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## Mechanistic study on the catalytic surface reaction of vibrationally-excited CO<sub>2</sub> in nonthermal plasma

A THESIS

## SUBMITTED TO THE FACILITY OF SCHOOL OF ENGINEERING, GRADUATE MAJOR OF MECHANICAL ENGINEERING OF TOKYO INSTITUTE OF TECHNOLOGY

BY

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#### Abstract

Nonthermal plasma (NTP) assisted catalysis is gaining attention as an attractive technology that can overcome the energy barriers involved in conventional thermal catalysis. However, the catalytic surface reaction dynamics of NTP-activated species are still primitive. Generally, interactions between catalytic surface and gas molecules follow three well-established mechanisms: Langmuir-Hinshelwood, Eley–Rideal, and Mars–van Krevelen type mechanisms. In this thesis, I present the elucidation of the microscopic mechanism of NTP-assisted catalysis. In particular, I focus on the interaction between vibrationally-excited molecules and the catalyst surface. First, I explore the CO<sub>2</sub> hydrogenation over Pd<sub>2</sub>Ga/SiO<sub>2</sub> alloy catalysts via the Eley–Rideal type mechanism. Then, I investigate the CO oxidation over wurtzite ZnO via the Mars–van Krevelen type mechanism.

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#### **Chapter 1. Introduction**

#### **1.1 Motivation and outline**

Nonthermal plasma (NTP) assisted catalysis is gaining increasing attention as emerging technologies can improve existing technologies in various applications, such as CO<sub>2</sub> hydrogenation<sup>1,2</sup>, CH<sub>4</sub> dry reforming<sup>3,4</sup>, ammonia synthesis<sup>5-7</sup>, and more (Figure 1.1). As summarized in various NTP-assisted catalysis review papers<sup>8-15</sup>, the advantages of NTPassisted catalysis over thermal catalysis are achieved by combining the high selectivity of the catalyst with the high reactivity of the NTP. NTP is characterized by having abundant vibrationally-excited molecules with various active species including ions, radicals, and free electrons which arise due to inelastic collisions between high-energy electrons and groundstate molecules<sup>9,14,16</sup>. This effectively makes thermodynamically challenging reactions possible by removing the thermal equilibrium limitations experienced in thermal catalysis. Moreover, the NTP process offers the advantage of integrating with renewable energy with high variabilities of energy production, such as solar and wind power, as it operates instantaneously and provides the flexibility to be turned on/off quickly as needed<sup>12,13,17</sup>. Therefore, the purpose of NTP-assisted catalysis is to synthesize the desired product with high selectivity and energy efficiency as well as high conversion of reactants by generating active species from NTP and reacting them on the catalyst surface.

Although the synergistic effects in NTP-assisted catalysis are elicited by the rational design of catalysts, they depend on an understanding of the surface activity and reaction mechanisms relationships at the molecular level. A search for the topic "Plasma catalysis" on the Web of Science provides 4279 papers from the last 10 years. Although a significant number of studies on NTP-assisted catalysis have shown synergistic effects of combining NTP and catalysis, However, Due to the complex interaction between the plasma discharge and the catalyst in NTP-assisted catalysis, the explanation of the fundamental mechanism has yet to be

established.

Catalytic surface chemistry is an important factor in NTP-assisted catalysis. The nature of the various reactions occurring on the catalytic surface determines the activity of the entire process of NTP-assisted catalysis<sup>11</sup>. The interactions at the catalytic surface of gas molecules (reactants) generally follow three well-established mechanisms: Langmuir–Hinshelwood (L–H); Two reactants adsorbed on catalyst surface react with each other, Eley–Rideal (E–R); Gas-phase reactants directly react with reactant previously adsorbed on catalyst surfaces, and Mars–van Krevelen (MvK) mechanisms; Reactants react with lattice components of catalysts, and spent components are recovered through second reactant (Figure 1.2). In the NTP conditions, vibrationally-excited molecules are dominant channels because of their low energy threshold compared with ionization or dissociation<sup>4,7,13</sup>. Accordingly, I believed that elucidating the interplay between vibrationally-excited molecules and catalytic surfaces is a great step forward for the clear-cut understanding of the synergistic effect and a prerequisite for the rational catalytic design for NTP-assisted catalysis.

In **Chapter 2**, I explored the reaction promotion of NTP-assisted catalysis by vibrationally-excited  $CO_2$  via the E–R type mechanism. I focused on the  $CO_2$  hydrogenation over  $Pd_2Ga/SiO_2$  intermetallic catalysts. Although both thermal and NTP conditions showed close to 100% CO selectivity, it is worth emphasizing that when activated by NTP,  $CO_2$  conversion not only improves more than 2-fold under thermal conditions but also breaks the thermodynamic equilibrium limitation. Mechanistic insight into NTP-activated species and intermetallic catalyst surface were investigated by using *in situ* transmission infrared (TIR) spectroscopy, where catalyst surface species were identified during NTP irradiation. Moreover, in *in situ* X-ray absorption fine-structure analysis under reaction conditions, the catalyst under NTP conditions not only did not undergo restructuring affecting  $CO_2$  hydrogenation but also could clearly rule out catalyst activation by heating. *In situ* characterizations of the catalysts during  $CO_2$  hydrogenation depict that vibrationally-excited  $CO_2$  significantly enhances the

catalytic reaction. the agreement of approaches combining experimental studies and density functional theory (DFT) calculations substantiates that vibrationally-excited  $CO_2$  reacts directly with hydrogen adsorbed on Pd sites (via E–R type mechanism) while accelerating formate formation due to neighboring Ga sites. Moreover, DFT analysis deduces the key reaction pathway that the decomposition of monodentate formate is promoted by plasma-activated hydrogen species. I believed that the understanding and insights in **Chapter 2** enable the high designability of  $CO_2$  hydrogenation catalysts toward value-added chemicals based on the electrification of chemical processes via NTP.

In **Chapter 3**, I focused on the reaction promotion of NTP-assisted catalysis by vibrationally-excited CO via the MvK mechanism. First, I was able to unambiguously identify vibrationally-excited CO species with *in situ* TIR diagnostics performed in a catalyst-free environment. The rotational temperature of CO remained unchanged at room temperature (ca. 300 K) at various NTP powers, while the vibrational temperature was increased from 1000 K to 1300 K with NTP power, showing that CO is excited into the vibrational quantum number of three. Then, the effect of NTP, or vibrationally-excited CO, was studied using surface reaction over wurtzite ZnO. A comparative study with ground-state CO by *in situ* TIR spectroscopy suggests that vibrationally-excited CO over the wurtzite ZnO surface promotes thermodynamically limited CO exhibits an unusual CO adsorption band due to strong binding energy with Zn<sup>2+</sup>, which improves the CO oxidation by activating the reaction with adjacent lattice oxygen in the wurtzite ZnO via the Mar–van Krevelen type mechanism at room temperature. The present findings provide new possibilities for achieving low temperature CO oxidation based on the electrification of chemical processes through NTP.



Figure 1.1. Application of NTP-assisted catalysis



**Figure 1.2.** Schematic illustrations of (a) Langmuir–Hinshelwood mechanism, (b) Eley–Rideal mechanism and (c) Mars–van Krevelen mechanism.

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# Chapter 2. Cooperative catalysis of vibrationally-excited CO<sub>2</sub> and alloy catalyst breaks the thermodynamic equilibrium limitation

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#### 2.1 Abstract

Using nonthermal plasma (NTP) to promote CO<sub>2</sub> hydrogenation is one of the most promising approaches that overcome the limitations of conventional thermal catalysis. However, the catalytic surface reaction dynamics of NTP-activated species are still under debate. The NTP-activated CO<sub>2</sub> hydrogenation was investigated in Pd<sub>2</sub>Ga/SiO<sub>2</sub> alloy catalysts and compared to thermal conditions. Although both thermal and NTP conditions showed close to 100% CO selectivity, it is worth emphasizing that when activated by NTP, CO<sub>2</sub> conversion not only improves more than 2-fold under thermal conditions but also breaks the thermodynamic equilibrium limitation. Mechanistic insights into NTP-activated species and alloy catalyst surface were investigated by using *in situ* transmission infrared spectroscopy, where catalyst surface species were identified during NTP irradiation. Moreover, in in situ Xray absorption fine-structure analysis under reaction conditions, the catalyst under NTP conditions not only did not undergo restructuring affecting CO<sub>2</sub> hydrogenation but also could clearly rule out catalyst activation by heating. In situ characterizations of the catalysts during CO<sub>2</sub> hydrogenation depict that vibrationally-excited CO<sub>2</sub> significantly enhances the catalytic reaction. The agreement of approaches combining experimental studies and density functional theory (DFT) calculations substantiates that vibrationally-excited  $CO_2$  reacts directly with hydrogen adsorbed on Pd sites while accelerating formate formation due to neighboring Ga sites. Moreover, DFT analysis deduces the key reaction pathway that the decomposition of monodentate formate is promoted by plasma-activated hydrogen species. This work enables the high designability of CO<sub>2</sub> hydrogenation catalysts toward value-added chemicals based on the electrification of chemical processes via NTP.

#### **2.2 Introduction**

Regarding the problem of climate change caused by CO<sub>2</sub> and future fossil fuel depletion, the capture, utilization, and storage of carbon dioxide, a representative global warming gas, offers significant benefits in reducing CO<sub>2</sub> emissions<sup>1-3</sup>. In particular, CO<sub>2</sub> capture and utilization (CCUS) is considered a sustainable technology in addition to reducing emissions, which can provide synthetic fuels and chemicals using CO<sub>2</sub> as a feedstock<sup>4,5</sup>. In this regard, CO<sub>2</sub> hydrogenation with renewable H<sub>2</sub> is being proven as an alternative fuel production technology<sup>6,7</sup>. Therefore, achieving a proper understanding of CO<sub>2</sub> hydrogenation and rational design of catalysts to improve conversion and selectivity efficiencies is an important task. Recent reviews focused on selective CO<sub>2</sub> conversion of heterogeneous catalysts in CO<sub>2</sub> hvdrogenation<sup>8,9</sup>. Meanwhile, for CO<sub>2</sub> hydrogenation, multimetallic catalysts can control CO<sub>2</sub>and hydrogen-bonding sites, charge transfer, and electronic structure properties through interactions between different monometallic catalysts, so the activity can be improved significantly over a monometallic catalyst<sup>10-13</sup>. In addition, nonthermal plasma (NTP) is considerably superior in activating thermodynamically stable molecules (e.g., CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>): NTP-assisted catalysis is recognized as a promising technology that can overcome the thermodynamic limitation or formation of new reaction pathways that cannot be achieved with thermal catalysis<sup>14-19</sup>. CO<sub>2</sub> hydrogenation to CO is endothermic, and a high temperature is needed thermodynamically. Meanwhile, high temperatures would be detrimental to multimetallic catalysts, especially alloy catalysts, because the high-temperature situation would induce irreversible phase separation of each metallic element which permanently deteriorates the activity of multimetallic catalysts<sup>20-22</sup>. NTP enables low-temperature activation of stable molecules, which accelerates the overall reaction rate without catalyst deactivation. Particularly, I focused on the Elev-Rideal (E-R) pathway where vibrationally activated CO<sub>2</sub> reacts directly with adsorbed hydrogen and promotes CO<sub>2</sub> conversion kinetically at low temperatures. The E–R pathway in  $CO_2$  hydrogenation has been proven by the molecular beam

study on Cu and Cu/ZnO well-defined surfaces<sup>23,24</sup>. In principle, CO<sub>2</sub> hydrogenation occurs via the E-R pathway with a small activation energy. However, the pre-exponential factor is quite small because formate formation is strongly coordinate- dependent and the bending-mode CO<sub>2</sub> vibration is critically important<sup>24</sup>. Such insight is quite courageous for efficient CO<sub>2</sub> conversion into formate, leading to final products such as methanol<sup>25,26</sup>, methane<sup>27,28</sup>, or CO<sup>29,30</sup>. However, at low temperatures, population of vibrationally-excited CO<sub>2</sub> is quite low and E-R is not anticipated, yielding a low CO<sub>2</sub> conversion. In the field of NTP-assisted catalysis, rationally designing catalysts that could enable more efficient interactions between NTP-activated species and catalysts remain a great challenge<sup>14,31</sup>. I propose an NTP-combined Pd<sub>2</sub>Ga/SiO<sub>2</sub> alloy catalyst system which produces a copious amount of vibrationally-excited species and has been proven experimentally in our previous study in CH<sub>4</sub> dry reforming. NTP realizes twotemperature reaction conditions where the system is kept at low temperatures, while the vibrational temperature of CO<sub>2</sub> would increase higher than the gas temperature which interacts directly with adsorbed hydrogen. A similar reaction enhancement mechanism is studied by Mehta et al., showing that vibrationally-excited N<sub>2</sub> promotes ammonia synthesis over the metal catalyst<sup>32</sup>. Meanwhile, Xu et al. confirmed the exceptional stability of metal-organic frameworks under NTP-assisted catalysis, which is also applicable to our reaction system with increased stability of alloy catalysts via low-temperature catalysis enabled by NTP<sup>33</sup>. Here, I first present the kinetic study in which the combination of NTP and the alloy catalyst yielded enhanced CO<sub>2</sub> conversion beyond the thermodynamic equilibrium limitation that could not be achieved under thermal catalysis. Intermetallic Pd<sub>2</sub>Ga was chosen as the catalyst because this material has been reported to be active for CO<sub>2</sub> conversion<sup>34,35</sup>. To gain mechanistic insight into the NTP-activated CO<sub>2</sub> and alloy catalyst interaction, I developed in situ transmission infrared (TIR) spectroscopy, where NTP is generated in the TIR cell, and surface species were identified during NTP irradiation. Furthermore, chemical and structural transitions of catalysts during CO<sub>2</sub> hydrogenation under both thermal and NTP conditions were investigated by *in situ*  X-ray absorption fine-structure (XAFS) analysis. Finally, through agreement between experimental and DFT calculation approach on the realistic model, I aim to provide fundamental mechanical insights into the role of vibrationally-excited CO<sub>2</sub> derived from NTP and alloy catalysts in significantly improving CO<sub>2</sub> hydrogenation.

