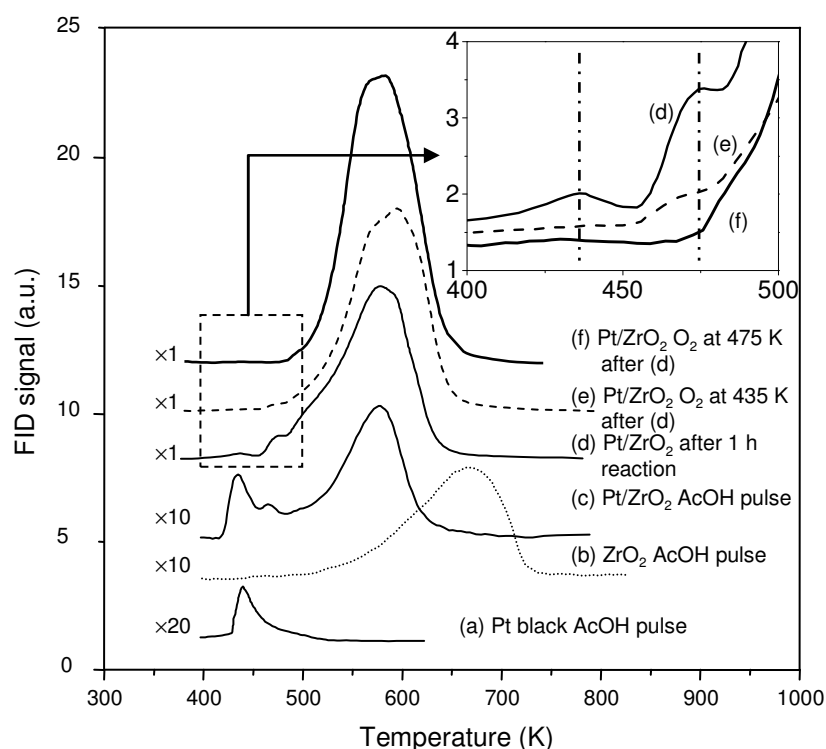


Fig. 6.2. Temperature programmed oxidation profiles of the catalysts used for the following reactions. (a) Pt black exposed to AcOH pulse; (b) ZrO₂ exposed to AcOH pulse; (c) Pt/ZrO₂ exposed to AcOH pulse; (d) Pt/ZrO₂ after 1 h reforming; (e) sample d treated in O₂ at 435 K after 15 min; (f) sample d treated in O₂ at 475 K. (AcOH pulse 3.8 μ mol, Reforming conditions: 625 K, H₂O/C = 5, GHSV = 320,000 h⁻¹, AcOH = 2.5 kPa)

The first peak in Fig. 6.2c can be assigned to carbon on the Pt surface based on the fact that the peak in the same temperature region is shown on Pt black (Fig. 6.2a). The high temperature peak on Pt/ZrO₂ (Fig. 6.2c) can be ascribed to the deposits on the support remote from Pt particles. Therefore, the second peak is tentatively assigned to the deposits on the perimeter of the Pt particles. Based on

the bi-functional mechanism, it would be expected that deposits at the perimeter would affect catalytic activity and other deposits would not. In order to investigate this, treatment of the used catalyst in O₂ at different temperature was demonstrated.

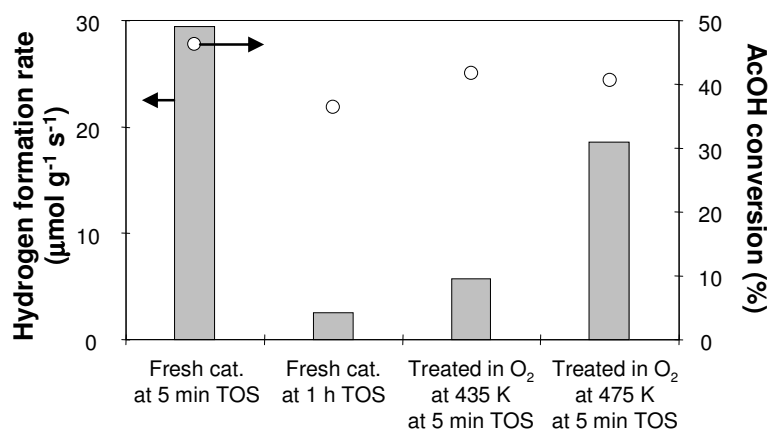


Fig. 6.3. Regeneration of Pt/ZrO₂ by treatment in O₂. (625 K, H₂O/C = 5, GHSV = 320,000 h⁻¹, AcOH = 2.5 kPa.)

As can be seen in Fig. 6.3, the catalytic activity for steam reforming decreased significantly after 1 h test (from 29.4 to 2.5 μmol g⁻¹ s⁻¹ for H₂ formation rate). TPO profile for the catalyst after 1 h test (Fig. 6.2d) exhibits three peaks (maxima at 436, 476, and 580 K, respectively). Compared to the TPO profiles after the pulse treatment (Fig. 6.2a-c), the high temperature peak exclusively increased in intensity since the deposition on ZrO₂ could still take place, as can be seen for high AcOH conversion (Fig. 6.3), even after the deactivation for the steam reforming. The catalyst was then treated in O₂ at two different temperatures, 435 and 475 K, for 15 min. After O₂ treatment at 435 K, the first peak disappeared from TPO profile (Fig. 6.2e) but the second peak remained present. However, the catalytic activity was only slightly recovered with this treatment (Fig. 6.3), which demonstrates that removal of carbon from the Pt surface has a small effect only. The fact that both the first and second peaks disappeared completely after oxidation at 475K (Fig. 6.2f), combined with the observation that the H₂ formation rate recovered significantly from 2.5 to 18.6 μmol g⁻¹ s⁻¹ (Fig. 6.3), supports the suggestion that the periphery sites of the metal particles are kinetically relevant active sites in steam reforming.

6.3.4. Active species derived from H₂O on the catalyst surface for steam reforming

Based on the assumption that ZrO₂ activates water to form hydroxyl groups, IR spectra of ν(OH)

region were measured when the Pt/ZrO₂ catalyst was exposed to water vapor, and the spectra are shown in Fig. 6.4. After reduction at 775 K (before H₂O introduction), isolated surface OH groups (ca. 3756, 3728, 3660 and 3643 cm⁻¹) were observed [9,10]. When H₂O was introduced (13 mbar), intensities of all the OH peaks increased (Fig. 6.4b), Even after thorough evacuation (Fig. 6.4c), intensities of these OH peaks were higher than those before H₂O introduction (Figs. 6.4a,c). Throughout the experiments, molecularly coordinated H₂O (δ HOH) at ca. 1630 cm⁻¹ was not observed.

