

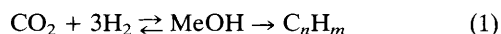
## Hydrocarbon Synthesis from Carbon Dioxide and Hydrogen over Cu–Zn–Cr Oxide/Zeolite Hybrid Catalysts

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The combination of Cu–Zn–Cr oxides and zeolites was effective for hydrocarbon synthesis *via* methanol by the hydrogenation of carbon dioxide, and the conversion of carbon dioxide into C<sub>2+</sub> hydrocarbons was much higher than the thermodynamic equilibrium conversion of methanol.

Hydrogenation of carbon dioxide is important for the utilization of carbon dioxide as a carbon resource.<sup>1</sup> Synthesis of C<sub>2+</sub> hydrocarbons such as liquefied petroleum gas (C<sub>2</sub>–C<sub>4</sub>) or gasoline (C<sub>5+</sub>) from carbon dioxide is especially important. However, C<sub>2+</sub> hydrocarbon synthesis has been considered difficult.<sup>2</sup> For example, methane was produced predominantly even in the case of Fischer–Tropsch catalysts.<sup>3</sup> The combination of the methanol synthesis and MTG (methanol to gasoline) processes used a hybrid catalyst system for hydrocarbon synthesis from carbon monoxide.<sup>4</sup> In these catalysts copper–zinc oxide catalysts and zeolites were used for the methanol synthesis and MTG processes, respectively. Such hybrid catalysts can be applied to the hydrogenation of carbon dioxide [eqn. (1)], because copper–zinc oxide catalysts have



been shown to be useful for methanol synthesis even from carbon dioxide.<sup>5</sup> In this system, the immediate conversion of methanol into hydrocarbons would be expected to shift the equilibrium of methanol synthesis to afford hydrocarbons to a greater extent than the thermodynamically estimated productivity of methanol formation from carbon dioxide.<sup>6</sup> This type of effect has already been observed in the hydrogenation of carbon monoxide using, for example, Cu–Zn/DAY (dealuminated Y-type zeolite).<sup>4</sup> The hydrogenation of carbon dioxide using the same hybrid catalysts was also examined.<sup>7</sup> However, yields of C<sub>2+</sub> hydrocarbons were very low compared with yields for the hydrogenation of carbon monoxide. Therefore, a suitable methanol synthesis catalyst must be employed in order to increase the yield of C<sub>2+</sub> hydrocarbons in the hydrogenation of carbon dioxide. We now report efficient hybrid catalysts obtained by physical mixing of zeolites and Cu–Zn–Cr oxides, prepared from CuO, ZnO and CrO<sub>3</sub>.<sup>8</sup>

As shown in Table 1, the novel hybrid catalysts composed of the Cu–Zn–Cr oxide were very effective for C<sub>2+</sub> hydrocarbon synthesis (runs 1–3) compared with other catalysts (runs

8–11). About 12% of carbon dioxide was converted into C<sub>2+</sub> hydrocarbons by the Cu–Zn–Cr (3:3:1) oxide/HY catalyst and the selectivity was very high (32.2%; run 3). Alkenes such as ethylene were not obtained. Even C<sub>5</sub> and C<sub>6</sub> hydrocarbons were formed with about 1% selectivity. It is noteworthy that C<sub>2+</sub> selectivities for all hydrocarbons exceeded 90% (92–95%; runs 1–3) and methane (C<sub>1</sub>) was a minor product. When a typical methanol synthesis catalyst, Cu–Zn oxide (3:7)<sup>9</sup> was used in a hybrid catalyst, yields of C<sub>2+</sub> hydrocarbons were low (0.4%; run 8). More remarkable is the fact that the Cu–Zn–Cr (2:2:1) oxide/HY catalyst (run 9) prepared from Cr<sub>2</sub>O<sub>3</sub><sup>10</sup> did not exhibit good catalytic activity in contrast with the similar catalyst prepared from CrO<sub>3</sub> (run 1). In addition, other catalysts such as Cu–Zn–SiO<sub>2</sub> and Cu–Zn–Al<sub>2</sub>O<sub>3</sub> were not favourable (runs 10 and 11). These results indicated that the use of CrO<sub>3</sub> as a starting material was important in order to prepare effective hybrid catalysts, although it seems that the real active species does not contain hexavalent chromium. The catalytic activity of these hybrid catalysts gradually decreased, probably because of coke formation in the HY zeolite. Cu–Zn–Cr oxide/HY catalysts nevertheless had moderate activity for hydrocarbon synthesis after 24 h (run 4).

