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Hydrocarbon synthesis from CO_2 over Fe–Cu catalysts

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Abstract

Hydrocarbons and carbon monoxide were produced from carbon dioxide and hydrogen at 400°C over copper-promoted iron catalysts containing sodium. The major surface phases of the catalysts were FeO and/or $FeCO_3$ although iron carbide is believed as an active phase of the hydrocarbon synthesis from carbon monoxide. Copper was present as metal on the surface and the surface density was considerably high even if the content of copper was less than 1 wt%. The surface density of sodium was not negligible in the catalysts containing sodium less than 0.1 wt% and the sodium ion can affect the surface basicity of the catalysts. The olefin content in the products is believed to relate to the surface basicity. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Fischer–Tropsch (F–T) type iron catalyst is often employed for the hydrocarbon synthesis from carbon oxides, and many researchers are still engaged in the development of both the catalyst and the reaction system [1–15]. Alkali metals are effective additives for iron catalysts to increase selectivity to olefin compounds [1–4,16–21]. It is known that the addition of alkali metals enhances adsorption of carbon oxides on the reduced iron but adsorption of hydrogen is rather weakened [22–24]. This may relate to the increase in the selectivity to olefins, and Arakawa and Bell [22] reported that the hydrogenation of carbon monoxide over iron catalysts results in formation of olefins in presence of potassium on the surface.

Although it is believed that iron carbide is an active phase for the F–T synthesis [25–27], formation of the carbide phase must be prevented in presence of carbon dioxide in the feedstock because the reaction between carbon and carbon dioxide to carbon monoxide is expected to take place. In this report, we have investigated the reaction with carbon dioxide over copper-promoted iron (Fe–Cu) catalysts, which is a typical F–T catalyst, to clarify the surface phase of the catalyst.

2. Experimental

Fe–Cu catalysts were prepared by coprecipitation from an aqueous solution containing iron and copper nitrates (the concentration of the metals was 1 M) and an aqueous solution of NaOH (1 M). The precipitates were washed with distilled water, then, dried in air at

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Table 1
Chemical composition of Fe–Cu catalysts

Sample	Content (wt%)				BET surface area ($m^2\ g^{-1}$)[a,b]
	Fe	Cu	Na	O	
$FeCu_{0.99}$	33.3	37.6	<0.01	29.1	5
$FeCu_{0.26}$	52.7	15.3	<0.01	32.0	5
$FeCu_{0.11}$	62.8	8.00	0.08	29.1	10
$FeCu_{0.06}$	64.8	4.77	0.06	30.4	8
$FeCu_{0.01}$	69.3	0.49	<0.01	30.2	5
$FeCu_{0.05}Na_{0.07}$	62.6	3.86	1.75	31.8	5
$FeCu_{0.01}Na_{0.01}$	68.7	0.74	0.40	30.2	6

[a] Determined by nitrogen physisorption.

[b] After reaction.

120°C for 6 h. The resulting solids were calcined in air at 350°C for 3 h, and were ground into powders (100–400 mesh). The bulk composition of the catalysts was determined by ICP emission spectrometry (Table 1).

The catalytic hydrogenation of carbon dioxide was performed with a fixed-bed flow reactor made of stainless steel tube with 9.0 mm ID. A catalyst (1.0 g) was pretreated with diluted hydrogen (1 vol% H_2 in N_2) at 250°C under atmospheric pressure for 12 h. After introduction of a reaction gas mixture (25 vol% CO_2 in H_2) at 250°C, the pressure was raised to 5 MPa (total flow rate, 3.0 $dm^3\ h^{-1}$ in STP); then, the reaction temperature was gradually raised to 400°C.

X-ray diffraction (XRD) patterns were recorded with a Rigaku ROTAFLEX diffractometer (Cu K_α). Surface analyses by X-ray photoelectron spectroscopy (XPS) were performed with a Shimadzu ESCA-3200. The spectra were recorded after Ar ion sputtering for 0.5 min (2 kV, 25 mA). Binding energies were corrected with that of C(1s) (284.6 eV) for carbon contaminant, and the peaks were identified by [28].

