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_2 and Re–Nb_2O_5 under moderate conditions (10 atm, 160—220 °C).

The hydrogenation of CO has been extensively investigated for the production of hydrocarbons and alcohols.[1] In comparison, however, there has been little study of CO_2 hydrogenation reactions.[2] There have been several attempts to make methanol from CO_2 + H_2, but only a few catalysts (*e.g.*, supported CuO[3] or Pd[4]) are known to form methanol in CO_2 hydrogenation.

We report herein the effectiveness of Re–ZrO_2 and Re–Nb_2O_5 for the production of methanol from CO_2 and H_2. Table 1 summarizes the results obtained over Re–ZrO_2, Re–Nb_2O_5, Re–SiO_2, 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_2 showed excellent reactivity and selectivity for the formation of methanol at 160 °C. Re–Nb_2O_5 showed selectivity for methanol (>50%)

Table 1. Hydrogenation of CO_2 over supported rhenium catalysts [CO_2(or CO) flow rate, 45 mmol h^{-1}].

Catalyst	Metal surface area[a]/m^2 g^{-1}	Reaction temp/°C	Rate[b] of alcohol + hydrocarbon formation	Selectivity/mol % δ							Rate[b] of CO formation
				CH_4	MeOH	Me_2O	EtOH	C_2	C_3	C_{4+}	
Re–ZrO_2	4.1	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
	(CO + H_2)	220	6.66	30.7	53.5	—	4.2	6.1	3.8	1.7	7.30[c]
Re–Nb_2O_5	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_2	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

[a] Calculated from the amount of H_2 adsorbed. [b] Rate × 10^{-2} mmol g-cat.$^{-1}$. [c] Rate of CO_2 formation.

and dimethyl ether (*ca.* 9%), but its activity was lower than that of Re–ZrO_2. Nb_2O_5 has surface acidic character and catalyses the dehydration of methanol to dimethyl ether,[5] which would account for the formation of dimethyl ether over Re–Nb_2O_5. Basic supports are reported to favour the production of methanol,[4] and in this work, the latter did not predominate on the other acidic supports, SiO_2 and Zeolon. The role of Nb_2O_5 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_2 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_2, 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_2 at 160 °C. Our results confirm these hydrogenations of CO_2 as a method for producing methanol with an activity comparable to those using Cu and Zn catalysts.[3]

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