#### **2.3 Experiment section**

#### 2.3.1 Materials and characterization

The  $Pd_2Ga/SiO_2$  (Pd/Ga = 2) catalysts were synthesized by the pore-filling (co-)impregnation method. Pd(NO)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> (Kojima Chemicals, 4.765 wt % in HNO<sub>3</sub> solution, Cas no. 14852-83-6<sup>36</sup> and Ga(NO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O (n = 7-9, Wako, 99.9%) were used as metal precursors. The loading amounts of Pd and Ga were fixed at 10 and 3.3 wt %, respectively (atomic ratio: Pd/Ga = 2). Aqueous solution of the metal precursor(s) was first added dropwise to SiO<sub>2</sub> (CARiACT G-6, Fuji Silysia,  $S_{\text{BET}} = 673 \text{ m}^2 \text{ g}^{-1}$ , grain size: 300–425  $\mu$ m), so that the solutions just filled the pore of SiO<sub>2</sub> (ca. 1.6 mL of solution per g of SiO<sub>2</sub>). The obtained mixtures were sealed by three pieces of plastic film and kept overnight at room temperature, followed by transferring to a round-bottom flask and subsequent freezing using liquid nitrogen. The frozen mixtures were dried in vacuum at ca. -5 °C and further dried in an oven at 90 °C overnight. The resulting powder was calcined at 500 °C for 1 h in dry air with a ramping rate of 20 °C min<sup>-1</sup>. The calcined powder was then reduced under flowing H<sub>2</sub> (0.1 MPa, 50 mL min<sup>-1</sup>) at 500 °C for 1 h with a ramping rate of 20 °C min<sup>-1</sup>. After the reduction, the catalyst bed was purged with N<sub>2</sub> and then exposed to air very slowly (overnight) for passivation. The crystalline phase in the prepared catalysts was obtained using powder X-ray diffraction (MiniFlex 700+D/teX Ultra; Cu Ka X-ray source). The main diffraction patterns to the intermetallic Pd<sub>2</sub>Ga phase were observed (Figure 2.1), indicating that the desired metallic phases were successfully formed. A small amount of monometallic Pd also remained as a minor phase. XAFS spectra of Pd<sub>2</sub>Ga/SiO<sub>2</sub> and reference samples were recorded at the BL9A beamline of the photon factory (PF) for the Ga K-edge and at the NW10A beamline of the Photon Factory Advanced Ring (PF-AR) for the Pd K-edge, respectively, in the Institute of Material Structure Science (IMSS) of High Energy Accelerator Research Organization (KEK). The XAFS spectra were recorded in a transmission mode. The formation of intermetallic Pd<sub>2</sub>Ga was also suggested by XAFS analysis, where Pd- Ga (Ga-Pd) interatomic bonds were

observed in the EXAFS results (Figure 2.2 and Table 2.1). The morphology of the prepared catalysts was observed by transmission electron microscopy (TEM, JEOL, JEM- ARM200F NEOARM, 200 kV). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with energy- dispersive X-ray spectroscopy (EDX) was performed. The HAADF-STEM images (Figure 2.3a) show that Pd<sub>2</sub>Ga nanoparticles with a size smaller than 8 nm were dispersed on the SiO<sub>2</sub> support (Figure 2.3d). The corresponding EDX elemental mapping confirms that Pd and Ga are distributed closely uniformly, indicating the intermetallic interaction between them due to the formation of a intermetallic phase (Figure 2.3b,c). Moreover, in Figure 2.3e, two clear lattice fringes spacings of 2.18 and 1.90 Å are observed, which correspond to the (211) and (203) planes of Pd<sub>2</sub>Ga, respectively, and the dihedral angle is measured to be 41°. Consequently, the series of characterization results confirm the successful formation of the desired Pd<sub>2</sub>Ga intermetallic catalysts.



**Figure 2.1.** (a) XRD patterns of Pd-Ga/SiO<sub>2</sub>. (Pd/Ga = 2) with the reference patterns of Pd and Pd-Ga intermetallic. (b) Peak deconvolution into the contribution of Pd, Pd<sub>2</sub>Ga, and SiO<sub>2</sub>. The crystallite sizes were determined using the Scherrer's equation for the peaks designated by arrows.



**Figure 2.2.** *In situ* XAFS results of the reduced Pd<sub>2</sub>Ga/SiO<sub>2</sub>. (a) Ga and (c) Pd K-edge XANES. (b) Ga and (d) Pd K-dege  $k^3$ -weighted EXAFS oscillation, Fourier-transformed (FT) EXAFS and inversely FT EXAFS are shown with the red fitted curves (see Table 2.1 for the details of the fitting). *k*-range for FT: 3.0–16.0 Å<sup>-1</sup>. The measurements were carried out at room temperature in H<sub>2</sub> flow after reduction at 500 °C in H<sub>2</sub> flow for > 1 h. H<sub>2</sub> = 150 mL min<sup>-1</sup>, pressure = 30 kPa.



**Figure 2.3.** TEM image of  $Pd_2Ga/SiO_2$ . (a) HAADF-STEM image and the corresponding elemental maps of (b) Pd and (c) Ga acquired by EDX. (d) Particle size distribution. (e) High resolution HAADF-STEM image of single  $Pd_2Ga$  nanoparticle. The average in parathesis indicates the volume-weighted average.

**Table 2.1.** Curve-fitting results for Ga and Pd K-edge EXAFS data of the reduce Pd<sub>2</sub>Ga/SiO<sub>2</sub> shown in Figure 2.2b and d, respectively<sup>a</sup>

Edge	Shell	Ν	r (Å)	$\Delta E (eV)$	$\sigma^2$ (Å <sup>2</sup> )	<i>R</i> -factor / %
Cak	Ga-O	$0.5 \pm 0.2$	$1.77 \pm 0.02$	(-10)	$0.0043 \pm 0.0025$	0.6
Ga K	Ga-Pd	3.6 ± 0.5	$2.52\pm0.02$	$0 \pm 1$	$0.0075 \pm 0.0003$	0.6
Pd K	Pd-Ga	$1.4 \pm 0.4$	$2.52\pm0.02$	(-9)	$0.0083 \pm 0.0025$	0.7
	Pd-Pd	6.1 ± 1.0	$2.76\pm0.02$	(-4)	$0.0072 \pm 0.0011$	0.7

<sup>a</sup>Parentheses indicate those values fixed during the fitting procedure. *k*-range for FT: 3.0-16.0 Å<sup>-1</sup>. *R*-range for back *k* fitting: 1.1-2.9 Å and 1.6-3.9 Å for Ga and Pd K-edge EXAFS analysis, respectively.

#### 2.3.2 Fluidized-bed dielectric barrier discharge

A fluidized-bed dielectric barrier discharge (FB-DBD) reactor was used for CO<sub>2</sub> hydrogenation over  $Pd_2Ga/SiO_2$  (Figure 2.4). The quartz reactor (20 mm i.d.  $\times$  23 mm o.d.), ground electrode (aluminum), and furnace were laminated to have a better contact, while the high-voltage (H.V.) electrode (stainless steel; 1 mm i.d.  $\times$  6 mm o.d.) was coaxially placed along the axis of the reactor, creating 7 mm gas gap for generation of DBD. The H.V. electrode was immersed in the static catalyst powder. The feed gas was introduced from the tip of the H.V. electrode which blows off the catalyst powder, initiating a stable fluidization of catalysts. Before the CO<sub>2</sub> hydrogenation reaction, 4 g of Pd<sub>2</sub>Ga/SiO<sub>2</sub> catalyst powder (300–425 µm) was reduced at 500 °C for 90 min in a 15% H<sub>2</sub>/Ar gas flow (total flow rate = 230 mL min<sup>-1</sup>). The reduced catalyst powder was placed into the quartz reactor, and FB-DBD was applied by a gas mixture of  $H_2/CO_2$  (molar ratio of 3:1). The total flow rate and the weight hourly space velocity (WHSV) of the gas mixture were 200 mL min<sup>-1</sup> and 3000 mL g<sup>-1</sup> h<sup>-1</sup>, respectively, under STP conditions (25 °C and 101 kPa). For each test, the total pressure was fixed at 15 kPa. An AC high-voltage power source (Logy Electric; LHV-13AC, Vp-p = +8 to -6 kV, 12 kHz) was used to generate DBD. The applied voltage and the mean current were measured using an oscilloscope (Agilent Technologies; DSO-X 3014A). The discharge power was obtained by the voltage-charge Lissajous figure method and was fixed to 30 W in this study. The catalyst temperature was measured using the infrared camera combined with an IR-reflecting mirror (TH5104; NEC Sanei Instrument, Ltd). The infrared camera was calibrated by the thermocouples without DBD, showing an emissivity of 0.76 which represents most likely the temperature of the fluidized catalyst powder<sup>15,37-40</sup>. The gas analysis was performed using a quadrupole mass spectrometer (QMS, Prisma Plus QMG 220).



**Figure 2.4.** Schematic diagram of the FB-DBD reactor. Thermoimage (left side) represents the temperature distribution of fluidized Pd<sub>2</sub>Ga/SiO<sub>2</sub> powder. Inset photograph (right side) represents discharge emission in FB-DBD reactor.

#### 2.3.3 Kinetic analysis

I analyzed the mean reaction rate assuming continuous plug-flow reactor model in which the reaction rate is characterized by the inlet and the outlet of gas components. The power-law equation was integrated numerically by considering reaction orders to yield the mean rate constant. Lee et al. analyzed fluidize-bed reactor as either plug flow or mixed flow model.<sup>41</sup> They found a similar kinetic behavior between plug and mixed flow reactor models because the mean reaction rate was analyzed in both cases. Barea et al. performed systematic analysis of char gasification in a fluidized-bed reactor, concluding that the plug-flow condition of gas is necessarily needed to distinguish the kinetic effect from that of mass transfer and fluid motion<sup>42</sup>. Considering the similarity between our study and cited literature, our analytical method evaluating the mean reaction rate is rational.

Before the fluidization (gas flow is zero), DBD was not generated in the dense layer of catalyst powder due to the restriction of gas breakdown phenomena known as Paschen's law. Likewise, small gas flow rate near the "minimum fluidization velocity" does not generate DBD either in the powder layer. In order to generate DBD over the entire fluidized bed, a large gas flow to generate bubble-phase fluidization is necessary. Due to the fact that DBD is generated in the bubble-phase fluidization with large gas flow, back mixing is suppressed in our fluidized-bed plasma reactor.

