# Hydrogenation of Carbon Dioxide and Carbon Monoxide over Supported Platinum Catalysts

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The production of methanol from reactions between  $CO_2 + H_2$  and  $CO + H_2$ has been studied over platinum catalysts supported on Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, MgO, SiO<sub>2</sub> and TiO<sub>2</sub>. Zirconia- and niobia-supported Pt catalysts showed the highest activity for reactions of both CO<sub>2</sub> and CO. The magnesia-supported Pt catalyst was less active compared with Pt/ZrO<sub>2</sub> and Pt/Nb<sub>2</sub>O<sub>5</sub>, but exhibited the highest selectivity towards MeOH formation. The activation energy of the CO<sub>2</sub> + H<sub>2</sub> reaction was always lower than that of the CO reaction. Thus, the reaction of CO<sub>2</sub> + H<sub>2</sub> occurs easily at lower temperature compared with the CO + H<sub>2</sub> reaction, but the rate of CO hydrogenation exceeds that of CO<sub>2</sub> hydrogenation at higher temperatures. The selectivity towards methanol was higher for CO<sub>2</sub> hydrogenation than that for the CO + H<sub>2</sub> reaction over all the catalysts used.

The hydrogenation reactions of CO over transition-metal catalysts have been extensively studied.<sup>1</sup> Most chemical studies have concentrated on maximizing the yields and optimizing the selectivity for the following main reactions: methanation,<sup>2</sup> methanol synthesis<sup>3</sup> and the synthesis of higher molecular-weight hydrocarbons.<sup>4</sup>

On the other hand, studies in the hydrogenation of  $CO_2^{5-10}$  have been much less extensive than those of CO hydrogenation. In particular, for the synthesis of methanol from  $CO_2$ , only a few papers have been published so far.<sup>1-14</sup> This paper reports a study of the reaction of  $CO_2 + H_2$  to form methanol and hydrocarbons in comparison to the hydrogenation of CO, using supported platinum as a catalyst.

#### Experimental

Supported platinum catalysts were prepared by impregnating Nb<sub>2</sub>O<sub>5</sub>,  $ZrO_2$ ,  $TiO_2$  or SiO<sub>2</sub> with an aqueous solution of hexachloroplatinic acid. For the preparation of Pt/MgO, a methanol solution of hexachloroplatinic acid was used to avoid the partial dissolution of MgO in water. The Pt content was 2.0 wt% on all the catalysts. Zirconium oxide was prepared by the hydrolysis of ZrOCl<sub>2</sub> with aqueous ammonia, followed by calcination at 500 °C for 2 h. Silica (a reference catalyst of the Catalysis Society of Japan, JRC-SiO-1) and TiO<sub>3</sub>(JCR-TiD-1) were used after the calcination at 500 °C for 2 h. Nb<sub>2</sub>O<sub>5</sub> was used after washing  $Nb_2O_5 \cdot nH_2O$  (CBMM-AD-108) with distilled water several times and drying at 100 °C. Magnesium oxide was prepared by the hydrolysis of  $Mg(NO_3)_2$  with an aqueous ammonia solution followed by calcinating at 500 °C for 2 h. The catalysts were reduced at 400 °C for 2 h in a stream of H<sub>2</sub> before use. The reactions were carried out by using a flow reactor under 10 atm pressure. A premixed gas comprising  $CO_2 + H_2$ (1/1 or 1/3) or CO+H<sub>2</sub> (1/1) (Nippon Sanso Co.) was used without purification. The flow rate of  $CO_2$  (or CO) was 50 mmol h<sup>-1</sup> as a standard experimental condition. The products were analysed by f.i.d. and t.c.d gas chromatographs. Adsorption experiments of CO to obtain the metal surface area were carried out by a conventional B.E.T. apparatus at room temperature. The adsorption uptake was determined as a function

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Fig. 1. Change in rate of CO<sub>2</sub> hydrogenation with time over  $Pt/Nb_2O_5$  ar 240 °C:  $\bigcirc$ , MeOH;  $\square$ , CH<sub>4</sub>.

of pressure and the linear portion of the isotherm was extrapolated to zero pressure to obtain the amount chemisorbed.