3. Results

Carbon dioxide was hydrogenated into carbon monoxide and hydrocarbons at 400°C over the Fe–Cu catalysts (Table 2). Methanol was also produced but the yield was negligibly small. When pure iron and copper oxides were used under reaction conditions, they showed a relatively low activity compared to those obtained over Fe–Cu catalysts and they gave only methane as hydrocarbon product. The conversions of carbon dioxide were ca. 40%, regardless of the catalyst composition and the surface area

Table 2
Hydrogenation of carbon dioxide over Fe–Cu catalysts

Catalyst	CO_2 conversion (%)	Yield (C-mol%)								
		CO	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
CuO	13	10.4	2.6	0	0	0	0	0	0	0
$FeCu_{0.99}$	39	11.6	10.0	4.6	5.2	3.4	2.2	1.5	0.7	0.3
$FeCu_{0.26}$	40	12.4	12.2	4.7	4.5	2.7	1.6	1.2	0.3	0.1
$FeCu_{0.11}$	40	8.3	7.7	3.9	5.6	5.0	3.9	3.3	1.9	0.8
$FeCu_{0.06}$	40	8.1	7.2	3.9	5.6	4.9	3.9	3.4	2.0	1.4
$FeCu_{0.01}$	39	12.1	13.7	4.4	4.0	2.1	1.5	0.7	0.3	0.1
$FeCu_{0.05}Na_{0.07}$	41	7.4	7.8	3.7	5.7	5.6	4.2	3.7	2.0	0.5
$FeCu_{0.01}Na_{0.01}$	40	6.8	7.1	3.9	6.1	6.0	4.3	3.7	2.3	0.4
Fe_2O_3	8[a]	6.3	1.0	0	0	0	0	0	0	0

Conditions: temperature, 400°C; pressure, 5 MPa; space velocity, 3000 ml g $cat^{-1}\ h^{-1}$; time-on-stream, 2 h

[a] MeOH was observed with 0.7% yield.

Table 3
Olefin content in the hydrocarbon products

Catalyst	Time-on-stream (h)	Olefin content (%)		
		C_2	C_3	C_4
$FeCu_{0.99}$	2	0	0	0
	24	0	0	0
$FeCu_{0.26}$	2	0	0	0
	27	0	0	0
$FeCu_{0.11}$	2	0.3	0.8	1.3
	24	2.6	24.1	32.4
$FeCu_{0.06}$	2	0	0.5	0.6
	25	1.8	11.3	20.8
$FeCu_{0.01}$	2	0	2.6	9.7
	24	1.6	27.9	37.9
$FeCu_{0.05}Na_{0.07}$	2	1.2	22.0	29.7
	23	34.2	71.7	74.0
	47	51.1	77.0	78.6
$FeCu_{0.01}Na_{0.01}$	2	21.8	62.0	63.7
	27	57.8	72.4	83.2

(5–$10\ m^2\ g^{-1}$ after reaction). The yields of methane and carbon monoxide related roughly and were essentially high in the products. When the molar ratio of Cu/Fe in the catalyst was 0.11 or less, olefins were formed in the reaction (Table 3). The olefin selectivity was always high in C_4 products and decreased with decrease in the carbon number. At the initial stage of the reaction over $FeCu_{0.01-0.11}$ the selectivities to olefins were small, but they increased with increasing in time-on-stream. The selectivities were significantly high with $FeCu_{0.05}Na_{0.07}$ and $FeCu_{0.01}Na_{0.01}$ and they also increased with increasing in time-on-stream.

XRD patterns were recorded with the catalysts taken out from the reactor after the reaction. There were peaks attributed to Fe_3O_4 (18.3, 30.1, 35.4, 37.1, 43.1, 53.4, and 56.9° in 2θ) in the patterns but no peaks attributed to metallic iron were observed [29]. The crystalline size of Fe_3O_4 was determined as ca. 40 nm for all samples from the width of the peak at 35.4 degree using the equation of Scherrer [30]. Slight peaks for iron carbide were present in the pattern for $FeCu_{0.01}Na_{0.01}$. The peaks attributed to metallic copper (43.3 and 50.4°) were also found in the patterns but the intensities were weak for the samples whose Cu/Fe molar ratios are 0.01–0.06 [29]. A discernible peak was recorded at 36° attributed to Cu_2O only with $FeCu_{0.99}$ [29]. It is noteworthy that there were peaks at 24.6 and 31.9° attributed to $FeCO_3$ in the pattern for $FeCu_{0.05}Na_{0.07}$ [29].

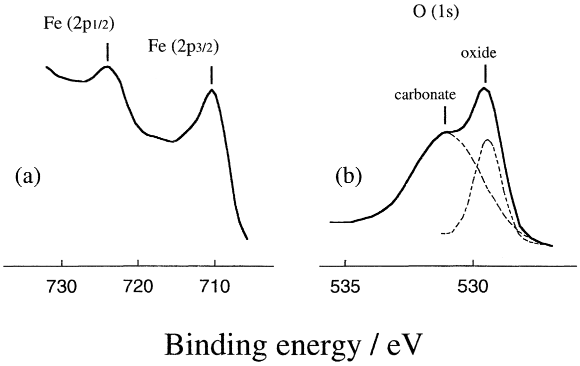

Fig. 1. X-ray photoelectron spectra for $FeCu_{0.01}Na_{0.01}$ after 27 h reaction: (a) $Fe(2p_{1/2})$ and $Fe(2p_{3/2})$ and (b) O(1s).

