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Hydrogenation of carbon dioxide over copper-pyrochlore/zeolite composite catalysts

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Abstract

The hydrogenation of CO_2 was studied over composite catalysts obtained by mixing Cu-based methanol synthesis catalyst and HY zeolite. A mechanism associating methanol synthesis and MTG (methanol to gasoline) reaction allowed the formation of C_1–C_4 hydrocarbons. It was found that the catalytic behaviors of the composite catalysts were favorably influenced by the characteristics of the methanol synthesis catalysts. The Cu–$La_2Zr_2O_7$ catalyst we recently developed associated with HY zeolite exhibited interesting performances in hydrocarbon synthesis. The addition of ZrO_2 to Cu–$La_2Zr_2O_7$/HY enhanced the ability to produce hydrocarbons. Comparing composite catalyst systems prepared with different Cu-based methanol synthesis catalysts, the effect of Na contamination on methanol and hydrocarbon formation over composite catalysts were also discussed.

Keywords: Cu–$La_2Zr_2O_7$ catalysts; HY zeolite

1. Introduction

The hydrogenation of CO_2 produces essentially C_1 compounds such as methane and methanol. C_{2+} hydrocarbons are sometimes obtained in CO_2 based Fischer–Tropsch like reaction. Another method to produce hydrocarbons in a non-Anderson–Schultz–Flory distribution consists in converting methanol formed from CO_2–H_2 into hydrocarbons by MTG (methanol to gasoline) reaction [1–4]. A challenge is to perform the reaction in the one stage reactor using composite catalyst comprised of methanol synthesis catalyst and zeolite in spite of the fact that these catalysts exhibit their catalytic activity under completely different conditions (e.g., $T = 250°C$, $P = 50$ atm; $T = 400°C$, $P = 1$ atm, respectively).

Recently, it was found that Cu–Zn–Cr oxide catalysts prepared by dissolving CuO and ZnO in CrO_3, were more effective components of the composite catalyst [2] and the decrease of activity for methanol synthesis during the catalytic test was lower than the same type of catalysts obtained by the conventional coprecipitation with Na_2CO_3 [4]. These results probably suggest that alkali metals contamination through the preparation, influence the catalytic activity of the composite catalysts. On the other hand,

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active and thermically stable Cu-pyrochlore (Cu–$La_2Zr_2O_7$) methanol synthesis catalysts were developed in our laboratory [5]. This alkali-metal-free preparation method by coprecipitation of the mixed oxalates gave us a presage for a good behavior with zeolite. In this paper, the hydrogenation of CO_2 over composite catalysts comprised of Cu–$La_2Zr_2O_7$ and zeolite is reported.

2. Experimental

Cu–$La_2Zr_2O_7$ catalysts were prepared by the coprecipitation of a mixed solution of $Cu(NO_3)_2 \cdot 3H_2O$, $La(NO_3)_3 \cdot 6H_2O$ and $Zr(OC_3H_7)_4$ by oxalic acid in ethanol [5]. The precipitate was washed by ethanol, dried at 60°C and calcined at 550°C for 5 h and at 700°C for 0.5 h. The same technique was used for the preparation of Cu–ZnO(Oxa), Cu–ZnO–$La_2Zr_2O_7$(Oxa), Cu–ZrO_2–$La_2Zr_2O_7$(Oxa) and Cu–ZrO_2(Oxa) catalyst. The Cu–ZnO(CO_3) catalyst, as well as Cu–ZnO–$La_2Zr_2O_7$(CO_3), was obtained by conventional coprecipitation using Na_2CO_3. All catalysts contain 33% Cu by weight. The promoted catalysts also contain 33% Cu, 33% (ZnO or ZrO_2) and 33% $La_2Zr_2O_7$ by weight.

All composite catalysts were obtained by the physical mixing of equal amounts of methanol synthesis catalyst and HY zeolite, the Reference Catalyst of the Catalysis Society of Japan (JRC-Z-HY4.8; Si/Al = 4.8) [4]. The hydrogenation of CO_2 was carried out (50 atm, SV = 3000 ml/g cat./h, $H_2/CO_2 = 3$) using a previously described stainless steel apparatus [4]. All values of metallic copper surface area (SCu) were based on the weight of methanol synthesis catalyst.

3. Results and discussion

3.1. Catalytic activity of Cu–$La_2Zr_2O_7$/HY composite catalyst

Composite catalysts prepared by mixing Cu-based catalysts with HY zeolite were active for the formation of hydrocarbons at 400°C in the presence of CO_2–H_2 (Table 1). During the process over the composite catalyst, methanol before decomposing into CO reacts over zeolite to form hydrocarbons. The results obtained on Cu–$La_2Zr_2O_7$ and Cu–$La_2Zr_2O_7$/HY are in accordance with the plausible reaction path given in Eq. 1 and support that the hydrocarbons were formed via methanol in the case of composite catalyst. Indeed in the absence of zeolite, only small amounts of hydrocarbons were formed (mainly methane) whereas on composite catalysts a higher hydrocarbon formation was observed. In this case, ethane was the major component in the hydrocarbon fraction at 400°C and the selectivities of other hydrocarbons were comparatively low. This distribution, which is analogous to the results previously obtained in Cu–Zn–Cr oxide systems [2,4], is different from that of MTG reaction [6]. A fast hydrogenation of intermediary ethylene into ethane in the presence of H_2 at high pressure and metallic Cu species depressing the formation of heavier hydrocarbons can explain

