Hydrogenation of Carbon Dioxide to Methanol by Titania-Supported Palladium Catalyst: Promotive SMSI Effect

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Synopsis. Pd/TiO_2 catalyst reduced by flowing hydrogen at 500 °C, appearing with a strong SMSI effect, was found to be an active and selective catalyst for hydrogenation of CO_2 to methanol while the catalyst showed poor activity and selectivity if it was reduced below 400 °C.

Considerable attention is now focused on CO_2 hydrogenation to CH_3OH for environmental consideration. Most of efforts were made on CuO–ZnO catalyst series until now.[1—7] Although supported Pd catalysts have been found to be effective for methanol synthesis from CO hydrogenation, hydrogenation of CO_2 on supported Pd catalyst under atmospheric pressure produce only methane.[8,9] Ramaroson et al. conducted this reaction under very severe condition (120 bar, 350 °C) using supported Pd catalyst but CH_3OH selectivity was low than 40% if produced CO was considered.[10,11] Solymosi et al. studied the supported Pd catalyst on Al_2O_3, SiO_2, TiO_2, and MgO but all of the methanol selectivity was lower than 30%.[12,13] We recently discovered that a Pd/CeO_2 catalyst reduced with hydrogen at high temperature exhibited high activity and long lifetime for methanol synthesis from CO_2 and H_2.[14] We report in this paper that a new Pd/TiO_2 catalyst which is prepared by being reduced with H_2 at 500 °C, where strong metal-support interaction (SMSI) appears, shows excellent activity and stability for CO_2 hydrogenation to CH_3OH.

Experimental

Commercially available TiO_2 powder (Aerosil) was moulded to 20—40 mesh, then it was impregnated with $PdCl_2$ from its hot acidic aqueous solution (Kojima Chemicals, 98.5%). Palladium loading was 4% by weight. After degasification and evaporation, the catalyst precursor was dried in air at 120 °C for 12 h and reduced by flowing hydrogen at 400 °C for 4 h to form Pd metal, and then passivated by argon containing 1% O_2. Before reaction the catalyst was reduced with flowing hydrogen in reactor in situ at the temperature varying between 550 and 200 °C for 1 h. Reactor was a fixed bed flow type one and was operated under pressurized conditions. Methanol analysis was conducted with a gas chromatograph (Shimadzu GC-9A) with a flame ionization detector (FID) equipped with a Porapak R column. Catalyst weight was 0.5 g.

X-Ray diffraction (XRD) measurements were conducted with a Rigaku RINT 2400 instrument. Measurements of CO chemisorption were carried out at room temperature by using a conventional gass-made vacuum system. The amount of CO required for a monolayer coverage of Pd metal surface (q_m) was estimated by extrapolating the flat part of an adsorption isotherm to the zero of the equilibrium pressure for adsorption. Assuming that each surface Pd atom can adsorb one CO molecule, the dispersion of Pd was calculated from the q_m value.

Results and Discussion

In Table 1, reaction performances of Pd/TiO_2 reduced by hydrogen at different temperature are compared. Reduction time for each catalyst was 1 h. When the reduction temperature was between 200 and 400 °C, no obvious change happened to its activity and selectivity. The selectivities of methane and CO were rather high. However, when it was reduced at 500 °C for 1 h, although the rate of CO_2 conversion was nearly the same, selectivity of methanol increased tremendously to 84.9%, which was accompanied by the marked decrease in the formations of CO and CH_4.

In Fig. 1 are compared the durability of the 400 °C-reduced catalyst and the 500 °C-reduced catalyst. Not only CO_2 conversion but also methanol selectivity of the 500 °C-reduced catalyst was very stable. But for the 400 °C-reduced catalyst, along with its gradually decreased CO_2 conversion, its CH_3OH formation capacity decreased very quickly as its CH_3OH selectivity was 2.1% after 8 h from reaction start.

In Fig. 2 are exhibited XRD patterns of fresh or used Pd/TiO_2 catalysts reduced at 400 or 500 °C, respectively. Pd metal and TiO_2 were recognized for all catalysts. New Ti_2O_3 phase was discerned in 500 °C-reduced Pd/TiO_2. No change happened to the XRD pattern of used 500 °C-reduced catalyst compared to its fresh state. But for the 400 °C-reduced catalyst, PdO appeared on the used catalyst besides Pd metal while only Pd existed on its fresh catalyst. No change occurred on the TiO_2 support of fresh or used 400 °C-reduced catalyst.

