Plasma-enhanced reverse water gas shift reaction over alloy catalyst: breaking the thermodynamic equilibrium limit

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Abstract: Here, nonthermal plasma (NTP) assisted catalysis of reverse water gas shift reaction was investigated over Pd₂Ga/SiO₂ alloy catalysts. Although both thermal and NTP conditions showed 100% CO selectivity, it is worth highlighting that under the NTP conditions, CO₂ conversion beyond the thermodynamic equilibrium limitation. The reaction mechanism is elucidated through an approach combining *in situ* characterizations and density functional theory (DFT) calculations, demonstrating that vibrationally excited CO₂ directly reacts with hydrogen adsorbed on Pd sites while accelerating formate formate formate decomposition is promoted by plasma activated H₂ is inferred. The findings highlight the opportunity to exploit the synergies between NTP and alloy catalysts to achieve CO₂ conversion inaccessible via thermal catalysis. Moreover, this study enables the designability of CO₂ hydrogenation catalysts toward value-added chemicals via NTP.

Keywords: Plasma catalysis, Nonthermal plasma, Alloy catalyst, Reverse water gas shift reaction, Thermodynamic equilibrium

1. Introduction

Catalytic CO_2 hydrogenation has attracted much attention as an important process that not only serves to alleviate the problem of CO_2 emissions but also helps alleviate the energy crisis caused by the depletion of fossil fuels [1, 2]. However, because CO_2 is thermodynamically stable, the efficient and economical high conversion of CO_2 is a challenge facing the scientific and industrial community. Therefore, it is necessary to develop breaking thorough technologies that can efficiently convert CO_2 based on the electrification of chemical processes.

Non-thermal plasma (NTP) assisted catalysis is an attractive new technology for CO₂ valorization [3]. Such NTP is characterized by nonthermal energy distribution and can generate reactive species, such as vibrationally excited molecules, radicals and ions, while maintaining low bulk gas temperatures [4]. This effectively can make thermodynamically challenging reactions possible by removing the thermal equilibrium limitations experienced in thermal catalysis [5]. However, the designing catalysts that can enable more efficient interactions between NTP active species and catalysts remains a great challenge.

Using Pd₂Ga/SiO₂ as a catalyst for NTP-assisted reverse water gas shift (RWGS) reaction, we present that the combination of vibrationally excited CO2 and alloy catalysts can achieve CO_2 conversion bevond thermodynamic equilibrium. In situ characterizations, including transmission infrared (TIR) spectroscopy and Xray absorption fine-structure (XAFS) combined with density functional theory (DFT) calculations were employed. Mechanistic insights into the vibrationally excited CO₂ from NTP and alloy catalysts in improving RWGS reaction are provided. We aim to enable the high designability of CO₂ hydrogenation catalysts toward valueadded chemicals based on electrification via NTP.



Figure 1. Kinetic study of reverse water gas shift reaction over the 3 and 10 wt % Pd₂Ga/SiO₂. (a) CO₂ conversion under thermal and DBD (12 and 100 kHz) conditions. (b) Arrhenius plot.

2. Result and Discussion

In this study, the fluidized-bed dielectric barrier discharge (DBD) reactor was chosen to improve plasmacatalyst interaction and heat and mass transfer efficiencies. First, we conducted the kinetics study for RWGS reaction over Pd₂Ga/SiO₂ with different Pd₂Ga loadings (3 and 10



Figure 2. *in situ* TIR spectra. (a) steady-state experiments with a CO_2+H_2 mixture. (b) thermal and (c) DBD transient experiments where the feed gas was switched alternately between H₂ and CO₂.