 $CO_2$  reaction rate was expressed by the power-law kinetics (eq 2.1). Take the natural logarithm of eq 2.1 and rewrite it into eqs 2.2–2.4.

$$-\frac{dP_{CO_2}}{dt} = r_{CO_2} = k_f P_{CO_2}{}^{\alpha} P_{H_2}{}^{\beta}$$
eq 2.1

$$\ln r_{CO_2} = \ln k_f + \alpha \ln P_{CO_2} + \beta \ln P_{H_2}$$
 eq 2.2

$$\ln \frac{r_{CO_2}}{P_{H_2}^{\beta}} \propto \alpha \ln P_{CO_2} \qquad \text{eq } 2.3$$

$$\ln \frac{r_{CO_2}}{P_{CO_2}} \propto \beta \ln P_{H_2}$$
 eq 2.4

Here,  $k_f$  and P expresses the forward reaction rate constant and the average concentration

of CO<sub>2</sub> and H<sub>2</sub>.  $\alpha$  and  $\beta$  represent the modified reaction order for CO<sub>2</sub> and H<sub>2</sub>, respectively.  $\alpha$  and  $\beta$  were unknown figures at this point: Assume arbitrary values for  $\alpha$  and  $\beta$  and performed iterative calculation until the deviation of  $\alpha$  and  $\beta$  becomes smaller than 1% error. The feasibility of this method had been verified in our previous research on dry methane reforming<sup>15</sup>.

Reaction order was estimated from Figure 2.5 at fixed total flow rate while varying H<sub>2</sub>/CO<sub>2</sub> ratio without dilution gas. Figure 2.6 represents the corresponding CO<sub>2</sub> and H<sub>2</sub> conversion while ca. 100% CO selectivity was obtained in all cases. Experimental conditions are provided in the figure caption of Figure 2.6. In Figure 2.5,  $\ln \frac{r_{CO_2}}{P_{H_2}\beta}$  v.s.  $\ln P_{CO_2}$  (a) and  $\ln \frac{r_{CO_2}}{P_{CO_2}\alpha}$  v.s.  $\ln P_{H_2}$  (b) express the linear relationship; the slope of each line corresponds to the modified reaction order as summarized in Table 2.2. As presented in Figure 2.5, the reaction order of CO<sub>2</sub> and H<sub>2</sub> over Pd<sub>2</sub>Ga/SiO<sub>2</sub> decreased clearly by applying DBD. First, smaller reaction order of H<sub>2</sub> than that of the thermal case implies the adsorption of H<sub>2</sub> is promoted by DBD. Second, smaller reaction order of CO<sub>2</sub> and adsorbed H increases.

Apparent activation energy  $(E_{app})$  of thermal and DBD catalysis was determined according to eqs 2-1 and 2-5.

$$k_f = Ae^{-\frac{E_{app}}{RT}}$$
eq 2.5

The A, R and T represent pre-exponential factor, universal gas constant and catalyst temperature (K), respectively.

Specific energy input (SEI) was calculated by following eq 2.6

$$SEI (eV molecule^{-1}) = \frac{Power (W)}{eN_A \times \frac{Q_{\text{total}}^{\text{in}}}{60 \times 10^6} \times \frac{P}{RT}} eq 2.6$$

The  $Q_{\text{total}}^{\text{in}}$  represents the total gas flow rate (mL min<sup>-1</sup>, STP) at the reactor inlet;  $e = 1.602 \times 10^{-19}$  (C);  $N_{\text{A}} = 6.02 \times 10^{23}$ ; R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>. Here, 1 eV molecule<sup>-1</sup> is equivalent to

96.5 kJ mol<sup>-1</sup>.  $CO_2$  and  $H_2$  conversion and CO selectivity were calculated by the following eqs 2.7–2.9.

$$CO_2 \text{ conversion } \% = \frac{F_{CO_2}^{in} - F_{CO_2}^{out}}{F_{CO_2}^{in}} \times 100$$
 eq 2.7

$$H_2 \text{ conversion } \% = \frac{F_{H_2}^{in} - F_{H_2}^{out}}{F_{CO_2}^{in}} \times 100 \text{ eq } 2.8$$

$$CO \text{ selectivity } \% = \frac{F_{CO_2}^{out}}{F_{CO_2}^{in} - F_{CO_2}^{out}} \times 100 \qquad \text{eq } 2.9$$

F (mol min<sup>-1</sup>) expresses mol flow rate at STP conditions (25 °C and 101 kPa).

The average reaction rate ( $r_i$ ; mol m<sup>-3</sup>s<sup>-1</sup>) was calculated using mole concentration of each species ( $P_i$ ; mol m<sup>-3</sup>) in eqs 2.10–2.12.

$$r_i = \frac{P_i^{in} - P_i^{out}}{\Delta t}$$
eq 2.10

$$\Delta t = \frac{2V}{Q_{\text{total}}^{\text{in}} + Q_{\text{total}}^{\text{out}}}$$
eq 2.11

$$V = V_0 - V_{cat}$$
eq 2.12

The  $V_{cat}$  (= 2.1 mL) expresses the total volume of 4 grams of catalyst powders used for reforming.



**Figure 2.5.** Modified reaction orders. (a)  $\alpha$  for CO<sub>2</sub>. (b)  $\beta$  for H<sub>2</sub>, respectively. Conditions: see Figure 2.6 caption.



**Figure 2.6.** CO<sub>2</sub> and H<sub>2</sub> conversion (%) with respect to the initial CO<sub>2</sub> flow rate on 10 wt% Pd<sub>2</sub>Ga/SiO<sub>2</sub>. (a) Thermal catalysis. (b) DBD catalysis. Catalyst temperature and input power were fixed at 465 °C and SEI = 2.28 eV molecule<sup>-1</sup>, respectively. Total flow rate = 200 mL min<sup>-1</sup> (STP); H<sub>2</sub>/CO<sub>2</sub> = 1, 3, and 9; WHSV = 3000 mL g<sup>-1</sup> h<sup>-1</sup> (STP); Pressure = 15 kPa.

 Table 2.2. Modified reaction orders obtained from Figure 2.5.

	α	β
Thermal catalysis	1.42	2.43
DBD catalysis	1.00	1.53
#### 2.3.4 In situ TIR

The in situ TIR characterization of catalyst CO<sub>2</sub> hydrogenation under plasma was measured using a DBD flow-type TIR cell under a pressure of 10 kPa (Figures 2.7 and 2.8). The *in situ* TIR cell was in the form of a cylindrical glass tube, and a K-type thermocouple (1 mm o.d.) was arranged to continuously monitor the temperature inside the reactor. The stainless-steel (1 mm o.d.) H.V. electrode and ground electrode were inserted inside the reactor. The ground electrode was wrapped in a quartz sheath. The electrical parameters of the DBD were monitored using an oscilloscope (RIGOL MSO5104) connected to the reactor via an H.V. probe. The gap between point-to-point electrodes was 10 mm. A high-voltage power supply was connected to the reactor and applied voltage and frequency for all catalyst tests were 2 kV and 19 kHz, respectively. The catalyst was powdered (25–30 mg), compressed with a pressure press, and manufactured in the form a pellet (10 mm o.d., 1 mm thickness). After that, the catalyst was fixed in a glass holder and inserted into the 5 mm downstream from the discharge zone. The in situ TIR spectra were collected using a Fourier-transform infrared spectrometer (FTIR, JASCO FTIR-6600) equipped with a mercury-cadmium-telluride (MCT) detector with 64 scans with a spectral resolution of 4  $\text{cm}^{-1}$  in the range 4000–650  $\text{cm}^{-1}$ . Spectra were recorded every 15 s. Background reference of the spectra of the reduced sample were acquired in a 6% H<sub>2</sub> in Ar flow. The catalyst pellet was reduced at 500 °C under a 6% H<sub>2</sub> in Ar flow for 1 h before testing. After reduction, the reactor was cooled to 250 °C under pure Ar. Then, CO<sub>2</sub> hydrogenation was performed by flowing CO<sub>2</sub> (10 mL min<sup>-1</sup>) + H<sub>2</sub> (30 mL min<sup>-1</sup>) diluted in Ar (150 mL min<sup>-1</sup>). Furthermore, to gain insights into the evolution of surface species adsorbed on the catalysts during thermal and DBD conditions, transient experiments were performed by alternatingly flowing H<sub>2</sub>/Ar (10/150 mL min<sup>-1</sup>) and CO<sub>2</sub>/Ar (10/150 mL min<sup>-1</sup>). Ar was used as a balance gas to dilute the reaction gas and avoid signal saturation of IR spectra. The gas flow was controlled using a programable mass flow controller. The outlet gas stream of the reactor was measured using a QMS (Prisma Plus QMG 220) with a response time of ca. 1 s.



**Figure 2.7.** Design for the *in situ* DBD-TIR cell. (a) Schematic of the *in situ* TIR cell capable of identifying surface species with and without DBD irradiation characterized in this work (b) and (c) cross-sectional schematic (b) and a corresponding photograph (c) during DBD irradiation under CO<sub>2</sub> (10 mL min<sup>-1</sup>) + H<sub>2</sub> (30 mL min<sup>-1</sup>) diluted in Ar (150 mL min<sup>-1</sup>). The high-voltage electrode is on the left exposing the metallic tip, while the grounded electrode is fully covered by glass sheath. The catalyst pellet is located behind the luminescence discharge channel which is separated by 5 mm to avoid direct contact of plasma channel to the catalyst surface.



Figure 2.8. Schematic diagram of the experimental set up.

#### 2.3.5 In situ XAFS

The *in situ* XAFS measurements were conducted using the identical TIR cell and experimental conditions shown in Figure 2.7 equipped with X-ray transparent windows made from Kapton (TX cell). Data analysis was performed with the REX 2000 software package (Rigaku Co., Japan). The XAFS oscillations  $\chi(k)$  were extracted using a spline smoothing method and normalized to edge height, where k is the photoelectron wavenumber and calculated from the photon energy, *E*, using eq 2.1.

$$k = \sqrt{2m(E - E_0)/\hbar^2} \qquad \text{eq } 2.1$$

where  $E_0$  and m are the threshold energy and the electron mass, respectively. The quantity  $k^3\chi(k)$  was Fourier transformed to R space, the peak in the transform was filtered, and then an inverse Fourier transform was applied to convert the filtered peak back to k space. The Fourier-filtered data were then analyzed with a curve-fitting technique using the following theoretical XAFS eqs 2.2 and 2.3.

$$k^{3}\chi(k) = \sum_{i} \frac{k_{i}^{2} S_{i} N_{i} F_{i}(k_{i}) e^{-2k_{i}^{2} \sigma_{i}^{2}} \sin(2k_{i} r_{i} + \varphi_{i}(k_{i}))}{r_{i}^{2}}$$
 eq 2.2

$$k_i = \sqrt{k^2 - 2m\Delta E_i/\hbar^2} \qquad \text{eq } 2.2$$

Here  $S_i$ ,  $N_i$ ,  $\sigma i$ ,  $r_i$ , and  $\Delta E_i$  are the amplitude reduction factor, coordination number, Debye–Waller factor, bond distance of the *i*th bond, and energy shift in the origin of the photoelectron kinetic energy of the ith bond, respectively. The backscattering amplitude,  $F_i(k)$ , and phase shift,  $\varphi_i(k)$  were calculated using the FEFF8.04 algorithm<sup>43</sup>. The amplitude reduction factors,  $S_i$ , were estimated using reference compounds or calculated using the FEFF8.04 algorithm.