It should also be noted that the state of Pt should remain the same after the H₂O introduction since dissociation of O-H bond in

H₂O on Pt is not plausible thermodynamically under the conditions investigated [11]. Therefore, it can be concluded that H₂O dissociatively adsorbs on the ZrO₂ exclusively, and forms supplementary hydroxyl groups.

Table 6.3 shows product distribution from AcOH or acetone pulse when the catalyst was either exposed or not exposed to H₂O prior to the pulse. In the case of AcOH, prior treatment with H₂O induced increasing H₂, CO₂ and CH₄ yields, decreasing CO yield, and did not affect acetone formation significantly. Note that oxygen content in CO_x produced increased by 0.24 μ mol. In the case of acetone pulse without H₂O pretreatment, H₂, CO and CH₄ were formed, which is in agreement with results reported for Pt foil [12]. In the case of H₂O pretreatment, more H₂, CO and CH₄ were produced and CO₂ was formed additionally. Similarly, additional 0.18 μ mol of oxygen was contained in CO_x produced. Increasing oxygen content in the product must be derived from surface hydroxyl groups. Fig. 6.5 shows the IR difference spectrum in the ν (OH) region when AcOH was introduced. It can be seen that when AcOH was introduced (1.3 mbar) to catalyst pre-treated with H₂O, intensity of the peaks for surface hydroxyl groups

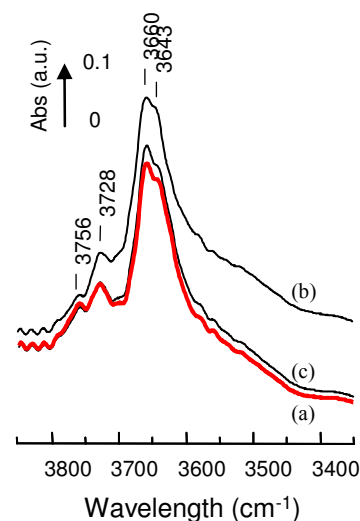


Fig. 6.4. IR spectra of Pt/ZrO₂ for H₂O treatment at 625 K. (a) before H₂O introduction, (b) in the presence of 13 mbar H₂O, (c) after evacuation for 15 min after (b).

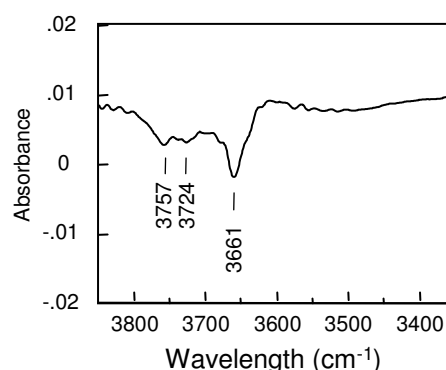


Fig. 6.5. IR difference spectra of Pt/ZrO₂ after exposure to AcOH (1.3 mbar), referred to after H₂O treatment (13 mbar) and evacuation at 625 K.

decreased significantly. Similar results were also observed with acetone (not shown). These results confirm the participation of hydroxyl groups derived from water for steam reforming/ WGS reactions.

Table 6.3

Effect of water pretreatment on product distributions for AcOH or acetone pulse reaction over Pt/ZrO₂ catalysts (625 K, AcOH 3.8 μ mol or acetone 4.3 μ mol, H₂O 22 μ mol)

Reactant	H ₂ O pulse prior to oxygenate pulse	Yield (μ mol)				
		H ₂	CO ₂	CO	CH ₄	Acetone
AcOH	Without	1.32	0.91	1.57	0.75	0.26
AcOH	With	1.59	1.24	1.15	0.84	0.31
acetone	Without	0.52	0.00	0.03	0.10	-
acetone	With	0.77	0.08	0.05	0.14	-

6.3.5. Kinetic relevance of possible secondary reactions during steam reforming of acetic acid

Under conditions for AcOH steam reforming, the products from AcOH decomposition (H₂, CO_x, CH₄) may undergo secondary reactions, which can affect hydrogen yield significantly. In order to elucidate kinetic relevance of the secondary reactions, the separate kinetic tests for CH₄ formation (CO/H₂) and CH₄ consumption (CH₄/H₂O) were carried out over the Pt/ZrO₂ catalysts (Table 6.4). It was found that CO hydrogenation was kinetically much slower to account for the methane formed, even when the reactant (CO, H₂) concentrations were considerably higher than those actually expected for the AcOH reforming (Table 6.1). Therefore, it is suggested that the CH₄ observed for AcOH reforming is derived not from the secondary CO hydrogenation, but from primarily AcOH decomposition on Pt. In addition, CH₄/H₂O reaction was relatively more rapid as compared to CO hydrogenation (especially when excess of water is present in the feed).

Table 5

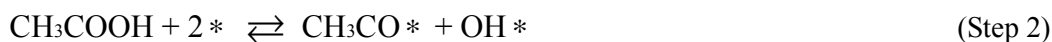
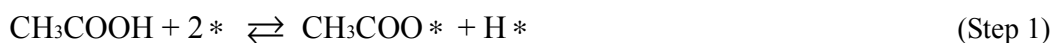
Production/ consumption rate of hydrogen and methane over Pt/ZrO₂ for various reactions. (625 K, H₂O/C = 5 or H₂/C = 3, GHSV = 1,600,000 h⁻¹)

	Initial formation/ consumption rate (μ mol g ⁻¹ s ⁻¹)		
	AcOH/H ₂ O	CH ₄ /H ₂ O	CO/H ₂
H ₂	38	27	2
CH ₄	3.6	6.6	1.1

Approach to equilibrium for WGS reaction ($\eta_{\text{WGS}} = ([P_{\text{CO}_2}][P_{\text{H}_2\text{O}}])/([P_{\text{CO}}][P_{\text{H}_2\text{O}}]K_{\text{WGS}})$) was <0.01 during the steam reforming of AcOH shown in Table 6.1 (at relatively short contact time), indicating that the gas composition was far from WGS equilibrium. However, at larger contact times, extent of WGS reaches the equilibrium, the Pt/ZrO₂ catalysts achieved thorough conversion of CO to CO₂, as can be seen, e.g., in the pulse experiment (Table 6.2, AcOH/H₂O pulse).

