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Studies on the catalytic conversion of xylose to value-added chemicals over solid acid catalysts

(和訳 : 固体酸触媒によるキシロースの有用化学品への転換反応に関する研究)

This thesis was submitted to Tokyo Institute of Technology for the degree of Doctor of Engineering

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Chapter 1

General introduction

1. Background

From considerations such as depletion of fossil resources and global warming, change from fossil energy resources to renewable ones and to environmentally friendly systems etc. are required and "renewable" is one of the most important and urgent matters for the earth. Before industrial revolution, all of human being's lives was supported by renewable resources; however, the introduction of coal and oil has caused the imbalance between consumption and reproduction of resources and has already brought the situation to the point of no return to ameriorable circumstances.

The technology change from fossil resources to renewable ones is currently very urgent but not quite new. Since the early stage of 20th century, the conversion of biomass resources not suitable for food, clothes and house-making have been realized. However, along the explosion of worldwide population, new needs for better environment have been increasing more and more and it is very urgent and important to change, on an industrial level, the processes and catalysts for utilization of biomass resources from the environmental point of view.

I have summarized the background of my study with reference to the paper reported by Avelinno Corma et al. [1, 2], as follows

2. Utilization of vegetable biomass

Vegetable biomass is generated from CO_2 and H_2O using sunlight as the energy source, producing O_2 as a byproduct. The primary products formed are C_6 - and C_5 -sugars that form cellulose (by polymerization of glucose) and hemicellulose (a polymer of glucose and xylose). There is a third component, lignin that is a highly cross-linked polymer built of substituted phenols and, together with cellulose and hemicellulose, gives strength to plants. Besides those components, plants are also able to elaborate energy storage products such as lipids, sugars, and starches as well

as other products relatively rich in hydrogen and carbon (terpenes) that are found in essential oils that are components of resins, steroids, and rubber.

The Kyoto protocol, together with the desire to reduce society's dependence on imported crude oil, has directed researchers' attention to the use of biomass as a source of energy and, more specifically, for transportation fuels [3, 4 5]. In this sense, ethanol has been used for some time already, blended with conventional fuels or transformed into ethyl *tert*-butyl ether. However, if one considers the energy content of the different biomass products, terpenes top the list, followed by vegetable oils, lignin, and sugars. Since the production of terpenes is too low to meet the requirements for biofuels, it is not surprising that the most attention has been focused on vegetable oils. However, the limited amounts of triglycerides available, together with ethical reasons, have directed future development for large-scale production of biofuels toward lignocellulose as the most interesting source. If lignocellulose can be used for biofuels, it can be employed for synthesizing products with a higher added value, such as chemicals and fine chemicals. In this sense, one can think of replacing existing chemicals competing directly with those derived from petroleum, or making use of the functional groups existing in biomass components to generate novel products with new and improved properties for replacement of existing chemicals or for new applications. When looking into biomass components, it is possible to see their potential for making building block intermediates that can be transformed into families of useful or potentially useful products. Of course, the final utility of a particular synthesis route or family of products will depend on the feedstock and processing cost, the current market volumes and prices, and the possibility of creating new market opportunities. In the present paper, the approach to review catalytic reactions that can help to transform carbohydrates, vegetable oils, animal fats, and terpenes into valuable or potentially valuable chemicals and fine chemicals, their applications also were examined. While most potential catalytic chemical routes have been considered, the attention was concentrated on chemical routes through heterogeneous catalysis; homogeneous and enzymatic processes are treated only marginally. Emphasis has been given to describing environmentally friendly catalytic

processes that can substitute older ones using mineral acids or bases, peracids, or stoichiometric hydrogen-donating molecules.

3. Chemicals from biomass: intermediate platforms

Nature produces the vast amount of 170 billion metric tons (t) of biomass per year by photosynthesis, 75% of which can be assigned to the class of carbohydrates. Surprisingly, only 3-4% of these compounds are used by humans for food and non-food purposes [6]. Biomass carbohydrates are the most abundant renewable resources available, and they are currently viewed as a feedstock for the Green Chemistry of the future [7]. Two types of sugars are present in biomass: hexoses (six-carbon sugars), of which glucose is the most common, and pentoses (five-carbon sugars), of which xylose is most common. There are two ways to transform sugars into bioproducts: one is the fermentation process, and the other is the chemical transformation. In the present section the discussions were directed to the main bioproducts coming from the most important sugars from biomass by both processes.

3.1 Chemicals from fermentation processes: glucose fermentation

Glucose can be obtained from starch, cellulose, sucrose, and lactose. On an industrial scale, glucose is produced from starch by enzymatic hydrolysis, corn being the main source of glucose. The United States alone produces 200-250 $\times 10^9$ t of corn annually, and 1 t of corn produces about 590 kg of glucose. The 250 $\times 10^9$ t of corn produced annually contains the carbon equivalent of 500 million barrels of crude oil, i.e., about two-thirds of that currently consumed annually for production of chemicals.

Another important source of glucose for chemical production is woody biomass. Improvement of processes for harvesting and processing wood cellulose could result in a glucose

source much less expensive than corn. Advances in woody biomass processing, along with enhancements in corn production, will make glucose an easily available raw material for the production of chemicals.

In recent years, due to the large increase in petroleum cost, there has been a re-emergence of interest in large-volume production of fermentation chemicals. Biotechnology is providing new, low-cost and highly efficient fermentation processes for the production of chemicals from biomass resources. Moreover, with a wide range of microorganisms available and many more recently discovered, fermentation of sugars represents an important route for the production of new bioproducts. However, the current economic impact of fermentation bioproducts is still limited, in large part owing to difficulties in product recovery. Thus, substantial improvements in the existing recovery technology are needed in order to allow the chemicals from fermentation to penetrate further in the organic chemical industry. In this section the description on the most important bioproducts coming from glucose fermentation and their conversion or potential conversion into important chemical building blocks was prepared (Fig. 1.1).

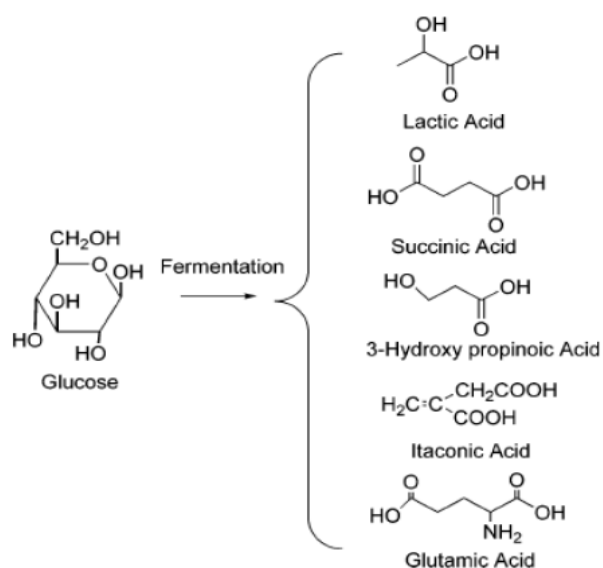


Fig. 1.1 Important products obtained by fermentation of glucose

3.2 Chemical transformations of monosaccharides

Since sugars, i.e., mono- and disaccharides, are readily available biomass primary compounds, in this section the discussions were directed to the most important chemical transformation of the most abundant monosaccharides including glucose, fructose and xylose. Thermal dehydration of pentoses and hexoses in acid media leads to the formation of three important basic nonpetroleum chemicals: furfural (2-furancarboxaldehyde) arising from dehydration of pentoses, 5-hydroxymethylfurfural (HMF) arising from dehydration of hexoses, and levulinic acid arising from hydration of HMF (Fig. 1.2).

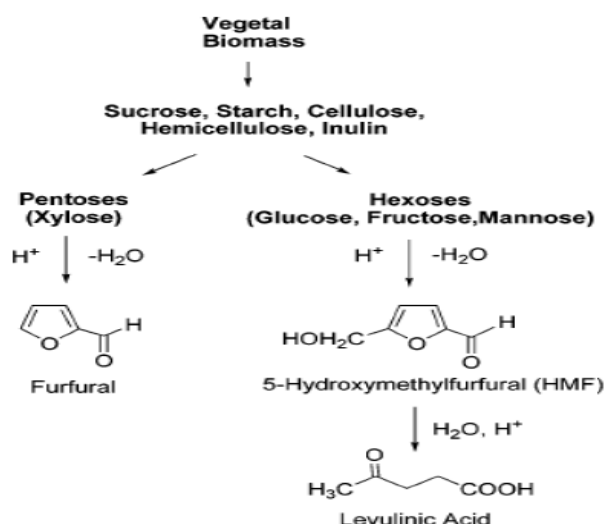


Fig 1.2 Products obtained by dehydration of monosaccharides

3.2.1 Dehydration to 5-Hydroxymethylfurfural.

In recent years, several extensive reviews dealing with the chemistry of HMF and its derivatives have been reported [8]. The synthesis of HMF is based on the acid-catalyzed triple dehydration of hexoses (mainly glucose and fructose, Fig. 1.2), although oligo- and polysaccharides as well as converted industrial wastes can be used as HMF sources. The acidcatalyzed dehydration leads, besides to HMF, to traces of various other dehydration products [9], such as levulinic acid and polymeric side products called humines or humic acids.

Concerning the mechanism of dehydration, Haworth and Jones [10] were the first to suggest the dehydration of fructose in HMF. Later, Van Dam, Antal [11], and Kuster [12] studied the dehydration of hexoses (fructose and glucose) and concluded that the dehydration could occur through two possible pathways (Fig. 1.3): (i) based on acyclic compounds and (ii) based on transformation of ring systems. Moreover, they demonstrated that the chemistry of the formation of HMF is very complex; besides dehydration, it includes a series of side reactions such as isomerization, fragmentation, and condensation which influence strongly the yield of the process [11, 12]. Van Dam [13] and Cottier showed that aqueous and nonaqueous dehydration processes led to about 37 products.

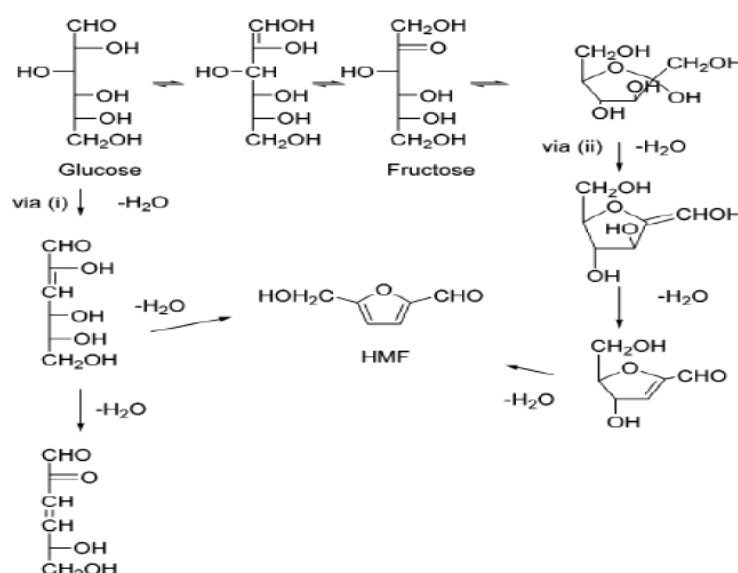


Fig 1.3 Pathways for the dehydration of hexoses

The dehydration process is more efficient and selective to HMF when started from ketohexoses than from aldohexoses. The aldohexose (glucose) enolyzes to a very low degree and the enolization is a determining step of the HMF formation from glucose (see Fig. 1.3). Besides, glucose can condense to form oligosaccharides, which can react with HMF, resulting in cross-polymerized materials. However, glucose is still used in industry as a source of HMF because its cost is lower than that of fructose.

The most convenient method for the preparation of HMF is the acid-catalyzed dehydration

of fructose. Fructose can be obtained by acid-catalyzed hydrolysis of sucrose and inulin or by selective isomerization of glucose to fructose. Many types of catalysts have been used for the dehydration of hexoses. Cottier divided the catalysts into five groups (see Table 1.1): organic acids, and inorganic (mineral) acids [8, 12], organic and inorganic salts, Lewis acids, and others (ion-exchange resins and zeolites).

Moreover, Cottier categorized several HMF processes into five types of methods, depending of the kind of solvent and processing temperature: (1) aqueous processes below 200 °C, (2) aqueous processes above 200 °C, (3) processes in nonaqueous media, (4) processes in mixed solvents, and (5) processes without solvent/microwave processes.

Table 1.1. Catalysts for dehydration of hexoses

organic acids	oxalic acid; levulinic acid; maleic acid; <i>p</i> -toluenesulfonic acid
inorganic acids	phosphoric acid; sulfuric acid; hydrochloric acid; iodine or hydro- iodic acid generated in situ
salts	(NH ₄) ₂ SO ₄ /SO ₃ ; pyridine/PO ₄ ³⁻ ; pyridine/HCl; aluminum salts; Th and Zr ions; zirconium phosphate; Cr, Al, Ti, Ca, In ions; ZrOCl ₂ ; VO(SO ₄) ₂ ; TiO ₂ ; V, Zr, Cr, Ti porphyrins
Lewis acids	ZnCl ₂ ; AlCl ₃ ; BF ₃
others	ion-exchange resins; zeolites

Aqueous processes are very convenient from an ecological point of view but, unfortunately, are not efficient. Under these conditions, rehydration of HMF to levulinic and formic acid occur easily, and yields of HMF are low (30%). Kuster and Van Dam performed in-depth studies of all parameters that might influence the dehydration of fructose in water under homogeneous catalysis. They found that, regardless of the operating conditions, the maximum selectivity to HMF (75%) was obtained when methyl isobutyl ketone was used as a simultaneous extraction solvent.

When acidic ion-exchange resins are used as catalysts in aqueous media, instead of mineral

acids, the yields and selectivity to HMF are not significantly improved.

Nonaqueous solvents such as dimethylformamide (DMF), acetonitrile, and poly(glycol ether) have been used in the HMF synthesis. However, the highest yields of HMF have been obtained in dimethylsulfoxide (DMSO) as the solvent under moderate operating conditions. Mussau et al. [14] performed the reaction without a catalyst in DMSO. Nakamura et al. obtained HMF in 80% yield using DMSO as a solvent and a strongly acidic ion-exchange resin as catalyst. Gaset et al. [32, 33] obtained HMF in 70-80% yield using Levait SPC-108, and Morikawa et al. reported 90% yield of HMF using Diaion PK-216 as catalyst. The advantage of using DMSO as solvent is that it prevents the formation of levulinic and humic acids; however, the main disadvantages of using DMSO are that this solvent is difficult to separate from HMF and there is a possibility of formation of toxic S-containing byproducts arising from the decomposition of DMSO.

The application of mixed solvents (water-organic) solves the problem arising from the low solubility of hexoses in organic solvents. Experiments performed in aqueous *n*-butanol, dioxane, and poly(ethylene glycol) showed a decrease in the levulinic acid formation; processes performed without a solvent show this behavior, too. Formation of levulinic and humic acids is decreased and HMF can be obtained in 70% yield when using equimolecular amounts of pyridinium salts. Cottier described the irradiation with microwaves of aqueous fructose mixed with inorganic phosphates, which produced HMF in 28% yield.

Despite the fact that dehydration of hexoses to HMF has been a well-known reaction for many years, researchers are still searching for both the most suitable catalytic system and the best reaction medium. In the past decade, new catalytic systems and processes for the synthesis of HMF have also been developed. For instance, acid zeolites (as heterogeneous catalysts) and related materials can be used as highly selective and active catalysts in the synthesis of bulk and fine chemicals. The possibility, in using these microporous materials, of tuning acidic and basic properties, hydrophilic and hydrophobic character, and adsorption and shape-selectivity properties make zeolites advantageous as heterogeneous catalysts compared to other catalysts. However,

zeolites of the faujasite family and acidic pillared montmorillonites were already tested as catalysts in the dehydration of hexoses, and only traces of HMF were detected, the main reaction products being levulinic and formic acids. Recently, interesting results on the dehydration of fructose using dealuminated zeolites as catalysts in a water-methyl isobutyl ketone mixture have been reported by Moreau et al. [15]. An acid mordenite zeolite with a Si/Al ratio of 11 was found to be optimal in terms of activity and selectivity to HMF. Working at 165 °C, a selectivity to HMF of 91-92% for a fructose conversion of 76% was achieved. However, it was also observed that selectivity was decreased by increasing the Si/Al ratio. This behavior was related to the increase in acid strength of the acid sites, allowing secondary reactions, such as the formation of levulinic and humic acids, to take place. When the starting reactants were fructose precursors, such as sucrose and inulin hydrolysates, instead of fructose itself, it was observed that glucose was not significantly dehydrated under the operating conditions, and selectivities to HMF between 92 and 97% for fructose conversion up to 54% were achieved.

The above findings were applied to the development of a pilot plant using a new solid-liquid-liquid reactor, where the zeolite is in suspension in the aqueous phase and the HMF is extracted continuously with methyl isobutyl ketone in a countercurrent manner with respect to the aqueous fructose phase and catalyst feed. Thus, the residence time of HMF in the aqueous phase is shortened, and an increase in selectivity of about 10% is achieved.

Vanadyl phosphate ($\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$), which is a layered material involving Lewis and Brønsted acid sites, has been recently tested as a heterogeneous acid catalyst in dehydration of fructose aqueous solutions at moderate temperature (80 °C) [16]. Selectivities to HMF of over 80% for fructose conversions around 50% were achieved.

When VO^{3+} was partially substituted by trivalent metal cations such as Fe^{3+} , the catalyst exhibited the best activity and selectivity. This system was able to convert highly concentrated fructose solutions with a performance of 376 mmol of HMF/ $\text{g}_{\text{cat}} \cdot \text{h}$ and selectivity around 90%, without formation of levulinic or humic acid. Inulin may also be converted to HMF with similar

performance.

Ribeiro et al. [17] have reported the catalytic one-pot cyclation and oxidation of fructose over bifunctional and redox catalysts, cobalt acetyl acetonate on sol-gel silica. The aim of this study was to prepare 2,5-furandicarboxylic acid directly from fructose. The authors found that, with SiO₂ gel catalyst, fructose in aqueous solution is selectively converted into HMF, achieving 50% yield within 1 h reaction time at 165 °C and under 2 MPa air pressure.

Considering that high selectivity to HMF is often obtained in high-boiling polar solvents such as DMSO, and the problems associated with the separation procedures when these solvents are used, Bicker et al. [18] studied the dehydration of fructose, glucose, sucrose, and inulin in suband supercritical fluids such as acetone/water mixtures, methanol, and acetic acid. When sub- and supercritical methanol and subcritical acetic acid were used as solvents, the corresponding furfural ether (78% yields) and furfural ester (37% yield) were obtained. Using acetone/water mixtures and working under optimized reaction conditions (90% v/v of acetone, 10 g/L of fructose, 10 mmol/L H₂SO₄, 183 °C, and 20 MPa), a nearly complete conversion of fructose with a 77% selectivity to HMF and no production of humic acids was obtained, in contrast to the reaction performed in supercritical water, where unsatisfactory yields of HMF were achieved with high production of humic acids. Also, in the case of dehydration of inulin, glucose, and sucrose, selectivities to HMF were high: at 100% conversion of the starting sugar, 78%, 48%, and 56% selectivities were obtained, respectively. These findings led to the authors to propose an acceptable price of about 2 euros/kg for HMF if fructose or fructose precursors are available at a price of 0.5 euro/kg.

Considering the good results obtained 20 years ago by Fayet et al. for the fructose dehydration (70% yield of HMF) over molten salts (pyridinium chloride) under mild operating conditions, Moreau et al.[19] investigated the dehydration of fructose over a novel class of salts that recently appeared, the ionic liquids. Preliminary studies showed that, when the reaction was performed using 1-butyl-3-methylimidazolium tetrafluoroborate as solvent and Amberlyst-15 as catalyst, a yield of up to 50% of HMF is obtained within around 3 h at 80 °C. However, using

DMSO as co-solvent, yields of HMF close to 80% were achieved within 24 h.