#### 2.3.6 Computational details

Periodic DFT calculations were performed using the CASTEP code<sup>44</sup> with Vanderbilttype ultrasoft pseudopotentials and the revised version of Perdew-Burke-Ernzerhof exchange-correlation functional based on the generalized gradient approximation<sup>45,46</sup>. The plane-wave basis set was truncated at a kinetic energy of 360 eV. A Fermi smearing of 0.1 eV was utilized. Dispersion correlations were considered using the Tkatchenko-Scheffler method with a scaling coefficient of  $s_R = 0.94$  and a damping parameter of  $d = 20^{47}$ . The reciprocal space was sampled using a k-point mesh with a spacing of typically 0.04  $Å^{-1}$ , as generated by the Monkhorst-Pack scheme<sup>48</sup>. Geometry optimizations were performed on supercell structures using periodic boundary conditions. I chose Pd<sub>2</sub>Ga(020) plane as the most stable (likely to be exposed) and low-mirror index surface because of the clear appearance of the diffraction peak assignable to this plane (44.5°). The stronger the diffraction is, the higher the atom density is, hence the lower the surface energy is. The surfaces were modeled using the Pd<sub>2</sub>Ga(020)-( $2 \times 1$ ) metallic slabs with a thickness of four atomic layers with 13 Å of vacuum spacing. The unit cell size of the bulk material (Pd<sub>2</sub>Ga) was first optimized, followed by modeling the slab structure and surface relaxation with the size of the supercell fixed. The convergence criteria for structure optimization and energy calculation were set to (a) an SCF tolerance of  $1.0 \times 10^{-6}$  eV per atom, (b) an energy tolerance of  $1.0 \times 10^{-5}$  eV per atom, (c) a maximum force tolerance of 0.05 eV Å<sup>-1</sup>, and (d) a maximum displacement tolerance of  $1.0 \times$ 10<sup>-3</sup> Å. For all calculations, the net charge was set to zero and spin polarization was considered. The adsorption energy was defined as follows:  $E_{ad} = E_{A-S} - (E_S + E_A)$ , where  $E_{A-S}$  is the energy of the slab together with the adsorbate,  $E_A$  is the total energy of the free adsorbate, and  $E_{\rm S}$  is the total energy of the bare slab. Transition-state search was carried out based on the complete linear synchronous transit/quadratic synchronous transit method<sup>49,50</sup> with the tolerance for all root-mean-square forces on an atom of 0.10 eV Å<sup>-1</sup>.

### 2.4 Result and discussion

#### 2.4.1 Kinetic study

I first carried out the kinetics study of CO<sub>2</sub> hydrogenation over Pd<sub>2</sub>Ga/SiO<sub>2</sub> under both thermal and DBD conditions. The FB-DBD reactor was used for enhancing plasma catalyst interactions, as well as the heat and mass transport efficiencies<sup>51</sup>.

Figure 2.9a shows the CO<sub>2</sub> conversion results over Pd<sub>2</sub>Ga/SiO<sub>2</sub> with different Pd<sub>2</sub>Ga loadings (10 and 3 wt %) under thermal and two types of DBD conditions which are generated by different frequencies (12 and 100 kHz) of power source. The CO<sub>2</sub> conversion increases with catalyst temperature, indicating similar trends under all conditions. In particular, in the case of both catalysts, the reaction activity was significantly improved under the DBD conditions compared to the thermal conditions. Meanwhile, SiO<sub>2</sub> and without catalyst (blank) is inactive under both thermal and DBD conditions (Figure 2.10). The CO selectivity was ca. 100% for all conditions (Figure 2.11). It is also worth highlighting that CO<sub>2</sub> conversion for 10 wt % Pd<sub>2</sub>Ga/SiO<sub>2</sub> under 100 kHz DBD conditions is higher than the thermodynamic equilibrium limitation. The dotted line indicates the equilibrium CO<sub>2</sub> conversion for the reverse water-gas shift (RWGS) reaction (H<sub>2</sub>/CO<sub>2</sub> molar ratio of 3) based on ground-state CO<sub>2</sub> at 15 kPa. This limitation curve would shift toward higher value than the thermal equilibrium when CO<sub>2</sub> is excited primarily into vibrational states. Estimation of the Gibbs energy for vibrationallyexcited CO<sub>2</sub>, or nonequilibrium two-temperature system (vibrational temperature > gas temperature), is not readily available. Assuming three fundamental vibration modes of CO<sub>2</sub> (bending, symmetric, and asymmetric stretching) with Boltzmann distribution of vibrational energy, approximately 34 mol % of CO<sub>2</sub> is excited into bending mode vibration at an equilibrium vibrational temperature of 1000 K. Such a unique condition is readily available in NTP without gas heating. Subsequently, bending-mode CO<sub>2</sub> would contribute additional conversion, yielding higher CO<sub>2</sub> conversion than that of the ground-state CO<sub>2</sub>. As for the corresponding Arrhenius plot (Figure 2.9b), regardless of the Pd<sub>2</sub>Ga loadings, the extracted

activation energy for the DBD conditions is clearly smaller than that of the thermal conditions. The activation energy of four NTP reactions does not change to a large degree. In other words, DBD conditions can be grouped together (the activation energy is determined as ca. 43 kJ mol<sup>-1</sup>). This implies that the reaction pathways, or the rate-determining step, for the two catalysts is not only identical but also not influenced by the concentration of vibrationallyexcited molecules. Moreover, from the fact that the slopes of Arrhenius plots for all of the NTP reactions can consist of one group, even if, for 10 wt % Pd<sub>2</sub>Ga/SiO<sub>2</sub>, CO<sub>2</sub> conversion goes beyond the thermodynamic equilibrium limitation, it may not be con-strained by the reverse reaction. The remarkable activity of 10 wt % Pd<sub>2</sub>Ga/SiO<sub>2</sub> under DBD conditions is further highlighted by comparison with mono-metallic catalysts (10 wt % Pd/SiO<sub>2</sub> and 3.3 wt % Ga/SiO<sub>2</sub>). Comparing the CO yield over the three catalysts (Figure 2.12), under both DBD and thermal conditions, CO yield for 10 wt % Pd<sub>2</sub>Ga/SiO<sub>2</sub> is much greater than the sum of the individual contribution of Pd and Ga catalysts. Moreover, the reaction is further enhanced under a DBD environment: the remarkable improvement in CO yield over Pd<sub>2</sub>Ga/SiO<sub>2</sub> further highlights the synergistic effect of Pd<sub>2</sub>Ga and DBD coupling. For Pd<sub>2</sub>Ga/SiO<sub>2</sub>, the tuning of the electronic structure of Pd by Ga can change the reaction barrier and catalyzing the reaction at a certain step, promoting intrinsic activity. This remarkable improvement in CO yield over Pd<sub>2</sub>Ga/SiO<sub>2</sub> makes the synergistic effect of intermetallic Pd<sub>2</sub>Ga and bending mode CO<sub>2</sub> more noteworthy.



**Figure 2.9.** Kinetic study of CO<sub>2</sub> hydrogenation over the 10 and 3 wt % Pd<sub>2</sub>Ga/SiO<sub>2</sub> with the FB-DBD reactor. (a) CO<sub>2</sub> conversion under thermal and DBD (12 and 100 kHz) conditions. (b) Arrhenius plot. Total flow rate = 200 mL min<sup>-1</sup> (STP); H<sub>2</sub>/CO<sub>2</sub> = 3; WHSV = 3000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup> (STP); pressure = 15 kPa; and SEI = 2.28 eV molecules<sup>-1</sup>.



**Figure 2.10.** CO<sub>2</sub> conversion over SiO<sub>2</sub> and without catalyst (Blank) under DBD (12 and 100 kHz) conditions with the FB-DBD reactor.



Figure 2.11. CO selectivity over the Pd<sub>2</sub>Ga/SiO<sub>2</sub> corresponding to Figure 2.9.



**Figure 2.12.** CO yield in CO<sub>2</sub> hydrogenation under thermal and 12 kHz DBD conditions over the 10 wt% Pd<sub>2</sub>Ga/SiO<sub>2</sub>, 10 wt% Pd/SiO<sub>2</sub> and 3.3 wt% Ga/SiO<sub>2</sub> with the FB-DBD reactor. (a) Thermal conditions. (b) DBD conditions.

#### 2.4.2 Steady-state in situ TIR

The surface-adsorbed species were investigated for the Pd<sub>2</sub>Ga/SiO<sub>2</sub> alloy catalyst using uniquely designed in situ TIR (Figure 2.7). Catalyst reaction experiments were conducted under both the thermal (at 250 °C) and DBD conditions. First, I performed steady-state experiments with a  $CO_2 + H_2$  mixture. Figure 2.13 shows a series of *in situ* TIR spectra with and without DBD irradiation. Under the thermal conditions ( $0 \min < t < 8 \min$ ), the catalyst can confirm the weak evolution of adsorbed CO over time. When the conditions changed from thermal to DBD at t = 8 min, two adsorbed peaks become intense remarkably, confirming the reaction promotion by DBD. IR peaks appear at 2077 and 1947 cm<sup>-1</sup>, which are assigned to monocoordinated linearly and dicoordinated bridging bonded CO (denoted as CO<sub>L</sub> and CO<sub>B</sub>) at the Pd site, respectively<sup>52-54</sup>. Upon switching back from the DBD to the thermal conditions (t = 16 min), an abrupt decrease in each peak is observed. In general, the CO adsorption properties and reactivity of multimetallic to monometallic catalysts can be determined by the distribution of surface atoms: geometric ensemble effect and changes in the electronic structure due to monometallic interactions: ligand effect<sup>55-58</sup>. The absence of triply coordinated bridging CO on hollow sites<sup>59,60</sup> in the Pd<sub>2</sub>Ga/SiO<sub>2</sub> indicates that the two metallic atoms, Pd and Ga, are well bonded and most of the surface-active sites contribute to the Pd<sub>2</sub>Ga. Moreover, the properties of the CO adsorption and desorption can be attributed to the stronger ligand effect of Ga on individual Pd atoms<sup>61</sup>. Other clear adsorbed species, except adsorbed CO, were not observed suggesting rapid formation and decomposition of reaction intermediates. Meanwhile, DBD can not only vibrationally-excite gas-phase  $CO_2$  but also dissociate it to  $CO^{14,18,31,62}$ . Therefore, the adsorbed CO species under the DBD conditions may not fully rule out the effect of gas-phase CO<sub>2</sub> dissociation to CO. I performed additional experiments combined with QMS analysis (Figure 2.14), showing that gas-phase CO generation is negligible because plasma input power was set 0.1 W so that the energy density becomes as small as 0.77 kJ mol<sup>-1</sup>. DBDinduced unique reaction behavior originates from the surface reaction.



**Figure 2.13.** Plasma enhancement of  $CO_2$  hydrogenation identified by *in situ* TIR. *In situ* TIR spectra of surface species on Pd<sub>2</sub>Ga/SiO<sub>2</sub>. A  $CO_2$  + H<sub>2</sub> mixture was introduced at a constant flow rate, while reaction conditions were switching from thermal to DBD to thermal for every 8 min.



**Figure 2.14.** Identification of the influence of gas phase CO<sub>2</sub> dissociation to CO under DBD conditions with QMS. QMS signal over the (a) Blank, (b) SiO<sub>2</sub> and (c) Pd<sub>2</sub>Ga/SiO<sub>2</sub> at 250 °C under CO<sub>2</sub> (10 mL min<sup>-1</sup>) + H<sub>2</sub> (30 mL min<sup>-1</sup>) diluted in Ar (150 mL min<sup>-1</sup>). DBD was turned on from 8 min to 12 min, comparing thermal and DBD hybrid reactions. To clarify the influence of the DBD-induced gas phase reaction, under the thermal and DBD transient experiments over the without catalyst (Blank), SiO<sub>2</sub>, and Pd<sub>2</sub>Ga/SiO<sub>2</sub> with CO<sub>2</sub> + H<sub>2</sub> mixture QMS studies were performed. Under these conditions, the plasma power was 0.1 W. Upon turning on DBD, a CO signal was not detected by QMS with Blank experiment. In the case of SiO<sub>2</sub>, compared to the Blank experiment, a faint CO signal was observed by QMS, indicating that CO<sub>2</sub> dissociation to CO by DBD is not promoted. In contrast, in the case of Pd<sub>2</sub>Ga/SiO<sub>2</sub>, a CO signal increased clearly during DBD treatment. Generation of CO originates DBD-induced catalyst reaction and gas phase CO<sub>2</sub> dissociation to CO by DBD is negligible.