6.3.6. Mechanistic scheme for steps involved in steam reforming of AcOH

In this section, the results are compiled up to give the entire image for the reaction. Fig. 6.6 illustrates a scheme of the possible steps involved in steam reforming of AcOH over Pt/ZrO₂. In the figure, the reaction which may occur on Pt is shown in the left box, and the reactions which are proposed to occur on Pt-ZrO₂ boundary is shown in the right box. Since the initial step of the reaction of AcOH occurring on Pt is very rapid, the data by Dumesic and co-workers [13] are adapted, that reported both experimental results and theoretical calculations for the reactions of AcOH on Pt. They suggested that the initial reactions of AcOH with Pt are steps 1 or 2; formation of acetate or acyl species, respectively;



where the symbol * denotes the metal site. Then, the acetate and the acyl groups may further decompose to give CO₂ and methyl (Step 3), and CO and methyl (Step 4), respectively. The CO₂ formed will desorb immediately (unstable on Pt), and the CO will adsorb and desorb (Step 5). Then, the methyl can be hydrogenated with adsorbed hydrogen to form CH₄ (Step 6). Adsorbed hydrogens can re-combine themselves to become di-hydrogen (Step 7). Both steps 1 and 2 seem to take place in parallel (Table 6.3), in agreement with the suggestions in the earlier report [13]. The steps 1 through 7 are considered to be the ways to form the decomposition products on the Pt. Alternatively, the methyl formed may be further dehydrogenated to coke precursor, CH_x species where $0 \leq x \leq 3$ (Step 8). The CH_x species can further undergo graphitization or oligomerization to become deposit, which can cause the deactivation for AcOH decomposition as shown in Fig. 6.1. On the other hand, ZrO₂ activates H₂O to form surface hydroxyl groups (Step 9) as seen in Fig. 6.4. This hydroxyl groups are consumed in the

reactions as shown in Table 6.3. In order to make catalytic action proceeds, CH_x on Pt has to be removed presumably by reacting with the hydroxyl groups formed on ZrO_2 . This reaction should happen via Pt- ZrO_2 boundary, to produce H_2 and CO , i.e., steam reforming (Step 10). Subsequently, WGS reaction may follow (Step 11). The scheme proposed here will continue until the boundary sites between Pt and ZrO_2 is blocked by deposits. Similar to AcOH decomposition, acetone decomposition on Pt may give methyl and CO may be formed as a primary step, and then follow the steps described for AcOH (Table 6.3 shows the results). It is accordingly proposed that the concept of this bifunctional mechanism can also be applied for steam reforming of other oxygenates. In order to improve the activity of the catalysts for steam reforming of oxygenates, the support should be designed to enhance the activation of H_2O .

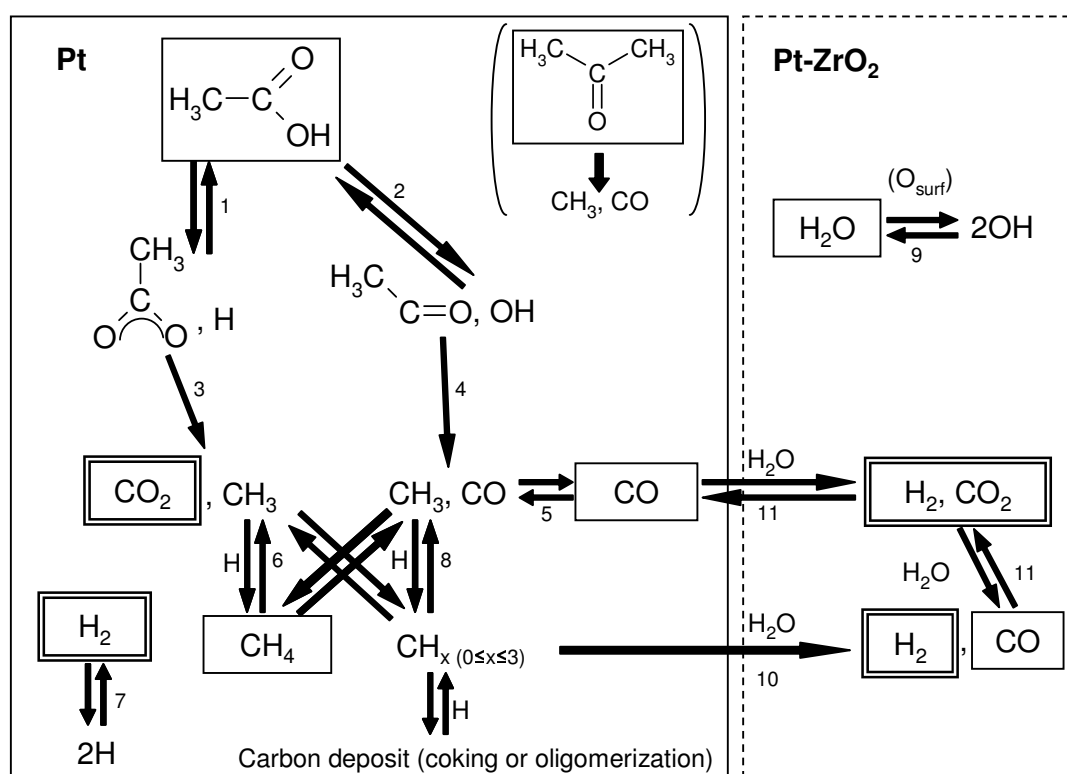


Fig. 6.6. The proposed schematic drawing for the mechanism of steam reforming of AcOH. The steps occurring on Pt are shown in the left box, while the steps which require the Pt- ZrO_2 boundary site to take place are shown in the right box. The primary step of acetone decomposition is shown in the parenthesis. The species in square are in the gas phase, those in double square are the desired products, and the others represent surface adsorbed species. Further details are described in the text.