3.2.2 Dehydration of Monosaccharides to Furfural.

Furfural is an important chemical readily accessible from biomass. It appears to be the only unsaturated large-volume organic chemical prepared from carbohydrate resources and is a key derivative for the production of important nonpetroleum- derived chemicals competing with crude oil [20-22].

The annual production of furfural is about 300 000 t/year, [23] and its price (250 euros/t) is in the range of basic petrochemicals such as benzene and toluene (225-250 euros/t). Furfural is produced from agricultural raw (or waste) materials rich in pentosan polymers (hemicellulose fraction) by acidic degradation. The reaction involves hydrolysis of pentosan into pentoses (mainly xylose) which under high temperatures (200-250 °C) and in the presence of acid catalysts, mainly sulfuric acid, [24] undergo a triple dehydration, giving furfural. Under these conditions, the selectivity to furfural is not higher than 70%, and only when continuous extraction with supercritical CO₂ is performed is 80% selectivity reached. According to the literature, the reaction mechanism involves the irreversible development of conjugation via the formation of enediol intermediates. [24]

The first commercial process for production of furfural, which is currently the main source of furfural, was developed by the Quaker Oats Co. in 1922, and uses concentrated sulfuric acid as catalyst. Other processes, such as the Petrole-chimie process, use phosphoric acid or superphosphate. These types of processes suffer from serious drawbacks, related to the use of extremely corrosive and highly toxic acid catalysts, the difficulty in their separation and recycling, and moreover the fact that extensive side reactions take place, resulting in loss of furfural yield due to long residence times. Therefore, improvement of the chemical technology is required in order to increase the possibilities of furan-based chemical industries.

Heterogeneous catalytic processes for dehydration of pentoses into furfural offer

environmental as well as economic advantages. Attempts have been made to develop such processes, and Moreau et al. [25] reported the use of zeolites (faujasites and mordenites) for the dehydration of xylose to furfural at 170 °C in a solvent mixture of water and methyl isobutyl ketone or toluene. Mordenite was more selective to furfural than faujasite, achieving selectivities between 90 and 95%; however, conversion was low (about 30%).

Kim et al. [26] reported that, using sulfated titania and sulfated zirconia as solid acid catalysts and supercritical CO₂ as the extracting solvent, furfural was synthesized with high yields even at high conversions of xylose. More recently, Dias et al. have studied the dehydration of xylose to furfural in the presence of heteropolyacids, MCM-functionalized sulfonic acid, [27] and microporous and mesoporous niobium silicates as catalysts at 140 °C, using DMSO and water/toluene as solvents. With MCM-functionalized sulfonic acid materials, conversions of xylose higher than 90%, with selectivity to furfural of about 82%, were obtained; however, the yields obtained with heteropolyacids were lower than and comparable with those obtained with sulfuric acid and *p*-toluenesulfonic acid, respectively, in terms of the yields of furfural achieved (58-67%). Dehydration of xylose over microporous AM-11 niobium silicates gives xylose conversions up to 90% and furfural yields up to 50%. These yields are significantly higher than those achieved under the same reaction conditions with HY or mordenite zeolites. However, mesoporous MCM-41-type niobium silicates were less selective than AM-11 (giving yields between 34 and 39%) and also less stable in recycling runs.

3.2.3 Furfural Derivatives.

The chemistry of furfural is well developed, and recently Zeitsch [28] reported an excellent and extensive revision on the furfural chemistry and its derivatives. Therefore, here we will discuss in brief the main transformation of furfural to the primary families of derivatives which can be obtained by simple straightforward operation (Fig. 1.4). One important chemical coming from furfural is furfuryl alcohol. This compound finds a variety of applications in the chemical industry.

It is mainly used in the manufacture of resins, as a starting material for the manufacture of tetrahydrofurfuryl alcohol, and it is also an important chemical intermediate for the manufacture of fragrances, Vitamin C, and lysine.

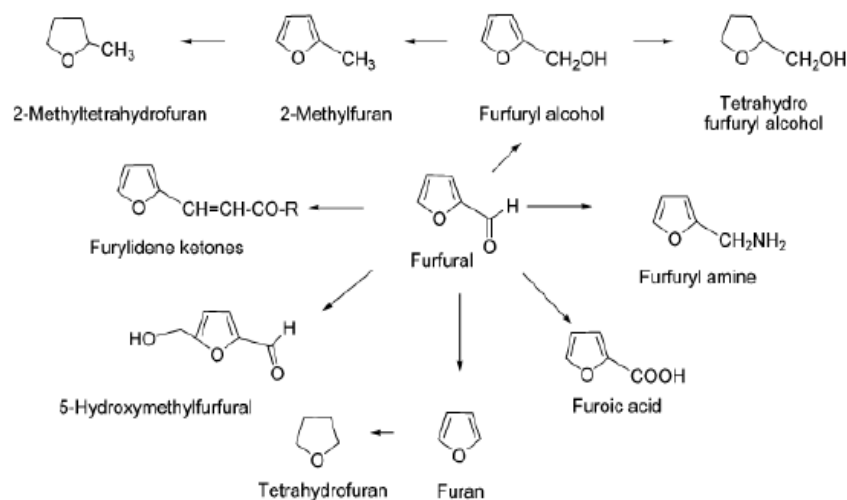


Fig 1.4 Primary products obtained by direct transformation of furfural

Furfuryl alcohol is prepared industrially by the catalytic hydrogenation of furfural. There are two ways to produce furfuryl alcohol by hydrogenation of furfural: vapor-phase hydrogenation and liquid-phase hydrogenation. In liquid-phase hydrogenation, high pressure and high temperature are required, and products from ring-opening and residues are formed. In vapor-phase hydrogenation, depending on the type of catalyst used, hydrogenation of furfural can give, besides furfuryl alcohol, a variety of products such as 2-methylfuran and tetrahydrofurfuryl alcohol. For over five decades, copper chromite has been the most successful commercial catalyst used in the furfural hydrogenation in liquid and gas phases. In gas-phase hydrogenation, selectivities to furfuryl alcohol between 35 and 98% have been reported [29], while in liquid-phase hydrogenation, selectivities in the order of 98% were found. The main problem with CuCr-based catalysts is their toxicity, which causes severe environmental pollution. Many attempts have been made to develop new catalysts that are environmentally friendly. Thus, while Raney nickel catalyst produces mainly

tetrahydrofurfuryl alcohol, Raney cobalt catalysts modified with various transition metals [30] and Raney nickel catalysts modified with $(\text{NH}_4)_6\text{MoO}_{24}$ or with salts of heteropolyacids can improve the catalytic activity and selectivity for the hydrogenation of furfural. For instance, in the case of Raney nickel catalysts modified with salts of heteropolyacids, conversions near 98%, with 98% selectivity to furfuryl alcohol, can be achieved in the liquid phase under a pressure of 20 atm.

Platinum has long been known as a furfural hydrogenation catalyst. However, commonly used platinum supported on oxides (and also other noble metals) catalyzes full furfural hydrogenation and favors side and consecutive reactions such as hydrogenolysis of the C-O bond, ring-opening, and decarbonylation. However, it has been shown that doping the platinum/metal oxide systems with electropositive transition metals (Sn, Fe, Ga) enhanced the selectivity to furfuryl alcohol up to 80%. Very recently, Pt deposited on monolayer supports (SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, MgO , TiO_2) was reported to yield a maximum selectivity of 93.8% toward furfuryl alcohol in the gas-phase hydrogenation of furfural at atmospheric pressure [31]. Pt/C catalyst was also shown to be an effective system for the liquid-phase hydrogenation of furfural to furfuryl alcohol.

Cu-based catalysts such as carbon-supported copper, Cu/MgO, CuLa supported on MCM-41, and Cu-Ca/SiO₂ have been developed recently and utilized for the selective gas-phase hydrogenation of furfural to furfuryl alcohol (98% conversion with nearly 98% selectivity was reported).

With the development of amorphous materials and nanomaterials, ultrafine amorphous powders such as Ni-P, Ni-B, and Ni-P-B have been used for the liquid-phase selective hydrogenation of furfural. In this direction, interesting results were reported by Li et al. using Fe-promoted Ni-B and Mo-doped Co-B amorphous alloy catalysts. Using these systems, and working at 100 °C and 1 MPa of hydrogen pressure, 100% yields of furfuryl alcohol were achieved. The promoting effect of the Fe and Mo dopants on the selectivity to furfural was attributed mainly to the acidic character of these metals, which favors the adsorption and activation of the CdO group of furfural. Furfurylamine is another useful compound derived from furfural that is used in the

manufacture of pharmaceuticals, pesticides, fibers, etc. Furfurylamine is industrially prepared by the reductive amination of furfural. This method allows the conversion of the carbonyl function to an amine by directly treating a mixture of the carbonyl compound and ammonia or an amine with the reducing agent in a single operation without preformation of an intermediate imine. Thus, furfural is reacted with NH_3 and H_2 in the presence of Co- and/or Ni-based catalysts. The reactions are usually performed in the liquid phase using dioxane or alcohols as solvents and at moderated temperatures (100°C). Under these conditions, complete furfural conversion with high selectivity to furfurylamine (97%) is obtained. More recently, electrochemical reduction of furfural derivatives such as furfuryl oxime has been reported for the preparation of furfurylamine; however, the yields of the amine are relatively low.

Furoic acid is used as a feedstock in organic syntheses and as an intermediate in the synthesis of medicines and perfumes. Methods reported to obtain furoic acid involve the Cannizzaro reaction from furfural and oxidation of furfural using oxidants such as KMnO_4 , Ag_2O , or mixtures of metallic oxides such as iron, copper, and noble metal oxides like platinum. However, such routes cannot be regarded as selective, and the catalysts in many cases are easily poisoned and their regeneration is difficult. Selective oxidation of furfural to furoic acid has been performed using hydrogen peroxide as oxidant in the presence of bases such as secondary and tertiary amines or pyridine, giving yields between 40 and 80%. Oxygen has also been employed to oxidize furfural to furoic acid. Verdeguer et al. performed the reaction in aqueous alkaline medium under a stream of oxygen in the presence of a bimetallic lead/platinum deposited on charcoal catalyst. Working at -35°C , pH 8, and 0.36 M solution of aqueous furfural, full conversion of furfural to furoic acid was obtained. The entire amount of furoic acid formed is recovered by acidification of the reaction mixture with concentrated HCl. The catalyst can be reused several times, without appreciable loss of activity.

Furfural is the starting material for the production of HMF. The commercial route to obtain HMF is by hydroxymethylation of furfural with formaldehyde. Furfural can be hydroxymethylated

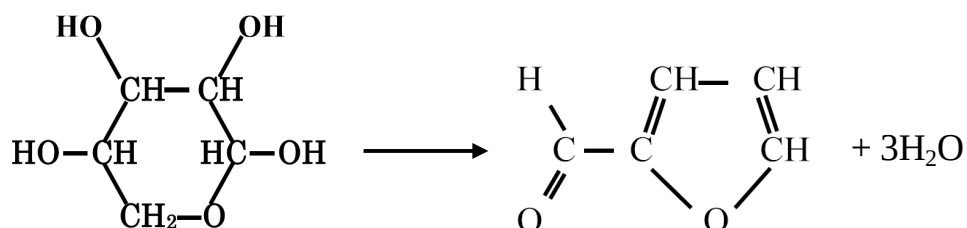
to HMF using acid zeolites with controlled structure and acidity. While ion-exchange resins were inactive, dealuminated mordenites were able to perform this reaction at 90 °C without solvent or by using an organic co-solvent for simultaneous extraction of HMF. Yields around 30% of HMF were obtained. The low yield was attributed to the deactivation of furfural by the presence of the electron-withdrawing aldehyde group at the C-5 position. However, by protecting the aldehyde function with an electron-donating 1,3-dithiolane group, the selectivity to the hydroxymethylated 1,3-dithiolane derivative was increased to 90%.

Furfural is also the key chemical for the commercial production of furan and tetrahydrofuran. Furan is obtained by catalytic decarbonylation of furfural. Hydrogenation of furan gives tetrahydrofuran, an important industrial solvent. Furan can also be used as an octane enhancer in gasoline blends. Catalytic decarbonylation of furfural is usually carried out using Pd supported on a basic support catalyst (BaSO_4 or Al_2O_3) in the presence of hydrogen at temperatures between 300 and 400 °C and at atmospheric pressure, achieving in this way yields of furan higher than 90%. Gaset et al. performed the liquid-phase (at 150-160 °C) decarbonylation of furfural in furan using Pd/C catalyst and hydrogen in the presence of K_2CO_3 as promoter, achieving high yields of furan. Increased activity was observed when the catalyst- K_2CO_3 mixture was activated by UV irradiation.

Vapor-phase decarbonylation of furfural in furan has also been performed over zeolites. Thus, passing furfural vapors (generated during cellulose pyrolysis) over ZSM-5 zeolite at temperatures between 350 and 550 °C, mixtures of furan and methylfuran are obtained. Supported metal oxides of Group VIII metal catalysts have also been used with different levels of success in the decarbonylation of furfuraldehyde to furan.

4. Targets of this study

Xylose, the starting material of this study, is a monosaccharide to be manufactured through hydrolysis of hemicellulose etc. as the biological raw materials. As the industrial field, the above hydrolysis has been realized mainly with sulfuric acid as the catalyst [21, 24]. The process from xylose to furfural has been established since 1920's, also over sulfuric acid as catalyst, as follows.



The sulfuric acid as catalyst 1) is difficult to be reclaimed or removed because of homogeneous catalyst and 2) gives a heavy load to environment because of its strong acidity. In order to minimize the influence to environment, the introduction of solid acid catalyst has been keenly expected, for easy reclaim or removal of catalyst and easy separation of furfural including easy purification.

Although there have been many studies and approaches shown in Table 3.1, unfortunately, no application to industries in actual has yet been realized. One of the reasons, I think, there has been little approach concerning the reaction conditions including reaction mechanism. It is the reason why I highlighted to the reaction conditions, especially the reaction solvents.

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Chapter 2

Dehydration of xylose to furfural over various solid acid catalysts

1. Introduction

At the beginning of this study, the selection of the kinds of catalysts was very important for the better continuity of study. Key points were considered as the acid amount, specific surface area and morphology. Former two items are considered to relate to activity of catalysts, i.e. the conversion of xylose and latter one is considered to relate the selectivity to furfural.

It was reported that furfural synthesized through dehydration from xylose was easily lost by reacting with the intermediates over catalysts [1]. In order to establish higher yield, it maybe essentially necessary to remove synthesized furfural from reacting solvent with catalysts and for this purpose 2-phase reacting system with water and toluene was tried in this study [2-7]. However, the details have not yet been reported and therefore it is absolute necessary to clarify the system and mechanism for 2 phase reacting method, which are reported and discussed in Chapter 3.

From these points of view, Mordenite with different Si/Al ratios and zirconia co-precipitated with SBA-15 were selected as catalyst for dehydration of xylose.

2. Mordenite

2.1 Experimental

2.1.1 Synthesis of Catalyst modified from [8-10]

NH_4NO_3 (Wako), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Wako), NaOH (Wako) and water were mixed in a Teflon beaker. The mixture was stirred for 10 minutes at room temperature. Silica source (Cab-O-SilM7D) and tetraethyl ammonium hydroxide (TEAOH, Wako) were added to the mixture with stirring for 30 minutes. The resultant mixture was additionally stirred at 60 °C for 60 minutes and transferred into Teflon lined autoclave. After the hydrothermal treatment at 170 °C for 1 week without mixing, the solid product was collected by centrifugal and washed with water. The

centrifugation and washing processes were repeated 4 times. Finally, the solid was dried at 120 °C for 24 hours and calcined at 500 °C for 10 hours. The molar composition of the mother gel was 1 SiO₂: 0.046 NH₄NO₃:0.10 or 0.067 of Al(NO₃)₃ · 9H₂O: 0.23 TEAOH: 0.3 NaOH: 7.4 H₂O. Thus obtained products were designated as Mordenite-10 and Mordenite-15, respectively.

Dealumination was made by adding 2 g of calcined mordenite into 40 mL of 6 M HCl aq., standing at 80 °C for 8 hours with reflux condenser and filtering solid. Such procedure was repeated 3 times and finally the solid was washed with water. Final thermal treatment was made including the calcinations at 140 °C for 2 hours, 300 °C for 2 hours and 540 °C for 4 hours. Thus obtained dealuminated catalysts were named as Mordenite-10-DA for 0.1 Al(NO₃)₃ · 9H₂O and Mordenite-15-DA for 0.067 Al(NO₃)₃ · 9H₂O.

2.1.2 Characterization

XRD patterns were collected on a Rint-Ultima III (Rigaku) using a Cu K α X-ray source (40 kV, 40 mA). Field-emission scanning electron microscope (FE-SEM) images of the powder samples were obtained on an S-5200 (Hitachi) microscope. The samples for FE-SEM observations were mounted on a carbon-coated microgrid (Okensoji Co.) without any metal coating. Nitrogen adsorption-desorption measurements were carried out to obtain information on the porosities. The measurements were conducted at -196 °C on a Belsorp-mini II (Bel Japan). The BET (Brunauer-Emmett-Teller) specific surface area was calculated from the adsorption data in the relative pressure ranging from 0.04 to 0.20. Elemental analyses of the samples (Si/Al ratio) were performed on an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000).

2.1.3 Catalytic reaction

Liquid-phase catalytic reactions were performed in a 25 mL glass flask using an oil-bath. In the one-phase system, 5 mL of DMSO was used as solvent. In the two-phase system, the

mixture of 5 mL of water and 5 mL of toluene was used as solvent (Fig. 2.1). Typically, 50 mg of catalyst and 150 mg (1 mmol) of xylose were added to the solvent. The mixture was stirred at 100 °C for 24 h by using a magnetic stirrer with a Teflon-coated stirring bar (10 × ø4 mm) at 400 rpm.

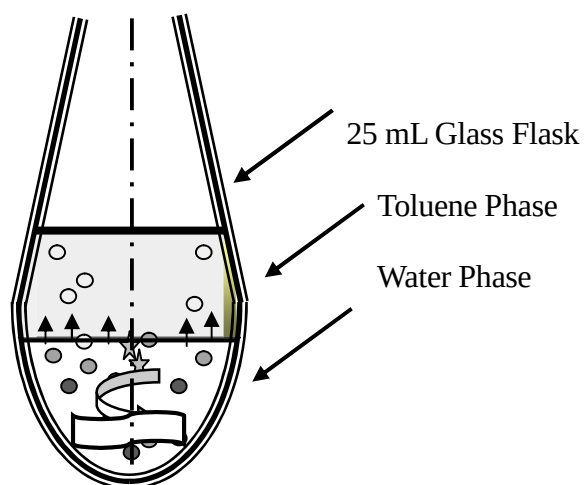
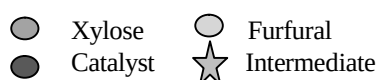


Fig. 2.1. 2-Phase reaction system



In the two-phase reaction system, the measurement shall be made separately to each phase. However it is relatively difficult to separate water and toluene phases precisely. Therefore I introduced co-solvent with polar aprotic liquid for uniform solution with water and toluene phase and realized only one time measurement. The process for this system was that co-solvent with 30 mL of DMSO and 0.8 g of cyclopentanone as inner standard were added to 2-phase liquid (approx. 10 mL in total of water and toluene phase) after catalytic reaction and stirred for 5 min.

Xylose and the products including furfural were analyzed on an HPLC (High Performance Liquid Chromatograph (Shimadzu, RID10A/SPD-10A) with column: Rezex ROA-Organic Acid H⁺ (8%), under conditions of temperature of 50 °C, flow rate of 0.4 mL·min⁻¹ detected by RID and UV (280 nm).