#### 2.4.3 Transient in situ TIR

To identify the reaction intermediates and to reach a deep insight into their reaction behavior, the transient in situ TIR was employed for DBD and thermal conditions over Pd<sub>2</sub>Ga/SiO<sub>2</sub>. In Figure 2.15a, similar to Figure 2.13, the CO<sub>L</sub> and CO<sub>B</sub> were observed upon introducing  $CO_2$  at t = 6 min. After ca. 2 min, the  $CO_L$  and  $CO_B$  were fully desorbed, followed by a new IR peak appeared at 1368 cm<sup>-1</sup>: the peak was assigned to an overlapped monodentate formate (m-HCOO) and bidentate formate (b-HCOO)<sup>63-65</sup>. When the feed gas was switched from CO<sub>2</sub> to H<sub>2</sub> at t = 12, the m-HCOO decreased immediately, but the b-HCOO (1355 cm<sup>-1</sup>) did not change significantly. Continuing with the switching back from  $H_2$  to  $CO_2$  at t = 18 min, the same trend of adsorbed CO species was observed. I used SiO<sub>2</sub>, which is generally regard as an inert support, and the surface species formed on SiO<sub>2</sub> could not be observed (Figure 2.16). The TIR spectra presented in Figure 2.15c show the evolution of the surface species with CO<sub>2</sub> + H<sub>2</sub> mixture and CO<sub>2</sub> under DBD conditions. When a CO<sub>2</sub> + H<sub>2</sub> mixture was introduced (0 min < t < 6 min) and when switching the gas stream from  $CO_2 + H_2$  to  $CO_2$  (6 min < t < 12 min), the IR peaks of adsorbed CO and HCOO were identical to those shown under the same conditions in Figures 2.13 and 2.15a, respectively. However, once the stream was switched back from CO<sub>2</sub> to CO<sub>2</sub> + H<sub>2</sub> mixture at 12 min, with an instantaneous decrease in m-HCOO, the evolution of adsorbed CO was observed, and significant change was not observed in b-HCOO, as presented in Figure 2.15d. Meanwhile, in Figure 2.15a, upon switching H<sub>2</sub> to CO<sub>2</sub> at 6 min, the sharp CO peak appears. On the other hand, when switching from CO<sub>2</sub> to H<sub>2</sub> at 12 min, the CO peak does not appear at all, indicating CO<sub>2</sub> and H<sub>2</sub> do not coexist at the moment of gas switching: the residual gas mixing effect is negligible in this study. Previously reported RWGS studies suggested that HCOO is the key intermediate surface species and that it decomposes by the H atom spillover from metallic particles<sup>29,66-68</sup>. The formation and desorption behavior of CO showed a correlation with m-HCOO. The adsorbed CO is formed from the decomposition of m-HCOO, and b-HCOO is quite stable at the reaction temperature.

Under the CO<sub>2</sub> + H<sub>2</sub> mixture, two points can be inferred from the absence of m- HCOO and b-HCOO: (i) from Figure 2.13, rapid formation and decomposition of m-HCOO through CO<sub>2</sub> hydrogenation over Pd<sub>2</sub>Ga/SiO<sub>2</sub>. (ii) From Figure 2.15a,c, reaction branching sequential from m-HCOO to b-HCOO or CO: adsorbed hydrogen is the key to determine the selectivity of b-HCOO and CO. When 6 min < t < 12 min (18 min < t < 24 min), there was an obvious shortage in hydrogen. Therefore, the formation of CO is suppressed and a sequential reaction from m-HCOO to b- HCOO occurs. This reaction pathway occurs under thermal conditions as well. In other words, the effect of DBD is highlighted during m-HCOO decomposition with sufficient surface hydrogen. All these observations are supported consistently by the DFT analysis as discussed later. Meanwhile, CO<sub>2</sub> is a molecule with a linear equilibrium structure in the groundstate, so it belongs to the D  $\infty$  h symmetry group. The molecular orbital energy according to the bonding angle of  $CO_2$  can be represented by a Walsh diagram<sup>69,70</sup> (Figure 2.17). The highest occupied molecular orbital (HOMO) is mainly confined to the terminal oxygen atom, while the antibonding lowest unoccupied molecular orbital (LUMO) is mostly located at the center of the carbon atom. Therefore, in this case, CO<sub>2</sub> can be considered an amphoteric molecule in which oxygen atoms exhibit Lewis basic properties and carbon atoms act as Lewis acid properties. CO<sub>2</sub> is an electron acceptor rather than a donor, and the reactivity of CO<sub>2</sub> depends on the electrophilic properties of the carbon atom. If the LUMO of CO<sub>2</sub> is filled through electron transfer, consequently the lowest energy state corresponds to a bent geometry. Obviously, this means that the CO<sub>2</sub>-bending mode formed by the electron impact in the plasma environment can promote the catalytic surface reaction (e.g., by a reaction with the metalhydride bond in which the metal center occupies the positive charge and the negative charge accumulates on the hydrogen). Recently, molecular beam study found that the OCO angle of vibrationally-excited  $CO_2$  was much larger than the angle of the transition state  $(TS)^{24}$ . In addition, based on DFT calculations, the bending vibration-driven CO<sub>2</sub> in HCOO formation occurs through the E-R pathway without barriers to the reaction with adsorbed hydrogen.

Indeed, it is possible to generate abundant vibrationally-excited CO<sub>2</sub> species by low-energy electron collision in DBD-type NTP and a lower reaction barrier is required for catalysis<sup>15,16,40,71</sup>. In other words, vibrationally- excited CO<sub>2</sub> generated in DBD under this experimental condition leads to the formation of CO<sub>2</sub>-bending mode and can form HCOO by directly reacting with hydrogen adsorbed on the catalyst surface.



**Figure 2.15.** Identification of the reaction intermediates for CO<sub>2</sub> hydrogenation over Pd<sub>2</sub>Ga/SiO<sub>2</sub>. (a,b) *In situ* TIR spectra where the feed gas was switched alternately between H<sub>2</sub> and CO<sub>2</sub> for 6 min interval under the DBD (a) and thermal (b) conditions. (c) *In situ* TIR spectra where the feed gas was switched alternately between CO<sub>2</sub> + H<sub>2</sub> mixture and CO<sub>2</sub> for 6 min interval. (d) Relative intensities attributed to CO<sub>L</sub> (2077 cm<sup>-1</sup>), m-HCOO (1368 cm<sup>-1</sup>), and b-HCOO (1355 cm<sup>-1</sup>) in (c) as a function of time.



**Figure 2.16.** *In situ* TIR spectra over  $SiO_2$  where the feed gas was switched alternately between H<sub>2</sub> and CO<sub>2</sub> for 6 min interval under the DBD conditions.



**Figure 2.17.** Walsh diagram of CO<sub>2</sub> orbital energies in linear and bent geometries<sup>69,70</sup>. Based on the linear geometry (180°), the schematics of the molecular orbitals are shown on the left side, and the symmetry properties of the orbital are shown on the right side. The molecular orbital most relevant to reactivity are the  $1\pi_g$  and  $2\pi_u$  orbitals roles as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. According to Walsh's rule, CO<sub>2</sub> adopts a linear shape. On the other hand, due to environmental factors, when LUMO is filled with electrons, the energy of the bent shape of CO<sub>2</sub> is more stabilized than linear shape. Also, the bending mode of vibrationally-excited CO<sub>2</sub> by plasma can induce changes in the shape and energy level of LUMO.

#### 2.4.4 In situ XAFS

I cannot rule out the contribution of catalyst restructuring and heating by NTP<sup>72</sup>, besides the vibrationally-excited CO<sub>2</sub>, in the significantly promotional CO<sub>2</sub> hydrogenation upon the NTP conditions. Therefore, I performed *in situ* Ga and Pd K-edge XAFS measurements to observe local structure around Ga and Pd atoms under both thermal and NTP conditions during the CO<sub>2</sub> hydrogenation.

The XANES and EXAFS spectra under thermal and NTP conditions did not show a significant difference for both Ga and Pd K-edge (Figure 2.18). The curve-fitting results of the EXAFS spectra shown in Tables 2.3 and 2.4 revealed that all the structural parameters such as the coordination number (*N*), bond distance (*r*), and square of Debye–Waller factor ( $\sigma^2$ ) were similar between thermal and NTP conditions within the margin of errors, suggesting that no catalyst restructuring was induced by NTP. It should be noted that no catalyst heating took place by NTP since the  $\sigma^2$  value did not change within the margin of errors under the thermal and NTP conditions<sup>72</sup>. Thus, the catalyst did not undergo any structural changes or heating affecting the NTP-assisted CO<sub>2</sub> hydrogenation. The *in situ* XAFS results strongly indicated that the significantly improved CO<sub>2</sub> hydrogenation by the NTP-combined catalyst system was achieved by vibrationally-excited CO<sub>2</sub>.



**Figure 2.18.** *In situ* XAFS results of the Pd<sub>2</sub>Ga/SiO<sub>2</sub> during CO<sub>2</sub> hydrogenation with and without DBD. (a) Ga and (c) Pd K-edge XANES. (b) Ga and (d) Pd K-edge  $k^3$ -weighted EXAFS oscillation, Fourier-transformed (FT) EXAFS and inversely FT EXAFS data are shown with the black fitted curves (see Tables 2.3 and 2.4 for the details of the fitting). *k*-range for FT: 3.0–15.0 Å<sup>-1</sup>; Ar = 100 mL min<sup>-1</sup>; H<sub>2</sub> = 30 mL min<sup>-1</sup>; CO<sub>2</sub> = 10 mL min<sup>-1</sup>; pressure = 10 kPa; Reaction temperature = 250 °C.

Edge	Shell	Ν	r (Å)	$\Delta E (\mathrm{eV})$	$\sigma^2({\rm \AA}^2)$	R-factor
Ga K	Ga-O	$0.7 \pm 0.2$	$1.77 \pm 0.02$	(-10)	$0.0071 \pm 0.0019$	0.8
	Ga-Pd	$3.6 \pm 0.3$	$2.51\pm0.02$	-1 ± 2	$0.0114 \pm 0.0008$	
Pd K	Pd-Ga	$1.7 \pm 0.3$	$2.53\pm0.02$	(-9)	$0.0119 \pm 0.0013$	0.2
	Pd-Pd	$6.6 \pm 0.7$	$2.74\pm0.02$	(-4)	$0.0117 \pm 0.0009$	

**Table 2.3.** Thermal reaction: Curve-fitting results for Ga and Pd K-edge EXAFS data of the Pd<sub>2</sub>Ga/SiO<sub>2</sub> during CO<sub>2</sub> hydrogenation (curves shown in Figure 2.18b and d)<sup>a</sup>

<sup>a</sup>Parentheses indicate those values fixed during the fitting procedure. *k*-range: 3.0-15.0 Å<sup>-1</sup>. *R*-range for back *k* fitting: 1.1-2.9 and 1.6-3.0 Å for Ga and Pd K-edge EXAFS analysis, respectively.

Edge	Shell	Ν	r (Å)	$\Delta E (eV)$	$\sigma^2$ (Å <sup>2</sup> )	R-factor / %
Ga K	Ga-O	$0.7 \pm 0.2$	$1.76 \pm 0.02$	(-10)	$0.0064 \pm 0.0014$	0.3
	Ga-Pd	$3.4 \pm 0.3$	$2.51\pm0.02$	$0 \pm 1$	$0.0110 \pm 0.0008$	
Pd K	Pd-Ga	$1.8 \pm 0.2$	$2.52\pm0.02$	(-9)	$0.0125 \pm 0.0009$	0.1
	Pd-Pd	$6.7 \pm 0.4$	$2.74\pm0.02$	(-4)	$0.0121 \pm 0.0005$	

**Table 2.4.** DBD reaction: Curve-fitting results for Ga and Pd K-edge EXAFS data of the Pd<sub>2</sub>Ga/SiO<sub>2</sub> during CO<sub>2</sub> hydrogenation (curves shown in Figure 2.18b and d)<sup>a</sup>

<sup>a</sup>Parentheses indicate those values fixed during the fitting procedure. *k*-range for FT: 3.0-15.0 Å<sup>-1</sup>. *R*-range for back *k* fitting: 1.1-2.9 Å and 1.6-3.0 Å for Ga and Pd K-edge EXAFS analysis, respectively.