6.4. Conclusions

The bifunctional mechanism has been claimed for steam reforming of AcOH over the Pt/ ZrO_2

catalysts, where both Pt and ZrO_2 have functions separately for the activation of AcOH and H_2O respectively, but complementarily for entire reaction sequence. It was found that, on Pt, AcOH is decomposed to release H_2 , CO , CO_2 , and CH_4 into gas phase and to leave carbonaceous residue which potentially deactivates the Pt surface. The residue can be gasified with water, forming additional H_2 and CO_2 (steam reforming), and thus, Pt surface is available for following AcOH decomposition. On the other hand, IR measurement confirmed that water is activated on the ZrO_2 , forming surface hydroxyl groups, which are consumed to react with carbon species derived from AcOH. It is considered that the hydroxyl group on the ZrO_2 surface should be the active intermediate of H_2O which reacts with the residue on the Pt. This reaction must occur through the Pt- ZrO_2 boundary sites, supported by the fact that the removal of carbon residue from the periphery of Pt particles might be essential to regenerate the catalyst for the steam reforming. Alternatively, hydrogen consumption by CO hydrogenation to CH_4 seems kinetically irrelevant under the AcOH reforming conditions investigated; i.e., CH_4 predominantly originates from decomposition of AcOH on Pt. The same mechanism is proposed for steam reforming of acetone, implying generality of the concept for the bifunctional mechanism proposed. Finally, the proposed bifunctional mechanism for steam reforming of AcOH over Pt/ ZrO_2 catalyst is illustrated in Fig. 6.7.

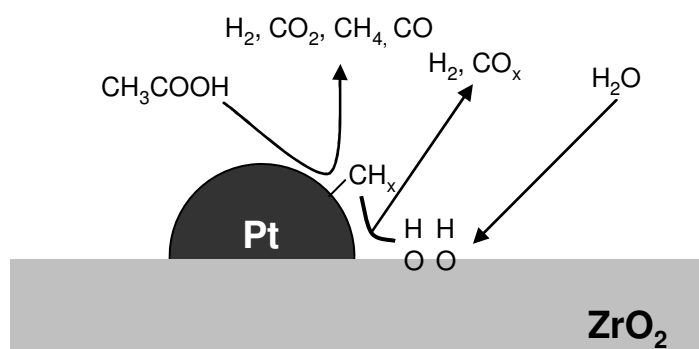


Fig. 6.7. The proposed bifunctional pathway for the steam reforming of AcOH over Pt/ ZrO_2 . Surface hydroxyl groups are formed from H_2O with the surface oxygen on the ZrO_2 .

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Chapter 7

Catalyst Deactivation during Steam Reforming of Acetic Acid over Pt/ZrO₂

Abstract

Steam reforming of acetic acid as a model compound present in bio-oil over Pt/ZrO₂ catalysts has been investigated. Pt/ZrO₂ yields steam reforming products (i.e., H₂, CO, CO₂) to the amounts predicted by thermodynamic equilibrium; however, conversion and yields dropped rapidly with time on course. The deactivation was due to blockage of active sites by coke/oligomer formed. This chapter clarifies cause of the deactivation during steam reforming of AcOH. It was found that many products can be formed from acetic acid on ZrO₂, such as acetone. The experimental results confirmed that aldol condensation of acetone took place on ZrO₂ to give larger compounds which can easily become deposits to block active sites for steam reforming. In order to develop durable catalysts for steam reforming of bio-oil, support should be designed to enhance activation of water, minimize dehydration reactions and thus oligomer formation.

7.1 Introduction

In chapters 5 and 6, it is discussed that mechanistic aspects during steam reforming of acetic acid (AcOH) over Pt/ZrO₂. A bifunctional mechanism was proposed wherein AcOH is activated on the Pt and H₂O is activated on the ZrO₂. The Pt/ZrO₂ catalyst was very active for steam reforming of AcOH, giving close to equilibrium yield of hydrogen. However, the catalyst showed severe deactivation even in the presence of excess amounts of steam due to blockage of active sites by coke/oligomers formed. ZrO₂ is an amphoteric oxide on which both medium-strength acid and basic sites coexist [1] and catalyze various oxygenate conversions [2]. For instance, it has been reported that ZrO₂ is active for acetone (CH₃COCH₃) formation from AcOH [3,4]. Thus, acetone, which is formed on the ZrO₂, may influence the performance of the catalyst. Steam reforming of AcOH and acetone over Pt/ZrO₂ has been investigated in order to study the reaction pathways that lead to deactivation of the Pt/ZrO₂ catalysts and help in the design of stable catalysts.

7.2 Methods

7.2.1 Catalyst preparation

The details of catalyst preparation method are described in chapter 5. Specific surface area of the ZrO₂ and the Pt/ZrO₂ catalysts used are 21 and 20 m² g⁻¹, respectively. Pt dispersion of 0.84 (H/Pt) was determined by hydrogen chemisorption.

7.2.2 Catalytic measurements

For catalytic measurements, 50-200 mg of catalysts was used. For reactions with water in the feed, an aqueous solution of AcOH or acetone giving a steam to carbon molar ratio (S/C) of 5 was introduced using a micro feeder (KD Scientific) and a syringe (Hamilton Co.). For reactions without water in the feed, AcOH or acetone was fed using a saturator. In both reactions with and without H₂O, AcOH and acetone were fed giving a vapor pressure of 2.5 and 1.7 kPa, respectively. The space velocity (SV) of 40000-160000 h⁻¹ was achieved with argon as a carrier gas. The same apparatus and analytical methods were used as that described in chapter 5.

In the case of AcOH conversion, steam reforming (Eq. 1), and water gas shift reactions (Eq. 2) occur simultaneously and the reaction stoichiometry is represented



Similarly, in the case of acetone reforming, the reaction stoichiometry is Eq. 3



The hydrogen yields were calculated based on Eq. 1 or 3. For carbon containing compounds, the yields were calculated based on C₁ equivalent values [5].

7.2.3 Quantification of deposits

Thermogravimetry (TG) (Mettler Toledo TGA/SDTA 851E) was used to determine the amount of deposits on the catalysts. The catalysts used for the reaction were heated from room temperature to 1075 K in 1%O₂/Ar and weight changes recorded.

7.3 Results

Blank experiments with inert quartz chips showed negligible conversions of AcOH and acetone under the conditions investigated. Thus, homogeneous decomposition of AcOH or acetone was not significant.

7.3.1 Steam reforming of AcOH and acetone over Pt/ZrO₂ catalysts

Fig. 7.1 shows conversions and yields obtained during steam reforming of AcOH over Pt/ZrO₂ catalyst at 875 K. Products observed were H₂, CO₂ and CO, and hydrogen yield (87.0%) was nearly at thermodynamic equilibrium (91.3%). However, a sharp drop in conversion was observed after 3 h time on stream.

