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Hydrogenation of Carbon Dioxide to Methanol by Lanthana-Supported Palladium Catalyst

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Pd/La_2O_3 catalyst reduced by flowing hydrogen at 500 °C for 1 h was found to be a promising catalyst for hydrogenation of CO_2 to methanol. At 230 °C and 30 bar, the CO_2 conversion was 4.8% while methanol selectivity reached 82.7% with extremely high durability, even if the composition of reactant gas was $CO_2 : H_2 = 1 : 3$.

Catalytic hydrogenation of CO_2 into valuable chemicals and fuels such as methanol has been recently recognized as one of demanding recycling technologies for emitted CO_2. Most of the research was focused on CuO-ZnO catalyst series. 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 produced only methane. 8,9) Ramaroson et al conducted this reaction under very severe condition (120 bar, 350 °C) using supported Pd catalyst, to report that little CH_3OH was formed if acidic oxide support was used. 10,11) When basic oxide support was utilized, methanol selectivity seemed to be enhanced. Unfortunately, the amount of CO formation was not taken into account in their calculation of methanol selectivity, as pointed out by other report. 12) The correct CH_3OH selectivity for their catalysts should not be higher than 55%, according to our re-calculation. 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) Iizuka et al. reported that Re/ZrO_2 and Re/Nb_2O_5 showed high activity for CO_2 hydrogenation to methanol with methanol selectivity higher than 50%. 14) We report here that a Pd/La_2O_3 catalyst which was reduced with hydrogen at 500 °C exhibited high activity and long lifetime for methanol synthesis from CO_2 and H_2 whereas the catalysts reduced with hydrogen at lower temperature showed quite low activity and short lifetime.

Commercially available La_2O_3 (Nacalai Tesque Inc., 99.99%) powder was moulded and crushed into 20-60 mesh, then it was impregnated with hot acidic aqueous solution of $PdCl_2$ (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 changing from 550 °C to 200 °C for 1 h. Reactor was a fixed bed flow type one, operated under pressurized conditions. Methanol analysis was conducted with gas chromatograph with a flame ionization detector (FID) equipped with a Porapak R column. Standard reaction conditions were: 30 bar, contact time W/F = 10 g-cat.h/mol, 220-240 °C, $H_2/CO_2 = 3$, catalyst weight was 0.5 g.

In Table 1, the reaction performances of Pd/La_2O_3 reduced by hydrogen at different temperature were compared. Reduction time for each catalyst was 1 h. When the reduction temperature was between 200 °C and 400 °C, no obvious change happened to the catalyst activity and selectivity. The CO_2 conversion was around 5.1%-5.5% with a methanol selectivity of ca. 18%. The selectivities of methane and CO were relatively high. Also the durability of the catalyst was poor as the methanol selectivity decreased from 19% to 6% after 10 hr from the reaction start (Fig. 1). But for the catalyst reduced at 500 °C for 1 h, although CO_2 conversion was 4.8%, selectivity of methanol increased remarkably to 82.7% with the CH_4 selectivity of 3.8%. For the catalyst treated by H_2 at higher temperature such as 550 ° C, further improvement was not realized as methanol selectivity was 78.5% with the conversion of 4.5%.

The durability of the catalyst which was reduced at 500 °C or 400 °C was compared in Fig. 1. Both the conversion and the methanol selectivity for the catalyst reduced at 500 ° C were kept stable through 80 h. Re-reduction by hydrogen at 500 °C for 1 h for this catalyst after 56 h reaction exhibited no effect on its reaction behavior. The activity and selectivity of the catalyst were so stable that repeated hydrogenation seemed to be unnecessary.

Also as displayed in Fig. 1, the catalyst reduced at 400 °C showed low methanol selectivity and short lifetime. Regeneration by reduction with H_2 at 400 °C could restore about 80% of the initial activity (15% for regenerated CH_3OH selectivity) but the activity dropped quickly, again.[15] The most likely explanation for the deactivation of this catalyst might be the oxidation of Pd metal, resulting from CH_4 formation or water formed through reverse water-gas shift reaction. The other possible route for oxidation of Pd was direct reaction of Pd with CO_2, because it was confirmed on the deactivated catalyst by X-ray diffraction (XRD) that a part of Pd was oxidized to form PdO, as shown in Fig. 2. It should be noted that no change of XRD pattern appeared for catalyst reduced at 500 °C before and after reaction and no oxidation of Pd occurred.