#### 2.4.5 Computational study

In order to obtain more detailed understanding regarding the influence of Ga–Pd-alloyed surface on the catalytic activity, I investigated further by performing DFT calculations. Starting from hydrogen atoms adsorbed on the Pd<sub>2</sub>Ga(020) surfaces, the calculated energy diagram and the corresponding structures are shown in Figure 2.19. In this model, CO<sub>2</sub> is assumed to be a ground-state in linear geometry. For the Pd<sub>2</sub>Ga(020) surface, because our calculations show that the carboxyl (COOH) formation (blue pathway) and direct CO<sub>2</sub> decomposition (orange pathway) have a much higher energy barrier than the HCOO formation barrier (red pathway), these two pathways are ruled out. Therefore, I focus on the HCOO formation as the most favorable pathway. For the initial activation of CO<sub>2</sub>(g) to HCOO formation on the surface of the Pd<sub>2</sub>Ga(020) surface, the E-R and Langmuir-Hinshelwood (L-H) pathways were considered. In the E-R pathway (green pathway), initial hydrogen atoms adsorbed on the surface migrate to the top side (59.2 kJ mol<sup>-1</sup>), and then CO<sub>2</sub>(g) reacts directly with the hydrogen to from m-HCOO (67.7 kJ mol<sup>-1</sup>). While climbing the activation barrier for TS, the C atoms at the center of the CO<sub>2</sub> molecule attach directly to hydrogen adsorbed to the Pd site. Subsequently, one of the O atoms is attached to the neighboring Ga atom that has affinity of the O atoms<sup>73</sup>. On the other hand, in the L–H pathway (pea green pathway), a  $CO_2(g)$  activation barrier of 52.2 kJ mol<sup>-1</sup> for surface adsorption then reacts with adsorbed hydrogen to form m-HCOO (81.9 kJ mol<sup>-1</sup>). Therefore, even under thermal conditions, the E–R pathway is more favorable than the L-H pathway for m-HCOO formation. The reaction of m-HCOO is branching to either b-HCOO formation or decomposition to CO, as discussed in Figure 2.15. The m-HCOO can be converted to b-HCOO via the bridge HCOO (br-HCOO, 31.3 kJ mol<sup>-1</sup>) in which two O atoms are bounded on Ga atoms (Ga–Ga). Subsequently, b-HCOO is stabilized further on Ga and Pd (Ga–Pd) with an activation barrier of 4.4 kJ mol<sup>-1</sup>. Because the energy barrier for the reverse reaction from b-HCOO to m-HCOO is so large, b- HCOO is quite stable: this is an agreement with *in situ* TIR (Figure 2.15d). The decomposition of m-HCOO undergoes a transformation from br-HCOO to side HCOO (s-HCOO), a form in which the C atom is bound to Pd atom lying down, and then is decomposed with an activation barrier of 74.1 kJ  $mol^{-1}$ . For Pd<sub>2</sub>Ga(020), the nucleophilic Pd atom with the ligand effect by Ga could enhance the interaction by promoting electron transfer to the LUMO centered at the C atom. As discussed above, when CO<sub>2</sub> coordinates with the metal or metal-hydride bond and fill the LUMO with electrons, the CO<sub>2</sub> results in a bent form, which is a lower energy state. At this time, HOMO, which has a localized electron density as lone pairs of oxygen atoms, forms a bond with an electrophilic Ga atom<sup>74</sup>. Note that this consideration is based on a fully thermal reaction: E-R pathway should be enhanced much stronger when CO<sub>2</sub> is primarily excited to bending-mode vibration. These DFT calculation results are in good agreement with the *in situ* TIR results and can strongly support the proposed plasma-enhanced reaction mechanisms. Meanwhile, in the kinetic study, the apparent activation energy of thermal conditions was determined as ca. 75 kJ mol<sup>-1</sup> (Figure 2.9b). This value is in good agreement with the DFT calculation (74.1 kJ mol<sup>-1</sup>), identifying the rate- determining step in the thermal reaction is the decomposition of m-HCOO. Interestingly, the apparent activation energy of the DBD reaction is estimated to be ca. 43 kJ mol<sup>-1</sup> which is smaller than the activation barrier for m-HCOO formation (67.7 kJ mol<sup>-1</sup>) and decomposition (74.1 kJ mol<sup>-1</sup>): not only HCOO formation via the E-R pathway but also HCOO decomposition is promoted by DBD. As discussed earlier, hydrogen spillover is essential to decompose HCOO to yield CO. The role of DBD is not limited to vibrational excitation of CO<sub>2</sub>, but activation of H<sub>2</sub> toward enhanced hydrogen spillover is highly anticipated.



**Figure 2.19.** DFT calculations of the  $CO_2$  hydrogenation reactions on  $Pd_2Ga(020)$ . (a) Energy diagram. (b) Corresponding DFT optimized geometries, showing the energy barriers. Color scheme: black, palladium; green, gallium; gray, carbon; red, oxygen; and white, hydrogen.

#### 2.4.6 Reaction mechanisms of the CO<sub>2</sub> hydrogenation under NTP conditions

Figure 2.20 summarizes the mechanism of CO<sub>2</sub> hydrogenation over Pd<sub>2</sub>Ga/SiO<sub>2</sub> under NTP conditions. The vibrationally-excited CO<sub>2</sub> promoted by plasma reacts directly with H atoms on the Pd site via the E–R pathway. Subsequently, the O atom is adsorbed to the Ga site eventually forming m-HCOO. As a subsequent step, H atoms adsorbed on the Pd site spillover to the Ga sites, and m-HCOO is decomposed into CO. The rate of formation and decomposition of m-HCOO is accelerated by NTP. As the hydrogen coverage has a shortage on the surface, the formation of CO is suppressed and part of m-HCOO is converted to b-HCOO. At this point, b-HCOO is quite stable. Under the NTP conditions, the decomposition of m-HCOO is further highlighted with sufficient H coverage on the surface. Other than the Pd<sub>2</sub>Ga intermetallic phase, a small amount of monometallic Pd and Ga oxide is present. Although the interfacial sites of them might also be active for the NTP-assisted RWGS reaction, the contribution to the overall reaction rate should be minor because of the limited number of the Pd–Ga interface compared with that of intermetallic Pd<sub>2</sub>Ga.



Figure 2.20. Proposed reaction mechanism of the  $CO_2$  hydrogenation. Schematic illustration showing the  $CO_2$  hydrogenation over the  $Pd_2Ga/SiO_2$  by the vibrationally-excited  $CO_2$  under NTP conditions via the E–R pathway.

## **2.5 Conclusions**

In summary, I have shown that compared with the conventional thermal catalyst, the NTPcombined Pd<sub>2</sub>Ga/SiO<sub>2</sub> alloy catalyst system significantly improve CO<sub>2</sub> hydrogenation. More precisely, I elucidated that the bending mode of vibrationally-excited CO<sub>2</sub> species derived from NTP could lower the energy barrier and react with hydrogen atoms adsorbed on Pd sites via the E–R pathway and then accelerate formate formation due to the strong oxyphilic nature of Ga sites. The coupled experimental–theoretical study highlights that the combination of alloy catalysts and NTP is the key to promoting CO<sub>2</sub> hydrogenation and thereby could be beyond the thermodynamic limitation that is impossible to achieve with thermal catalysis. Our results demonstrated the reaction mechanism of fast formation and decomposition of m-HCOO for CO<sub>2</sub> hydrogenation over Pd<sub>2</sub>Ga/SiO<sub>2</sub> alloy catalysts, implying that not only CO<sub>2</sub> activation but also H<sub>2</sub> activation is necessary for the enhanced spillover. Moreover, *in situ* XAFS results confirmed that a structural change of the alloyed catalyst and plasma heating effect are fully ruled out. The present study enables the high designability of CO<sub>2</sub> hydrogenation catalysts toward value-added chemicals based on the electrification of chemical processes via NTP.

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# Chapter 3. *In situ* infrared absorption probing of plasma catalysis: vibrationally-excited species induced Mars-van Krevelen type mechanism

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### **3.1 Abstract**

Nonthermal plasma (NTP) assisted catalysis has recently received attention as an attractive technology that can overcome the energy barriers involved in conventional thermal catalysis. It is important to obtain fundamental insight into the synergistic effects arising from interactions between NTP-activated species and catalysis. However, it remains a challenge due to difficulties associated with the *in situ* characterization of NTP-activated species. In this study, CO was explored in dielectric barrier discharge by applying *in situ* transmission infrared (TIR) absorption spectroscopy; TIR enables the measurement of the vibrational temperature of CO while observing the surface reaction of excited CO to form intermediates species over wurtzite ZnO. The reaction behavior of activated CO correlates with the vibrational temperature of CO, showing vibrationally-excited CO reacts with lattice oxygen via the Mars–van Krevelen mechanism; thus, leading to higher activity compared with conventional thermal catalysis. This work helps to understand the fundamental chemistry and provides new insight into NTP-activated CO and its catalysis.

## **3.2 Introduction**

Nonthermal plasma (NTP) assisted catalysis, which combines NTP and heterogenous catalysts, has been attracting attention as an alternative to conventional thermal catalysis in various environmental and energy fields<sup>1-10</sup>. NTP is characterized by having abundant vibrationally-excited molecules with various active species including ions, radicals, and free electrons which arise due to inelastic collisions between high-energy electrons and ground-state molecules<sup>11-13</sup>. NTP-assisted catalysis generates activated species that are inaccessible at bulk thermal temperatures. This effectively makes thermodynamically challenging reaction possible by removing the thermal equilibrium limitations experienced in conventional catalysis<sup>14</sup>. Although the synergistic effects in NTP-assisted catalysis are elicited by the rational design of catalysts, they depend on a fundamental understanding of the surface activity and reaction mechanisms relationships at the molecular level.

In the NTP environment, vibrationally-excited molecules are dominant channels because of their low energy threshold compared with ionization or dissociation<sup>15</sup>. This point is particularly important as unique reaction pathways arise<sup>15-19</sup>. However, the lack of direct spectral evidence for vibrationally-excited molecules for catalysis is controversial and the reaction mechanism of NTP-assisted catalysis is poorly understood. As the elucidation of interactions between the catalytic surfaces and NTP-active species is challenging, it is essential to develop spectroscopic techniques that enable the *in situ* analysis of the catalytic surface reaction in the NTP environment. *In situ* Fourier transform infrared spectroscopy (FTIR) is one of the most powerful spectroscopic techniques to investigate the reaction mechanism through *in situ* monitoring of catalytic surface reactions<sup>20-22</sup> and to gain insight into the vibrationallyexcited state of molecules<sup>23-25</sup>.

The interactions at the catalytic surface of gas molecules (reactants) generally follow three well-established mechanisms: Langmuir–Hinshelwood (L–H), Eley–Rideal (E–R) and Mars– van Krevelen (MvK) mechanisms. Previously reported NTP-assisted catalysis studies have

reported that vibrationally-excited and dissociation species activated by NTP can promote catalytic reactions via E–R and/or L–H type mechanisms<sup>8,14,16,26,27</sup>. In contrast, thus far, there have been no reports of MvK type mechanisms in NTP-assisted catalysis. ZnO is considered a major component in various catalytic processes<sup>28-30</sup>. In particular, the catalytic surface chemistry of CO over ZnO can be oxidized via the MvK mechanism<sup>31-33</sup>; CO molecules adsorbed at Zn ions directly react with adjacent lattice oxygen atoms to form CO<sub>2</sub> and oxygen vacancies (R3.1). The oxygen vacancies are then healed by. Gas phase O<sub>2</sub> (R3.2)

$$CO + ZnO \rightarrow CO_2 + ZnO_{1-x}$$
 R3.1

$$O_2 + ZnO_{1-x} \rightarrow ZnO + O$$
 R3.2

The reducibility of ZnO is an essential property of oxidation reactions and is of interest to researchers in the field of catalysis<sup>32-35</sup>. A typical descriptor of this reducibility is the formation of oxygen vacancies, which can be measured by the observation of adsorbed species, along with the resulting change in the surface composition<sup>34</sup>. However, the process in (1) above is generally endothermic and at low temperatures may be unfavorable<sup>33,36,37</sup>.

Herein, I compare the catalysis of NTP-activated CO with the conventional thermal catalysis over wurtzite ZnO. By applying *in situ* transmission infrared (TIR) absorption spectroscopy, where the catalytic surface can be identified during dielectric barrier discharge (DBD) irradiation, the detection of the IR-activated vibrationally-excited CO and their catalytic surface evolution was directly correlated at room temperature (ca. 300 K). I found that in the DBD conditions, the rotational temperature of CO remained close to room temperature, while the vibrational temperature increased by higher than 1000 K. Furthermore, the density of the vibrationally-excited CO species was controlled by the DBD power. These insights eliminated the effect of gas heating by DBD and allowed us to quantitatively confirm the surface reaction channels of vibrationally-excited CO over ZnO. From the observation of the catalytic surface reaction of the ZnO through *in situ* TIR, ZnO remains inert with CO in the ground-state at room temperature, whereas CO oxidation is promoted under DBD conditions to promote the

formation of carbonate. Through this study, I report that DBD-activated vibrationally-excited CO promotes thermodynamically limited CO oxidation via the MvK type mechanism.