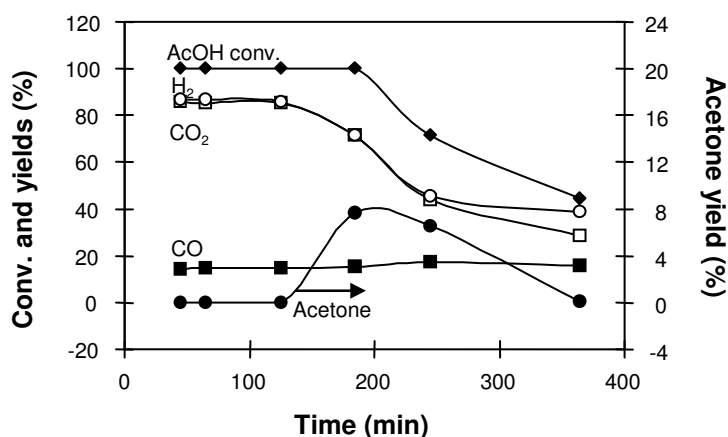


Fig. 7.1. Steam reforming of AcOH over Pt/ZrO₂. (875 K, H₂O/C = 5, GHSV = 40000 h⁻¹, AcOH = 2.5 kPa)

H₂ and CO₂ yields decreased correspondingly, while the CO yield remained constant. Notably, acetone

was observed as deactivation set in. Carbon loss (<15%) was observed throughout the catalytic test, indicating that deposits remained on the catalyst surface. After 6 h time on stream, yields of acetone, H₂ and CO₂ decreased whereas the yield of CO remained constant in smaller amounts.

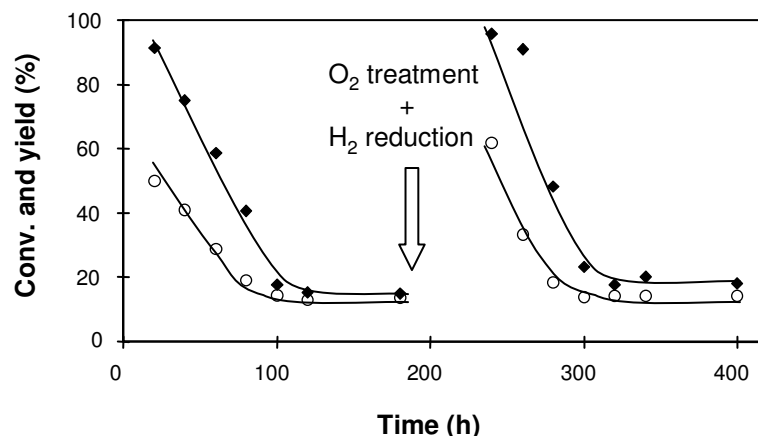


Fig. 7.2. Regeneration of Pt/ZrO₂ for steam reforming of AcOH. The catalyst was treated in flowing air at 875 K, then reduced in H₂ at 925 K. (875 K, H₂O/C = 5, GHSV = 160000 h⁻¹, AcOH = 2.5 kPa) (♦) AcOH conversion, (○) H₂ yield.

The catalyst activity could be regenerated with oxygen at 875 K (Fig. 7.2), suggesting that deactivation was caused by carbonaceous deposits which blocked active sites. Sintering of Pt particles was excluded from Pt dispersion measurements. TG analysis of deactivated catalyst showed that the deposits (amounting to 1.56 wt% after 3 h test) could be removed by combustion in air below 700 K.

Fig. 7.3 shows acetone conversion and H₂ yield for steam reforming of acetone over Pt/ZrO₂ catalyst at 875 K; results for AcOH are given in the same figure for comparison. In order to be able make proper comparison, feed rates for carbon, steam to carbon ratios and space velocity were kept identical. It is seen from Fig. 7.3 that, in the beginning of the reaction, acetone could also be

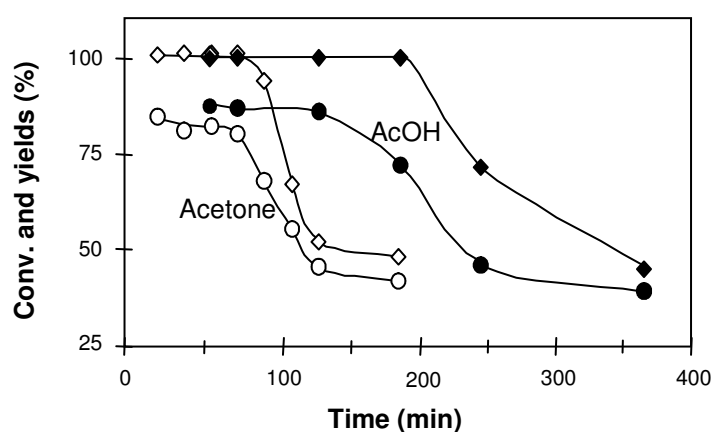


Fig. 7.3. Comparison of conversions and H₂ yields between steam reforming of AcOH and acetone over Pt/ZrO₂ catalyst. (875 K, S/C = 5, GHSV = 40000 h⁻¹, AcOH = 2.5 kPa, Acetone = 1.7 kPa) (♦, ◇) Conversion, (●, ○) H₂ yield, closed symbols for reforming of AcOH, open symbols for reforming of acetone.

steam reformed. However, the Pt/ZrO₂ catalyst showed more rapid deactivation as compared to steam reforming of AcOH (85 min versus 3 h). The catalyst experienced 1.47 wt% of deposits after 3 h test.

Table 7.1

Conversion, selectivity for carbon containing materials, and hydrogen yields for steam reforming of AcOH or acetone over Pt/ZrO₂ catalyst (875 K, 200 mg-cat, SV = 40000 h⁻¹)

Reactant	Conv. (%)	Selectivity (mol%) ^a			Yield (%)
		CO ₂	CO	CH ₄	H ₂
AcOH/H ₂ O	100	85.5	14.5	0	87.0
Acetone/H ₂ O	99.8	71.1	28.1	0.5	83.7

^a Selectivity for carbon containing compounds calculated excluding carbon loss

Table 7.1 summarizes the catalytic results after 5 min time on stream for the two steam reforming reactions. In the case of acetone, CH₄ was observed additionally and H₂ yield of 83.7% observed was close to thermodynamic equilibrium (88.3%) value.