XPS analyses were performed with the Fe–Cu catalysts after the reaction. Although the XRD analysis shows the presence of Fe_3O_4, the binding energy of $Fe(2p_{3/2})$ for the catalysts taken out after the reaction was 710.3–709.9 eV which is significantly smaller than that for Fe_3O_4 at 711 eV [28,31,32]. The binding energy is rather close to that for FeO [28,31,32], appearing that the surface of the Fe–Cu catalysts is reduced to FeO [28,31]. No peak or shoulder attributed to iron carbide or metallic iron was recorded in the spectra (Fig. 1(a)) while the binding energy of $Fe(2p_{3/2})$ reported is ca. 707 eV [20]. The binding energy of $Cu(2p_{3/2})$ for the catalysts after reaction was 932.5–932.6 eV almost identical with that for metallic copper (932.7 eV) and far from that for $CuFe_2O_4$ (933.8 eV) [32].

The peak for O(1s) can be divided into two peaks at 529.5–530.2 eV and 531.0–532.3 eV; the former can be attributed to iron oxide and the latter carbonate species (see Fig. 1(b)) [28]. The peak at 287.6–288.9 eV attributed to carbonate species can be also separated from that for carbon contaminant [28]. The surface composition was calculated from the XPS peak areas using atomic sensitivity factors, 3.00 for $Fe(2p_{3/2})$, 0.66 for O(1s), 6.30 for $Cu(2p_{3/2})$, 0.25 for C(1s), and 2.30 for Na(1s) (Table 4). The surface compositions of Cu in $FeCu_{0.01}$ and $FeCu_{0.01}Na_{0.01}$ were 10 and 7 mol%, respectively, significantly larger than the chemical contents. A single peak of Na(1s) was recorded and the binding energy was 1071.5–1072.1 eV. The surface concentrations of sodium were 3–5 mol% for $FeCu_{0.01-0.99}$ and 13 mol% for $FeCu_{0.05}Na_{0.07}$ and $FeCu_{0.01}Na_{0.01}$, showing that

Table 4
Surface composition (mol%) of the Fe–Cu catalysts determined by XPS

Catalyst	Na	Cu	Fe	O		C
				Oxide	Carbonate	Carbonate
$FeCu_{0.99}$	3	31	11	18	28	9
$FeCu_{0.26}$	2	30	17	24	21	6
$FeCu_{0.11}$	3	20	17	16	35	9
$FeCu_{0.06}$	5	4	25	25	31	10
$FeCu_{0.01}$	3	10	28	20	31	8
$FeCu_{0.05}Na_{0.07}$	13	13	14	13	34	13
$FeCu_{0.01}Na_{0.01}$	13	7	17	14	36	13

sodium is dominantly present on the surface. However, the values for $FeCu_{0.01-0.99}$ were considerably smaller than the concentration of carbonate species, the carbonate species are rather $FeCO_3$ than Na_2CO_3.

4. Discussion

When carbon dioxide is used as a carbon source in the hydrocarbon synthesis, it is known that carbon monoxide is formed in the reverse water gas shift reaction and further hydrogenated to hydrocarbons [33]. Hence the reaction mechanism with carbon dioxide should be similar to that of the Fischer–Tropsch reaction, however, the distribution of produced hydrocarbons over the Fe–Cu catalyst whose Cu/Fe molar ratio is less than 0.11 ($FeCu_{<0.11}$) did not follow the Schulz–Flory distribution function. As described above the olefin content in the product was high over $FeCu_{<0.11}$, and this might lead to the deviation from the Schulz–Flory equation. The detail reaction mechanism is under investigation.