# **3.3 Experiment section**

#### **3.3.1 Material and Characterization**

CO activation was performed over commercial ZnO powder (Kanto Chemical Co. Inc). The experiments were performed with a CO-Ar mixture (10 % CO by volume) and the Ar. ZnO powder was characterized by X-ray diffraction (XRD) measurements. The XRD of ZnO powder was performed on a Rigaku SmartLab diffractometer, using a Cu K $\alpha$  radiation source ( $\lambda = 0.15418$  nm). The diffraction patterns to the wurtzite ZnO structure were observed (Figure 3.1).



**Figure 3.1.** XRD patterns of ZnO. The inset shows the SEM image of ZnO, indicating it is hexagonal.

#### 3.3.2 In situ TIR

*In situ* TIR absorption spectroscopy over ZnO pellet was performed using an IR reactor equipped with a DBD system (Figure 3.2) under a pressure of 5 kPa. The reactor was composed of quartz glass with an inner diameter of 25 mm, and the path length was 11.6 cm. ZnSe windows were set on both ends of the reactor. Stainless steel (1 mm o.d.) high voltage and ground electrodes were inserted inside the reactor center. The high voltage electrode was wrapped with an alumina tube and only the metal tip was exposed to the gas flow, while the grounded electrode was fully covered by a quartz sheath. A K-type thermocouple (1 mm o.d.) was arranged at the 12 o'clock position above the high voltage and ground electrodes to detect the temperature inside the reactor (Figure 3.2c). The electrical parameters were monitored using an oscilloscope (RIGOL MSO5104) connected to the reactor via a high voltage probe. The gap between the point-to-point electrodes was 10 mm. A high voltage power supply was connected to the reactor and the applied power was 0.058, 0.066, and 0.078 W.

To prepare the ZnO powder (ca. 50 mg) in the form of a pellet (10 mm o.d., 1 mm thickness), the powder was uniformly transferred to a disk kit and compressed at ca. 1.5 MPa. Thereafter, the catalyst was fixed in a glass holder and inserted into the TIR reactor. The TIR spectra were measured using a JASCO FTIR-6600 spectrometer equipped with a mercury–cadmium–telluride (MCT) detector with a spectral resolution of 4 cm<sup>-1</sup>. Prior to the IR absorption spectroscopic experiments, the ZnO pellet was treated with H<sub>2</sub> (flow rate, 3 cm<sup>3</sup> min<sup>-1</sup>) and Ar (flow rate, 40 cm<sup>3</sup> min<sup>-1</sup>) at ca. 770 K for 1 h. The pellet was subsequently cooled to room temperature in an Ar atmosphere and the background spectra were obtained. For CO activation experiments, the CO and Ar mixture was introduced at 5 kPa (flow rate, CO = 1 cm<sup>3</sup> min<sup>-1</sup> and Ar = 49 cm<sup>3</sup> min<sup>-1</sup>).



**Figure 3.2.** (a) 3D Schematic illustration of *in situ* TIR DBD reactor which is capable of identifying catalytic surface species with and without DBD irradiation. Gas-phase IR absorption spectroscopy is also possible using blank TIR reactor (without catalyst pellet). (b) 3D schematic diagram electrodes and ZnO pellet geometry. (c) Photograph emission from DBD (0.058W).

## 3.4 Result and discussion

#### 3.4.1 Measurement of vibrational temperature

First, I performed *in situ* TIR in 2 % CO in Ar steam at 5 kPa in a blank (without catalyst) TIR reactor at room temperature (ca. 300 K) to gain insight into vibrationally-excited CO species under DBD conditions (Figure 3.3a). At this time, the spectral resolution was set to 0.5 cm<sup>-1</sup>. An increase in absorbance can be clearly observed at the lower wavenumber band resulting from the transition of the quantum number of vibrationally-excited CO ( $v_{co} = 1 \rightarrow 2$ ) under a DBD power of 0.058 W. The vibrational temperature (Tvib) of CO was estimated from the modeled optimal spectra using a fast line-by-line code RADIS<sup>38</sup> assuming a Boltzmann distribution of vibrational energy. As shown in Figure 3.3b, the best fit of DBD power of 0.058 W at 5 kPa under a 2 % CO in Ar stream is obtained with a rotational temperature  $(T_{rot}) = 300$  $\pm$  10 K and T<sub>vib</sub> = 1000  $\pm$  100 K. The temperature of the vibrationally-excited CO was further investigated for higher DBD power of 0.066 and 0.078 W (Figure 3.3c). Trot remains close to room temperature while T<sub>vib</sub> increases with the DBD power developing toward 1300 K at 0.078 W. The DBD power dependence on T<sub>rot</sub> is weak. This is explained by the low excitation efficiency of the rotational degree of freedom because the transfer of momentum from highenergy electrons to the ground-state molecules is limited due to the conservation of angular momentum<sup>39</sup>. I also measured the reactor temperature via a thermocouple, and a negligible temperature increase of ca. 10 K was observed under DBD conditions. Vibrationally-excited CO species can be efficiently induced via energy transfer from low energy electrons to the ground-state CO under the DBD conditions. Therefore, T<sub>rot</sub> and T<sub>vib</sub> are generally different in nonequilibrium excited molecules. When the anharmonicity of the diatomic molecules is large and the high vibrational temperature exceeds 3000 K, due to the strong nonequilibrium excitation of the molecules, the vibrational-vibrational process is non-resonant<sup>15,40</sup>. Due to this occurrence, the population of the high-vibration states has a large deviation from the Boltzmann distribution<sup>41,42</sup>. Thus, a non-resonant vibrational-vibrational process should be considered through the Treanor distribution. However, the population of the first few vibrational states has a small anharmonicity, so the vibrational-vibrational process can resonate. Therefore, the deviation of the Boltzmann distribution can be kept below the sensitivity limit. I assumed the Boltzmann distribution for the weak nonequilibrium discharge condition applied in this work and showed good fitting results as shown in Figure 3.3b. Moreover, at the measured low vibrational temperature of approximately 1000–1300 K, the population in the high vibration state is very low, so it cannot be evaluated with the Treanor distribution because of the nonresonant vibrational-vibrational process<sup>40</sup>. From theses insight, I can rule out the effects on ionization and ions. Moreover, the first excited electronic state, CO(a<sup>3</sup>II), can be ruled out due to its high potential energy of 6.006 eV, which is nearly isoenergetic at high vibrational levels above 26<sup>43</sup>. That is, our DBD system can selectively activate the vibrational excitation mode of CO molecules.



**Figure 3.3.** (a) Vibrationally-excited CO TIR spectra taken at DBD power of 0.058 W at 2 % CO in Ar (50 cm<sup>3</sup> min<sup>-1</sup>) stream at room temperature. (b) Comparison between simulated and experimental CO TIR spectra at same conditions with (a). (c) Rotational and vibrational temperatures measured at DBD power of 0.058, 0.066, and 0.078 W at 2 % CO in Ar stream.

#### 3.4.2 Population quantification of vibrationally-excited CO

The population quantification of vibrationally-excited CO provides useful information about the energy exchange processes occurring under DBD conditions. The density of the vibrationally excitation levels was predicted via a partition function assuming that the vibrational energy follows the Boltzmann distribution (Figure 3.4). The density of the vibrationally-excited CO shows the dependence on DBD power, and the population distribution of the main vibrationally-excited CO up to a quantum number of three. A higher DBD power results in either a high electron energy or electron number density; in both cases, a collision between electrons and CO would be enhanced and a higher vibrational temperature is possible. This makes DBD suitable for investigating the ZnO surface reaction channel supported by vibrationally-excited CO. Moreover, in our previous work, the temperature of nanometer-sized metallic components of catalyst was measured by *in situ* X-ray absorption fine-structure (XAFS), showing that a DBD-induced temperature increase was not confirmed<sup>14</sup>. Therefore, our DBD system excludes even the influence of unwanted surface reactions by heating the ZnO surface.



**Figure 3.4.** Density distribution of vibrationally-excited CO calculated at vibrational temperatures of 1000, 1100 and 1300 K while gas temperature is assumed to be constant at 300 K. Y-axis represents mol % of density of vibrationally-excited CO relative to total CO density.

#### 3.4.3 Investigation of the surface response by vibrationally-excited CO

Subsequently, I discuss the *in situ* TIR spectra of the wurtzite ZnO surface response to vibrationally-excited CO and thereby the evolution of the surface species; I compared it with the surface reaction with ground-state CO. Figure 3.5 shows the temporal evolution of the spectra recorded during the reaction with ground-state CO (labeled as thermal) and vibrationally-excited CO (labeled as DBD). As shown in Figure 3.5a, it is difficult to identify a clear peak due to carbonate in the region of 1800 to 1200 cm<sup>-1</sup> under thermal conditions. Moreover, in the CO-related spectral region of 2300 to 2000 cm<sup>-1</sup>, a small peak at 2060 cm<sup>-1</sup>, due to adsorbed CO, is observed in addition to the CO gas phase (CO<sub>(g)</sub>). However, the 2060 cm<sup>-1</sup> peak disappears when the CO flow is turned off. As a result, ground-state CO has a weak interaction with the ZnO surfaces. However, the reactivity of CO changes prominently under DBD conditions. When the ZnO surface is exposed to vibrationally-excited CO by a DBD power of 0.058 W, a sharp increase in the bands of adsorbed bicarbonate (HCO<sub>3</sub><sup>\*</sup>: 1635, 1411 and 1225 cm<sup>-1</sup>)<sup>44,45</sup> and carbonate (CO<sub>3</sub><sup>\*</sup>: 1514 and 1341 cm<sup>-1</sup>)<sup>46</sup> are detected. Bicarbonate is formed when the surface OH groups are consumed<sup>47</sup> (Figure 3.7).

When the surface OH. Groups are removed by strict pretreatment conditions; the formation of bicarbonate is suppressed (Figure 3.6). It has been demonstrated by previous theoretical and FTIR experiments studies that CO<sub>2</sub> produced through CO oxidation on the catalyst can react with the surface to from (bi)carbonate<sup>48-52</sup>. The appearance of (bi)carbonate suggests that the oxidation of vibrationally-excited CO is responsible for the generation of intermediate species. Vibrationally-excited molecules have a higher energy level than the ground-state molecules corresponding with the vibrational energy. The internal vibrational energy can provide more reactivity by reducing or removing the activation barrier at the catalyst surface. Moreover, upon the chemisorption of the vibrationally-excited molecules on the catalyst surface, the catalyst surface can retain sufficient energy to supply endothermic energy<sup>53</sup>. The CO oxidation on the reducible metal oxides mainly occurs via the reaction of lattice oxygen

species and CO, known as the MvK mechanism<sup>31-34</sup>. The experiments were performed at room temperature; therefore, ground-state CO does not react with the lattice oxygen of ZnO. At a relatively high temperature of 470 K, carbonate formation is observed under thermal conditions (Figure 3.6). Conversely, the evolution of the (bi)carbonate species observed even at room temperature under DBD conditions suggests that vibrationally-excited CO promotes a thermodynamically limited MvK type mechanism. This is further confirmed in the CO spectral region from 2300 to 2000 cm<sup>-1</sup> (Figure 3.5b). The evolution of bands attributed to CO adsorption (CO<sup>\*</sup>) at 2106 and 2155 cm<sup>-1</sup> was initiated in approximately 5 min. I can find a correlation between the immediate formation of carbonate and the appearance of a late CO adsorption band. The CO oxidation reaction by the MvK type mechanism is a reaction that forms oxygen vacancies. Therefore, to predict the activity of the catalytic CO oxidation, the formation energy of the oxygen vacancies is taken as the main indicator<sup>34</sup>. That is, the late evolution of the CO adsorption band suggests a decrease in the CO oxidation reaction rate by the formation of oxygen vacancies. This occurrence can be supported by a decrease in the formation rate of (bi)carbonate over time (e.g. Figure 3.8). It must be discussed further that the observed wavenumber at 2106 cm<sup>-1</sup> is unexpectedly red-shifted, and the adsorbed CO on Zn<sup>2+</sup> is generally characterized between 2200 to 2170 cm<sup>-154,55</sup>. Similar observations have been previously reported by Schott et al<sup>56</sup>. The authors report that a distorted ZnO, different from wurtzite ZnO, exhibits significant charge flow, and this chemical property increases the CO binding energy with  $Zn^{2+}$  and is accompanied by a red-shift of the CO adsorption band<sup>56</sup>. The CO adsorption band observed in this study did not disappear even after the CO flow was turned off (Figure 3.5b), confirming the high stability. This observation represents a reasonable agreement with the study of Schott et al. Therefore, I suggest that vibrationally-excited CO promotes adsorption on  $Zn^{2+}$  and is generally recognized as an active site for Zn, and subsequently reacts with adjacent lattice oxygen. Additionally, CO can more strongly adsorb to metal ions that are not shielded (or less shielded) by oxygen on the oxide surface<sup>57-59</sup>. That is, the CO adsorbed on  $Zn^{2+}$  observed under DBD conditions can be derived from the subsequent adsorption of ground-state CO to unshielded  $Zn^{2+}$  formed by the reaction with vibrationally-excited CO. Therefore, I investigated the behavior of the CO adsorption band by exposing the ZnO surface to CO for a specific time under DBD conditions and then switching to thermal conditions (Figure 3.5c). When the ZnO surface was exposed to vibrationally-excited CO with a DBD power of 0.058 W for 10 min, CO adsorption bands at 2155 and 2106 cm<sup>-1</sup> are observed (yellow spectra at the top). Thereafter, when switched to ground-state CO (DBD off, black spectra), the CO adsorption band at 2155 and 2106 cm<sup>-1</sup> gradually disappear, and when the CO gas is turned off after 10 min, no CO adsorption band is observed. These observations support the premise that the CO adsorption bands appearing under DBD conditions are due to the adsorption of vibrationally-excited CO to  $Zn^{2+}$ , and the effect of ground-state CO adsorption is excluded.