7.3.2 Reactions of AcOH and acetone over ZrO₂

In order to establish the role of the support, reactions were carried out on the bare ZrO₂ support. Results of the steam reforming of AcOH over ZrO₂ (without Pt) are shown in Fig. 7.4. The product distribution changed drastically in time. In the beginning, CH₄ and CO₂ were mainly obtained. After 45 min time on stream, CH₄ disappeared,

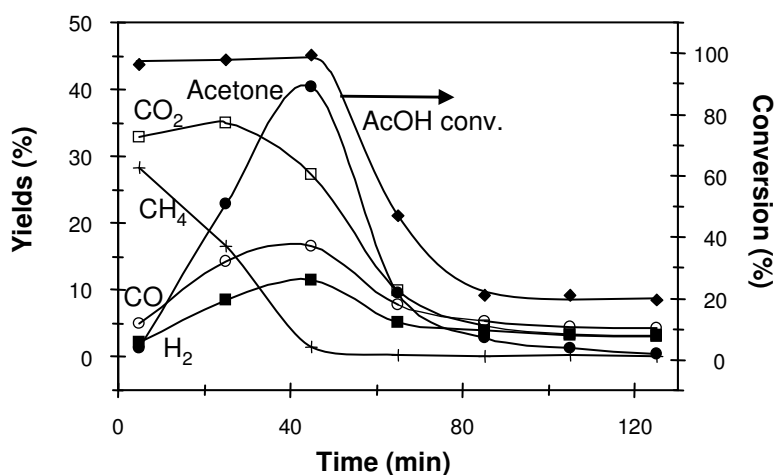


Fig. 7.4. AcOH conversion in the presence of water over ZrO₂. (875 K, H₂O/C = 5, SV = 40000 h⁻¹, AcOH = 2.5 kPa)

acetone yield increased and CO₂ yield remained high. After 85 min., AcOH conversion decreased and yields of all the products decreased correspondingly. Throughout the test, H₂ and CO were observed only in smaller quantities, confirming that ZrO₂ has no appreciable activity for steam reforming (Pt is

essential for steam reforming as discussed in chapter 5). Larger carbon loss was observed throughout the catalytic test (<30%). TG analysis in air indicated 2.1 wt% of deposits after 3 h test and the deposits could be removed below 725 K.

In the absence of water (Table 7.2) AcOH was extensively dehydrated over ZrO_2 , producing ketene (Eq. 4). At a lower temperature (725K) acetone was observed according to Eq. 5.



In the case of steam reforming acetone over ZrO_2 , CH_4 and CO_2 were mainly observed (Eq. 6).



In the absence of water, in spite of the nearly complete acetone conversion, no products were observed in any significant quantities. Indeed, carbon loss was more than 90%. This suggests that the acetone conversion resulted in deposits on the catalyst. At a lower temperature (725 K), mesityl oxide and mesitylene could be observed. Lippert *et al.* [6] describe the formation of mesitylene from acetone due to the following reactions (Eq. 7 and 8)

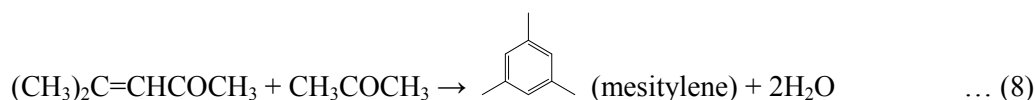
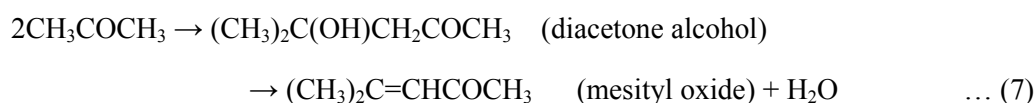


Table 7.2
Reactions of acetic acid or acetone over ZrO_2 at 875 K with ($\text{H}_2\text{O}/\text{C} = 5$) or without H_2O at 5 min time on stream (200 mg-cat, $\text{SV} = 40000 \text{ h}^{-1}$)

Reactant	Conv. (%)	Yield (%)						
		H_2	CO_2	CO	CH_4	ketene	isobutene	acetone
AcOH/ H_2O	96.1	4.9	32.9	2.2	28.4	0.2	1.5	1.3
Acetone/ H_2O	99.8	4.3	22.4	3.0	40.9	0.5	3.1	-
AcOH	98.6	10.4	15.1	3.8	3.1	43.0	0.9	11.1
Acetone	84.6	2.0	1.4	1.3	0.7	2.6	0.1	-

Isobutene was observed over ZrO_2 in small amounts at 875 K (Table 7.2). Isobutene has been reported to be the main reaction product of the acid-catalyzed condensation reaction of acetone [7-9], and known to undergo polymerization to form higher hydrocarbons and aromatics which can become

deposits over acidic catalysts [10]. However, in the current situation this must be a small contribution as the amounts of isobutene observed are much smaller than the other coke/oligomer precursors, ketene or mesityl oxide.

7.4 Discussion

In chapters 5 and 6, it was shown that both Pt and ZrO₂ have a role in the catalysis of steam reforming of AcOH; AcOH activation occurs on Pt and water is activated on ZrO₂. Thus, the active sites are suggested to be located at the Pt-ZrO₂ boundary. It has also been established from the facts (i) catalyst could be reactivated by oxidative regeneration and (ii) Pt dispersion measurements did not indicate sintering of Pt, that loss in activity during steam reforming of AcOH is due to coke/oligomer deposition. As the active sites are located at the Pt-ZrO₂ boundary, coke/oligomer formation in these locations will deactivate the catalyst most effectively. In order to extend catalyst life, it is essential to understand how coke/oligomer formation occurs so that catalyst design can take into consideration ways to overcome this.

During steam reforming of AcOH (Fig. 7.1), initially only steam reforming products are observed. Acetone is observed only after the catalyst deactivates, even though ZrO₂ is capable of catalyzing the formation of acetone from AcOH. This implies the catalyst is able to steam reform acetone formed initially. However, during the steam reforming of acetone (Fig. 7.3) catalyst deactivation occurred more rapidly. This suggests that acetone can play a key role in the deactivation of steam reforming. Indeed, acetone was observed in large quantities from AcOH over ZrO₂ (Fig. 7.4). According to available information [5,6,11,12] most oxides catalyze this reaction (Eq. 6). In the experiments at 875 K, over ZrO₂ (Table 7.2) AcOH undergoes transformation to form CO₂, CH₄, acetone and ketene. The last three products have the potential to form coke/oligomers *via* consecutive reactions.

Earlier works [13, 14] have shown that Pt/ZrO₂ is a very stable catalyst for the steam reforming of methane. Further, the catalyst is even stable and resistant to coke forming during the dry reforming of methane with CO₂ where coke formation is favored by thermodynamics. It is concluded from this that CH₄ itself (formed on ZrO₂) can be considered less important for deactivation here during steam reforming of AcOH.

Ketene, on the other hand, contains two unsaturated bonds and has been proposed to be a

coke-precursor [5]. However, this reaction is known to be a reversible reaction [11], so that excess of water in the feed could prevent its formation (only traces of ketene were observed during the experiments investigated, Table 7.2).