Various types of zeolites were employed in the preparation of hybrid catalysts. The HY-type of zeolite was most effective in our studies. NaY had no ability to convert methanol into hydrocarbons because of the absence of acid sites (run 5). H-ZSM-5, the most widely used zeolite for the MTG process,<sup>11</sup> was not suitable because C<sub>3+</sub> hydrocarbons were hardly obtained (run 6). This is because of its high hydrogenation ability to reduce alkenes to alkanes.<sup>12</sup> In addition, the catalytic activity of Cu–Zn–Cr oxide/HM for C<sub>2+</sub> hydrocarbon synthesis was very low (run 7). C<sub>4</sub> hydrocarbons were not obtained with the NaY, H-ZSM-5 or HM based catalysts (runs 5–7), but they were with Cu–Zn–Cr oxide/HY catalysts (runs 1–4). It seems that these hydrocarbons arose from carbon-chain extension processes.

**Table 1** Hydrogenation of carbon dioxide using hybrid catalysts<sup>a</sup>

Run	Hybrid catalyst <sup>b</sup> (MSC <sup>c</sup> /Zeolite <sup>d</sup> )	Conv. <sup>e</sup> of CO <sub>2</sub> (%)	Selectivity (%) <sup>f</sup>							Conv. <sup>f</sup> to C <sub>2+</sub> (%)	Select. <sup>g</sup> of C <sub>2+</sub> (%)
			CO	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4+</sub>	MeOH	Me <sub>2</sub> O		
1	Cu–Zn–Cr (2:2:1)/HY	35.9	70.3	1.8	7.0	9.5	3.9	0.7	6.8	7.3	91.9
2	Cu–Zn–Cr (3:3:1)/HY	37.1	69.0	1.1	6.2	10.5	6.0	0.7	6.5	8.4	95.4
3	Cu–Zn–Cr (3:3:1)/HY <sup>h</sup>	36.0	56.5	2.1	8.5	12.9	10.8	0.0	9.2	11.6	93.9
4	Cu–Zn–Cr (3:3:1)/HY <sup>h</sup>	34.9	73.7	6.0	5.0	6.1	5.3	0.0	3.95	5.7	73.2
5	Cu–Zn–Cr (3:3:1)/NaY	34.1	96.7	1.5	0.2	0.0	0.0	1.6	0.0	0.1	11.8
6	Cu–Zn–Cr (3:3:1)/H-ZSM-5	34.0	89.5	1.8	7.5	0.0	0.0	1.2	0.0	2.6	80.6
7	Cu–Zn–Cr (3:3:1)/HM	34.8	94.8	1.9	0.7	0.6	0.0	2.0	0.0	0.5	40.6
8	Cu–Zn (3:7)/HY	30.0	97.7	0.7	1.2	0.2	0.0	0.2	0.0	0.4	66.7
9	Cu–Zn–Cr (2:2:1) <sup>h</sup> /HY	24.4	96.0	0.9	0.9	1.1	0.9	0.2	0.0	0.7	76.3
10	Cu–Zn–SiO <sub>2</sub> (2:2:1)/HY	26.6	99.4	0.0	0.6	0.0	0.0	0.0	0.0	0.2	100
11	Cu–Zn–Al <sub>2</sub> O <sub>3</sub> (2:2:1)/HY	25.9	99.4	0.0	0.6	0.0	0.0	0.0	0.0	0.2	100