The most probable explanation for the deactivation of the catalyst reduced at lower than 400 °C should be the oxidation of Pd metal, resulting from water formed through CH_4 or CO formation, or CO_2, because the PdO was confirmed on the deactivated catalyst.

Also it should be noted that the particle size of Pd determined by Scherrer method from XRD peaks was the same for both catalysts. Considering the Pd particle size determined from CO chemisorption (Table 2), it is able to conclude that partially-reduced support of 500 °C-reduced catalyst, Ti_2O_3, migrated back onto

Table 1. Hydrogen Reduction Temperature Effect on Pd/TiO_2 Catalyst

Reduced temp	CO_2 conversion	MeOH selectivity	CH_4 selectivity	CO selectivity
°C	%	%	%	%
200	4.4	1.0	50.7	48.3
400	4.9	4.2	44.6	51.2
500	4.7	84.9	7.4	7.7
550	4.5	81.2	10.3	8.5

All data was recorded when MeOH selectivity was highest. Total pressure: 30 bar; temperature: 230 °C; catalyst weight: 0.5 g; $W/F=10$ g-cat h mol^{-1}.

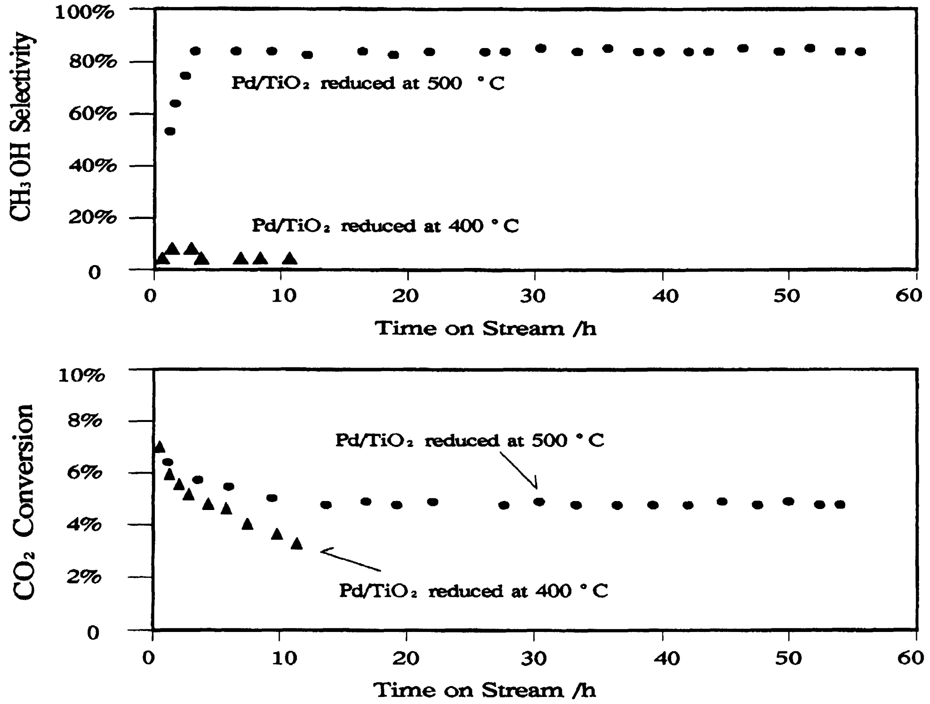

Fig. 1. Durability of Pd/TiO_2 catalysts reduced under different temperatures. The same reaction condition as in Table 1.

Table 2. CO Chemisorption and XRD Results of Pd/TiO_2

	400 °C-reduced Pd/TiO_2	500 °C-reduced Pd/TiO_2
CO uptake[a] (μmol g^{-1})	1.15	0.17
Dispersion (%)	0.31	0.045
Pd size from CO adsorption (Å)	3005	20690
Pd size by XRD (Å)	2840	2840

a) CO uptake here contains no physically-adsorbed CO.

Pd surface and covered most exposed Pd surface, which is an indicative property of SMSI effect.[15] As a result, CO uptake of 500 °C-reduced catalyst was so small that calculated Pd particle size from CO chemisorption was too big.