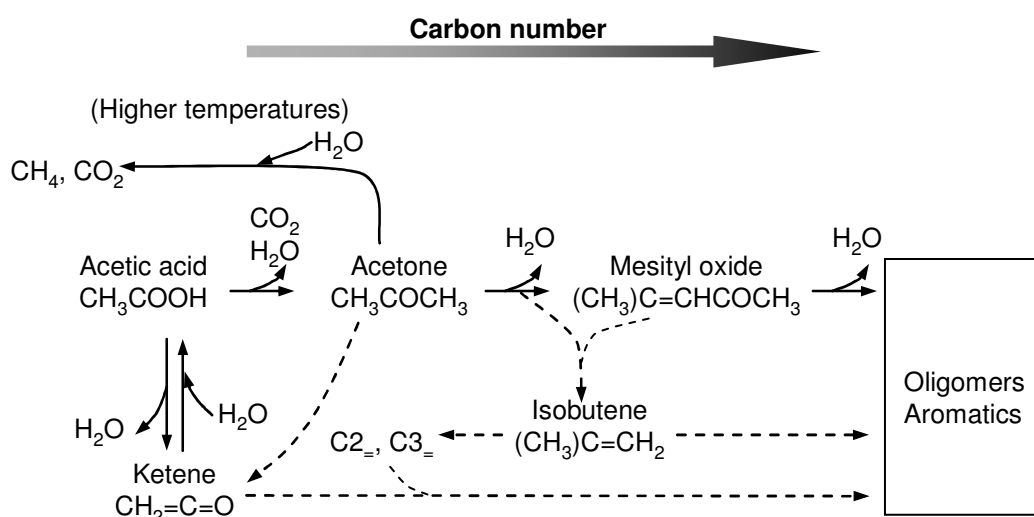


Fig. 7.5. Diagram for the possible reactions of acetic acid (and acetone) over ZrO_2 catalysts.

Discussions so far point out fact that a route to form deposits from acetone should exist. Based on the results obtained in this study, a reaction sequence that AcOH undergoes over ZrO_2 is proposed as illustrated in Fig. 7.5. Carbon number in a compound increases to the right of the figure. It can be noted from Fig. 7.5 that all the dehydration reactions are undesirable for the steam reforming because these reactions are related to the oligomerization (new C-C bond formation). This is in agreement with the fact that the presence of water in the feed significantly suppressed the rate of deposition and total amounts of deposits (Fig. 7.6). However, high ratio of steam to carbon of 5 could still not suppress the coke/oligomer deposition completely.

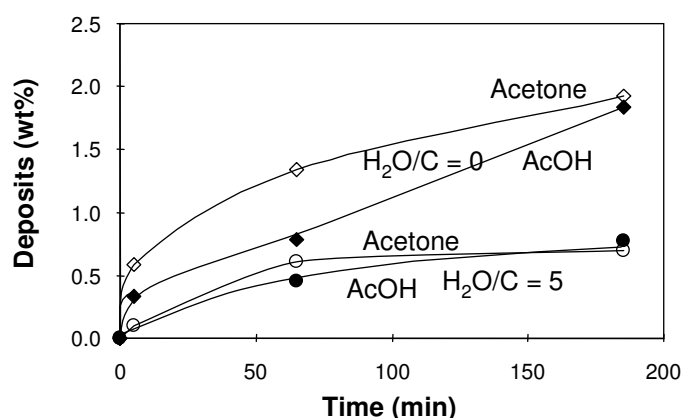


Fig. 7.6. Influence of reactant (AcOH or acetone) and of water on the amount of deposits on ZrO_2 catalyst. (725 K, GHSV = 160000 h^{-1} , AcOH = 2.5 kPa, Acetone = 1.7 kPa) ($\diamond, \diamond$) $\text{H}_2\text{O}/\text{C} = 0$, ($\bullet, \circ$) $\text{H}_2\text{O}/\text{C} = 5$, closed symbols for AcOH reaction, open symbols for acetone reaction.

It is thus proposed that the major route to deactivation is the formation of oligomers by the dehydration of AcOH *via* acetone and mesityl oxide as intermediates. Separate studies indeed show that Pt/ZrO₂ catalyst could be deactivated very effectively by contacting with trace amounts of mesityl oxide (chapter 5). Fig. 7.7 represents overall picture for the proposed reactions over Pt/ZrO₂, some of them also adapted from chapter 6. In the proposed mechanism, deactivation for steam reforming occurs when the boundary sites are blocked. Since acetone is the precursor for oligomer formation, and since acetone is formed from AcOH by acidic or basic oxides, the more plausible way to enhance the life of the catalyst is to enhance steam reforming activity of acetone than prevent its formation. Enhancement of the ability to activate water might help in minimizing the dehydration type reactions which leads to oligomer formation.

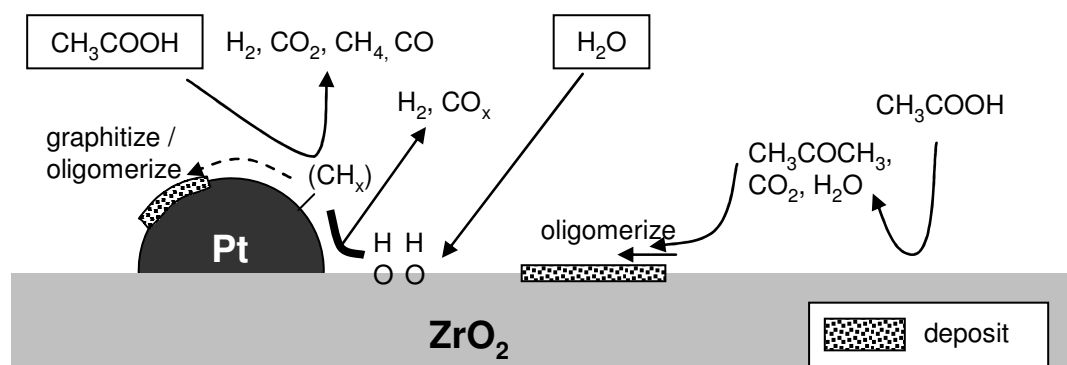


Fig. 7.7. The schematic of bifunctional pathway for AcOH/H₂O reaction over Pt/ZrO₂. Surface hydroxyl groups are formed from H₂O with the surface oxygen on the ZrO₂.