<sup>a</sup> Conditions: 400 °C, 50 kg cm<sup>-2</sup>, space velocity = 3 dm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>, H<sub>2</sub>/CO<sub>2</sub> = 3. <sup>b</sup> Equal amounts of methanol synthesis catalysts (MSC) and zeolites were mixed physically, then were pressed into disks and finally were crushed into granules (24–40 mesh). <sup>c</sup> Methanol synthesis catalyst. Catalysts of runs 1–7 were prepared according to the described method<sup>8</sup> using CuO, ZnO and CrO<sub>3</sub>. Catalysts of runs 8–11 were prepared by coprecipitation method from copper and zinc nitrate in the presence of an oxide.<sup>9,10</sup> <sup>d</sup> Zeolites used were from the Reference Catalysts of the Catalysis Society of Japan: HY(JRC-Z-HY 4.8; Si/Al = 4.8), NaY(JRC-Z-Y 4.8; Si/Al = 4.8), H-ZSM-5 (Si/Al = 70.8) and HM(JRC-Z-HM10; Si/Al = 10). <sup>e</sup> Carbon %. <sup>f</sup> Selectivity of C<sub>2+</sub> hydrocarbons in all hydrocarbons. <sup>g</sup> SV = 1.5 dm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>. <sup>h</sup> After 24 h. <sup>i</sup> Cr<sub>2</sub>O<sub>3</sub> was used.

**Table 2** Methanol synthesis from carbon dioxide and hydrogen<sup>a</sup>

Run	Catalyst	Conv. CO <sub>2</sub> (%)	Selectivity (%)			Yield MeOH (%)
			MeOH	CO	HC <sup>c</sup>	
1	Cu-Zn-Cr (2:2:1)	37.8 (18.8)	3.7 (45.8)	93.5 (54.2)	2.8 (0.0)	1.4 (8.6)
2	Cu-Zn-Cr (2:2:1)	38.1 (14.8)	4.7 (44.0)	92.4 (56.0)	2.9 (0.0)	1.8 (6.5)
3	Cu-Zn (3:7)	37.3 (19.4)	1.5 (34.5)	95.2 (65.5)	3.3 (0.0)	0.56 (6.7)
4	Cu-Zr-Cr (2:2:1) <sup>b</sup>	37.5 (16.1)	1.8 (45.0)	95.7 (55.0)	2.5 (0.0)	0.68 (7.2)
5	Cu-Zr-SiO <sub>2</sub> (2:2:1)	37.0 (18.7)	1.8 (50.1)	96.0 (49.9)	2.2 (0.0)	0.67 (9.4)
6	Cu-Zr-Al <sub>2</sub> O <sub>3</sub> (2:2:1)	37.3 (8.8)	1.4 (59.7)	97.0 (40.3)	1.6 (0.0)	0.52 (5.3)

<sup>a</sup> Conditions: 400 °C; 50 kg cm<sup>-2</sup>, space velocity = 3 dm<sup>3</sup> h<sup>-1</sup> g<sup>-1</sup>; H<sub>2</sub>/CO<sub>2</sub> = 3, other conditions as in Table 1. Results in parentheses at 250 °C. <sup>b</sup> Cr<sub>2</sub>O<sub>3</sub> was used. <sup>c</sup> HC = hydrocarbon.

The pathway of C<sub>2+</sub> hydrocarbon production *via* methanol was based on the formation of dimethyl ether which is regarded as an intermediate in the MTG process.<sup>13</sup> Unmodified zeolite (HY) had no ability for hydrocarbon formation, and only carbon monoxide was obtained in 3% yield under the same conditions. Table 2 shows the results for methanol synthesis using the copper-zinc catalysts in Table 1. Although the productivity for methanol formation using Cu-Zn-Cr oxides was inferior to that of Cu-Zn-SiO<sub>2</sub> or other reported catalysts,<sup>5</sup> at 250 °C, a suitable temperature for methanol synthesis, Cu-Zn-Cr catalysts (runs 1 and 2) had higher catalytic activity than other catalysts (runs 3-6) at 400 °C. However it seems that the specific character of the Cu-Zn-Cr oxide/HY catalysts could not be simply related to the differences in productivity for methanol formation at 400 °C.