2.2 Result and discussion

2.2.1 Characterization

Figs. 2.2 and 2.3 shows the XRD patterns of Mordenite-10-DA and Mordenite-15-DA, respectively, indicating that both catalysts are typical mordenite crystals. The BET specific surface area and total pore volume of Mordenite-10-DA were estimated as $555 \text{ m}^2 \text{ g}^{-1}$ and $0.3 \text{ cm}^3 \text{ g}^{-1}$, respectively. The BET specific surface area and total pore volume of Mordenite-15-DA were estimated as $540 \text{ m}^2 \text{ g}^{-1}$ and $0.3 \text{ cm}^3 \text{ g}^{-1}$, respectively.

FE-SEM images of Mordenite-10-DA and Mordenite-15-DA are shown in Figs. 2.4 and 2.5, respectively. Particle morphology of Mordenite-10-DA is aggregates of many small platelets 2000 nm in length and 200-400 nm in width. Although Mordenite-15-DA is also aggregates of many small platelets, small platelets were not clearly observed compared to Mordenite-10-DA.

The Si/Al ratios before and after dealumination are listed in Table 2.1. After the dealumination, the content of Al was dramatically decarsed. Thus, Mordenite catalysts with different Si/Al ratos were prepared.

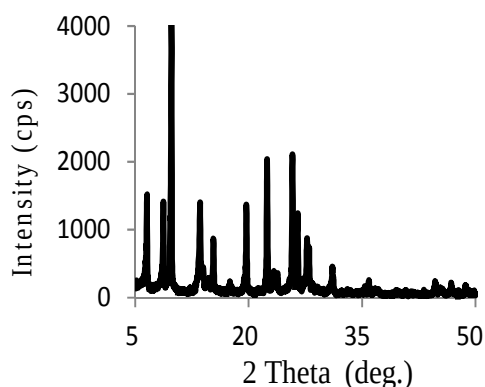


Fig. 2.2 XRD pattern Mordenite-10-DA

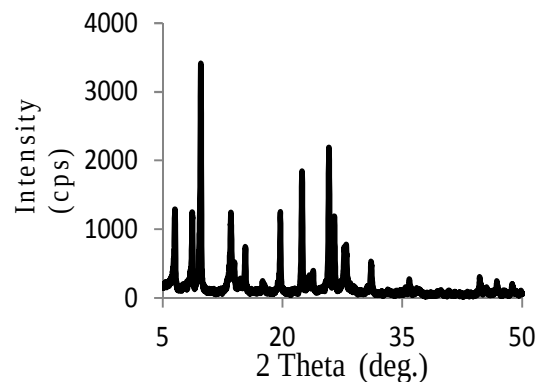


Fig. 2.3 XRD pattern Mordenite-15-DA

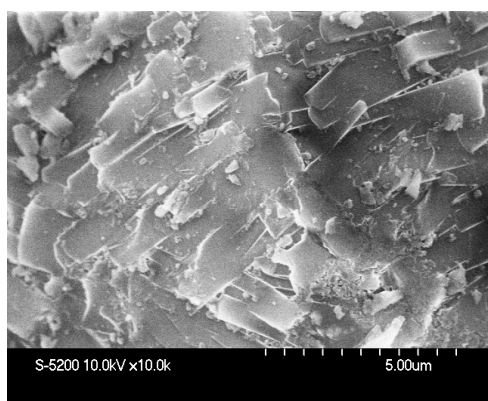


Fig. 2.4 SEM image of Mordenite-10-DA

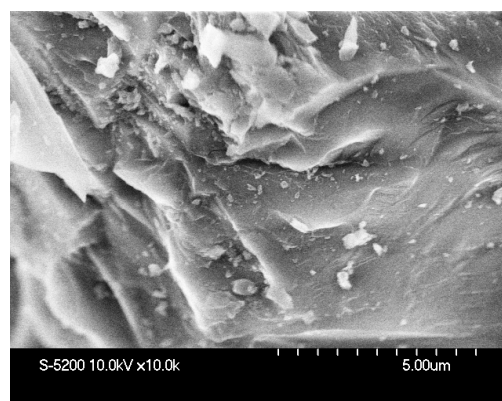


Fig. 2.5 SEM image of Mordenite-15-DA

Table 2.1 Si/Al ratios before and after dealumination

Catalyst	Before	After
Mordenite-10-DA	5.7	20.2
Mordenite-15-DA	6.7	21.6

2. 2. 2 Results of catalytic reaction

As shown in Table 2.2, both catalysts showed a low catalytic performance. It is very difficult to evaluate the possibility of these catalysts for applicability to synthesis of furfural from xylose. The reaction conditions may not be suitable for these catalysts.

Table 2.2 Results of catalytic reactions (48 hours)

	Conversion of Xylose (%)	Yield of Furfural (%)	Selectivity to Furfural (%)
Mordenite-10-DA	4.6	0.9	20.5
Mordenite-15-DA	4.7	2.2	46.6

Reaction conditions: catalyst, 50 mg; xylose, 1 mmol; solvents, water 5 ml and toluene 5 ml; temperature, 100 °C; reaction time, 48 h

3. Zirconia co-precipitated with SBA-15

3.1 Experimental

3.1.1 Synthesis of zirconia co-precipitated with SBA-15

Zirconia-silica-mesoporous composite has been investigated as catalyst for the dehydration of xylose [11-17]. Therefore, zirconia co-precipitated with SBA-15, which is named as Zr(x)-SBA-15, has been applied to this study, where x means the atomic % ratio of Zr/Si in the mother gel. In a typical synthesis, the surfactant, P123 from (Aldrich, $M_n = 5800$), was dissolved into 2 M of HCl aq. TEOS (tetraethyl orthosilicate) was added to the solution with stirring at 40 °C for 1 hours. Then $ZrOCl_2 \cdot 8H_2O$ was added to the mixture with stirring at 40 °C for 4 hours.

Thus obtained mother gel was stirred 100 °C for 48 hours with pH of 7.5 kept by adding 28% of NH_4OH and allowed to stand for further condensation at 100 °C for 48 hours. After the thermal treatment, the solid was collected by filtration, washed with water, dried at 100 °C and calcined at 500 °C for 5 hours. The molar composition of the reactants was 0.017 P123: 1 TEOS: 0.1 or 0.2 $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$: 6.13 HCl: 158.7 H_2O . Thus obtained products were designated as Zr(10)-SBA-15 and Zr(20)-SBA-15.

3.1.2 Characterization

The structural characterizations were conducted with the processes shown in the section 2.1.2 of this chapter.

3.1.3 Catalytic reaction

The catalytic performances were evaluated by the same method as the section 2.1.3 of this chapter.

3.2 Result and Discussion

3.2.1 Structural characterization

The low diffraction angle of the XRD pattern of Zr(10)-SBA-15 and Zr(20)-SBA-15 shows the same pattern as that of SBA-15 although the intensities of the peaks were decreased (Fig. 2.6). In Zr(10)-SBA-15 and Zr(20)-SBA-15, no specified peaks was observed at the high diffraction angle, suggesting that the Zr species was incorporated into the silica network of SBA-15 and that the independent ZrO_2 crystals were not formed. Table 2.3 summarizes the data of the N_2 adsorption-desorption measurements. Although the addition of Zr species led to the decrease in the surface areas, the pores sizes were unchanged.

Table 2.4 showed the acid amount and density, estimated by the ammonia TPD method. The acid amount of Zr(20)-SBA-15 is higher than that of Zr(10)-SBA-15. The acid sites of

SBA-15 would be ascribed to the abundant Si-OH groups on the surface of mesopores. In the zirconia co-precipitated with SBA-15, the Zr-O-Si species in addition to Si-OH groups would contribute to the acid sites.

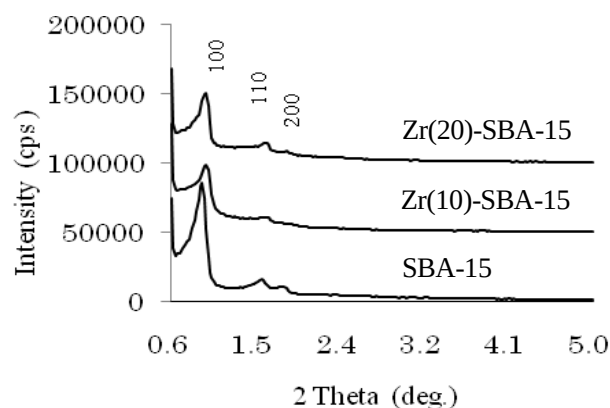


Fig. 2.6 XRD patterns of SBA-15, Zr(10)-SBA-15 and Zr(20)-SBA-15.

Table 2.3 Results of N₂ adsorption-desorption isotherms measurement

Sample	$S_{BET}^{1)}$ (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Pore size (nm)
SBA-15	777	1.13	8.6
Zr(10)-SBA-15	429	1.39	9.7
Zr(20)-SBA-15	441	1.23	8.0

*¹⁾ S_{BET} : BET surface area

Table 2.4 Acid amount and acid density by ammonia TPD

	Acid amount (mmol·g ⁻¹)	S_{BET} (m ² ·g ⁻¹)	Acid density (μmol·g ⁻¹)
SBA-15	0.03	777	0.36
Zr(10)-SBA-15	0.10	399	0.90
Zr(20)-SBA-15	0.29	446	1.09

3.2.2 Results of catalytic reaction

As shown in Table 2.5, Zr(20)-SBA-15 showed the best results in terms of the conversion of xylose and yield of furfural because Zr(20)-SBA-15 had relatively high acid amount and acid density. For converting xylose to intermediate, not only acid amount but also acid density seemed to have a significant influence.

Table 2.5 Results of catalytic reaction (48 hours)

	Conversion of xylose (%)	Yield of furfural (%)	Selectivity to furfural (%)
SBA-15	16.2	3.5	21.6
Zr(10)-SBA-15	18.9	6.9	36.5
Zr(20)-SBA-15	20.8	8.9	42.8

Reaction conditions:

catalyst, 50 mg; xylose, 1 mmol; solvents, water 5 ml and toluene 5 ml; temperature, 100 °C; reaction time, 48 h

4. Conclusion

1. Zirconia containing SBA-15 catalyst with the Zr/SiO₂ atomic ratio of 0.2 was confirmed as one of the candidates for replace of H₂SO₄ catalyst used in industry for synthesizing furfural from xylose.
2. Mordenite did not show any advantage to better yield and selectivity.
3. For further investigation, the acidity level and also acid density level were suggested to be improved remarkably for better yield of furfural and also selectivity to furfural excluding the so-called furfural loss indicated in paper [1].

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Chapter 3

Investigation of reaction system for synthesis of furfural from xylose

1. Introduction

The synthesis for furfural from xylose in industry has been executed by using sulfuric acid as catalysts for dehydration. There are two reaction systems -- one is batch system and the other is continuous system. However in case of research purpose by using solid acid catalyst, I know also two systems -- one is 1(one) phase system, the other is 2 (two) phase system. As shown in Ref. [1], the system for analytical chemistry can achieve even 100 % of furfural yield from xylose by using sulfuric acid, nevertheless the yield in industries has been staying on approx. 60 %. The investigation of the reaction system is very important parallel to investigation of solid acid catalyst itself.

As described in Chapter 2, the reaction conditions have a significant influence to the performance of solid acid catalysts for synthesis of furfural from xylose and therefore in this chapter, the reaction conditions were studied. The systems used in many researches had 3 methods shown in Table 3.1, the 1st of which was 1(one) phase system with DMSO for reaction solvent, the 2nd of which was 2 (two) phase system with water for reacting phase and toluene for extracting phase in autoclave and 3rd of which was 2 (two) phase system also with water and toluene but in micro reactor. The details of reacting system were not clarified and there I had to start to clarify the details. I wish to report the investigation results as follows.

1. Comparison between 1 and 2-phases reaction system,
2. Effect of the volume ratio between water and toluene in the 2-phase system
3. Consideration on the furfural loss during the reaction.

Table 3.1 Reaction conditions and results from Paper

Catalyst		Reactor	Solvent		D-xylose (mg)	Reaction conditions		Results	
Kind	Weight		Kind	Vol. Ratio		Temperature °C	Time	Conv. (%) of xylose	Select. (%) to furfural
H-mordenite	1000	Autoclave	T/W	3/1	200	170	30 min.	30	83
H-mordenite	1000		T/W	3/1	200	170	50 min.	41	82
MCM-41	20	Micro-Reactor	DMSO	-	1	140	4 Hrs.	30	4
MCM41-SO ₃ Hs	20	Micro-Reactor	DMSO	-	1	140	4 Hrs.	81	49
Amberrite	20	Micro-Reactor	DMSO	-	1	140	4 Hrs.	87	68
MP34PWb	30	Micro-Reactor	DMSO	-	1	140	4 Hrs.	49	47
MP34PWb	30		T/W	0.7/0.3	1	140	4 Hrs.	47	80
MP34PWb	30		T/W	0.7/0.3	1	160	4 Hrs.	80	42
exfoliated H ₄ Nb ₆ O ₁₇	20	Micro-Reactor	T/W	0.7/0.3	1	160	4 Hrs.	95	55
Mesoporous persulfated zirconia	20	Micro-Reactor	T/W	0.7/0.3	1	160	4 Hrs.	80	48
Mesoporous sulfated zirconia	20		T/W	0.7/0.3	1	160	4 Hrs.	60	45
Persulfated zirconia grafted on MCM-41	20		T/W	0.7/0.3	1	160	4 Hrs.	95	45
Mesoporous silica-supported 12- BEA	30	Micro-Reactor	T/W	0.7/0.3	1	160	4 Hrs.	40-80	15-50
BEA0.4/TUD0.6	30	Micro-Reactor	T/W	0.7/0.3	1	170	4 Hrs.	85	65
BEATUD	30	Micro-Reactor	T/W	0.7/0.3	1	170	4 Hrs.	85	59
	30	Micro-Reactor	T/W	0.7/0.3	1	170	4 Hrs.	80	75

Note:

MPxxPWb; Mesoporous silica loaded with xx wt % of 12-tungstophosphoric acid (PW)

BEA; Zeolite H-Beta, BEATUD; H-Beta embedded on mesoporous silica and BEA0.4/TUD0.6; physical mixture 0.6 of former and 0.6 of latter

2. Effect of solvent on dehydration of xylose over Zr(20)-SBA-15 catalyst and H₂SO₄

2.1. Experimental

2.1.1 Catalyst:

Zirconia co-precipitated with SBA-15, Zr(20)-SBA-15, which was developed in Chapter 2, was used as catalyst for this investigation. [2,-5]

2.1.2 Reaction method

Liquid-phase catalytic reactions were performed in a 25 mL glass flask using an oil-bath. In the one-phase system, 5 mL of DMSO was used as solvent. In the two-phase system, the mixture of 5 mL of water and 5 mL of toluene was used as solvent (Fig. 2.1). Typically, 50 mg of catalyst and 150 mg (1 mmol) of xylose were added to the solvent. The mixture was stirred at 100 °C for 48 h by using a magnetic stirrer with a Teflon-coated stirring bar (10 × ø4 mm) at 400 rpm.

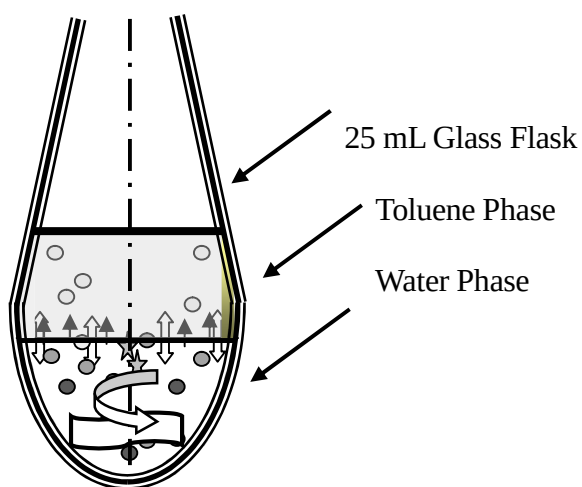


Fig. 3.1. 2-Phase reaction system



In the two-phase reaction system, the measurement shall be made separately to each phase. However it is relatively difficult to separate water and toluene phases precisely. Therefore I introduced co-solvent with polar aprotic liquid for uniform solution with water and toluene phase and realized only one time measurement. The process for this system was that co-solvent with 30

mL of DMSO (dimethyl sulfoxide) and 0.8 g of cyclopentanone as inner standard were added to 2-phase liquid (approx. 10 mL in total of water and toluene phase) after catalytic reaction and stirred for 5 min. [6-14]

Xylose and the products including furfural were analyzed on an HPLC (High Performance Liquid Chromatograph (Shimadzu, RID10A/SPD-10A) with column: Rezex ROA-Organic Acid H+ (8%), under conditions of temperature of 50 °C, flow rate of 0.4 mL·min⁻¹ detected by RID and UV (280 nm).

Table 3.2 List of chemicals used

	chemical composition	molecular weight	melting point (°C)	boiling point (°C)
Xylose	C ₅ H ₁₀ O ₅	150.13	144-145	-
Furfural	C ₅ H ₄ O ₂	96.08	-36.5	161.7
DMSO	(CH ₃) ₂ SO	78.-13	18.5	189
Water	H ₂ O	18.02	0	100
Toluene	C ₆ H ₅ CH ₃	92.14	-93	110.6

2.2 Result and Discussion

The results were shown in Table 3.3. In case of 1 phase, synthesized furfural stay in reaction phase with intermediates and catalyst and as the result, the reaction between furfural and intermediates (condensation) and the reaction among furfurals themselves (polymerization / resinification), were possible.

In case of 2-phase solvent system with water and toluene, both solvents make a boundary due to very little solubility to each other. Furfural solves easily into toluene phase and can also solve into water phase but its solubility is much less than that into toluene. And therefore almost all portions (approx. 80 %) of furfural shall be transferred into toluene phase and there shall be much less opportunity for furfural to contact with the intermediates, which cannot solve into toluene,

and to contact with catalyst, which has much bigger specific gravity than water. As the results, the loss of furfural shall be limited and bigger yield of furfural and selectivity to furfural shall become possible. Even in case of 2-phase system, the combination of DMSO and water and the combination of DMSO and toluene were similar to 1 phase because two kinds of solvent were mixed up completely and same considerations as those for 1 phase shall be applied.

Note: Rough estimation of distribution of furfural into water and toluene at 85 °C (as azeotrope temperature between water and toluene) showed 19.5 % and 80.5 %.

Table 3.3 Solvent effect on dehydration of xylose over ZrO₂-SBA-15 catalyst and H₂SO₄

solvent	(vol. %)	conversion	selectivity
H ₂ O	100	13.4	16.2
DMSO	100	31.8	18.9
toluene	100	< 0.1	< 0.1
DMSO/H ₂ O	50/50	8.8	21.8
Toluene/H ₂ O	50/50	20.8	42.8
DMSO/toluene	50/50	32.0	23.9
DMSO(*2)	100	100	59.7
H ₂ O (*3)	100	33.8	3.1

*1) Reaction conditions: xylose: 1.0 mmol, catalyst: 50 mg, temperature: 100 °C, time: 48 h. each solvent: 5 ml, *2) *3) catalyst: H₂SO₄.

In case of 2-phase reaction, two kinds of mixing are considered as necessary, i.e. the horizontal mixing for accelerating the contact between xylose and catalysts and the vertical mixing for accelerating the extraction of furfural from water phase to toluene phase. In case of Fig. 3.1, it seems that the horizontal mixing is realized mainly by the rotation of magnetic stirring rod and the vertical mixing is realized mainly by azeotrope of water and toluene. This consideration shall be confirmed from chemical engineering point of view, separately.