7.5 Conclusions

Pt/ZrO₂ is an active catalyst for the steam reforming of AcOH. During reaction AcOH is also converted to acetone over ZrO₂. Subsequently, acetone undergoes condensation/oligomerization reactions which result in deposits on the catalysts. The Pt/ZrO₂ catalyst is initially active to steam reform AcOH as well as all the compounds formed on ZrO₂, yielding hydrogen close to thermodynamic equilibrium. However, the catalyst is deactivated rapidly for the steam reforming after certain time on stream, due to the blockage of the Pt related active sites by the deposits. Oligomerization (new C-C bond formation) causing the deactivation is related to dehydration reactions (e.g., aldol condensation reactions of acetone), which are undesirable for the steam reforming (where

C-C, C-H bond splitting is necessary). In order to develop efficient and durable catalysts for the steam reforming of AcOH, special attention should be given to the surface properties of the support to enhance activation of water which might suppress undesirable dehydration reactions.

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Chapter 8

Summary

In this dissertation, reforming of methane and biomass derived oxygenates over titania or zirconia supported transition metal catalysts has been investigated.

In chapter 2 to 4, the objective of the study was set to eliminate unfavorable carbon deposition completely during CO₂ reforming of methane. It was revealed that the Co/TiO₂ catalysts showed strong resistance against coke deposition. The studies on influence of reduction temperature strongly suggested that the large difference observed in the initial activities could be ascribed to the differences in the TiO₂ bulk crystal structure. As a result, oxidation of cobalt supported on rutile is more favored than that of cobalt supported on anatase during CH₄/CO₂ reforming. This indicates that TiO₂, together with Co, strongly participate in the reaction and is of importance to optimize a balance of reactions between CH₄ and CO₂.

Although the cobalt is oxidized during CH₄/CO₂ reaction, replacement of cobalt with nickel, i.e., the bimetallic Co-Ni/TiO₂ catalysts, drastically improved the catalytic activity and stability for stable activity. XRD and XPS analyses revealed that homogeneous alloy of cobalt and nickel was formed after the H₂ reduction and remained after the reaction. Compared to the mono-metallic cobalt catalyst, the bimetallic catalysts improved the reactivity toward CH₄ decomposition on the metal, giving the more reductive atmosphere over the catalyst (e.g., H₂ formation from CH₄). The excess of nickel content (> 80 mol%), on the other hand, resulted in carbon formation. By adjusting the ratio of cobalt and nickel loading appropriately, the long-life Co-Ni/TiO₂ catalysts without inducing carbon formation as well as metal oxidation have been developed for the CH₄/CO₂ reforming.

The Co-Ni catalysts were then tested for the CH₄/CO₂ reaction under 2.0 MPa which is practical conditions in industry. The Co/TiO₂ reduced at 1123 K showed relatively stable activity and

experienced only a slight amount of coke. However, slow deactivation ascribed to the oxidation of metallic Co was observed. The addition of trace amounts of noble metals (Pt or Ru) to Co/TiO₂ improved the reducibility of cobalt, resulting in improved catalytic stability, whereas the strong resistant nature of Co/TiO₂ to coke deposition was also retained. Alternatively, the replacement of Co by small amounts of Ni in Co/TiO₂ also enhanced the catalytic stability by inhibiting the oxidation of metallic Co, but replacement by an excess amount of Ni resulted in the decrease of stability due to serious coke deposition. CoNi/TiO₂ with an optimum Co:Ni ratio showed high stability without a significant amount of carbon deposit. It is proposed that the reactions between the reductive and oxidative reactants are balanced kinetically over the catalyst containing proper amounts of Co and Ni, even under the high pressure of 2.0 MPa where coke formation is thermodynamically highly favorable.

In chapter 5 to 7, hydrogen production via steam reforming of acetic acid as a model compound present in bio-oil was investigated on predominantly Pt/ZrO₂ catalysts which exhibit high activity and stability for CO₂ reforming of methane. The objective of this series of study was aimed at elucidating the reaction and deactivation mechanisms to provide knowledge base to develop efficient catalysts. The Pt/ZrO₂ catalysts showed high activities at initial time on stream, but lost its activity for steam reforming (H₂ production) rapidly. It is revealed that Pt is essential for the steam reforming, and ZrO₂ is needed to extend the catalyst life. A bifunctional mechanism is proposed for steam reforming of acetic acid on Pt/ZrO₂, i.e., acetic acid activation takes place on Pt and steam activation on ZrO₂, and the active sites for the steam reforming of acetic acid are located at the boundary between Pt particles and the supports. This proposal is based on the results that (1) hydrogen formation rates correlated strongly with the number of Pt atoms in the close proximity of the support, (2) the support influenced the intrinsic activity (TOF) per Pt periphery site for hydrogen formation, probably due to different water affinity of the support, (3) the catalysts deactivate due to blocking of active sites by oligomers derived from acetic acid/acetone on ZrO₂, (4) the catalyst was regenerated only when deposits on the Pt-ZrO₂ boundary sites were removed.

During steam reforming of acetic acid over Pt/ZrO₂, acetic acid is decomposed on Pt to release H₂, CO, CO₂, and CH₄ into gas phase and to leave carbonaceous residue (most likely CH_x species). It was clearly shown that the residue potentially deactivates the Pt surface unless removed efficiently with

water. On the other hand, IR and pulse reaction experiments confirmed that water is activated on the support, forming hydroxyl groups, which reacted with the carbonaceous residue on the Pt particles. It is considered that this reaction should take place mostly at the boundary between the Pt and the support (active sites for steam reforming) and thus, catalytic sequence continues until the boundary sites will be deactivated by deposits. The CO and CH₄ formed from decomposition of acetic acid may subsequently undergo WGS and steam reforming reactions, respectively, to form additional hydrogen under the acetic acid reforming conditions (when excess of water is present), while hydrogen consumption by CO_x hydrogenation (H₂ consumption) seems by far less kinetically relevant. The concept of the bifunctional mechanism can be extended to steam reforming of other oxygenates, including acetone, over supported Pt catalysts. During reaction acetic acid is also converted to acetone over ZrO₂. Subsequently, acetone undergoes condensation/oligomerization reactions which result in deposits on the catalysts. Oligomerization (new C-C bond formation) causing the deactivation is related to dehydration reactions (e.g., aldol condensation reactions of acetone). In order to develop efficient and durable catalysts for the steam reforming of acetic acid, special attention should be given to the surface properties of the support to enhance activation of water, which improves the catalytic activity as well as which might suppress undesirable dehydration reactions.

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