Since the equilibrium conversion of carbon dioxide to carbon monoxide under the reaction conditions (400°C, 5 MPa) is 46%, the equilibrium could govern the total conversion because the conversions of carbon dioxide in Table 2 are close to the equilibrium value regardless of the catalysts. Despite the similar conversion, the total yields of hydrocarbons do not always the same. The catalytic activity does not depend on the content or surface concentration of copper in $FeCu_{0.01-0.99}$ but does on the concentration of sodium, that is, $FeCu_{0.05}Na_{0.07}$ and $FeCu_{0.01}Na_{0.01}$ produced 32–34% of total hydrocarbons. Kölbel et al. [19] showed that copper is an important promoter for iron catalysts but the content is not affect to the activity, and Wachs et al. [20] also reported that the product distribution do not change when copper is incorporated into an iron catalyst. These are consistent with our results. It is known that significant promotional effect appears with simultaneous presence of copper and alkali metal in the hydrogenation of carbon monoxide over iron catalysts [33], and it is consistent with our results. In general, presence of alkali metals on iron catalysts results in formation of olefin compounds in the Fischer–Tropsch synthesis and it is pointed out

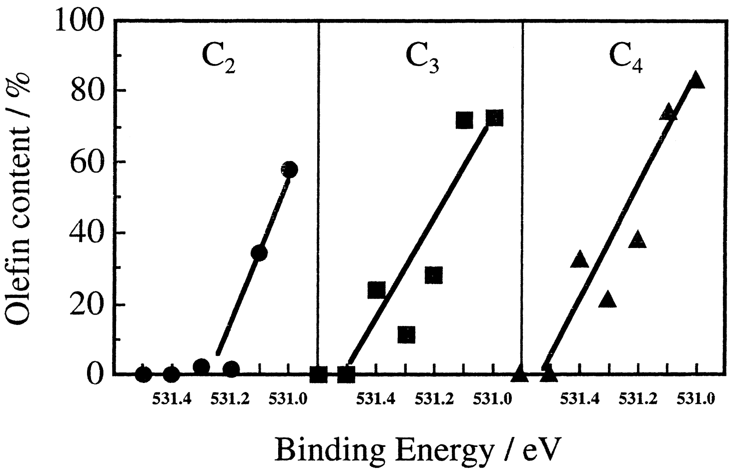

Fig. 2. Relationship between the binding energy of O(1s) for carbonate species and olefin content.

that basic sites on the catalysts play an important role for production of olefins [34]. Actually, the formation of carbonate species found in the XPS analyses of the used catalysts suggests the presence of basic sites on the surface. The strength of the basicity can relate to the binding energy of O(1s) for the carbonate species because the electron density of oxygen is expected to be high on basic sites. Fig. 2 shows the relation between the olefin contents in the C_2–C_4 products and the binding energy of O(1s) for carbonate species, and the olefin contents at the end of the reaction evidently increase with a decrease in the binding energy, that is, an increase in basicity.

Since the binding energy of O(1s) for the carbonate is low in the catalysts with high surface concentration of sodium ($FeCu_{0.05}Na_{0.07}$ and $FeCu_{0.01}Na_{0.01}$), sodium ions on the catalysts are the source of the basicity. The binding energies of Fe($2p_{3/2}$) for these catalysts were low, showing interaction between iron and sodium ions. However, $FeCu_{0.99}$ and $FeCu_{0.26}$ whose surface concentrations of sodium are not negligible did not produce olefin compounds. Although the binding energies of Fe($2p_{3/2}$) evidence that FeO is the dominant species on these catalysts, the atomic ratios of O(oxide)/Fe are significantly larger than one while the ratios for other catalysts producing olefins are close to one (see Table 4). This suggests that the dominant surface phases of FeO in these two catalysts are different from the others. Sodium ions are considered to coordinate to iron via oxygen atoms, hence, high density of oxygen may increase the coordination number of sodium and decrease basicity. Formation of $FeCO_3$ is evidenced from the XRD pattern of $FeCu_{0.01}Na_{0.01}$ taken out after the reaction of 47 h. The absence of the peak attributed to $FeCO_3$ in other patterns for the catalysts endured for 27 h or less suggests gradual reduction of Fe_3O_4 on the surface to FeO or $FeCO_3$. Hence, it may be supposed that the gradual phase transfer results in increase in the olefin selectivity with time-on-stream. The surface densities of copper for $FeCu_{0.99}$ and $FeCu_{0.26}$ are high and it could be possible that hydrogenation activity of copper suppresses olefin formation. Formation of olefin has been proposed to be caused by stronger adsorption of carbon monoxide on basic sites where carbon monoxide is not perfectly reduced to alkanes [35]. However, in the hydrogenation of carbon dioxide the ratio of H_2/CO is very high, and this implies the presence of different mechanisms such as stabilization of olefinic species on basic sites, while further investigation is necessary to clarify it.

5. Conclusion

The catalytic hydrogenation of carbon dioxide over Fe–Cu catalysts was carried out. In conclusion it was found that the surface density of sodium was not negligible in the catalysts containing sodium less than 0.1 wt% and that the major surface phases of the catalysts were FeO and/or $FeCO_3$ after reaction. The clear relationship was revealed between the surface basicity of the catalyst and the olefin content in the product.