### **Results and Discussion**

The rate change for hydrocarbon and alcohol production in the course of  $CO_2$ hydrogenation over  $Pt/Nb_2O_5$  is shown in fig. 1. In the initial stage of reaction, methane was formed predominantly. However, the formation of methane decreased and the selectivity to methanol formation increased gradually. Along with the formation of methanol, dimethyl ether formation was also observed. Since the Nb<sub>2</sub>O<sub>5</sub> support has acidic properties,<sup>15</sup> the formation of dimethyl ether can be ascribed to the dehydration of methanol molecules produced on the oxide support. The activity and selectivity are summarized along with the metal dispersion in table 1.  $Pt/ZrO_2$  and  $Pt/SiO_2$  showed higher metal dispersions than the others. Although  $Pt/ZrO_{2}$  exhibited the highest activity for CO and CO<sub>2</sub> reactions, there is nothing to choose between the activities of  $Pt/ZrO_2$ and  $Pt/Nb_2O_5$  on the basis of metal dispersion because of the low dispersion on  $Nb_2O_5$ . The selectivity of Pt/ZrO<sub>2</sub> to methanol was 70% at 200-240 °C, but it decreased considerably at higher temperatures. In fig. 2 the effect of space velocity on the selectivity is shown. At lower space velocities, methanol selectivity decreased slightly. However, the selectivity change with space velocity was far less compared with the case of the  $CO_2 + H_2$ reaction over Re/ZrO<sub>2</sub>.<sup>14</sup> Thus, over Pt catalysts, although the possibility that some methane is formed via methanol cannot be ruled out, methane and methanol will mainly form via independent routes.  $Pt/Nb_2O_5$  and  $Pt/TiO_2$  showed almost the same selectivity to methanol plus dimethyl ether (> 60%) at 240 °C. Pt/MgO had the highest selectivity to methanol, although the activity was least.  $Pt/SiO_2$  showed a high selectivity to methanol at 260 °C, but the selectivity decreased drastically at higher temperatures and methane and higher hydrocarbons were formed.

The results of CO hydrogenation are summarized in table 2. In CO hydrogenation over Pt catalysts, methanol formation with a high selectivity is known to occur.<sup>16, 17</sup> Pt/ZrO<sub>2</sub> and Pt/Nb<sub>2</sub>O<sub>5</sub> also showed the highest activity in this reaction, but the selectivity to methanol was lower than in CO<sub>2</sub> hydrogenation. In this reaction the selectivity to higher hydrocarbons increased in comparison with the case of CO<sub>2</sub>

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Table 1.  $CO_2$  hydrogenation over supported Pt catalysts<sup>*a*</sup>

rate of CO	formation /mmol h <sup>-1</sup> g-cat <sup>-1</sup>	2.34	0.64	3.25	2.72	2.39	5.36	3.41	10.10	2.52	2.62	3.28
	Me <sub>2</sub> O	3.4		-						trace	0.3	0.3
(%)	C <sub>3+</sub>	0.4	0.2	0.1	0.1	trace	0.1	0.6	5.0	trace	trace	0.1
tivity (mol	C <sup>3</sup>	2.9	0.8	0.9	0.8	trace	0.4	1.3	8.5	0.3	0.2	0.3
selec	МеОН	56.2	71.7	48.8	47.3	78.5	60.9	52.7	4.5	72.9	65.8	55.6
	CH4	37.1	24.3	48.8	50.5	21.5	32.7	44.8	81.8	26.8	33.7	43.5
turnover	frequency $/10^{-4} \text{ s}^{-1}$	6.7	2.5	6.9	7.5	5.0	6.7	0.6	6.1	2.5	3.6	4.7
rate of hydrocarbon and alcohol	formation $/$ mmol h <sup>-1</sup> g-cat <sup>-1</sup>	0.06	0.05	0.14	0.15	0.03	0.04	0.01	0.12	0.04	0.06	0.08
reaction	temperature /°C	240	200	235	260	260	300	260	300	200	240	260
	catalysts (dispersion) <sup>b</sup>	Pt/Nb <sub>8</sub> O <sub>5</sub> (0.24)	Pt/ZrO, (0.55)	1		Pt/MgO (0.16)	, , ,	Pt/SiO <sub>3</sub> (0.54)	, I	Pt/TiO <sub>2</sub> (0.46)	, •	

<sup>a</sup>  $CO_2/H_2 = 1/1$ . <sup>b</sup> Calculated from the amount of CO adsorption.

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Fig. 2. Effect of space velocity on selectivity over  $Pt/ZrO_2$  at 240 °C:  $\bigcirc$ , MeOH;  $\square$ , CH<sub>4</sub>.



