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NOTE

Promotive SMSI Effect for Hydrogenation of Carbon Dioxide to Methanol on a Pd/CeO_2 Catalyst

This article reports strong metal support interaction (SMSI) appearing in supported palladium catalysts which improves greatly the selectivity and lifetime of the catalysts for methanol synthesis from CO_2 hydrogenation.

SMSI was suggested by Tauster and co-workers (1, 2) to interpret the diminished H_2 and CO chemisorption on titania-supported platinum group metals reduced above 700 K. There exists a large volume of literature about the SMSI effect in the past decade (3–5). It has been found that SMSI decreases activities for hydrocarbon hydrogenolysis, isomerization, and hydrogenation reactions but does not effect the turnover frequency of structure-insensitive reactions like hydrogenation of olefins and aromatics (6, 7). But SMSI can enhance reaction activity involving hydrogenation of CO and carbonyl bonds. SMSI behavior has been observed with a lot of reducible oxides including Pd on rare earth oxides used for CO hydrogenation. Vannice *et al.* studied SMSI behavior in Pd/rare earth oxides catalysts as well as its influence on CO hydrogenation to both CH_4 and CO_3OH (8, 9). Rieck and Bell found by XPS that Pd supported on La_2O_3 is more electronegative than zero-valent Pd alone due to the electropositive nature of La (10). Also they studied interactions of H_2 and CO on Pd/SiO_2 catalysts promoted with rare earth oxides and declared that the rare earth oxide moieties have a slight influence on the distribution of H_2 adstates but cause a significant change in the distribution of CO adstates (11).

Catalytic hydrogenation of carbon dioxide into valuable chemicals and fuels such as methanol has been recently recognized as one of the promising recycling technologies for emitted CO_2. Most of the research was focused on CuO–ZnO catalysts (12–14). Supported Pd catalysts are regarded as demanding catalysts for methanol synthesis from synthesis gas (15, 16). On the other hand, under atmospheric pressure, hydrogenation of CO_2 on supported Pd catalysts produced only methane (17, 18). Solymosi *et al.* studied Pd supported on Al_2O_3, SiO_2, TiO_2, and MgO for CO_2 hydrogenation but methanol selectivity was insufficient (19, 20). Here we find that a Pd/CeO_2 catalyst which was reduced with hydrogen at 500°C exhibited high activity and long lifetime for methanol synthesis from CO_2 and H_2.

Commercially available CeO_2 powder (99.99%) was moulded and crushed into 20–60 mesh; then it was impregnated with $PdCl_2$ from its hot acidic aqueous solution kept at 250°C. Palladium loading was 4% by weight. After degasification and evaporation, the catalyst precursor was dried in air at 120°C for 12 h and then reduced by flowing hydrogen at 400°C for 4 h to remove chlorine. Chlorine was not detected if the catalysts at this step were washed by hot water and the washing solution was analyzed by ion chromatography. Before reaction the catalyst was reduced with flowing hydrogen in the reactor with the temperature set at values between 550°C and 200°C for 1 h.

The reactor was a fixed-bed flow type, operated under high pressure conditions. Products were analyzed by a gas chromatography. Standard reaction conditions were: 30 bar, contact time W/F = 10 g cat · h/mol, 230°C, $H_2/CO_2 = 3$, catalyst weight: 0.5 g.

In Table 1, reaction performances of Pd/CeO_2 reduced by hydrogen at different temperatures were compared. Reduction time for each catalyst was 1 h. When the reduction temperature was between 200 and 400°C, no obvious change happened to the activity and selectivity of the catalysts. The selectivities to methane and CO were high and the durability of the catalyst was poor as the methanol selectivity decreased from 18 to 6% after 14 h from the start of the reaction. For the catalyst reduced at 500°C for 1 h, although the CO_2 conversion was nearly the same, the selectivity to methanol increased drastically from 18.1 to 91.7%, accompanied by a marked decrease in the formation of CO and CH_4. For a Pd/CeO_2 catalyst treated by H_2 at higher temperature such as 550°C, further improvement was not attained. Both the conversion and the methanol selectivity for the catalyst reduced at 500°C were kept constant over 100 h. From turnover frequency data listed in Table 1, it is found that TOF increased from 0.95 to 14.3 s^{-1} with the change of reduction temperature from 400°C to 500°C.