wt%) and two types of DBD conditions (12 and 100 kHz). The CO₂ conversion increases with catalyst temperature (Figure 1a). Notably, the reaction activity was improved under the DBD conditions compared to the thermal conditions for both catalysts. The CO selectivity was 100% for all conditions. It is worth emphasizing that CO2 conversion for 10 wt % Pd2Ga/SiO2 under 12 and 100 kHz DBD conditions are higher than the thermodynamic equilibrium limit. As for the corresponding Arrhenius plot (Figure 1b), regardless of the Pd₂Ga loadings and DBD frequencies, the activation energy for the DBD conditions is smaller than that of the thermal conditions. Moreover, the activation energy of all thermal and DBD conditions does not change to a large degree. That is, thermal and DBD conditions can be grouped together respectively. This suggests that regardless of Pd2Ga loadings the reaction pathways, or the rate-determining step, are not only identical but also not influenced by the concentration of vibrationally excited molecules. This suggests that regardless of Pd2Ga loadings the reaction pathways, or the rate-determining step, are not only identical but also not influenced by the concentration of vibrationally excited molecules. Moreover, from being able to group the slopes of Arrhenius plots for all the DBD conditions, it indicates that even if for 10 wt % Pd2Ga/SiO2, CO2 conversion goes beyond the thermodynamic equilibrium limit, it may not be constrained by the reverse reaction.

The adsorbed species were investigated over 10 wt% Pd₂Ga/SiO₂ catalyst using uniquely designed *in situ* TIR

(Figure 2). We conducted steady-state experiments with a CO_2+H_2 mixture under the thermal (at 250 °C) and DBD conditions (Figure 2a). Under the thermal conditions, the weak peaks of adsorbed CO (2077 and 1947 cm⁻¹) can be confirmed over time [6, 7]. When conditions changed from thermal to DBD conditions, the peaks of adsorbed CO become intense. Upon switching back from the DBD to the thermal conditions, the peaks decrease immediately. Meanwhile, except for the adsorbed CO, other adsorbed species were not observed, which suggests the rapid formation and decomposition of reaction intermediates.

To identify the reaction intermediates, the transient in situ TIR was conducted over Pd2Ga/SiO2. Under DBD conditions (Figure 2b), the peaks of adsorbed CO were observed upon switching from H₂ to CO₂. After 2 min, the peaks of adsorbed CO were fully desorbed, followed by a new peak appearing at 1368 and 1355 cm⁻¹, which can be assigned to monodentate formate (m-HCOO) and bidentate formate (b-HCOO) respectively [8, 9]. When switching from CO2 to H2, the m-HCOO decreased immediately, but the b-HCOO was not changed. Continuing with the switching from H₂ to CO₂, the same behavior of the peaks of adsorbed CO was observed. From these measurements, it can be seen that the adsorbed CO is formed from the decomposition of m-HCOO and b-HCOO is quite stable. It also indicates that m-HCOO can be converted to b-HCOO or CO. At this point, the adsorbed hydrogen is key to determining the selectivity of b-HCOO and CO. When only CO₂ flowed, the adsorbed hydrogen was an obvious



Figure 3. In situ XAFS results. (a) and (c) XANES. (b) and (d) k³-wetighted EXAFS oscillation and Fourier-transformed EXAFS.

shortage. Therefore, the formation of CO is suppressed and a sequential reaction from m-HCOO to b-HCOO occurs. This reaction occurs under thermal conditions as well. In other words, the effect of DBD is emphasized during m-HCOO decomposition with sufficient adsorbed hydrogen.

Subsequently, to investigate the contribution of catalyst restructuring and heating by DBD, we conducted in situ XAFS with the same reactor with TIR, to observe the local structure around Pd and Ga atoms during the RWGS reaction under thermal and DBD conditions (Figure 3). The XANES and EXAFS spectra did not present a difference for both Pd and Ga K-edge under thermal and DBD conditions. The curve fitting results of the EXAFS spectra showed that all the structural parameters (coordination number, bond distance, and Debye-Waller factor) were similar between thermal and DBD conditions, which suggests catalytic restructuring was not affected by DBD. Moreover, it should be noted that catalyst heating was not occurred by DBD because the σ^2 value did not change compared to the thermal conditions. The series in situ characterization indicated that the improved RWGS reaction by DBD combined Pd2Ga/SiO2 system was achieved by vibrationally excited CO₂.

