

## Support Effects in the Formation of Methanol from Carbon Dioxide and Hydrogen over Rhenium Catalysts

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In the hydrogenation of carbon dioxide over supported Re catalysts the selectivity for methanol formation was high over Re-ZrO<sub>2</sub> and Re-Nb<sub>2</sub>O<sub>5</sub> under moderate conditions (10 atm, 160—220 °C).

The hydrogenation of CO has been extensively investigated for the production of hydrocarbons and alcohols.<sup>1</sup> In comparison, however, there has been little study of CO<sub>2</sub> hydrogenation reactions.<sup>2</sup> There have been several attempts to make methanol from CO<sub>2</sub> + H<sub>2</sub>, but only a few catalysts (*e.g.*, supported CuO<sup>3</sup> or Pd<sup>4</sup>) are known to form methanol in CO<sub>2</sub> hydrogenation.

We report herein the effectiveness of Re-ZrO<sub>2</sub> and Re-

Nb<sub>2</sub>O<sub>5</sub> for the production of methanol from CO<sub>2</sub> and H<sub>2</sub>. Table 1 summarizes the results obtained over Re-ZrO<sub>2</sub>, Re-Nb<sub>2</sub>O<sub>5</sub>, Re-SiO<sub>2</sub>, Re-MgO, and Re-Zeolon. The catalysts were prepared by a conventional impregnation method to obtain an Re content of 7 wt %. The reactions were carried out using a flow reactor under 10 atm. Re-ZrO<sub>2</sub> showed excellent reactivity and selectivity for the formation of methanol at 160 °C. Re-Nb<sub>2</sub>O<sub>5</sub> showed selectivity for methanol (>50%)

**Table 1.** Hydrogenation of CO<sub>2</sub> over supported rhenium catalysts [CO<sub>2</sub>(or CO) flow rate, 45 mmol h<sup>-1</sup>].

Catalyst	Metal surface area <sup>a</sup> /m <sup>2</sup> g <sup>-1</sup>	Reaction temp/°C	Rate <sup>b</sup> of alcohol + hydrocarbon formation	Selectivity/mol % $\delta$							Rate <sup>b</sup> of CO formation
				CH <sub>4</sub>	MeOH	Me <sub>2</sub> O	EtOH	C <sub>2</sub>	C <sub>3</sub>	C <sub>4+</sub>	
Re-ZrO <sub>2</sub>	4.1 (CO + H <sub>2</sub> )	160	9.95	25.5	73.2	—	—	0.9	0.4	trace	11.41
		220	119.82	68.5	25.6	—	0.2	3.5	1.5	0.7	163.96
		220	6.66	30.7	53.5	—	4.2	6.1	3.8	1.7	7.30 <sup>c</sup>
Re-Nb <sub>2</sub> O <sub>5</sub>	1.1	220	5.04	37.6	52.0	8.7	—	1.3	0.4	—	21.10
		260	20.34	74.0	17.4	5.0	—	2.7	0.7	0.2	90.68
Re-MgO	0.7	260	4.50	80.6	17.5	—	—	1.9	trace	—	23.97
		298	22.07	91.2	5.3	—	—	2.9	0.6	trace	141.55
Re-SiO <sub>2</sub>	1.6	180	10.40	74.7	22.6	—	—	1.9	0.7	0.1	11.46
		220	68.57	88.8	6.6	—	—	3.3	1.0	0.2	88.10
Re-Zeolon	2.9	220	19.98	75.7	18.2	0.1	—	4.0	1.4	0.6	68.10

<sup>a</sup> Calculated from the amount of H<sub>2</sub> adsorbed. <sup>b</sup> Rate  $\times 10^{-2}$  mmol g-cat.<sup>-1</sup>. <sup>c</sup> Rate of CO<sub>2</sub> formation.

and dimethyl ether (*ca.* 9%), but its activity was lower than that of Re-ZrO<sub>2</sub>. Nb<sub>2</sub>O<sub>5</sub> has surface acidic character and catalyses the dehydration of methanol to dimethyl ether,<sup>8</sup> which would account for the formation of dimethyl ether over Re-Nb<sub>2</sub>O<sub>5</sub>. Basic supports are reported to favour the production of methanol,<sup>4</sup> and in this work, the latter did not predominate on the other acidic supports, SiO<sub>2</sub> and Zeolon. The role of Nb<sub>2</sub>O<sub>5</sub> as a support, then, is peculiar and interesting. Rhenium supported on MgO which is a typical basic oxide showed very poor activity; a higher reaction temperature was required and consequently the selectivity for methanol was not high.

Conversion of CO<sub>2</sub> into methane predominated in initial stages of the reaction, but the formation of methanol gradually increased and reached a steady state in 1–2 h for all the catalysts. This suggests the gradual change of surface active sites to favour methanol formation.

In the comparable reaction of CO over Re-ZrO<sub>2</sub>, CO

exhibited almost no reactivity at 160 °C and even at 220 °C, the CO reaction was less active and selective compared to that of CO<sub>2</sub> at 160 °C. Our results confirm these hydrogenations of CO<sub>2</sub> as a method for producing methanol with an activity comparable to those using Cu and Zn catalysts.<sup>3</sup>

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