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References

[1] M. Röper, in: W. Keim (Ed.), Catalysis in C_1 Chemistry, Reidel, Dordrecht, 1983.

[2] H. Pichler, in: Frankenburg, Komarewsky, Rideal (Eds.), Advances in Catalysis, vol. 4, Academic Press, New York, 1952, p. 271.

[3] M.E. Dry, in: J.R. Anderson, M. Boudart (Eds.), Catalysis Science and Technology, vol. 1, Springer, New York, 1982, p. 159.

[4] M.-D. Lee, J.-F. Lee, C.-S. Chang, Bull. Chem. Soc. Jpn. 62 (1989) 2756.

[5] J. Barrault, C. Forquy, J.C. Menezo, R. Maurel, React. Kinet. Catal. Lett. 17 (1981) 373.

[6] M. Fujiwara, Y. Souma, J. Chem. Soc., Chem. Commun. (1992) 767.

[7] D.J. Dwyer, G.A. Somorjai, J. Catal. 52 (1978) 291.

[8] M. Pijolat, V. Perrichon, M. Primet, P. Bussiére, J. Mol. Catal. 17 (1982) 367.

[9] A. Kiennemann, R. Kieffer, E. Chornet, React. Kinet. Catal. Lett. 16 (1981) 371.

[10] R.C. Everson, H. Mulder, J. Catal. 143 (1993) 166.

[11] J.-C. Carlu, C. Caze, React. Polym. 12 (1990) 187.

[12] G.D. Weatherbee, C.H. Bartholomew, J. Catal. 87 (1984) 352.

[13] T. Inui, T. Takeguchi, A. Kohama, K. Kitagawa, in: L. Guczi (Ed.), New Frontiers in Catalysis, vol. B, 1993, p. 1453.

[14] R.J. Madon, W.F. Taylor, J. Catal. 69 (1981) 32.

[15] T. Inui, T. Takeguchi, Catal. Today 10 (1991) 95.

[16] S. Soled, E. Iglesia, R.A. Fiato, Catal. Lett. 7 (1990) 271.

[17] N.O. Egiebor, W.C. Cooper, Appl. Catal. 17 (1985) 47.
[18] D.J. Dwyer, G.A. Somorjai, J. Catal. 56 (1979) 249.
[19] H. Kölbel, P. Ackermann, E. Ruschenburg, R. Langheim, F. Engelhardt, Chem. Ing. Tech. 23 (1951) 153.
[20] I.E. Wachs, D.J. Duyer, E. Iglesia, Appl. Catal. 12 (1984) 201.
[21] D.B. Bukur, D. Mukesh, S.A. Patel, Ind. Eng. Chem. Res. 29 (1990) 194.
[22] H. Arakawa, A.T. Bell, Ind. Eng. Chem. Process Des. Dev. 22 (1983) 97.
[23] J. Benziger, R.J. Madix, Surf. Sci. 94 (1980) 119.
[24] M.E. Dry, T. Shingles, L.J. Boshoff, G.J. Oosthuizen, J. Catal. 15 (1969) 190.
[25] P. Biloen, J.N. Helle, W.M.H. Sachtler, J. Catal. 58 (1979) 95.
[26] J.W. Niemantsverdriet, A.M. van der Kraan, W.L. van Dijk, H.S. van der Baan, J. Phys. Chem. 84 (1980) 3363.
[27] R.A. Dictor, A.T. Bell, J. Catal. 97 (1986) 121.
[28] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg (Eds.), Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer, Eden Praine, 1978.
[29] JCPDS powder diffraction file: Fe_3O_4, 19-629; Cu, 4-836; Cu_2O, 35-1091; $FeCO_3$, 29-696.
[30] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures, Wiley, New York, 1954.
[31] J.P. Baltrus, J.R. Diehl, M.A. McDonald, M.F. Zarochak, Appl. Catal. 48 (1989) 199.
[32] C.D. Wagner, in: D. Briggs, M.P. Seah (Eds.), Practical Surface Analysis, vol. 1, p. 595.
[33] M. Pijolat, V. Perrichon, M. Primet, P. Bussiére, J. Mol. Catal. 17 (1982) 367.
[34] M.E. Dry, G.J. Oosthuizen, J. Catal. 11 (1968) 18.
[35] M.E. Dry, T. Shingles, L.J. Boshoff, G.J. Oosthuizen, J. Catal. 15 (1969) 190.