SMSI model is still a subject of controversy. One kind of 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 formation of the reducible support.[16,17] The other kind of theory is the migration and dispersion of partially-reduced oxide support on metal.[18,19] The SMSI effect behaved here should belong to the latter category. SMSI is generally regarded as a reason for catalyst deactivation due to its remarkable suppression for reactants adsorption.[20] Interestingly, SMSI showed positive effect here to increase astonishedly methanol formation from CO_2+H_2.

As a different evidence supporting SMSI phenomenon in 500 °C-reduced Pd/TiO_2, repeated reduction–oxi-

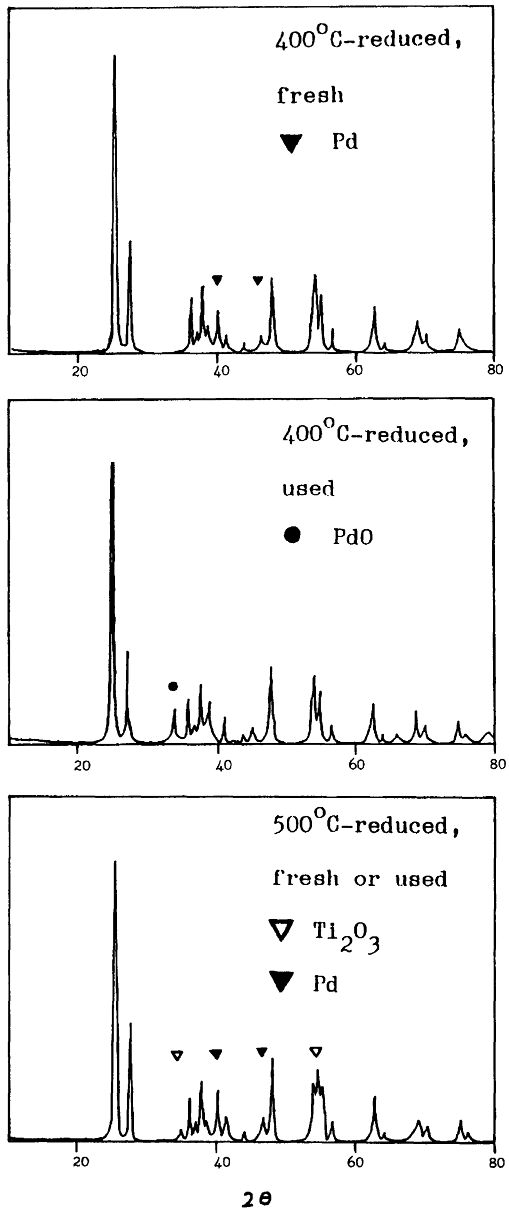

Fig. 2. XRD patterns of Pd/TiO_2 catalysts.

dation was performed to investigate the chemisorption behavior of this catalyst, which is also regarded as an indicative property of SMSI.[15] As demonstrated 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 make itself clear of Cl in the catalyst preparation would lead to sintering of Pd which resulted 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. Reducing the sample at 400 °C following the 500 °C reduction did not restore hydrogen sorption. However the oxidation of the 500 °C-reduced sample at 400 °C for 1 h followed by the 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. The H/Pd ratios in Table 3 are slightly higher than the CO/Pd ratios in Table 2. This should be attributed to hydrogen dissolution in Pd metal. These facts show clearly the occurrence of SMSI phenomenon.

Table 3. Reversibility of SMSI Effect by Oxidation for Pd/TiO_2

Treatment[a]	H/M
LTR[b]	0.67%
HTRc)	0.057%
LTR	0.057%
O_2, 400 °C, 1 h	
LTR	0.62%
HTR	0.055%

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.

In our experiments with a Pd/TiO_2 catalyst, no hydrocarbons other than methane were detected. So the carbon chain growth could be neglected. We think that CO_2 was adsorbed disassociately on reduced palladium–titania surface, to form adsorbed CO and surface oxygen atom on Ti_2O_3. The formed surface oxygen could react with hydrogen to form water and active site Ti^{3+} was kept stable to produce CO and oxygen atom. If the surface oxygen atom reoxidized Ti_2O_3 to restore original TiO_2 state, catalyst activity based on Ti_2O_3 will drop irreversibly, as happened at Pd/TiO_2 reduced at temperature ranging from 200 to 400 °C. It is speculated from CO chemisorption data that CO formed from CO_2 on Ti_2O_3 migrated to Pd site and was successively hydrogenated to methanol there. In a word, Ti_2O_3 originated from SMSI reduced CO_2 to CO and Pd metal hydrogenated the CO to methanol.

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