Next, to obtain a more detailed understanding the reaction mechanism of Pd_2Ga/SiO_2 , we investigated by performing DFT calculations. Starting from adsorbed hydrogen on the $Pd_2Ga(020)$ surfaces, the calculated energy diagram and the corresponding structures are shown in Figure 4. In this model, CO_2 is assumed to be a ground state. Because our calculations present that the carboxyl and direct CO_2 decomposition pathway have a much higher energy barrier than the HCOO formation

barrier, we focus on the HCOO pathway. Eley-Rideal and Langmuir-Hinshelwood pathways were considered for the initial reaction of CO2 with adsorbed hydrogen to m-HCOO formation, and the Eley-Rideal pathway is more favorable than the Langmuir-Hinshelwood pathway. The m-HCOO can be converted to b-HCOO via the bridge HCOO (br-HCOO). b-HCOO is quite stable, because the energy barrier for the reverse reaction from b-HCOO to m-HCOO is large. The decomposition of m-HCOO undergoes a transformation from br-HCOO to side HCOO (s-HCOO). Then s-HCOO is decomposed with an activation barrier of 74.1 kJ mol-1. For Pd₂Ga(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. when CO₂ coordinates with the metal-hydride bond and fill the LUMO with electrons, the CO₂ results in a bent, 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. It means that the reaction can be further enhanced when CO₂ is excited in bending mode. Recently, a molecular beam study found the bending mode of CO2 in HCOO formation occurs through the Eley-Rideal pathway without barriers to the reaction with adsorbed hydrogen [10]. Indeed, vibrationally excited CO₂, particularly bending mode, can be generated abundantly by low-energy electron collision in DBD. That is, the bending mode of CO2 generated under DBD conditions leads to the formation of m-HCOO through the Eley-Rideal pathway.

Meantime, the activation energy of thermal conditions was determined as ca. 75 kJ mol⁻¹ in the kinetic study (Figure 1b). This value is in good agreement with the DFT



Figure 4. DFT calculations of the reverse water gas shift reaction on $Pd_2Ga(020)$. (a) Energy diagram. (b) Corresponding optimized geometries, showing the energy barriers. Color scheme: black, palladium; green, gallium; gray, carbon; red, oxygen; and white, hydrogen.

calculation (74.1 kJ mol⁻¹), confirming the ratedetermining step in the thermal reaction as the decomposition of HCOO. It means that HCOO formation through the Eley–Rideal pathway as well as HCOO decomposition is promoted by DBD. As observed in *in situ* TIR, adsorbed hydrogen is essential to decompose HCOO to produce CO. In other words, not limited to the vibrational excitation production of CO₂ in the DBD, an increase in surface adsorbed hydrogen is also expected.

3.Conclusion

We have shown that the combination of NTP and alloy Pd_2Ga/SiO_2 catalysts could be beyond the thermodynamic limit which is impossible to achieve with thermal catalysis. Through an approach that combines in situ characterization and DFT studies, we elucidated that the reaction mechanism of fast formation and decomposition of m-HCOO for reverse water gas shift reaction. More precisely, the bending mode of vibrationally excited CO₂ from NTP could lower the energy barrier and react with adsorbed hydrogen on the Pd₂Ga via the Eley–Rideal pathway. In addition, it was suggested that under NTP conditions, adsorbed hydrogen on the catalyst surface can increase. we believe that this study enables the high designability of CO₂ hydrogenation catalysts toward value-added products based on electrification via NTP.

4. Acknowledgments

This study was supported by JST CREST (JPMJCR19R3) and KAKENHI (21K18615, 22K18336). DY. Kim was supported by the JSPS Research Fellowship for Young Scientists (DC2, 22J10360). X Chen was supported by the Japanese Government (MEXT) Scholarship Program (201807090002).

5. References

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