3. Volume ratio between water and toluene

3.1 Experimental

3.1.1 Catalyst

Zirconia co-precipitated with SBA-15, Zr(20)-SBA-15, which was developed in Chapter 2, was used as catalyst for this investigation.

3.1.2 Reaction method

Water was used as the reacting phase and toluene was used as an extracting phase. Because the volume ratio between water and toluene was considered to have some influence to the results, I studied the volume ratio (water/toluene) of 1/0, 4/1, 3/1, 2/1 1/1, 1/2, 1/3, 1/4 and 0/1 with the amount of total solvent of 10 ml kept.

3.2 Result and discussion

Fig. 3.2 shows the influence of volume ratio of toluene and (water + toluene) on the catalytic performance, indicating that most preferable volume ratio of toluene and (water + toluene) was near 50 to 60 %. Many papers showed the ratio used actually was 3/1 (toluene/water) [3, 4] and it is not clear whether such ratio was most preferable or not. The most preferable ratio may be fluctuated according to shape (dimension) and volume of reactor, reaction conditions, mixing speed and other parameters.

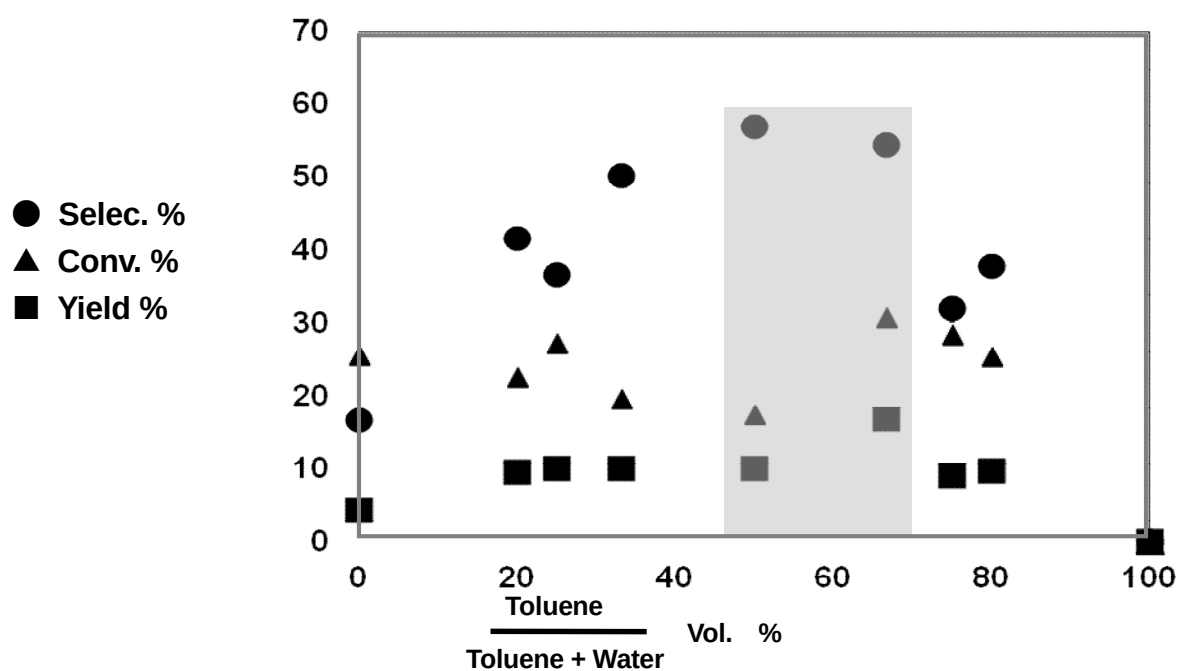


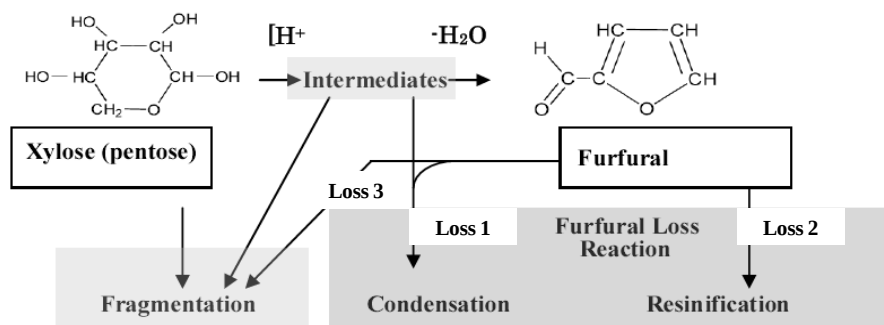
Fig. 3.2 Influence of volume ratio between toluene and water

Reaction conditions: catalyst (Zr(20)-SBA-15), 50 mg; xylose, 1 mmol; solvents, mixture of toluene and water (total solvent of 10 ml); temperature, 100 °C; reaction time, 48 h

4. Furfural loss

4.1 Experimental

There may be so-called "furfural loss" in the course of synthesis from xylose to furfural shown in Fig. 3.3. In order to clarify "furfural loss", the followings were studied.



Dias, A. S.; Lima, S.; Carriazo, D.; Rives, V.; Pillinger, M.; Valente, A. A, *Journal of Catalysis* 244 (2006) 230–237, *) line 1) & 2) were added by T. Suzuki

Fig. 3.3 Synthesis route from xylose to furfural.

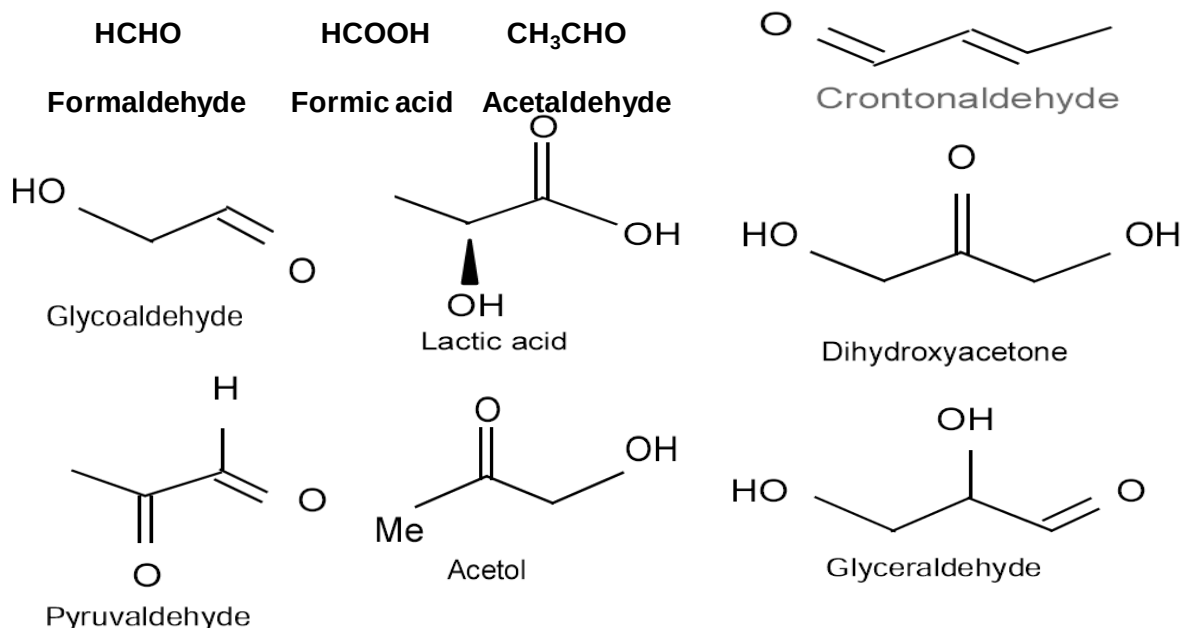


Fig 3.4 Plausible by-products (Loss-3 and by-products fragmented from xylose) [15]

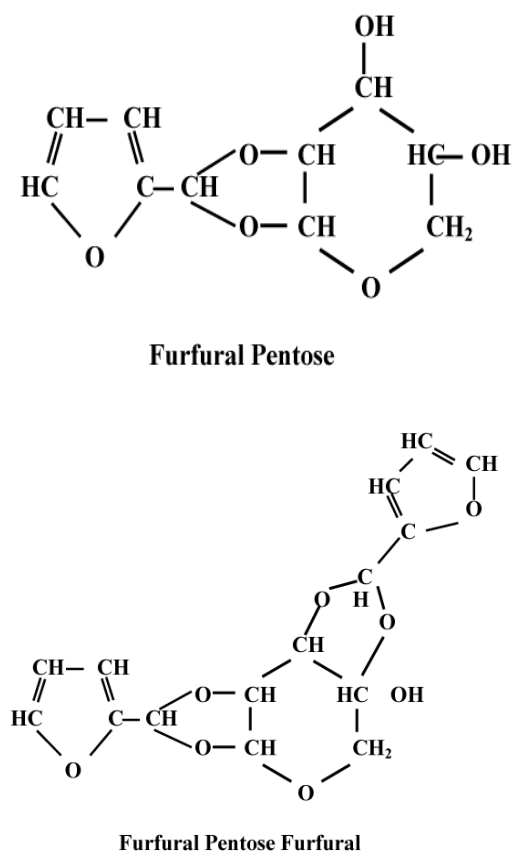


Fig. 3.5 Plausible by-products (Loss-1) [1]

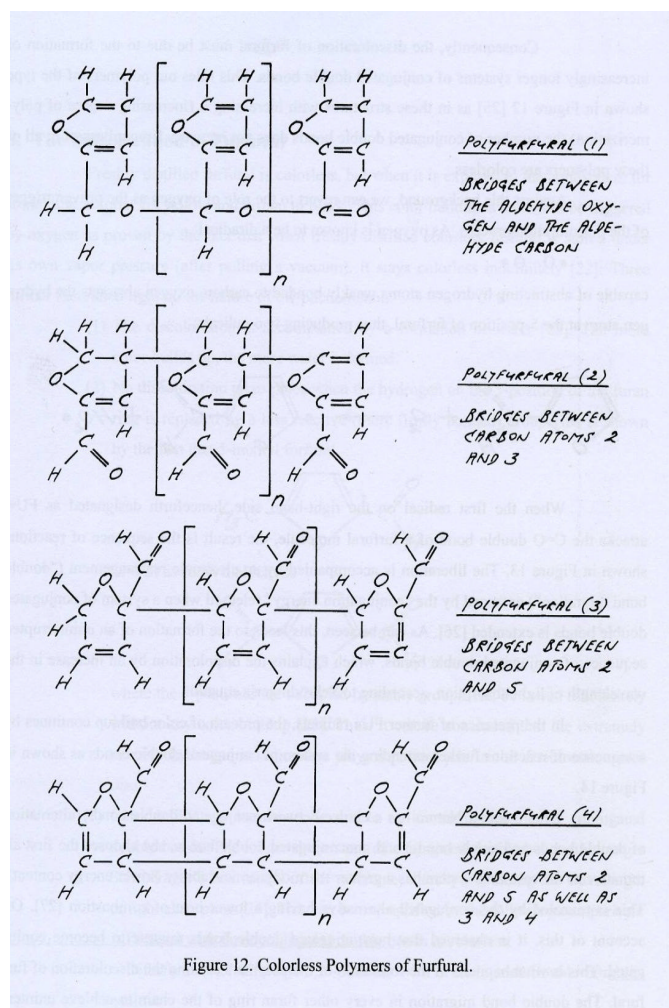


Fig. 3.6 Plausible by-products (Loss-2) [1]

The retention times of fragmentation, the candidates of which are shown in Fig. 3.4, are considered to come between that for xylose and that for furfural, if detections are executed with HPLC (UV). Unfortunately, it is impossible or very difficult to isolate intermediates, in case of consecutive reaction. Therefore, the investigation had to stay to confirm of condensation with furfural.

It may be not negligible that the loss of furfural comes from the condensation between intermediates and furfural shown in Fig. 3.5 [1] and from the resinification among furfurals shown in Fig. 3.6 [1]. However the details have not yet been reported in terms of quantitative analysis. If any quantitatively confirmed amount of furfural is added to reaction phase, the loss of furfural can be determined as the difference between total of the estimated amount to be synthesized and of the added amount and actually detected amount of furfural on the assumption that the loss occurs with same ratio against synthesized furfural and added furfural.

4.1.1 Analysis of the loss of furfural:

Furfural produced was converted to unknown chemicals during the reaction. In this study, furfural loss was defined as follows (Fig. 3.3).

Loss-1: the loss from the condensation between intermediates and furfural

Loss-2: the loss from the resinification among furfurals

Loss-3: the loss from fragmentation of furfural itself

In order to clarify the above 3 losses, the "Reaction-1"(basic reaction) with ca. 1 mmol of xylose and 50 mg of catalyst, the "Reaction-2" with the addition of 0.2 mmol (*) of furfural to the basic reaction and the "Reaction-3" with 0.2 mmol (*) of furfural instead of ca. 1 mmol of xylose of the basic reaction were executed. (*)The amount of furfural to be added was decided according

to the average yield value (approx. 20%) of furfural from the basic reaction. The details are shown in Table 3.4.

Table 3.4 Experimental and reaction conditions

	Reaction-1 (with catalyst)	Reaction-2 (with cat. and furfural)	Reaction-3 (with cat. & furfural, without xylose)
xylose (1 mmol)	X1	X2	-
catalyst Zr(20)-SBA-15	50 mg	50 mg	50 mg
solvent : DMSO, or water	5 mL	5 mL	5 mL
co-solvent: toluene	5 mL	5 mL	5 mL
added furfural	—	0.2 mmol: Fad	0.2 mmol: Fad
reaction temperature	100 °C.	100 °C	100 °C
Reaction Time	12, 24, 36, 48 Hrs.	12, 24, 36, 48 Hrs.	12, 24, 36, 48 Hrs.
stirring rod, stirring speed	4 x 10, 400 rpm.	4 x 10, 400 rpm	4 x 10, 400 rpm
conversion: consumed xylose / input xylose	C1	C2	-
yield: residual furfural / input xylose	Y1	Y2	

Furfural loss calculations were as follows.

1. Furfural loss is based on the sum of Loss 1 + Loss 2+ Loss3. T is defined as the ratio of loss of furfural against to total furfural to be synthesized if no loss and to be added (**Fad**)

$$T = 1 - \{X2*[(Y2*(1-C1)-Y1*(1-C2))]/[(C2-C1)*X2+(1-C1)*\mathbf{Fad}]\}$$

2. Total of loss2 and loss3 -- not concerned to xylose/intermediates

$$\text{Loss} = \text{Detected furfural} / \text{Input furfural} (\mathbf{Fad})$$

3. **Unknown loss** means total of xylose fragmentation and residual intermediates = 1 – total of loss1, loss2 and loss3.

Note: the above calculation is based upon following assumptions.

- 1) Same furfural loss comes from synthesized furfural from xylose and from the added furfural.
- 2) The concentration of intermediates depends upon the concentration of residual (not

converted) xylose.

4.1.2 Catalyst

Zirconia co-precipitated with SBA-15, Zr(20)-SBA-15, which was developed in Chapter 2, was used as catalyst for this investigation.

4.1.3 Furfural loss related to reaction phase

Three reactions were conducted as follows (see also Table 3.4)

Reaction 1 for reference

xylose: ca.1.0 mmol water and/or & toluene: each 5 mL, catalyst: ZrO₂20-SBA-15: 50 mg

temperature: 100 °C, time: (3), (6), 12, 24, 36, 48 Hrs.

mixing rod: 4 x 10 mixing speed: 400 rpm

Reaction 2 for detection of furfural total loss in combination to the above

Additional furfural: 0.2 mmol to the conditions of Reaction 1.

Reaction 3 for detection of furfural loss-2

Water and or Toluene: each 5 mL Catalyst: ZrO₂20-SBA-15: 50 mg,

furfural: 0.2 mmol temperature: 100 °C, time: (3), (6), 12, 24, 36, 48 Hr

mixing rod: 4 x 10, mixing speed: 400 rpm

Note: Reaction time (3) and (6) were applied only to 2phase toluene/water system

4.2 Result and Discussion

4.2.1 Fragmentation

Fragmentations shown in Fig. 3.3 are considered as fragmentation directly from xylose, fragmentation of intermediates and fragmentation of materials due to condensation between intermediates and furfural.

Fragmentation of synthesized furfural -- From the investigation with HPLC, the retention

time of fragmentation will become between the retention time of xylose and that of furfural. By analyzing the maximum plot of UV detection, I reached to the results shown in Table 3.7.

Table 3.7 Solvent, xylose, catalysts, furfural, reaction conditions fragmentation

Symbol	Solvent	Xylose	Catalyst	Furfural	Temp x Time	Fragmentation
1P-W85	D.I.W	ca.1 mmol	50 mg	none	85 x 48.	Peak found
1P-W	D.I.W.	ca.1 mmol	50 mg	none	100 x 48	Peak found
1PX-WF	D.I.W.	none	50 mg	0.5 mmol	100 x 48	none
1P-WC	D.I.W.	ca.1 mmol	none	none	100 x 48	none
1P-D85	DMSO	ca.1 mmol	50 mg	none	85 x 48	Peak found
1P-D	DMSO	ca.1 mmol	50 mg	none	100 x 48	Peak found
1PX-DF	DMSO	none	50 mg	0.5 mmol	100 x 48	none
1P-D140	DMSO	ca.1 mmol	50 mg	none	140 x 3	Peak found
1PD-OC	DMSO	ca.1 mmol	none	none	100 x 48	Peak found
1PX-D140	DMSO	none	50 mg	0.5 mmol	140 x 3	none
2P-WT	D.I.W/T	ca.1 mmol	50 mg	none	100(85)x48	none
2PX-WTF	D.I.W/T	none	50 mg	0.5 mmol	100(85)x48	none

1 phase reaction with DMSO and 1 phase reaction with water showed the peaks of substances from fragmentation. Out of them, the results of 1 phase DMSO with 140 °C x 3 Hrs. and 100 °C x 48 Hrs. showed the peaks with almost same retention time (approx. 22min.) of HPLC.

1 phase with water, of 100 °C x 48 Hrs. and 85 °C x 48 Hrs. showed the peaks with almost same retention time (approx. 16 min.) as that of 1 phase of DMSO 85 °C x 48 Hrs. but the peak heights were much lower. The kind of such substances has not yet been identified, but has some possibility as a glyceraldehyde.

2-phase system with water and toluene showed no typical peak like those of 1 phase system. Actual reaction temperature of this system was considered as 85 °C due to azeotrope between water and toluene, and therefore I examined 85 °C also in case of 1 phase as mentioned above.

4.2.2 Intermediates

It is impossible or very difficult to isolate the intermediates and also it is not clear how long the intermediates survive.

From such background this study had to stay to consider the intermediates as "Unknown".

4.2.3 The results of analysis of the furfural loss

The results for 1 phase with DMSO were shown in Fig. 3.7

Along to reaction time, furfural total loss increased and "Unknown Loss" decreased. The reason of this phenomenon seemed that synthesized furfural and intermediates stayed in reaction solvent with catalyst due to single (1) phase and due to the big specific gravity of catalyst and seemed that, as the result, furfural loss also increased due to the condensation between furfural and intermediates and due to the resinification (polymerization) of furfural, even though yield of furfural increased slightly.