Fig. 3. Arrhenius plots of (a) CO<sub>2</sub> and (b) CO hydrogenations. Activation energies are given in parentheses (kJ mol<sup>-1</sup>). (a) ▲. Pt/ZrO<sub>2</sub> (40.1); ●, Pt/TiO<sub>2</sub> (22.6) and ■, Pt/MgO (41.6); (b) ▲, Pt/ZrO<sub>2</sub> (107.8); ●, Pt/TiO<sub>2</sub> (87.4) and ■, Pt/MgO (95.6).

hydrogenation. In particular,  $Pt/Nb_2O_5$  tends to stimulate the propagation of C—C bonds towards higher hydrocarbons. This higher propagation ability in the CO reaction is a marked difference between the CO and CO<sub>2</sub> hydrogenation reactions over all the catalysts. This will be due to the higher concentration of adsorbed CO species on the surface in the CO reaction. In the case of CO<sub>2</sub> hydrogenation over  $Pt/SiO_2$  at 300 °C, the propagation towards higher hydrocarbons was faster than on the other catalysts. This is also due to the higher production rate of CO from the  $CO_2 + H_2$  reaction over  $Pt/SiO_2$  at 300 °C. The formation of ethanol was observed in CO hydrogenation over all the catalysts, in contrast to the case of CO<sub>2</sub> hydrogenation.

Arrhenius plots of the reactions are shown in fig. 3. The activation energy of  $CO_2$  hydrogenation was always lower than that of the CO reaction. Thus the reaction of  $CO_2 + H_2$  towards methanol and hydrocarbons occurs easily at lower temperatures compared with the cases of CO reaction, but at a higher reaction temperature the rates of CO hydrogenation exceed those of the reactions of  $CO_2$ . In previous studies the higher

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oo to Lueto	reaction	rate of hydrocarbon and alcohol	turnover			select	tivity (me	ol%)			rate of CO <sub>2</sub>
(dispersion) <sup>b</sup>		/mmol h <sup>-1</sup> g-cat <sup>-1</sup>	$/10^{-4}  {\rm s}^{-1}$	$CH_4$	МеОН	$C_2$	C3	$C_{4+}$	Me₂O	EtOH	/mmol h <sup>-1</sup> g cat <sup>-1</sup>
Pt/Nb <sub>3</sub> O <sub>5</sub> (0.24)	240	0.13	14.7	64.1	12.2	10.1	5.3	3.2	3.6	1.3	0.04
Pt/ZrO, (0.55)	200	0.03	1.39	33.0	62.8	2.2			ļ		0.01
	240	0.30	14.7	42.8	48.0	4.5	2.1	0.5	1	1.4	0.11
	260	0.63	31.1	54.0	32.0	7.1	3.1	1.6		1.1	0.47
Pt/MgO (0.16)	260	0.06	10.0	16.7	78.6	1.1	1.3	0.8		1.1	0.14
, , ,	280	0.20	33.9	30.1	57.7	3.5	3.5	2.9	ļ	2.4	0.29
	300	0.32	54.2	47.9	33.4	7.6	5.3	3.7		2.1	0.47
Pt/TiO <sub>3</sub> (0.46)	200	0.04	2.22	25.8	72.2	0.6	0.1	ļ	0.2	1.1	0.04
2	240	0.15	8.89	51.0	44.8	2.5	0.2	trace	1.2	0.9	0.12
	260	0.33	19.4	56.3	3.9	2.6	0.3	trace	1.2	0.6	0.30

<sup>*a*</sup> CO/H<sub>2</sub> = 1/1. <sup>*b*</sup> Calculated from the amount of CO adsorption.

**Table 2.** CO hydrogenation over supported Pt catalysts<sup>a</sup>

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reactivity of CO<sub>2</sub> towards H<sub>2</sub> compared with that of CO was emphasized and the reason for the higher reactivity of CO<sub>2</sub> was ascribed to the low CO coverage on the surface in  $CO_2 + H_2$  reaction.<sup>9, 10</sup> In the CO + H<sub>2</sub> reaction, CO strongly absorbs on the metal surface and even acts as a poison for hydrogenation. This situation will occur even on a Pt catalyst surface; thus  $CO_2$  reacts easily with  $H_2$  at lower temperatures. In the reaction of  $CO_2 + H_2$ , the product mainly comprises  $C_1$  compounds, in contrast to the formation of higher hydrocarbons and alcohols in the  $CO+H_2$  reaction. This is also due to the low probability of C-C propagation in the lower surface coverage of CO in the  $CO_2$ reaction, because CO formed from CO<sub>2</sub> might be surrounded by hydrogen atoms on the surface and be easily hydrogenated before propagation.

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