I further investigated the evolution of *in situ* TIR spectra for CO adsorption and (bi)carbonate formation on the ZnO surfaces at higher DBD powers. Figure 3.8a shows the spectra of the CO adsorption band recorded at 5 min after CO exposure under different DBD powers. At a DBD power of 0.058 W, the CO adsorption bands at 2106 and 2155 cm<sup>-1</sup> are difficult to observe as they are not strong enough to distinguish from  $CO_{(g)}$ . However, from a DBD power of 0.066 W, CO adsorption bands distinguishable from  $CO_{(g)}$  begin to appear and appear to increase further at 0.078 W. Figure 3.8b presents a two-dimensional plot of the normalized intensity versus the temporal evolution of carbonate (1514 cm<sup>-1</sup>) formed on the surface. Of note is that at higher DBD power, higher density vibrationally-excited CO species are formed. As might be expected, carbonate formation on the surface of the ZnO further increases with DBD power. When the electrons are charged to ZnO, some of the electrons are donated to the ZnO conduction band and IR photons are absorbed due to interactions with bulk plasmons, resulting in an increase in the background absorbance signal<sup>60</sup>. However, in the TIR spectra of the (bi)carbonate region after 5 min (Figure 3.9), no increase in the background

absorbance signal of the spectra is observed with increasing DBD power. In our previous work in which *in situ* XAFS was performed under DBD conditions<sup>14</sup>, the structure of the catalyst did not change even when the catalyst was charged. In addition, in this study, I set the DBD so as not to directly contact the pellet (Figure 3.2). That is, the effect on the charge of ZnO by DBD in the reaction of CO to ZnO under DBD conditions is excluded. This evidence provides rational support for promoting CO oxidation via the MvK type mechanism by vibrationallyexcited CO induced under DBD conditions.



**Figure 3.5.** *In situ* TIR spectra of (a) (bi)carbonates and (b,c) CO-related region over ZnO under thermal and DBD (0.058 W). ZnO was exposed to 2 % CO in Ar (50 cm<sup>3</sup> min<sup>-1</sup>) stream at 300 K for 20 min.



Figure 3.6. In situ TIR spectra over ZnO under thermal DBD (0.058 W). The ZnO was pretreated the at 770 K in Ar atmosphere for 1 h, and thereafter exposed to 2 % CO in Ar (50  $\text{cm}^3 \text{min}^{-1}$ ) stream at 470 K for 20 min.



**Figure 3.7.** *In situ* TIR spectra OH groups region over ZnO under DBD conditions corresponding Figure 3.6 (yellow) and Figure 3.7 (purple).



**Figure 3.8.** (a) *In situ* TIR spectra of CO-related region at different DBD power after 5 min and (b) corresponding evolution of carbonate ( $1514 \text{ cm}^{-1}$ ). ZnO was exposed to 2 % CO in Ar (50 cm<sup>3</sup> min<sup>-1</sup>) stream at 300 K for 20 min with DBD power of 0.058, 0.066, and 0.078 W.



Figure 3.9. In situ TIR spectra over ZnO of (bi)carbonate-related region at different DBD power.

## **3.5 Conclusions**

In summary, I were able to unambiguously identify vibrationally-excited CO species with *in situ* TIR diagnostics performed in a catalyst-free environment. The rotational temperature of CO remained unchanged at room temperature at various DBD powers, while the vibrational temperature was increased from 1000 K to 1300 K with DBD power, showing that CO is excited into the vibration quantum number of three. The effect of DBD, or vibrationally-excited CO, was studied using surface reaction over wurtzite ZnO. A comparative study with ground-state CO by *in situ* TIR spectroscopy suggests that vibrationally-excited CO over the ZnO surface promotes thermodynamically limited CO exhibits an unusual CO adsorption band due to strong binding energy with  $Zn^{2+}$ , which improves the CO oxidation by activating the reaction with adjacent lattice oxygen in the ZnO via the MvK type mechanism at room temperature (Figure 3.10). The present findings provide new possibilities for achieving low temperature CO oxidation based on the electrification of chemical processes through NTP.



**Figure 3.10.** Schematic illustration of the promoting CO oxidation via Mars–van Krevelen type mechanism by vibrationally-excited CO over ZnO.  $V_0$ : oxygen vacancies,  $O_L$ : lattice oxygen. I. Generation of vibrationally-excited CO by electron impact. II. Adsorption of vibrationally-excited CO to  $Zn^{2+}$ . III. (Bi)Carbonate formation by reaction with adsorbed CO and adjacent lattice oxygen.

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# Chapter 4. Summary and future work

## 4.1 Summary

In this thesis, I focused on elucidating the reaction mechanism of NTP-assisted catalysis, especially the interplay between vibrationally-excited molecules (e.g.  $CO_2^{vib}$  and  $CO^{vib}$ ) and catalytic surfaces. The content includes (i) surface reaction of vibrationally-excited  $CO_2$  and alloy catalysts via the E–R type mechanisms, and (ii) probing of vibrationally-excited CO-induced MvK type mechanisms over reducible catalysts.

In the first part, I presented that compared with the conventional thermal catalysis, the NTP-assisted Pd<sub>2</sub>Ga/SiO<sub>2</sub> alloy catalysis improve CO<sub>2</sub> hydrogenation. It is worth highlighting that the combination of alloy catalyst and NTP could be beyond the thermodynamic limitation that is impossible to achieve with conventional thermal catalysis. Upon the agreement of approaches coupling experimental–theoretical study, the bending mode of vibrationally-excited CO<sub>2</sub> could lower the energy barrier and react with hydrogen atoms adsorbed on Pd sites via the E–R type mechanisms and then accelerate formate formation due to the oxyphilic nature of neighboring Ga site. The results demonstrated the reaction mechanism of fast formation and decomposition of monodentate formate, not only CO<sub>2</sub> activation but also H<sub>2</sub> activation is expected. In addition, the *in situ* XAFS results confirmed that a structural change of the alloy catalyst and NTP heating affecting the CO<sub>2</sub> hydrogenation are fully ruled out. I believed that the present study enables the high designability of CO<sub>2</sub> hydrogenation catalysts toward value-added chemicals based on electrification via NTP.

In the second part, I investigated CO in DBD by applying *in situ* TIR diagnostics and identified vibrationally-excited CO with a catalyst-free environment. The rotational temperature of CO remained at room temperature (ca. 300 K) with various DBD power, while the vibration temperature increased from 1000 K to 1300 K. The density of the vibrational excitation levels was predicted under the assumption that the vibrational energies followed the

Boltzmann distribution, indicating the density of the vibrationally-excited CO was controlled by the DBD power and the population distribution of vibrationally-excited CO up to a quantum number of three. These insights allowed the quantitatively identification of the surface reaction channels of vibrationally-excited CO. Subsequently I carefully examined the effect of DBD or vibrationally-excited CO on the surface reaction on wurtzite ZnO. From the comparative studies through with ground-state CO suggest that vibrationally-excited CO over the surface of wurtzite ZnO promotes thermodynamically limited CO oxidation. More precisely, ZnO remains inert with ground-state CO, whereas vibrationally-excited CO exhibits an unusual CO adsorption band due to strong binding energy with  $Zn^{2+}$ , which promotes the CO oxidation by activating the reaction with adjacent lattice oxygen via the MvK type mechanism. These findings show that new pathway for achieving low temperature based on the electrification of via NTP. Furthermore, in addition to the L–H and E–R type mechanisms, the findings support the utility of MvK type mechanism, which is one of the three basic catalytic surface reaction mechanisms of vibrationally-excited molecules in NTP-assisted catalysis.

## 4.2 Future work

In the long-term low carbon strategies announced by major countries around the world, CO<sub>2</sub> capture, and utilization technology was included as a key strategic tool. Meanwhile, as renewable energy spreads, the demand for chemical conversion using electric power increases<sup>1,2</sup>, low-carbon technology related to electrification of chemical process such as NTP or Power-to-Gas are attracting attention in the environment and energy fields<sup>3-7</sup>. In particular, as a long-term strategy for carbon recycling, fundamental study using nonthermal plasma is being actively conducted in China and Europe<sup>5,8-16</sup>. However, most of the studies are dominated by the chemical conversion of CO<sub>2</sub>, so study on mineralization or utilization as an energy material is relatively weak.

As a future plan, the content includes  $CO_2(i)$  chemical conversion, (ii) energy conversion, and (iii) mineralization.

In the first part, adopting the nonthermal plasma assisted catalysis conducted in the doctoral course, accelerates the study of using  $CO_2$  as a reactant and converting it into various carbon compounds such as fuels and basic chemicals through chemical conversion. In more detail, I plan to conduct a study focusing on the promotion of catalysis through the Langmuir–Hinshelwood type mechanism of vibrationally-excited  $CO_2$ , which is not covered in this thesis. Furthermore, I explore the effect of nonthermal plasma activated  $H_2$  on the reaction in depth.

The second part is the conversion of  $CO_2$  as an energy material. Carbon black is used as black pigments, as a reinforcing filler in tires and in a variety of rubber applications<sup>17</sup>. Carbon black also has high electrical conductivity, and the porosity and surface chemistry can be altered to achieve the properties that best suit the application<sup>18</sup>. These properties can be very suitable for renewable energy applications. Therefore, I plan to conduct research on synthesizing carbon black from  $CO_2$  via NTP and applying it as an anode material or conductive additive for Li, Na and K ion batteries.

Finally, the third part is CO<sub>2</sub> mineralization. CO<sub>2</sub> mineralization is the storage process of CO<sub>2</sub> in the form of water insoluble Ca/MgCO<sub>3</sub>. In particular, CO<sub>2</sub> mineralization by alkaline solid waste is a promising option for climate change mitigation in countries with enormous amounts of waste<sup>19</sup>. Alkaline ash, a byproduct of fuel combustion in thermal power plants, such as coal fly ash and municipal solid waste incineration ash, is a promising feedstock for CO<sub>2</sub> mineralization due to its high alkalinity and abundance<sup>20,21</sup>. In addition, with the additional utilization of carbonate ash as a construction material, CO2 mineralization can be integrated with the utilization of carbonate ash in the manufacture of building materials to achieve a waste-to-resource supply chain<sup>22</sup>. However, the biggest obstacle to the large-scale application of CO<sub>2</sub> mineralization is the slow. The key steps involved in CO<sub>2</sub> mineralization are energy intensity<sup>23</sup>. Thus, the energy demand for CO<sub>2</sub> mineralization may offset potential greenhouse gas emission reductions. In this thesis, I presented that thermodynamically limited reactions can be improved by NTP. From these insights, the application of NTP can be a promising solution to achieve CO<sub>2</sub> removal efficiencies for the slow kinetics of CO<sub>2</sub> mineralization. Therefore, I investigate the screening of optimal alkaline ashes in NTP and the utilization of products of NTP-assisted mineralization in the production of construction materials.

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