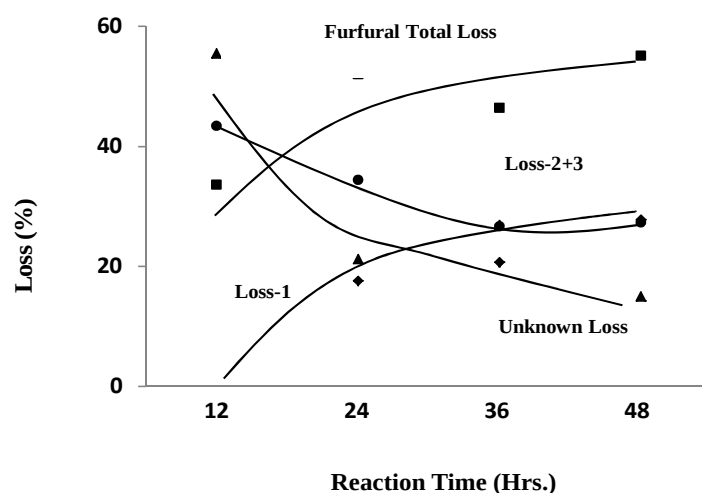


Fig. 3.7 Furfural loss of 1Phase DMSO

The results for 1 phase with D.I. water were shown in Fig. 3.8

Furfural total loss was high level but showed almost stable along to reaction proceeding.

And "Unknown Loss" showed a high level but was almost stable against reaction proceeding. The reasons were considered that synthesized furfural and intermediates stay in reaction solvent with catalyst due to single (1) phase and due to the big specific gravity of catalyst, and that water and catalyst can supply enough proton for making intermediates but not enough for convert the intermediates to furfural.

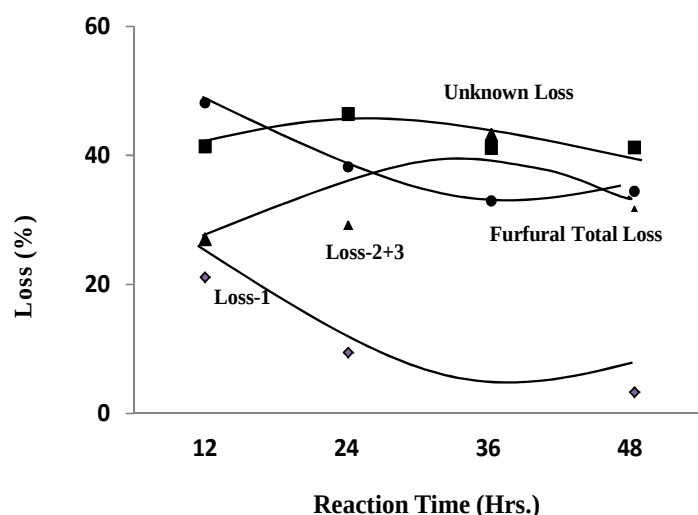


Fig. 3.8 Furfural loss of 1Phase D.I. water

The results for 2-phase with D.I. water and toluene were shown in Fig. 3.9

Just after synthesis, furfural stayed in water phase same as that in 1 phase D.I. water but was extracted within relatively short term by toluene phase due to its bigger solubility in toluene.

Almost all xylose and intermediate stayed into water phase because of low solubility of xylose into toluene phase, low solubility of intermediates also into toluene phase due to several OH groups similar to xylose and a separated layer of toluene phase on water phase due to a low solubility of toluene into water and a lower specific gravity (0.866) of toluene. In addition, the bigger specific gravity (approx. 2.5 - 3.5) of catalyst introduced a low contact opportunity of catalyst with furfural in toluene phase even under mixing and minimized the possibility of condensation and resinification. The data of furfural total loss in Fig. 3.9 showed very low level.

From the results, almost all portions of by-products were considered as "Unknown Loss", i.e. the intermediates. However the quantitative study has not yet been realized because of the difficulty of isolation of intermediates.

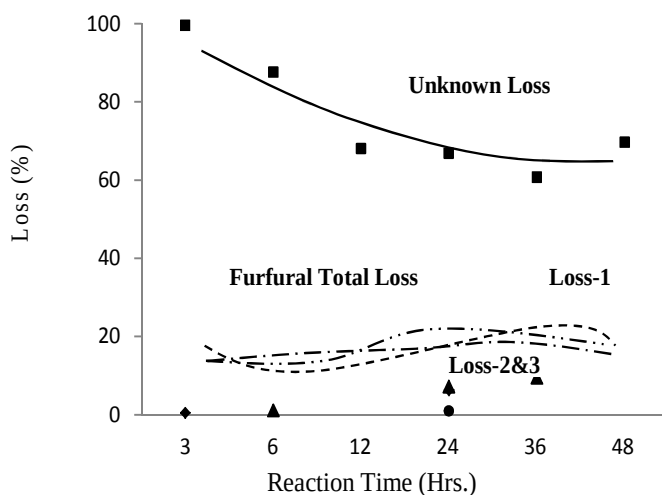


Fig. 3.9 Furfural loss of 2-phase D.I. water and toluene

5. Conclusion of Chapter 3

1. From reaction system investigation, 2-phase system with water and toluene was confirmed as a better system for higher selectivity to furfural, minimizing "Furfural Loss".
2. The volume ratio between toluene and (toluene+water) for best selectivity to furfural was shown as near 50 -60% but depended upon reaction conditions.
3. "Furfural Loss" due to condensation between intermediates and furfural, resinification among furfurals and fragmentation of xylose/intermediates can be reduced by introduction of 2-phase system.
4. Fragmentation of xylose/intermediates shall be taken into consideration in case of 1 phase system.
5. The reduction of "Furfural Loss" seems to depend upon minimizing the contact opportunity, including residence time of furfural with xylose/intermediates/catalysts and therefore further investigation shall be concentrated on 1) much higher activity of catalyst and 2) much suitable

reaction conditions.

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Chapter 4

Dehydration of xylose to furfural over various sulfated metal oxides

1. Introduction

There are a large number of reports on the catalytic dehydration of xylose to furfural over solid-acid catalysts. First, Moreau *et al.* successfully achieved the dehydration of xylose into furfural over zeolite solid-acid catalysts; H-type faujasite and mordenite catalysts gave a high selectivity (90–95%) with the conversion kept at about 30% at the reaction temperature of 170 °C [1]. Later, there have been great efforts given on the dehydration of xylose over various solid-acid catalysts. Valente *et al.* reported that sulfonic acid-anchored MCM-41 has been found to be an effective catalyst for the dehydration of xylose to furfural [3]. Kim *et al.* reported the use of sulfated metal oxides as catalysts for the conversion of xylose into furfural; the furfural yield of about 60% was achieved at the conversion of ca. 90% at the reaction temperature of 180 °C and high pressure of 200 atm. by using conventional sulfated zirconia or titania as solid acid catalysts in combination with supercritical carbon dioxide as an extracting solvent [3]. Recently, various zeolite-based catalysts have extensively been applied to this reaction [4-11]. However, thus developed methods have required high reaction temperature and pressure and/or supercritical solvent to attain the selective production of furfural with a high yield. Such harsh reaction conditions sometimes cause the deactivation of catalysts due to the formation of humins during the reaction. Furthermore, the correlation of the catalytic performance and acid properties of the catalyst is still unclear.

Recently, the importance of the presence of Lewis acid sites (LASs) as well as Brønsted acid sites (BASs) on the catalytic conversion of sugars into value-added chemicals has been claimed. Metal halides effectively have catalyzed the isomerization of glucose to fructose in ionic liquid solvents or organic solvents [12, 13]. LASs on Sn-containing Beta also enhanced the isomerization of glucose to fructose through intramolecular hydride transfer [14]. Moreover, the steam-treated Beta zeolite effectively promoted the Meerwein-Ponndorf-Verley reduction [15-17], which was known to progress through intermolecular hydride transfer from alcohols to ketones. It has been also found that the modification of acid properties on the Beta catalyst by a

steam-treatment has been found to be an effective way to improve catalytic performance in the dehydration of xylose to furfural [18]; LASs on the Beta catalyst accelerate isomerization of aldose, resulting in the formation of ketose, and BASs assist the dehydration of ketose to furfural.

Based upon the results of Chapter 2 and 3, the introduction of new catalysts with higher acidity and with reasonable specific surface area was considered necessary. The strong candidates were the sulfated metal oxides, especially sulfated zirconia, which has been eagerly studied, and sulfated tin oxide, the sulfation of which was executed with higher concentration of sulfuric acid than that for sulfated zirconia.

Sulfated metal oxides (SMOs) including *e.g.*, ZrO_2 , SnO_2 , TiO_2 and Fe_2O_3 possess both BASs derived from sulfates fixed on the surface of metal oxides and LASs derived from metal oxides, and have been widely used as a solid-acid catalyst in a variety of organic transformations [19] due to its high efficiency, non-pollutant and non-corrosive aspects, lower cost and greater stability. They can also be easily recovered from the reaction mixture by simple filtration and re-used after activation. Among them, sulfated tin oxide ($\text{SO}_4^{2-}/\text{SnO}_2$) has been superior to other SMOs [19-26]; it is used in hydrocracking of paraffins, dehydration of alcohols, esterification, alkylation of olefins, photochemical catalysis and protection of aldehydes, ketones and alcohols and olefin polymerization.

Here, the report comes concerning the preparation of various SMOs and their catalytic application in the dehydration of xylose to furfural under milder conditions. On the basis of the fact that sulfated SnO_2 exhibited the highest catalytic activity, the influences of the preparation conditions of sulfated SnO_2 were extensively investigated.

2. Experimental

2.1. Preparation of SMOs

2.1.1. Preparation of metal oxides.

SnO_2 was prepared by using $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Wako) as Sn source according to the literature

with modifications [21, 22]. In 300 mL of water was dissolved 10 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. The pH of this aqueous solution was adjusted to be about 8.5 by adding 28 % NH_3 aqueous solution. The resultant solution was stirred for 2 h at ambient temperature. The precipitate was collected by filtration and suspended in the aqueous solution containing 4% $\text{CH}_3\text{COONH}_4$ with stirring for 2 h. The precipitate was again filtered by suction and dried at 100 °C for 24 h.

For preparing ZrO_2 , Al_2O_3 , Fe_2O_3 , HfO_2 and Nb_2O_5 , 10 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Kanto Kagaku), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Wako), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Kanto Kagaku), $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ (STREM CHEMICALS) and NbCl_5 (Wako) were dissolved in 100 mL of water, respectively. The pH of this aqueous solution was adjusted to be about 9 by adding 28 % NH_3 aqueous solution. The resultant solutions were stirred for 24 h ambient temperature. The precipitate was collected by removing the solution *via* evaporation, washed with water and dried at 100 °C for 24 h.

SiO_2 and TiO_2 were prepared from $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ (Tokyo Kasei) and $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$ (Tokyo Kasei) *via* a typical sol-gel method under acidic conditions using HCl and HNO_3 , respectively. After stirring the gel for 24 h at ambient temperature, the precipitate was collected by filtration, washed with water and dried at 100 °C for 24 h.

2.1.2. Sulfation of metal oxides.

A 1 g of the prepared metal oxides was placed in a glass flask with 15 mL of 0.5 M H_2SO_4 aqueous solution stirred for 1 h. The solid was collected by filtration and dried at 100 °C for 2 h under vacuum conditions. The resultant products were calcined for 3 h in air with the temperature of 500 °C, leading to the formation of SMOs. Thus obtained SMOs were designated as *e.g.*, $\text{SO}_4^{2-}/\text{SnO}_2$.

2.2. Characterization of catalysts

XRD patterns were collected on a Rint-Ultima III (Rigaku) using a $\text{Cu K}\alpha$ X-ray source (40 kV, 40 mA). Field-emission scanning electron microscope (FE-SEM) images of the powder

samples were obtained on an S-5200 (Hitachi) microscope. The samples for FE-SEM observations were mounted on a carbon-coated microgrid (Okensoji Co.) without any metal coating. Nitrogen adsorption-desorption measurements were conducted to obtain information on the mesoporosities. The measurements were conducted at -196 °C on a Belsorp-mini II (Bel Japan). The BET (Brunauer-Emmett-Teller) specific surface area was calculated from the adsorption data in the relative pressure ranging from 0.04 to 0.20. The content of sulfur was evaluated via CHNS elemental analysis using a vario Micro Cube (Elementar).

Acid property on sulfated tin oxide was evaluated by *in-situ* FT-IR technique using CO as probe molecule [27, 28]. The sample disk was pretreated at 500 °C for 1 h under evacuation. The temperature was then decreased to -120 °C under evacuation. FT-IR spectra of clean samples before adsorption experiments were measured in He atmosphere at -120 °C and were used as background spectra. Then, CO probe molecule was introduced into the cell. IR spectra were measured with increasing the CO pressure up to 100 Torr. FT-IR spectra were obtained by use of a Jasco FT-IR 4100 spectrometer equipped with an MCT detector at a 4 cm⁻¹ resolution. Difference IR spectra between the background spectra and those with the adsorbed are shown in this paper.

2.3. Catalytic application

Liquid-phase catalytic reactions were performed in a glass flask using an oil-bath. Typically, 50 mg of catalyst and 1 mmol of xylose were added to a two-phase system consisting of 5 mL of water and 5 mL of toluene with stirring at the temperature of 100 °C. After the reaction, in addition to 0.8 g of cyclopentanone as an internal standard, 30 mL of DMSO was added to the reaction system with stirring for 5 min at ambient temperature, resulting in a homogeneous solution. Xylose and the products including furfural were analyzed on a Shimadzu RID10A/SPD-20A high performance liquid chromatograph (HPLC) with a Rezex ROA-Organic Acid (8%) column under conditions of temperature of 50 °C and flow a rate of 0.4 mL·min⁻¹, with UV (280 nm) and refractive index detectors.

3. Results and discussion

3.1. Dehydration of xylose over various SMOs

First, here is the evaluation for the catalytic performance in dehydration of xylose at the reaction temperature of 100 °C under an ambient pressure over various SMOs synthesized. The structural properties and the catalytic performance of the SMOs prepared are summarized in Table 4.1. As a control, the conversion of xylose in the absence of any catalysts was ca. 13 %, but the yield of furfural was low (ca. 2 %). When a homogenous acid catalyst, conc. H₂SO₄ of 0.027 ml, which has ca. 1 weight % of conc. H₂SO₄, (0.0018 mL of conc. H₂SO₄ has almost equivalent of acidity to the SO₄²⁻/SnO₂ catalyst), was used, the conversion and the yield were 13 and 2 %, respectively. Because SiO₂ was hard to sulfate; the content of SO₄²⁻ was *ca.* 0.04 mmol·g⁻¹ and SO₄²⁻/SiO₂ showed negligible catalytic performance. Although the content of SO₄²⁻ group on SO₄²⁻/Al₂O₃ was high (*ca.* 0.92 mmol·g⁻¹), it exhibited a low catalytic performance. SO₄²⁻/Fe₂O₃ gave the conversion of 16.1 % but the yield was low (ca. 1.1 %). The SO₄²⁻/TiO₂, SO₄²⁻/ZrO₂, SO₄²⁻/Nb₂O₅ and SO₄²⁻/HfO₂ samples gave the conversion of over 19 % but the yield was low (below 20 %). Among all the samples tested, the SO₄²⁻/SnO₂ exhibited the highest catalytic performance; the conversion was 57 % with the yield of 27 %. Based on these screening tests, we have focused on the sulfated tin oxide as the catalyst for the dehydration of xylose.

Table 4.1 Structural properties and catalytic performances of various SMOs

	S_{BET}^{*1} $\text{m}^2 \cdot \text{g}^{-1}$	SO_4^{2-} content ^{*2} $\text{mmol} \cdot \text{g}^{-1}$	Conv. %	Yield %
No catalyst	-	-	13.4	2.2
$\text{H}_2\text{SO}_4^{*3}$	-	-	22.5	18.7
/Al ₂ O ₃	209	0.92	7.1	2.4
/SiO ₂	147	0.04	2.2.	0.9
/TiO ₂	126	0.64	38.6	16.8
/Fe ₂ O ₃	67	0.37	16.1	1.1
/ZrO ₂	152	0.39	20.7	9.3
/Nb ₂ O ₅	39	0.58	19.7	7.8
/SnO ₂	127	0.64	57.3	26.6
/HfO ₂	158	0.22	41.7	9.8

$^{*1}S_{\text{BET}}$: BET surface area

^{*2} estimated by CHNS elemental analysis

^{*3} conc. H_2SO_4 (96%) of 0.027 ml was used.

(0.0018 mL of conc. H_2SO_4 has almost equivalent of acidity to the $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst)

Reaction conditions: catalyst, 50 mg; xylose, 1 mmol; water 5 ml, toluene 5 ml; temperature, 100 °C; reaction time, 48 h

3.2. Effect of preparation conditions of sulfated tin oxide

3.2.1. Concentration of H_2SO_4

To investigate the effect of the content of SO_4^{2-} group on the catalytic performance, the sulfation was conducted with the concentration of H_2SO_4 varied and with the calcination temperature of 500 °C kept. Thus obtained products were designated as *e.g.*, $M\text{-500-SO}_4^{2-}/\text{SnO}_2$, where M is the concentration of H_2SO_4 . When the concentration of H_2SO_4 was varied in the range of 0.25 to 3 M, the contents of group were changed from 0.52 to 0.77 $\text{mmol} \cdot \text{g}^{-1}$ (Table 4. 2). As a control, as-synthesized SnO_2 (designated as “as- SnO_2 ”) was calcined at 500 °C without sulfation (“cal- SnO_2 ”).

Fig. 4. 1 shows the XRD patterns of the as- SnO_2 , cal- SnO_2 and the $M\text{-500-SO}_4^{2-}/\text{SnO}_2$

samples. The peaks for the as-SnO₂ sample were weak and broad, indicating the presence of very small crystalline particle. After sulfation, three distinct X-ray diffraction peaks at $2\theta = 27, 34$ and 52° were observed. These peaks can be indexed as the 110, 101 and 221 reflections based on the tetragonal structure [29]. The intensity and width of the peaks were almost similar irrespective of H₂SO₄ concentration. Note that the calcination without sulfation led to a marked increase in the peak intensity and decrease in the peak width, implying that the sulfation inhibits the sintering of the particles. The particle size of SnO₂ (*S*) was estimated by the Scherrer's equation using the 101 reflection:

$$S = 0.9\lambda / \beta \cos\theta$$

where λ is the wavelength of the CuK α radiation, β is the full-width at half-maximum (FWHM) of the diffraction peak and θ is the Bragg's diffraction angle of the peak. The particle sizes of the as-SnO₂ and *M*-500-SO₄²⁻/SnO₂ samples were estimated at 3.3 and 6.1-6.4 nm, respectively. The calcination without sulfation led to the marked increase in the particle size (ca. 11.8 nm), as a result of the sintering of the particles.

By the nitrogen adsorption-desorption isotherms, the BET (Brunauer-Emmett-Teller) specific surface area were estimated and listed in Table 4. 2. The surface area was slightly increased with an increase in the content of SO₄²⁻ group; the surface areas of the 0.25- and 3.0-*M*-500-SO₄²⁻/SnO₂ samples were 115 and 169 m²·g⁻¹, respectively. The surface area of the cal-SnO₂ was decreased to ca. 52 m²·g⁻¹. The presence of the SO₄²⁻ group on the surface of SnO₂ suppressed the sintering of the SnO₂ particles.

Table 4.2 Influence of the concentration of H₂SO₄ on the structural properties and catalytic performances of the SO₄²⁻/SnO₂ sample.

Concentration M	S_{BET}^{*1} $m^2 \cdot g^{-1}$	SO ₄ ²⁻ content $mmol \cdot g^{-1}$	Particle size ^{*2} nm	Conv. %	Yield %
cal-SnO ₂ ^{*3}	52	-	11.8	33.3	13.3
0.25	115	0.52	6.3	50.6	21.5
0.5	127	0.64	6.4	57.3	26.6
1.0	139	0.64	6.2	61.3	28.7
2.0	144	0.68	6.1	60.8	28.6
3.0	169	0.77	6.1	60.1	31.1

^{*1} S_{BET} : BET surface area, ^{*2} Particle size: estimated by Scherrer's equation, ^{*3} SnO₂ calcined at 500 °C without sulfation.