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TABLE 1

Hydrogen Reduction Temperature Effect on Pd/CeO_2 Catalyst[a]

Reduced Temp. (°C)	CO_2 conversion (%)	Turnover frequency[b] (s^{-1})	MeOH selectivity (%)	CH4 selectivity (%)	CO selectivity (%)
550	3.1	14.3	87.8	1.9	10.3
500	3.1	14.3	91.7	1.1	7.1
400	3.2	0.95	18.1	72.5	9.4
200	3.2	0.93	17.8	73.1	9.1

[a] Total pressure: 30 bar; temperature: 230°C; catalyst weight: 0.5 g; W/F = 10 g cat · h/mol.

[b] Turnover frequency was obtained by using Pd dispersion data partly listed in Table 2.

TABLE 2

CO Chemisorption and XRD Results of Pd/CeO_2

	400°C-Reduced Pd/CeO_2	500°C-Reduced Pd/CeO_2
CO uptake[a] (μmol/g)	0.94	0.06
Dispersion (%)	0.25	0.016
Pd size from CO adsorption (Å)	3720	58,200[b]
Pd size by XRD (Å)	3260	3,260
Pd loading by ICP (%)	4.89	4.74

[a] CO uptake here contains no physically adsorbed CO

[b] Calculated value only.

The most probable explanation for the deactivation of the catalyst reduced at temperatures lower than 400°C should be the oxidation of Pd metal, resulting from water formed through CH_4 or CO formation, or CO_2, as the PdO was confirmed on the deactivated catalyst by X-ray diffraction (XRD).

In Fig. 1 are exhibited XRD patterns of fresh Pd/CeO_2 catalysts reduced at 400 or 500°C, respectively. Pd metal and CeO_2 were discerned in both catalysts, but a new Ce_2O_3 phase was formed in the 500°C-reduced Pd/CeO_2. Also it should be noted that the particle size of Pd determined by the Sherrer method from the XRD peaks was the same for both catalysts. Considering the Pd particle size determined from CO chemisorption (Table 2), one is able to conclude that the partially-reduced support of the 500°C-reduced catalyst, Ce_2O_3, migrated onto the Pd surface and covered most of the exposed Pd surface. As a result, CO uptake on the 500°C-reduced catalyst was so small that the calculated Pd particle size from CO chemisorption was too big. It is noteworthy also that Pd loadings measured by ICP listed in Table 2 were nearly the same, although they were higher than the original designed loading of 4% in catalyst preparation, which should be attributed to the loss of hydroxyl groups on the support or the reduction of the support.

The SMSI model is still a subject of controversy. One opinion is that metal particles are hexagonal in outline, of uniform thickness and very thin, indicating a pill-box morphology, accompanied by partially reduced oxide for-

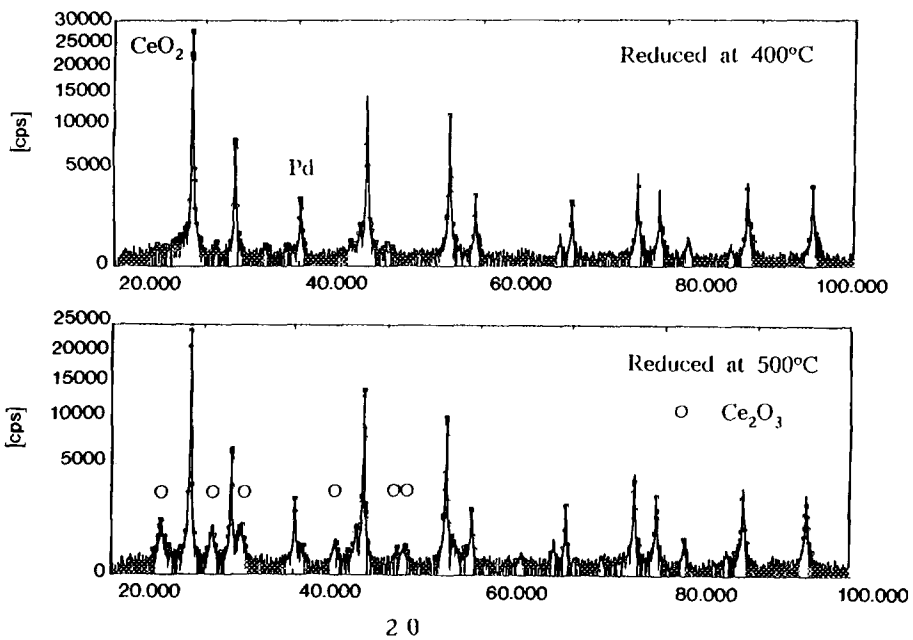

FIG. 1. XRD patterns for Pd/CeO_2 catalysts reduced at different temperatures.