The role of Pd here was to facilitate the reduction process and to activate H_2 for hydrogenation reaction, as suggested by Trovarelli et al[16,17] who studied metal-oxide interactions by transient condition. They confirmed that high-temperature reduction of some ceria-supported platinum group metal catalysts (i.e. Rh/CeO_2, Pt/CeO_2) induced a metal-support interaction which enhanced activity of CO or CO_2 hydrogenation as well as acetone hydrogenation. But this behavior existed only over the virgin catalyst operating in transient conditions. Strong metal-support interaction (SMSI) resulting from high temperature reduction[18] should contribute principally to the methanol selectivity improvement here. SMSI effect, ocurring through reduction by hydrogen under high temperature such as 500 °C, could decrease adsorption strength of CO and H_2, which prevented formation of surface carbide and hydrocarbons and was favorite for methanol formation. Also it is known that in SMSI phenomenon, sintering of metal did not occur even if reduced at high temperature but migration of oxide support to metal surface was often observed.[19] No change of Pd particle size showed in XRD results in Fig. 2. And mean Pd particle size determined from XRD was 1090 A for both catalysts. But from CO chemisorption at room temperature, the dispersion of 400 °C-reduced catalyst was 0.91% (Pd particle size was calculated to be 1023 A), which was much higher than that of 500 °C-reduced catalyst (0.11%, 8464 A). This should be attributed to the migration of support to metal surface. Meanwhile, it is speculated that, considering slight drop of CO_2 conversion (from 5.5% to

Table 1. Hydrogen Reduction Temperature Effect on Pd/La_2O_3 Catalyst

Reduced Temp °C	CO_2 Conv. %	MeOH Selec. %	CH_4 Selec. %	CO Selec. %
200	5.1	17.8	73.1	9.1
400	5.5	19.1	65.4	15.5
500	4.8	82.7	3.8	13.5
550	4.5	78.5	4.4	17.1

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

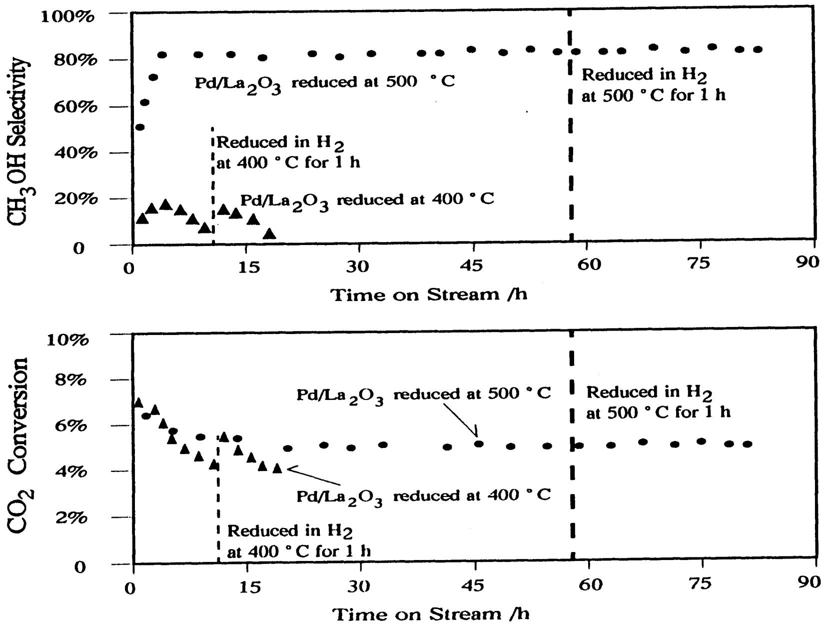

Fig. 1. Durability Test of Pd/La_2O_3 catalysts.
Reaction Conditions: 230 °C, Standard Conditions

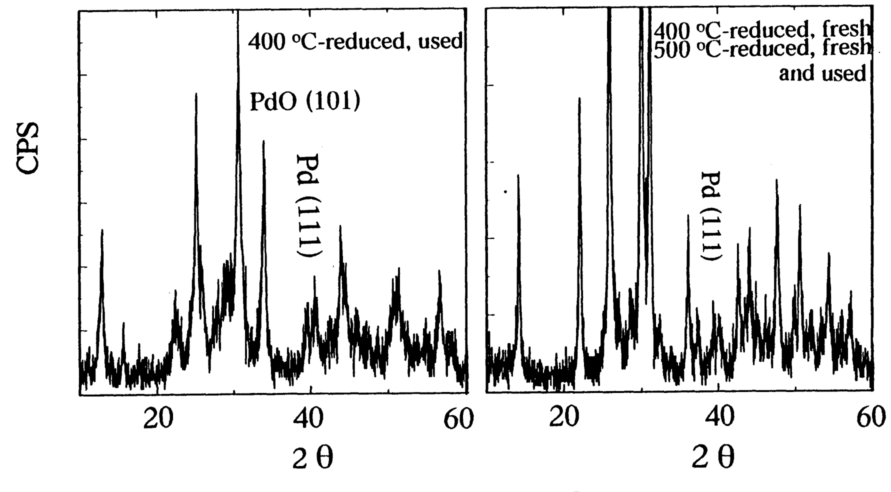

Fig. 2. XRD Patterns of Pd/La_2O_3.
(the numbers in parentheses are surface indexes)

4.5%) concomitant with reduction temperature rising from 400 °C to 550 °C, contribution from Pd metal surface decrease could not be excluded.

Finally, reduction temperature variance showed remarkable effect onto the catalytic performances of Pd/La_2O_3 catalyst in hydrogenation of carbon dioxide to methanol. Reduction in flowing hydrogen at high temperature such as 500 °C of Pd/La_2O_3 catalyst resulted in the high activity of methanol synthesis, especially its selectivity (about 83%) and durability.

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