Reaction conditions: catalyst, 50 mg; xylose, 1 mmol; water 5 ml, toluene 5 ml; temperature, 100 °C; reaction time, 48 h

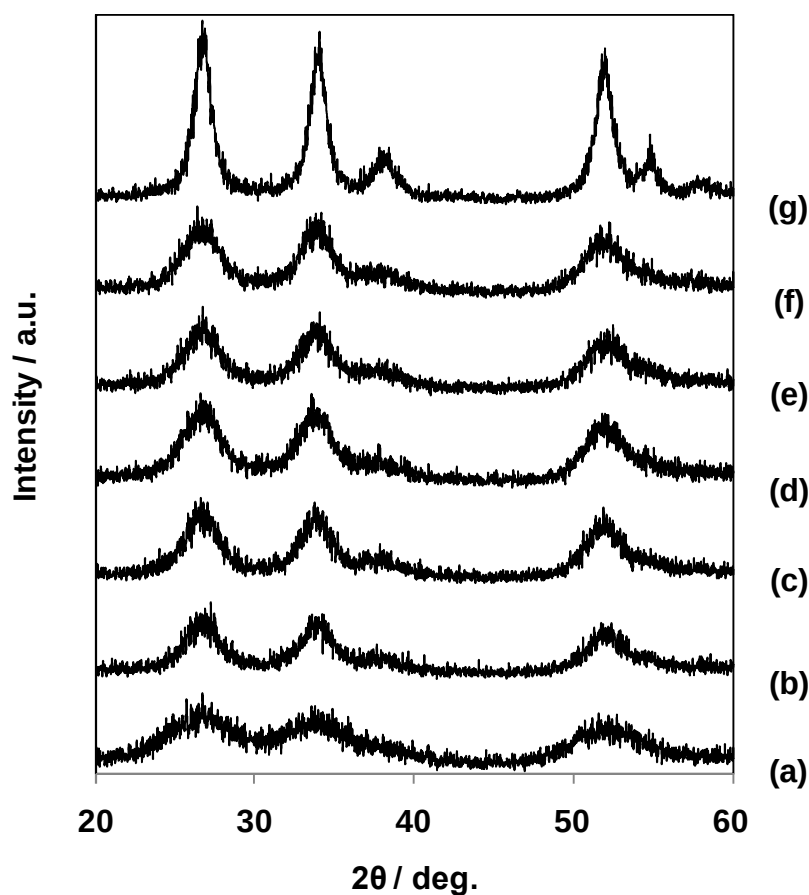


Fig. 4.1 XRD patterns of (a) as-SnO₂, (b) cal-SnO₂ and (c)-(g) the M-500-/SnO₂ samples (M = (c) 0.25, (d) 0.5, (e) 1.0, (f) 2.0 and (g) 3.0)

The high-resolution SEM images of the as-SnO₂, cal SnO₂, 0.5M-500-/SnO₂ and 3.0M-500-/SnO₂ were shown in Fig. 4. 2. The particle morphology of the as-SnO₂ sample was an aggregation of the small particles 3-4 nm in size with voids 2-8 nm in size were formed. In both of the 0.5M-500-/SnO₂ and 3.0M-500-/SnO₂ samples, small particles 5-6 nm in size were observed. Furthermore, the voids were retained after the sulfation process. It has been reported that SnO₂ prepared by the hydrolysis of SnCl₄ with ammonia water assumed the form of fine particles [29]. These morphological features would contribute to the high surface area. On the other hand, the cal-SnO₂ sample was an aggregation of the particles 12-13 nm in size. Thus particle sizes estimated by the SEM images are in accordance with those by the Scherrer's equation.

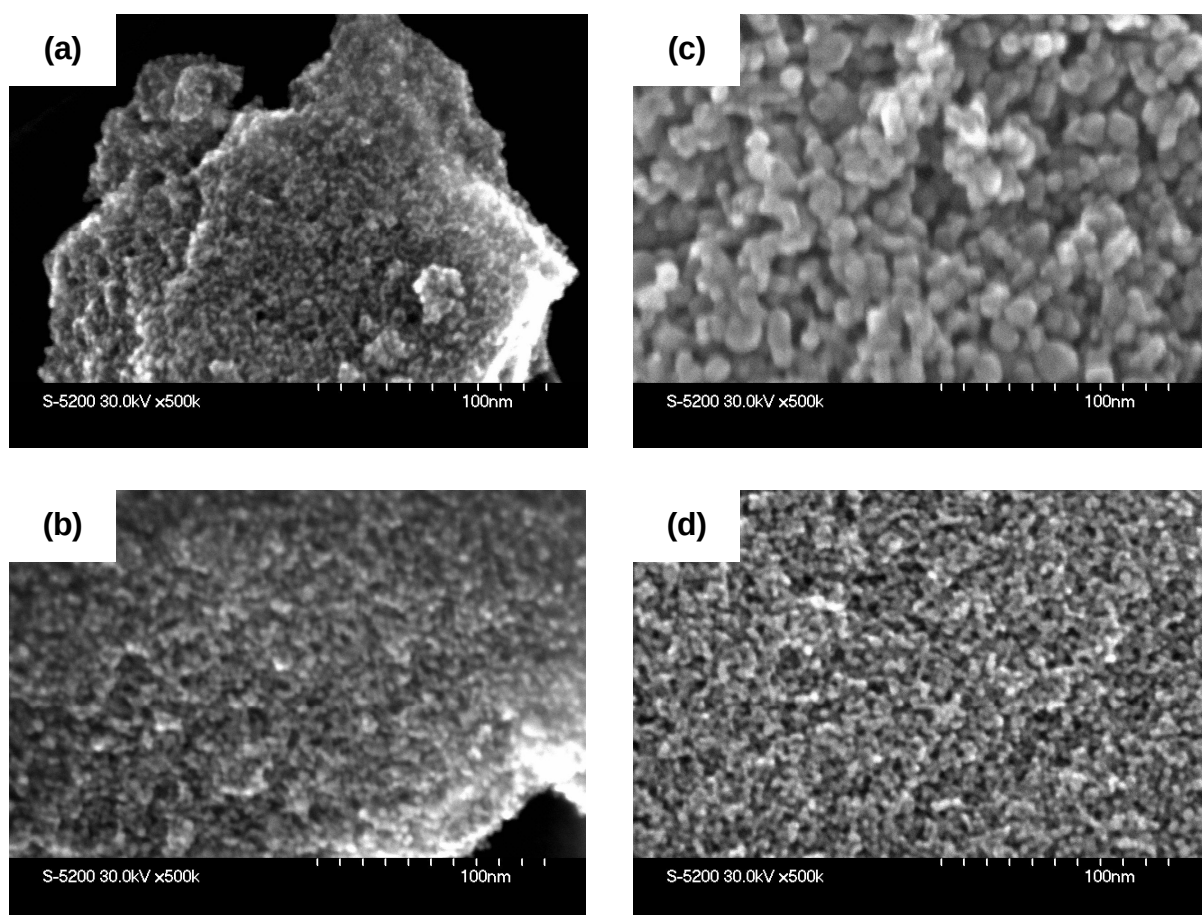


Fig. 4.2 SEM images of the (a) as-synthesized SnO₂, (b) calcined SnO₂ without sulfation, (c) 0.5M-500-/SnO₂ and (d) 3.0M-500-/SnO₂.

The influence of the content of the SO_4^{2-} group on the catalytic performance was investigated. Fig 4. 3 and Table 4. 2 show the results of the dehydration of xylose over the cal-SnO₂ and the M-500-/SnO₂ samples. In the cal-SnO₂ sample, the conversion of xylose was 33 % but the yield of furfural was 13 %. The conversion and the yield were increased along with the content of SO_4^{2-} group, while the conversion and the yield finally leveled off at 60 and 29 %, respectively. The SO_4^{2-} group on SnO₂ plays an important role in producing furfural through the dehydration of xylose. In the 3.0M-500- SO_4^{2-} /SnO₂ catalyst, the changes in the conversion of xylose and the yield of furfural along with the reaction time were investigated (Fig. 4.4). The conversion was increased along with the reaction time, while the yield leveled off at 40 %.

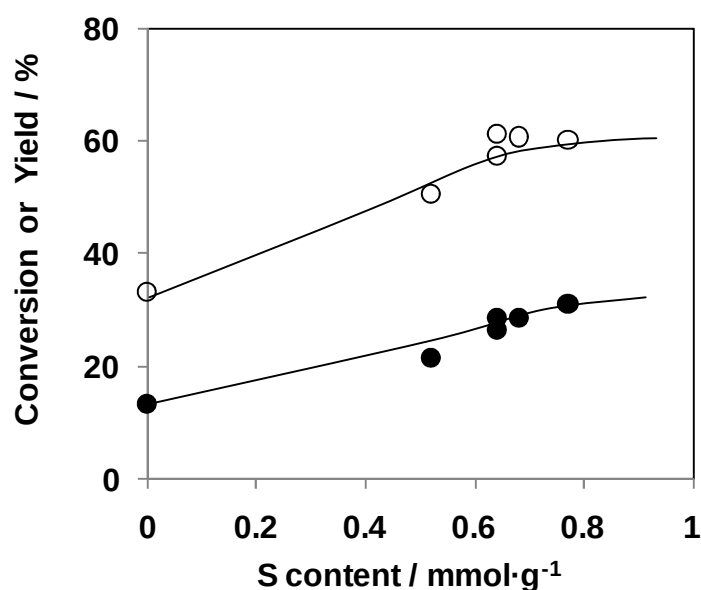


Fig. 4.3 Influence of the content of group on the catalytic performance
(○: conversion of xylose and ●: yield of furfural).

Reaction conditions: catalyst, 50 mg; xylose, 1 mmol; water 5 ml, toluene 5 ml; temperature, 100 °C; reaction time, 48 h

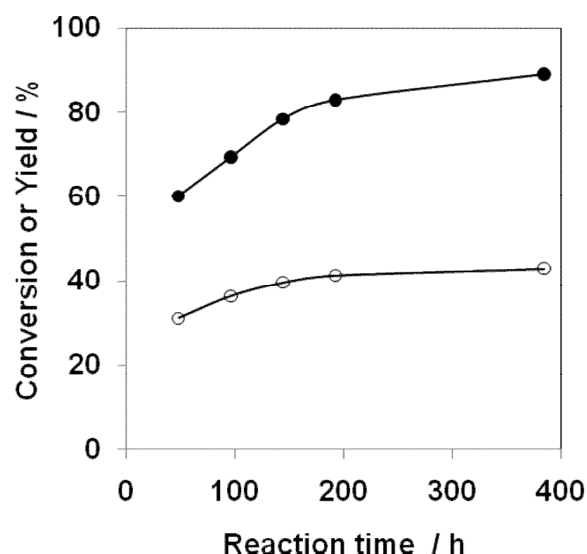


Fig. 4.4

Dehydration of xylose over 3.0M-500-SO₄²⁻/SnO₂ catalyst (●conversion of xylose, ○ yield of furfural).

Reaction conditions: catalyst, 50 mg; xylose, 1 mmol; water 5 ml, toluene 5 ml; temperature, 100 °C.

3.2.2. Calcination temperature

The influence of the calcination temperature on the structural properties and catalytic performance were investigated; the calcination temperature in the sulfation process was varied in the range of 350 to 700 °C with the concentration of H₂SO₄ of 0.5 M kept. Thus obtained products were designated as *e.g.*, 0.5-*T*-SO₄²⁻/SnO₂, where *T* is the calcination temperature. The contents of the SO₄²⁻ group were decreased with an increase in the calcination temperature (Table 4.3). Especially, when the calcination temperature was over 600 °C, the contents of SO₄²⁻ group were dramatically decreased, suggesting that the thermal stability of groups would be below 600 °C.

The XRD patterns of the 0.5-*T*-SO₄²⁻/SnO₂ samples (*T* = 350 - 700 °C) are shown in Fig. 4.5, indicating that the intensities of the three distinct peaks were increased and their widths were decreased along with the calcination temperature. The particle size estimated by the Scherrer's equation is listed in Table 4. 3, indicating that the particle size was increased along with the calcination temperature. The high-resolution SEM images of the 0.5-*T*-SO₄²⁻/SnO₂ samples

support the increase in the particle size by the increase in the calcination temperature (Fig. 4.6). At the calcination temperature of 700 °C, aggregated particles 30-40 nm in size were formed. This result implies that higher temperature enhance the sintering of the small SnO₂ particles. Tunstall *et al.* reported a relationship between the particle size and sintering temperature in detail, being similar to our results [29].

Table 4.3 Influence of the calcination temperature on the structural properties and catalytic performances of the SO₄²⁻/SnO₂ sample.

Temp. °C	S _{BET} ^{*1} m ² ·g ⁻¹	SO ₄ ²⁻ content mmol·g ⁻¹	Particle size ^{*2} nm	Conv. %	Yield %
350	125	0.75	4.2	56.2	30.5
400	125	0.78	4.4	62.1	27.1
450	125	0.68	5.0	75.3	28.9
500	127	0.64	6.4	57.3	26.6
600	74	0.25	15.1	38.9	18.3
700	28	0.06	33.2	17.7	7.9

^{*1}S_{BET}: BET surface area

^{*2} Particle size: estimated by Scherrer's equation

Reaction conditions:

catalyst, 50 mg; xylose, 1 mmol; water 5 ml, toluene 5 ml; temperature, 100 °C; reaction time, 48 h

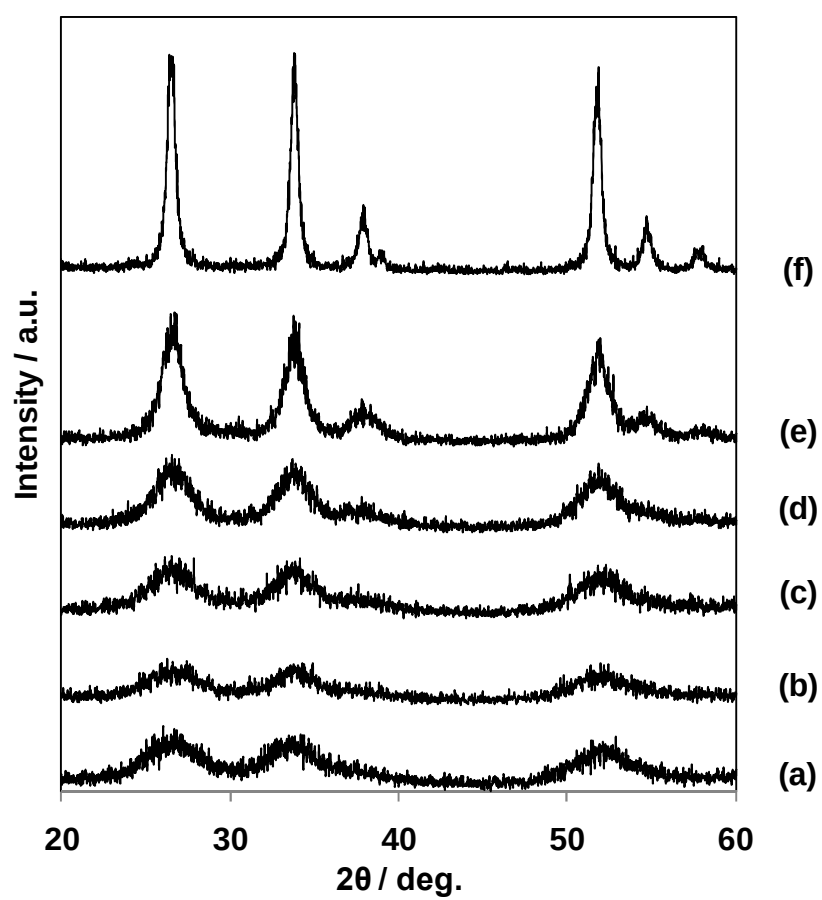


Fig.4.5 XRD patterns of the 0.5M-T/SnO₂ samples
($T = 350$ (a), 400 (b), 450 (c), 500 (d), 600 (e) and 700 (f)).

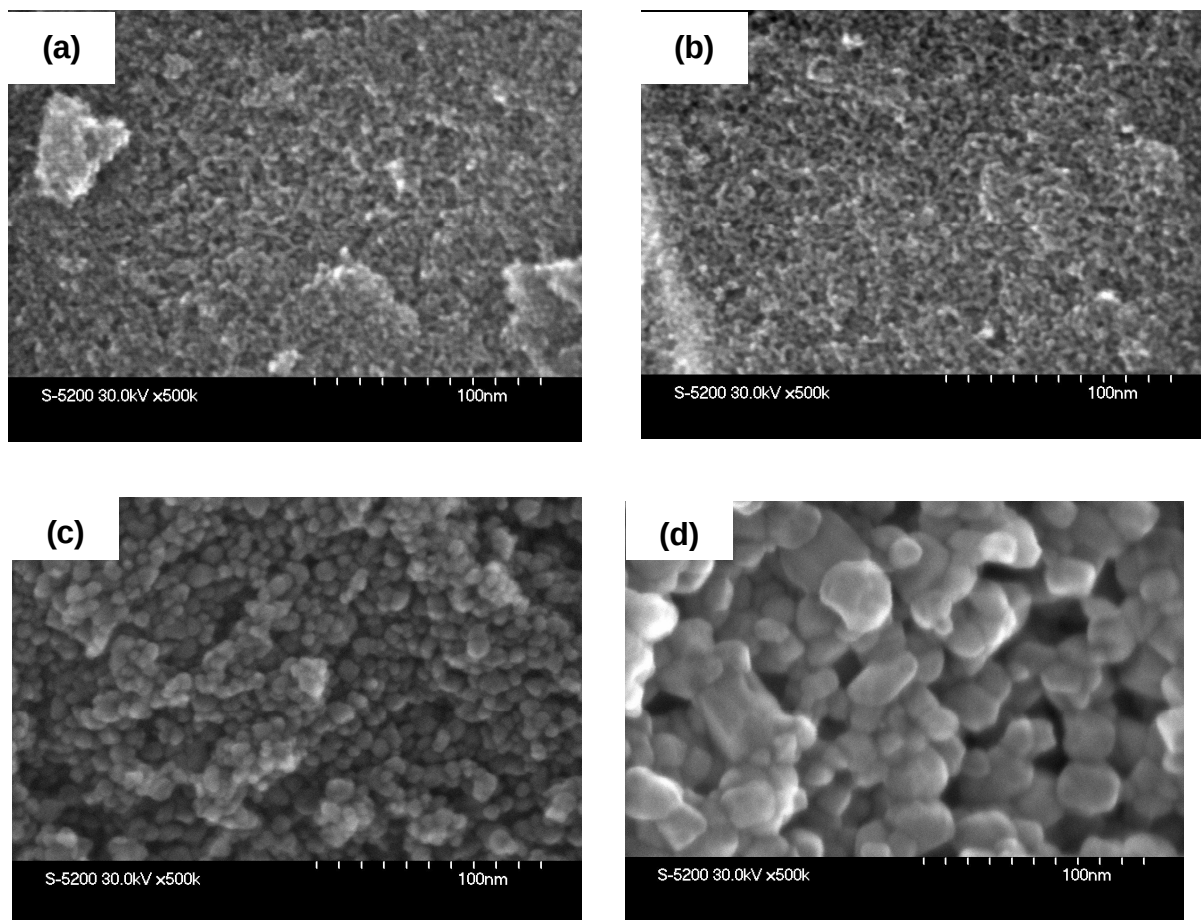


Fig. 4.6 SEM images of the 0.5M-T/SnO₂ samples ($T = 350$ (a), 400 (b), 600 (c) and 700 (d)).