In the case of the novel hybrid catalysts, the total conversion of carbon dioxide into methanol, dimethyl ether and C<sub>2+</sub> hydrocarbons (14.9%; run 3 in Table 1) greatly exceeded the level estimated from the thermodynamic equilibrium of methanol productivity from carbon dioxide and hydrogen (6.5% under our conditions). This is the first example of hybrid catalysts which had excellent ability for C<sub>2+</sub> hydrocarbon synthesis in the hydrogenation of carbon dioxide.

In conclusion, C<sub>2+</sub> hydrocarbons were obtained using Cu-Zn-Cr oxide/zeolite hybrid catalysts in good yields. In these catalysts, the use of CrO<sub>3</sub> as a starting material was extremely important.

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## References

- 1 For review: see W. M. Ayers, *Catalytic Activation of Carbon Dioxide*, American Chemical Society, New York, 1988.
- 2 For some exceptions: J. Barrault, C. Forguy, J. C. Menezo and R. Maurel, *React. Kinet. Catal. Lett.*, 1981, **17**, 373; F. Nozaki, T. Sodesawa, S. Satoh and K. Kimura, *J. Catal.*, 1987, **104**, 339.
- 3 For example: G. D. Weatherbee and C. H. Bartholomew, *J. Catal.*, 1984, **87**, 352.
- 4 C. D. Chang, W. H. Lang and A. J. Silvestri, *J. Catal.*, 1979, **56**, 268; T. Inui, T. Hagiwara, O. Yamase, K. Kitagawa, H. Yamaguchi and Y. Takegami, *J. Jpn. Pet. Inst.*, 1985, **28**, 225; K. Fujimoto, H. Saima and H. Tominaga, *Ind. Eng. Chem. Res.*, 1988, **27**, 920.
- 5 For example: E. Ramarosan, R. Kieffer and A. Kiennemann, *Appl. Catal.*, 1982, **4**, 281; T. Tagawa, G. Pleizier and Y. Amenomiya, *Appl. Catal.*, 1985, **18**, 285; B. Denise and R. P. A. Sneed, *Appl. Catal.*, 1986, **28**, 235.
- 6 P. B. Weisz, *Adv. Catal.*, 1962, **13**, 137.
- 7 T. Inui, K. Kitagawa and T. Hagiwara, *Chem. Express*, 1986, **1**, 107; K. Fujimoto and T. Shikada, *Appl. Catal.*, 1987, **31**, 13.
- 8 Methanol synthesis from carbon monoxide: Y. Ogino, M. Oba and H. Uchida, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 358; methanol synthesis from carbon dioxide using Zn-Cr oxide: Y. Ogino and M. Tani, *Nippon Kagaku Kaishi*, 1975, 1878.
- 9 R. G. Herman, K. Klier, G. W. Simmons, B. P. Finn, J. B. Bulko and T. P. Kobylinski, *J. Catal.*, 1979, **56**, 407.
- 10 E. Ramarosan, R. Kieffer and A. Kiennemann, *Appl. Catal.*, 1982, **4**, 281.
- 11 S. L. Miesel, J. P. McCullough, C. H. Lechthaler and P. B. Weisz, *CHEMTECH*, 1976, 86.
- 12 M. L. Poutsma, in *Zeolite Chem. Catal.*, ed. J. Rabe, American Chemical Society, 1976, 437.
- 13 C. D. Chang and A. J. Silvestri, *J. Catal.*, 1977, **47**, 249.