TABLE 3

Reversibility of SMSI Effect by Oxidation for Pd/CeO_2

Treatment[a]	H/M
LTR[b]	0.41%
HTR[c]	0.021%
LTR	0.021%
O_2, 400°C, 1 h	
LTR	0.39%
HTR	0.020%

[a] Sequential experiments on one sample.
[b] H_2 reduction, 400°C, 1 h; evacuation, 400°C, 1 h.
[c] H_2 reduction, 500°C, 1 h; evacuation, 500°C, 1 h.

mation of the reducible support (21, 22). The other theory is the migration and dispersion of partially reduced oxide support on the metal (23–25). The SMSI effect here should belong to the latter category.

As different evidence supporting an SMSI phenomenon in 500°C-reduced Pd/CeO_2, repeated reduction–oxidation was performed to investigate chemisorption behavior of this catalyst, which is regarded as an indictive property of SMSI (1). Experimental conditions were similar to those in the literature (1). In Table 3, the fresh sample reduced at 400°C shows a normal H/Pd ratio. It should be mentioned that reduction of the catalyst by H_2 at 400°C for 4 h to remove Cl leads to sintering of Pd which results in the low H/Pd ratio. Reduction at 500°C suppressed the sorption of hydrogen, leading to the very low H/Pd ratio which is inconsistent with the XRD result. Rereducing the sample at 400°C following the 500°C reduction did not restore hydrogen sorption. However, oxidation of the 500°C-reduced sample at 400°C for 1 h followed by reduction at 400°C completely restored the hydrogen sorption capacity. A second reduction at 500°C suppressed hydrogen sorption once more demonstrating the reversibility of the effect by oxidation.

Although the reduction temperature for our catalyst was only 500°C, lower than the reduction temperature for many reported catalysts in the literature, SMSI effect here is obvious (Table 3). This should be attributed partly to the low metal dispersion of the catalyst as it was first prepared by reduction at 400°C for 4 h to remove Cl, because larger Pd particles can exhibit stronger SMSI effect, at least for Pd/La_2O_3 as reported by Bell and coworkers (10).

In our experiment using Pd/CeO_2 catalysts, no hydrocarbons other than methane were detected, so carbon chain growth could be neglected. Dumesic and co-workers proposed that an electronic effect was involved in SMSI behavior (26, 27). It was suggested that new active sites were created at the interface between the metal and the support (23, 28). This explanation is also successful in elucidating the observed SMSI on the irreducible supports. In fact, it is reported that partially reduced TiO_2 can aid the dissociation of CO for CH_4 synthesis from syngas on Pd/TiO_2 (29). Although detailed discussion on the catalytic mechanism is impossible here, we think that CO_2 was adsorbed dissociatively on the interface between Pd and the reduced ceria surface, with the aid of hydrogen spilled over from Pd, to form adsorbed CO and a surface oxygen atom (30, 31). CO could be hydrogenated to methanol on Pd surface and surface oxygen atom might be involved into a redox cycle on Ce, as pointed out by Vannice *et al.* on Pd/rare earth oxide catalysts for CO hydrogenation (9).

As a blank experiment, CeO_2 was used as a catalyst in the absence of Pd for the same reaction, but it showed no activity even if it was reduced at 500°C by H_2. This blank experiment led to the conclusion that Pd could lower the formation temperature of Ce_2O_3 from CeO_2 via hydrogen spillover because formation of Ce_2O_3 by reduction of CeO_2 with H_2 needs a high temperature of 1000 K and a long time. It is also considered that rare earth oxides here have propensity to form surface carbonates if exposed to CO_2 (32, 33). These carbonates can form at low temperatures and decompose at higher temperatures. From our blank experiment, this alternative route for CO_2 activation is not possible for CeO_2 surface only. But it is difficult to comment on its possibility where Ce_2O_3 coexists with Pd at the present stage.

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