Fig. 4.7 and Table 4. 3 show the results of the dehydration of xylose over the 0.5-T-SO₄²⁻/SnO₂ samples. The catalytic performance was strongly affected by the calcination temperature. The conversion of xylose was increased, reached to the maximum at the calcination temperature of 450 °C and then was decreased along with the calcination temperature. The yield of furfural was continuously decreased along the calcination temperature. These results support that the content of the SO₄²⁻ group governs the catalytic performance. Corma *et al.* reported the effect of sulfation conditions and activation temperature of sulfate-doped ZrO₂, TiO₂ and SnO₂ catalysts during isobutene/2-butene alkylation [31]; the calcination temperature over 600 °C resulted in the marked decrease in the catalytic performance although the source of sulfur and sulfur concentration also affected the catalytic performance.

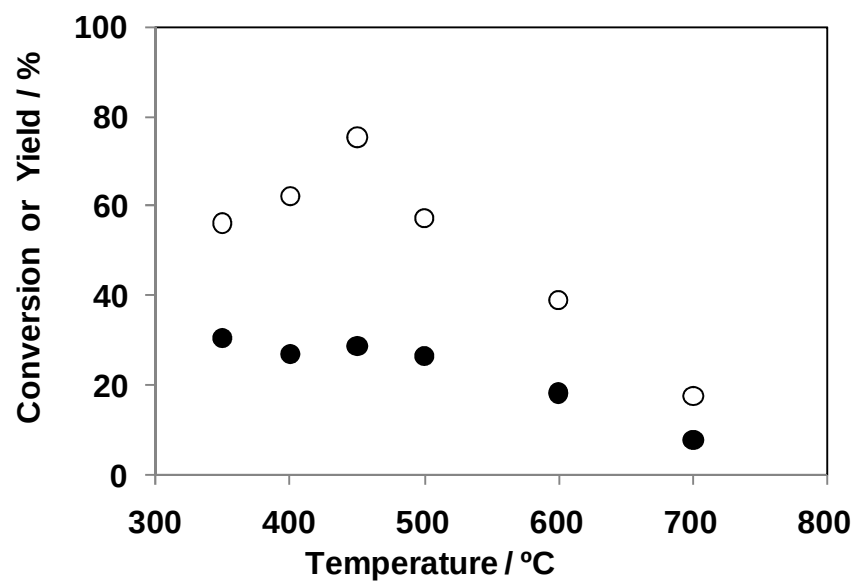


Fig. 4.7 Influence of the calcination temperature on the catalytic performance

(○: conversion of xylose and ●: yield of furfural).

Reaction conditions:

catalyst, 50 mg; xylose, 1 mmol; water 5 ml, toluene 5 ml; temperature, 100 °C; reaction time, 48 h

3.2.3 Comparison between the sulfated tin catalyst and sulfuric acid

In order to evaluate the level of sulfated tin oxide catalyst, the comparison was made according to the scheme shown in Table 4.4. The concentration of sulfuric acid used in industry was reported as 1 to 6 weight %.

Table 4.2 Catalytic reaction conditions for comparison

	Input quantity to 5 mL water	Acid amount (mmol)	Remarks
3.0M-500-SO ₄ ²⁻ /SnO ₂	50 mg	0.13	
Sulfuric acid (96%)	0.027 mL	1.04	ca. 1 weight %
Sulfuric acid (96%)	0.0018 mL	0.07	equivalent to 0.5M -500-SO ₄ ²⁻ /SnO ₂

Reaction conditions other than Catalysts:
Xylose; 1 mmol, water: 5 mL, toluene; 5 mL, temperature; 100 °C, reaction time; 48 – 192 h

The activity of sulfated tin oxide catalyst seems higher than those of sulfuric acid catalyst, as shown in Fig. 4.8.

Sulfated tin oxide catalyst and 1 weight % sulfuric acid catalyst showed almost same level of the relation between conversion of xylose and selectivity to furfural,

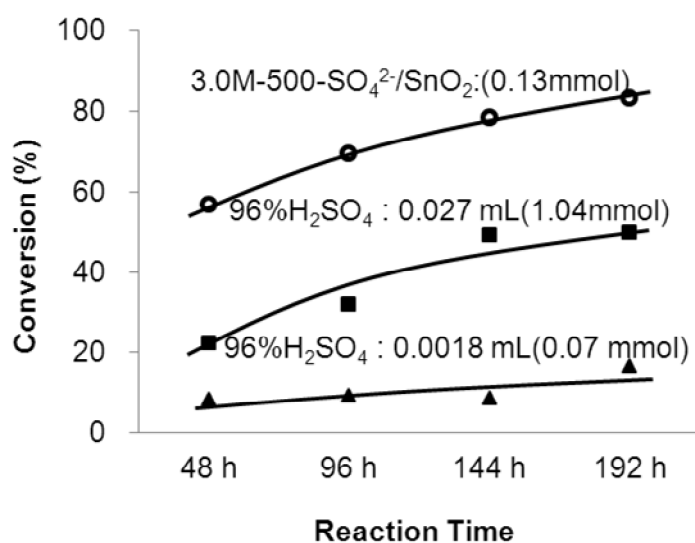


Fig 4.8 Conversion of xylose against reaction time

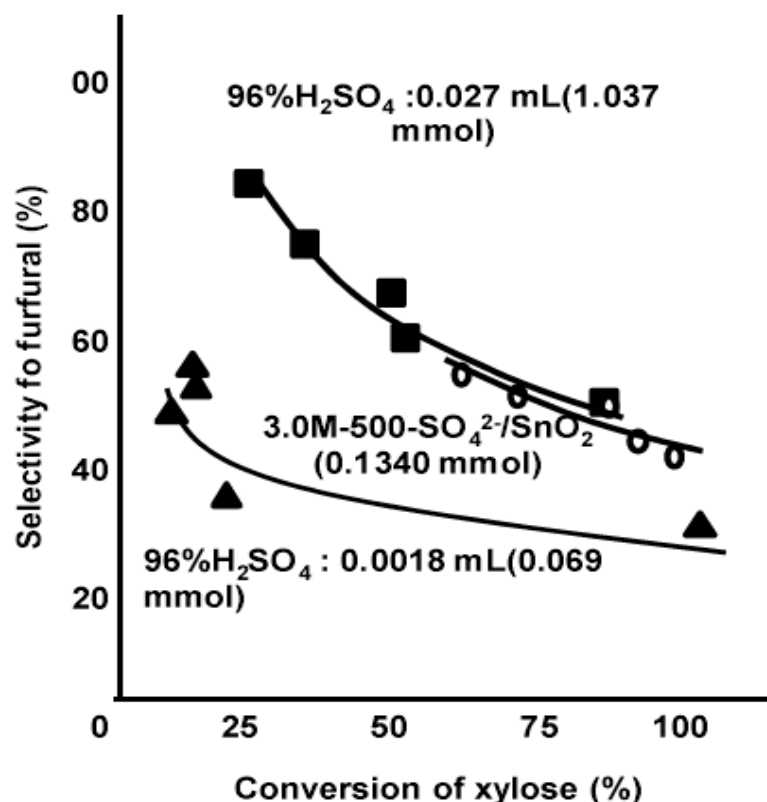


Fig. 4.9 Selectivity to furfural vs. conversion of xylose

3.3. Reaction mechanism

Finally, the reaction mechanism of dehydration of xylose over the $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst was considered. Sergent *et al.* characterized the acid property of SnO_2 by FTIR study of low-temperature CO adsorption in detail [32]. To characterize the acid property of the $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst, *in-situ* FT-IR observations of the CO-adsorbed sample were conducted. As a control, the IR spectrum of the calcined SnO_2 without sulfation in the range of $2000 - 2300 \text{ cm}^{-1}$ is shown in Fig. 4.10 (a), exhibiting the distinct four bands centered at $2210, 2190, 2182$ and 2169 cm^{-1} . Based on the refs. 32 and 33, these bands would be ascribed to CO molecules on very strong LASs, strong LASs, weak LASs and weakly acidic Sn-OH groups, respectively. Fig. 4.10 (b) shows the IR spectrum of the calcined the $0.5\text{M-500-SO}_4^{2-}/\text{SnO}_2$ sample. In this spectrum, the band at 2182

cm^{-1} almost disappeared but a band at 2173 cm^{-1} was newly observed. This new band would be attributed to the CO molecules on BASs, which are derived from SO_4^{2-} groups on the catalyst.

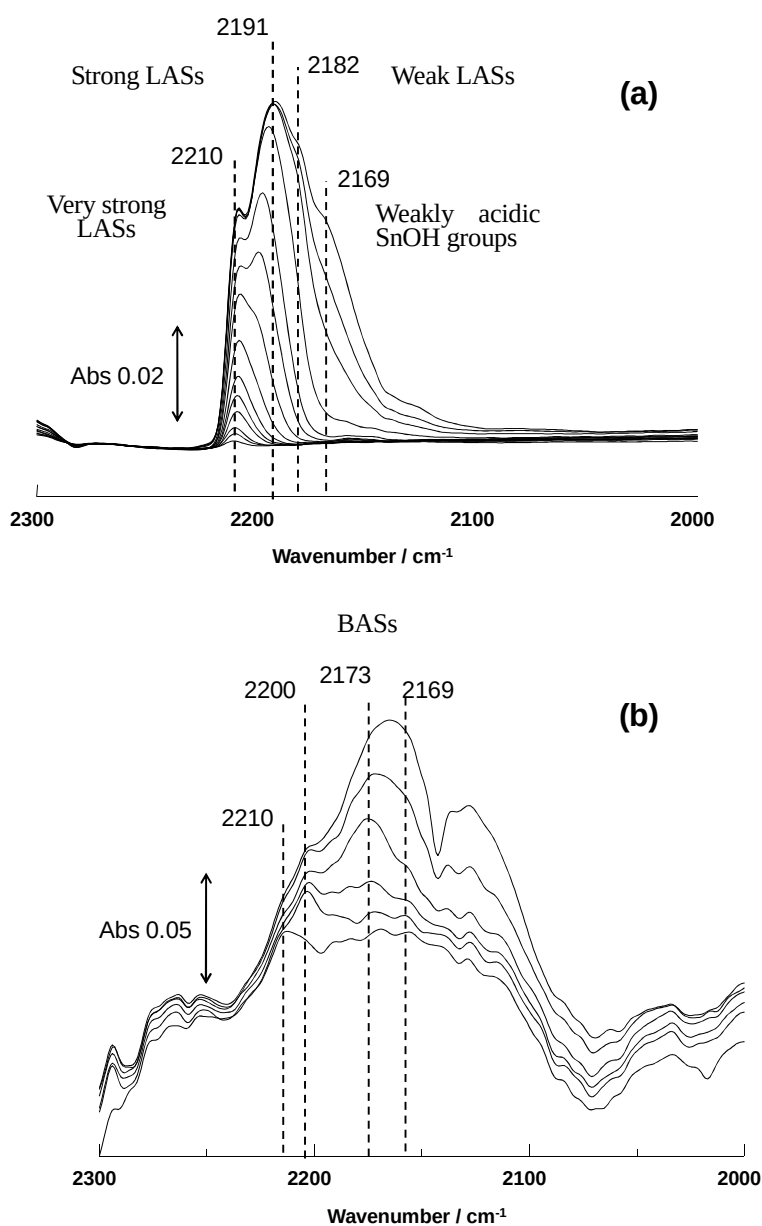


Fig.4.10 CO-adsorbed FT-IR spectra of (a) the SnO_2 calcined at 500 °C without sulfation and the $\text{S}(0.5-500)\text{-SnO}_2$ samples.

Considering the fact that the calcined SnO_2 without sulfation exhibited the high conversion but low yield (Table 4. 2), I concluded that LASs derived from SnO_2 contribute to the consumption of xylose but not to the production of furfural and that the presence of BASs derived from SO_4^{2-} group is indispensable for the production of furfural. The changes in the conversion

and yield along with the reaction time (Fig. 4.4) support this conclusion. The reason why the yield of furfural was not increased would be attributed to the leaching of SO_4^{2-} group during the reaction.

Furthermore, the $0.5\text{M-700-SO}_4^{2-}/\text{SnO}_2$ sample exhibited a lower conversion than the cal-SnO_2 sample, which was obtained by the calcination at 500°C without sulfation (Tables 4. 2 and 4. 3). The calcination at 700°C leads to the decrease in the amount of Sn-OH groups, which contribute to the formation of LASs, as well as the improvement of the crystallinity although the SO_4^{2-} group introduced was almost removed. This implies that LASs plays a certain role in the conversion of xylose. Based on the refs. 12-17 and my experimental results, a plausible reaction mechanism of dehydration of xylose is depicted in Fig. 4.11 [33]. It is considered that LASs and BASs on the $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst could act as active sites independently. LASs would promote the isomerization of xylose to xylulose and then BASs would accelerate the dehydration of xylulose to furfural although the formation of xylulose was not quantitatively observed probably because xylulose is immediately converted into furfural by BASs. In my developed $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst, the leaching of SO_4^{2-} species during the reaction is not negligible. It is to be noted that thus formed H_2SO_4 species would act as a homogenous Brønsted acid catalyst for the direct production of furfural from xylose without the formation of xylulose [34].

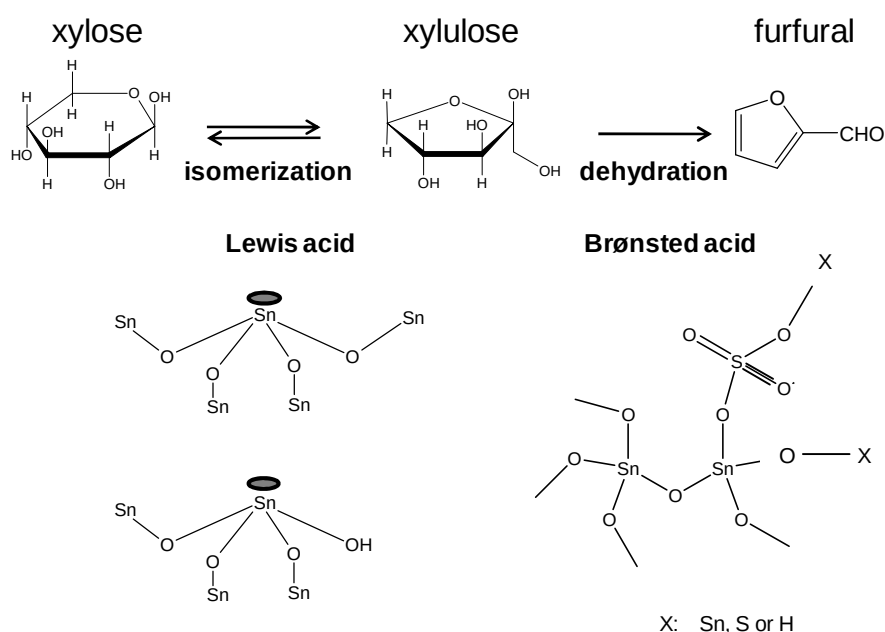


Fig. 4.11 Plausible reaction mechanism of dehydration of xylose over sulfated tin oxide catalyst.

4. Conclusion of chapter 4

It was found that sulfated tin oxide is found to be an effective catalyst for the dehydration of xylose to furfural. Both of LASs derived from SnO₂ and BASs derived from SO₄²⁻ groups are indispensable for the production of furfural by the dehydration of xylose. The preparation conditions including the concentration of H₂SO₄ and/or the calcination temperature in the sulfation process strongly affect the structural properties, which governed the catalytic performance.

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Chapter 5

Investigation of reusability of sulfated metal oxide catalysts

1. Introduction

Reusability is also very important item parallel to the initial performance of catalysts, especially in case of industrial use. Concerning gas phase reaction, generally speaking the possibility of re-using is relatively high. However, in case of liquid phase reaction, in addition of carbon deposition on catalyst, the active points of catalyst may be destroyed by liquid itself including dissolving. From papers directly concerned to synthesis of furfural from xylose, the usability specified as residual activity was shown to vary from 40 % to 90 % according to the catalysts and reaction systems.

In this chapter, the reusability itself and the reason of decreasing of activity were studied.

2. Experimental

2.1 Preparation of recycled catalysts

Tin oxide was synthesized with the same manners as described in Chapter 4. The oxide was sulfated with 0.5 M of H_2SO_4 aq. and calcined at 500 °C.

The reusability of the $\text{SO}_4^{2-}/\text{SnO}_2$ catalyst was tested by two methods; one is the reuse without re-sulfation and the other is the reuse with re-sulfation. First, after each reaction, the catalyst was filtered off, washed with ethanol, dried at 100 °C, calcined at 500 °C and then the catalysts were reused, as 1st method shown in Fig. 5.1.

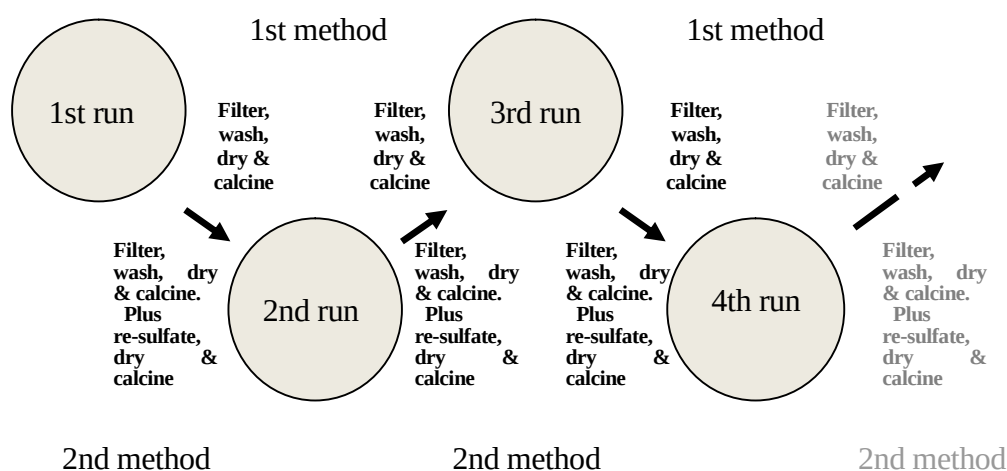


Fig. 5.1 Catalyst reusability flow

2.2 Characterization and catalytic reaction

Same methods were applied as those in chapter 4.

3. Results and discussion

After the first run, structural and morphological changes were hardly observed. However, the content of SO_4^{2-} group was significantly decreased from 0.64 to 0.27 $\text{mmol}\cdot\text{g}^{-1}$ (Table 5.1 (a)). Considering the fact that conc. H_2SO_4 of 0.027 ml gave the conversion and the yield of only 13 and 2 %, respectively (Table 5.1), the contribution of the SO_4^{2-} species in the aqueous phase to the total conversion of xylose and the yield of furfural is estimated to be below 8 and 1 %, respectively.

The catalyst after the first run exhibited a lower catalytic performance compared to the first run; the conversion was 38.8 % with the yield of 16.2 %. After the second run, the content of SO_4^{2-} group was further decreased from 0.27 to 0.18 $\text{mmol}\cdot\text{g}^{-1}$ and the third use resulted in the lower catalytic performance. Thus, the content of SO_4^{2-} group was decreased along with the use, resulting in decrease in the catalytic performance. The presence of organics on the catalyst would

also contribute to the decrease in the catalytic performance.

Based on the results above, the re-sulfation was conducted after the each catalytic run in expectation of a recover of the content of SO_4^{2-} group; after the reaction, the catalyst was reacted with 0.5 M H_2SO_4 followed by the calcination of 500 °C, as 2nd method shown in Fig. 5.1. By N_2 adsorption-desorption measurements and SEM observations, the re-sulfation enhanced the aggregation of the particle and decrease in the surface area (Table 5.1 (b)). Although the perfect recovery of the content of SO_4^{2-} group was not attained, the content of SO_4^{2-} group was successfully kept to be $0.30 \text{ mmol}\cdot\text{g}^{-1}$. This is because of the decrease in the surface area. The catalyst after the first run followed by the re-sulfation exhibited a lower catalytic performance compared to the first run; the conversion was 48.0 % with the yield of 21.0 %. However, the catalytic performance nearly kept this level even after the fourth run.

Table 5.1 Reusability of the $\text{SO}_4^{2-}/\text{SnO}_2$ sample

(a) without re-sulfation

	S_{BET}^{*1} $\text{m}^2\cdot\text{g}^{-1}$	SO_4^{2-} content $\text{mmol}\cdot\text{g}^{-1}$	Conv. %	Yield %
1 st run	127	0.64	57.3	26.6
2 nd run	125	0.27	38.8	16.2
3 rd run	125	0.18	30.5	15.8
4 th run	123	0.13	27.3	12.7

(b) with re-sulfation ^{*2}

	S_{BET}^{*1} $\text{m}^2\cdot\text{g}^{-1}$	SO_4^{2-} content $\text{mmol}\cdot\text{g}^{-1}$	Conv. %	Yield %
1 st run	127	0.64	57.3	26.6
2 nd run	105	0.30	48.0	21.0
3 rd run	95	0.27	39.9	16.5
4 th run	97	0.30	43.8	17.4

^{*1} S_{BET} : BET surface area

^{*2}Re-sulfation: the catalyst was reacted with 0.5 M H_2SO_4 followed by the calcination of 500 °C.

Reaction conditions:

catalyst, 50 mg; xylose, 1 mmol; water 5 ml, toluene 5 ml; temperature, 100 °C; reaction time, 48 h

4. Conclusion of chapter 5

The sulfated tin oxide catalyst can be reused through the re-sulfation process after the reaction. The performance of sulfated tin oxide catalyst for original run and that of the recycled catalyst showed the big possibility of replacement of sulfuric acid used in industry with continued improvement study of performance in future.

Chapter 6

Effects of addition of ionic salts into the reaction system on the catalytic performance

1. Introduction

It was suggested that the addition of NaCl into water (till to almost saturation) was effective to increase boiling point of water approx. 10 °C higher and also higher yield of furfural, in analytical furfural synthesis process, with the catalyst of HCl [1].

In case of azeotrope temperature between water and toluene, approx 10 deg. higher condition, i.e. from 85 °C to 95 °C was realized by adding NaCl into water (till to almost saturation). As the result, the yield of furfural and selectivity to furfural were expected to be improved.

In addition, as investigated in Chapter 3, 2-phase reaction system showed a better selectivity to furfural than that of 1-phase reaction system, due to the extraction of synthesized furfural by toluene phase. If water phase has any effects to depart synthesized furfural into toluene phase, the distribution ratio of furfural in water phase shall decrease and that in toluene phase shall increase and as the result, the selectivity to furfural is considered to be improved.

2. Preliminary Investigation

2.1 Experimental

1 mmol of furfural, 5 mL of toluene and 5 mL of water were mixed in 25 mL glass flask. The mixture was stirred at 100°C for 24 hours. After stirring, water and toluene phases were individually analyzed by HPLC.

2.2 Result and Discussion

2.2.1 Distribution of Furfural between Water and Toluene phase

As shown in Fig. 6.1, the distribution ratio of furfural into toluene was shown as approx. 80 % in case of water without NaCl and approx. 95 % in case of water saturated with NaCl.

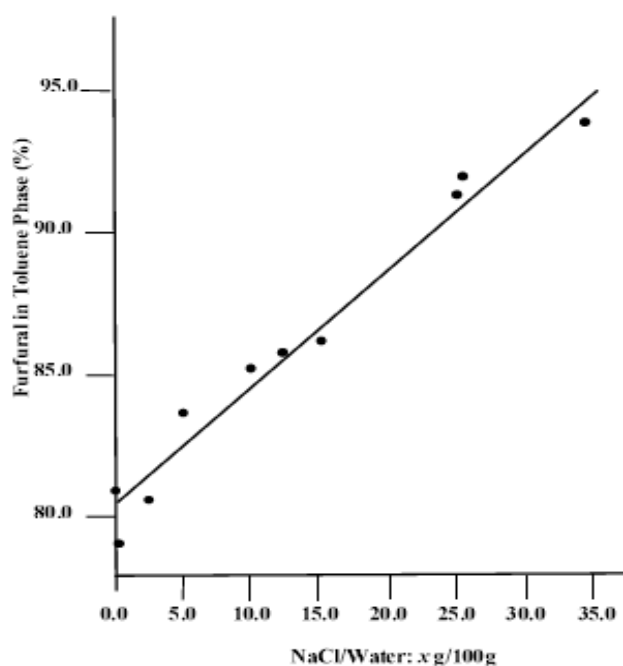


Fig. 6.1 Furfural Distribution ratio in Toluene vs. NaCl content in Water

2.2.2 Effect of the addition of NaCl into the reaction system

In order to confirm of the effect of NaCl, the reaction was conducted in the absence of catalyst. As shown in Table 6.1, the addition of NaCl as almost saturation level to water seemed to have not so big harmful influence to the results of reaction, without some heating effect (from 85 °C to 95 °C) to conversion of xylose and small effect to selectivity to furfural due to the high distribution ratio of furfural into toluene.

Table 6.1 Results of blank test

Solvent	Conversion of xylose (%)	Yield of furfural (%)	Selectivity to furfural (%)
N0	4.3	3.1	73.2
N3	5.5	4.2	75.9

Reaction conditions:

Xylose: 150 mg(0.999 m-mol) , Catalyst: none,
 Solvent: Water without NaCl: N0 and saturated with NaCl: N3
 Co-solvent: Toluene; 5 mL,
 Stirring Rod: 4 x 10, Stirring Speed: approx 400 rpm
 Temp: 100 °C , Duration: 48 Hrs.

From the above, the addition of NaCl into water phase may have good influence for much higher yield and selectivity but further investigation shall be made with accurate stirring speed control etc.

3. Investigation under ambient pressure

3.1 Experimental

Sulfated tin oxide, which was developed in Chapter 4, was used as catalyst for this investigation; tin oxide was sulfated with 3.0 M of H₂SO₄ aq. and calcined at 500 °C (3.0-500-SO₄²⁻/SnO₂). [2, 3]

Typically, 50 mg of catalyst and 1 mmol of xylose were added to a two-phase system consisting of 5 mL of water and 5 mL of toluene with stirring at the temperature of 100 °C. When NaCl was not added to the reaction system, the reaction was designated as “N0”. On the other hand, NaCl was added to the water phase with saturated concentration, the reaction was designated as N3.

After the reaction, in addition to 0.8 g of cyclopentanone as an internal standard, 30 mL of DMSO was added to the reaction system with stirring for 5 min at ambient temperature, resulting in a homogeneous solution. Xylose and the products including furfural were analyzed on a Shimadzu RID10A/SPD-20A high performance liquid chromatograph (HPLC) with Rezex ROA-Organic Acid H+ (8%) column under conditions of temperature of 50 °C and flow rate of 0.5 mL·min⁻¹, with UV (280 nm) and refractive index detectors.

3.2 Results and Discussion

3.2.1 Results

The results of catalytic reaction were shown in Figs. 6.2 to 6.4.

Conversion of Xylose with 25 mL Reactor

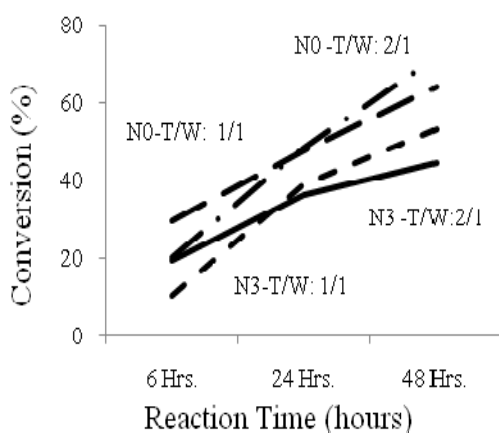


Fig 6.2 Conversion of xylose

Yield of Furfural with 25 mL

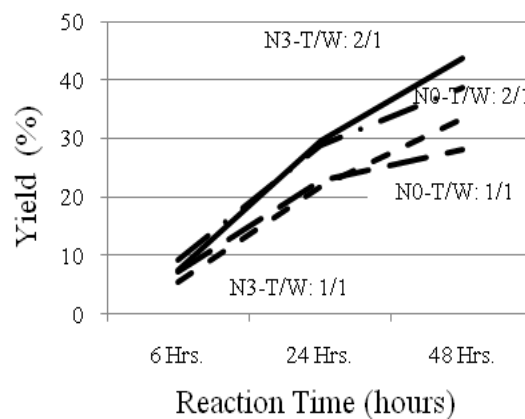


Fig 6.3 Yield of furfural

Selectivity to Furfural with 25 mL

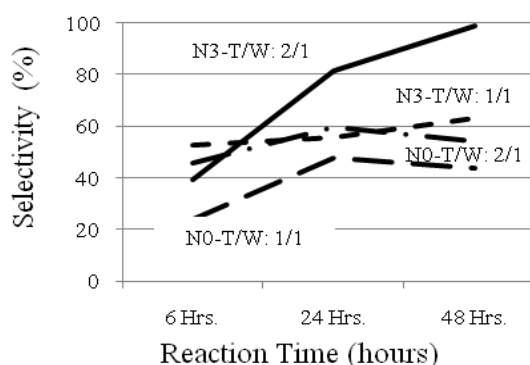


Fig 6.4 Selectivity to furfural

3.2.2 Discussion

The addition of NaCl to water phase is considered to have positive effects to yield of furfural and selectivity to furfural.

The addition of large volume of extraction phase (toluene) showed relatively high positive effect to yield of furfural and selectivity to furfural especially in combination with reaction

phase with NaCl, which seems to accelerate the departure of furfural from polar solvent. The problem is considered as the decrease of conversion of xylose probably due to the some inhibition or negative effect of protonation of xylose influenced by very high concentration of Na⁺ and Cl⁻ ion.

Maximum yield of furfural was 43 % and higher yield may be realized with much higher temperature including improvement of conversion of xylose and with shorter residence time of furfural contacted with reaction phase. In order to confirm the possibility of much higher yield of furfural, higher reaction temperature may be necessary and was examined by using autoclave.

4. Investigation by using autoclave

4.1 Experimental

It was confirmed that there are big possibility to realize same level yield of furfural by the reaction with high temperature of same level in industry. For the confirmations, an autoclave system shown in Fig. 6.5 was introduced.

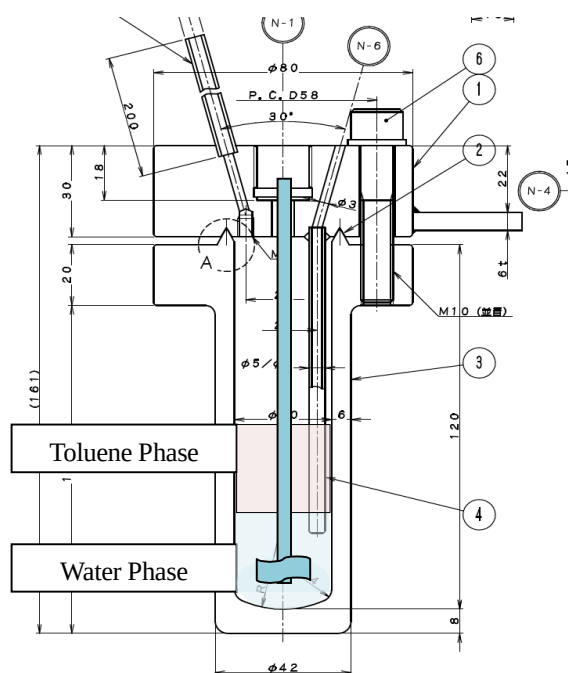


Fig. 6.5 Autoclave for High Temp. Reaction

Sulfated tin oxide, which was developed in Chapter 4, was used as catalyst for this investigation; tin oxide was sulfated with 3.0 M of H_2SO_4 aq. and calcined at 500°C ($3.0\text{M}-500\text{-SO}_4^{2-}/\text{SnO}_2$). [2, 3]

Typically, 250 mg of catalyst and 5 mmol of xylose were added to a two-phase system consisting of 25 mL of water and 25 mL of toluene with stirring at the temperature of 160°C . When NaCl was not added to the reaction system, the reaction was designated as “N0”. On the other hand, NaCl was added to the water phase with saturated concentration, the reaction was designated as N3. The analyses method of xylose and furfural was the same as section 3.1 of Chapter 6.

4.2 Results and Discussion

The results of catalytic reaction were shown in Fig. 6.6 to Fig.6.8

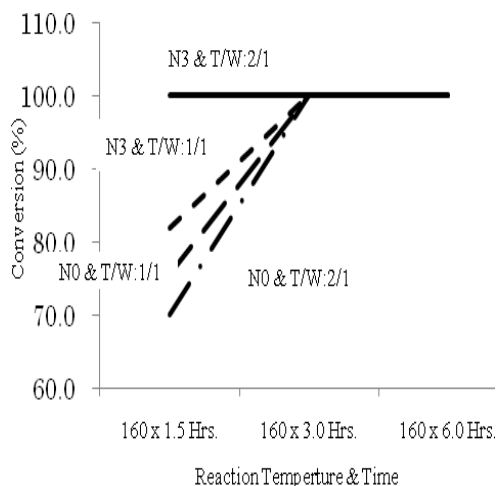


Fig. 6.6 Conversion of xylose

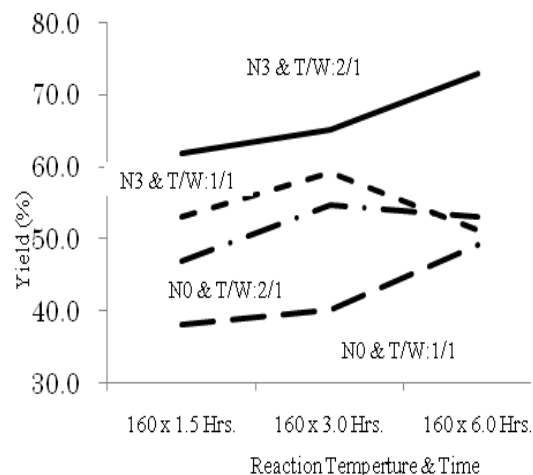


Fig 6.7 Yield of furfural

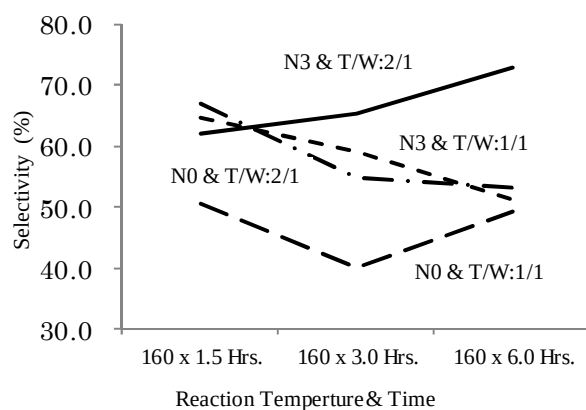


Fig 6.8 Selectivity to furfural

The conversion of xylose reached to 100 % in case of temp.:160 °C with reaction time of 1.5 hours by N3 and T/W: 2/1, and with reaction time of 3 hours by all other cases.

The yield of furfural showed the tendency of increment along reacting time. About the combination of N3 and T/W: 2/1 and of N0 and T/W: 1/1, the reason of such increment is considered as the higher acceptance capacity for furfural in former case and as the lower yield in latter case. The combination of N3 and T/W: 1/1 showed the tendency of saturation of increment

probably due to the poor accepting capacity for furfural.

The achieved yield value as 62 to 73 % in the combination of N3 and T/W ratio: 2/1, seems same to or higher than that of the industry with sulfuric acid as catalyst and additional investigations are expected to bring much higher yield than that in industry.

The selectivity to furfural showed similar tendency come from the above. The combination of N3 and T/W: 2/1 may have some possibility for higher selectivity and yield,

For further high yield and selectivity, the approach from chemical engineering may be essential including continuous reaction system instead of batch system with the continuous feeding mechanism of xylose and toluene and continuous taking out system of synthesized furfural in toluene and distillatory equipment etc..

5. Conclusion of chapter 6

1. The addition of NaCl to water phase to almost saturation in case of 2 phase reaction system with toluene and water showed positive effects to increase yield of furfural and selectivity to furfural, due to the departure effect of furfural from water phase.
2. The volume ratio between toluene and water was considered to have also very important parameter, due to acceleration of the extraction of furfural from water phase to toluene phase and to the possibility of contact of synthesized furfural with intermediates and catalyst. The detailed study may be necessary for designation of reactor and distillatory equipment.
3. The decreasing effect of conversion of xylose due to the addition of NaCl to water can be recovered by increasing reaction temperature from 100 °C to 160 °C and the yield of furfural can reach to almost same level as those of industry.
4. The residual items seem as 1) investigation of by products in case of 2-phase reaction with toluene and water phase with volume ratio of toluene/water with 2/1 with catalysts of tin oxide sulfated with 3 Mol. /L of H₂SO₄, 2) Investigation of repeatability of the above reaction, 3) Investigation of scale factor and 4) others including chemical engineering approach..

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Chapter 7

Summary

Chapter 2 Dehydration of xylose to furfural over various solid acid catalysts

1. As a part of screening of various catalysts from papers, Mordenite and zirconia co-precipitated with SBA-15(mesoporous silica) were studied as a catalyst for dehydration of xylose.
2. Mordenite could not show any positive direction however it was suggested that zirconia co-precipitated with SBA-15 has some possibility and relatively high acid amount prepared by zirconia was important parameter.
3. In addition to catalyst, the importance of reaction conditions prepared the direction for the development of new catalysts.

Chapter 3 Investigation of reaction system for synthesis of furfural from xylose

1. 2-phase reaction system with water and toluene was confirmed as a suitable system for higher selectivity to furfural under minimizing "Furfural Loss".
2. The volume ratio between toluene and water for best selectivity to furfural was shown as near 1/1 but depended upon reaction conditions.
3. "Furfural loss" was recognized one of the key point for the synthesis of furfural from xylose. Main reasons of "Furfural Loss" were considered as the condensation between intermediates and furfural, the resinification among furfurals and the fragmentation of xylose/intermediates. These may be reduced by introduction of 2-phase reaction system.
4. The reduction of "Furfural Loss" seems to depend upon minimizing the contact opportunity, including residence time of furfural with xylose/intermediates/catalysts.

Chapter 4 Dehydration of xylose to furfural over various sulfated metal oxides

1. Sulfated metal oxides (SMOs) including ZrO_2 , SnO_2 , TiO_2 and Fe_2O_3 have been extensively considered as solid acid catalyst for the dehydration of xylose. Consequently,

it was found that sulfated tin oxide exhibited the highest catalytic performance.

2. Both of LASs derived from SnO_2 and BASs derived from SO_4^{2-} groups are indispensable for the production of furfural by the dehydration of xylose.
3. The preparation conditions including the concentration of H_2SO_4 for sulfation and/or the calcination temperature at sulfation process strongly affect the structural properties followed by the catalytic performance

Chapter 5 Investigation of reusability of sulfated metal oxide catalysts

1. The sulfated tin oxide catalyst was recognized to be reused through the re-sulfation process after the reaction. The performance of the original sulfated tin oxide catalyst and of the recycled catalyst suggested the possibility of replacement of sulfuric acid used in industry.
2. For reuse of the catalyst, dissolving of SO_4^{2-} group fixed on tin oxide during catalytic reaction was investigated. The SO_4^{2-} groups were partially dissolved from the metal oxides after the 1st run. However, such dissolving can be almost recovered after re-sulfation.

Chapter 6 Effects of addition of ionic salts into the reaction system on the catalytic performance

1. The addition of NaCl to water phase to almost saturation for 2 phase reaction system with toluene and water showed positive effect to increase yield of furfural and selectivity to furfural.
2. The volume ratio between toluene and water was considered to have also very important parameter.

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Takeshi Suzuki