Table 1
Hydrogenation of CO_2 over composite catalysts at 400°C

Catalyst	Conversion of CO_2 (%)	Conversion to (C mol-%)			Ratio of HC (C mol-%)				
		HC	Oxy [a]	CO	C_1	C_2	C_3	C_4	C_{5+}
Cu–ZnO(CO_3)/HY	36.5	2.4	0.2	33.9	9	61	22	6	2
Cu–$La_2Zr_2O_7$/HY	37.9	4.1	0.3	33.5	20	63	14	3	0
Cu–$La_2Zr_2O_7$	32.8	0.9	0.4	31.5	95	4	1	0	0

[a] MeOH + Me_2O.

this particular distribution [7] and the low coke formation as mentioned later.

$$CO_2 + 3H_2 \xrightarrow{\text{Cu - based catalyst}} (\text{MeOH}) \xrightarrow{\text{Zeolite}} \text{Hydrocarbon} \tag{1}$$

It can be observed on Table 1 that a better conversion into hydrocarbons was obtained over Cu–$La_2Zr_2O_7$/HY than over conventional Cu–ZnO(CO_3)/HY, although the Cu–ZnO(CO_3) has a comparable activity to Cu–$La_2Zr_2O_7$ catalyst in the absence of HY zeolite [5]. The yields of methanol over Cu–$La_2Zr_2O_7$ or Cu–ZnO(CO_3) were 5.9% and 6.0%, respectively, at 250°C and 50 atm.

Working at increasing temperature stepwise from 250 to 400°C (Fig. 1), it can be seen that methanol and dimethylether (by dehydration of methanol) were formed at 250–300°C. Hydrocarbons were predominant at higher temperatures (350–400°C) where the MTG reaction occurs. In both cases, the catalytic activities at low temperature (250–300°C), were fairly different between the beginning and the end (after reaction at 400°C) of the test. The deactivation was particularly drastic in the case of the Cu–ZnO(CO_3)/HY. This deactivation has been already discussed in our previous paper [4]. This can be explained by (i) sintering of metallic Cu and (ii) solid–solid interaction between methanol synthesis catalyst and zeolite. The evolution of the metallic Cu surface areas (SCu) [8] of Cu–ZnO(CO_3) and Cu–Zn(Oxa) under the different reaction conditions (but at comparable working times), in the presence or in the absence of HY, showed a drastic decrease of SCu in Cu–ZnO(CO_3)/HY after CO_2–H_2 reaction (Table 2), which can be related with the equivalent diminution of catalytic activity (Fig. 1b). In this case, the thermal sintering was low compared with the deactivation by the interaction with zeolite. The moderate decrease of SCu observed in the Cu–$La_2Zr_2O_7$/HY seems to be mainly due to the thermic effect.

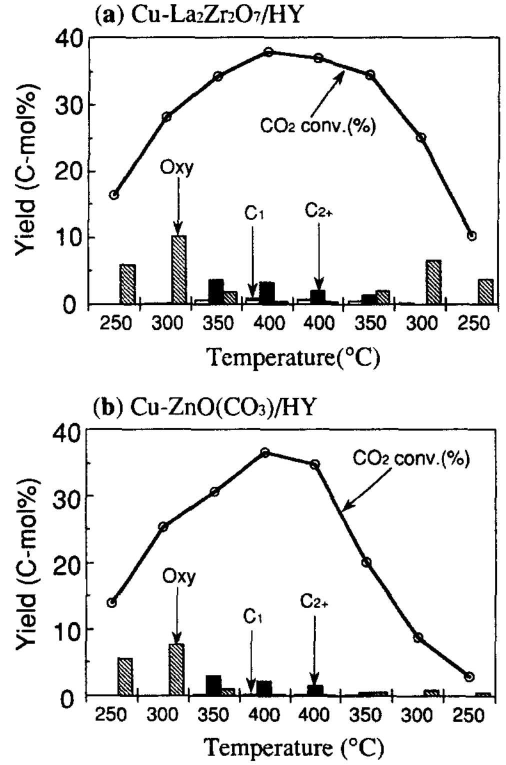

Fig. 1. Temperature dependence of $CO_2 + H_2$ reaction over composite catalysts.

3.2. Influence of the preparation technique

Table 3 which summarizes the characteristics of various composite catalysts suggests some important influences of the preparation method (i) on the initial methanol formation at 300°C, (ii) on the hydrocarbon formation at 400°C and (iii) on the deactivation of the catalytic activity evidenced by the decrease of SCu and methanol yield at 300°C during the catalytic test. Comparing Cu–ZnO(CO_3)/HY (containing 0.1 wt.-% of Na in Cu–ZnO) with the Na free Cu–ZnO(Oxa)/HY, we observe an important disparity in the catalytic behavior after the reaction at 400°C in spite of the slight difference in initial oxygenates formation. It seems that Na in Cu-based catalysts is an important factor of deactivating the composite catalyst. The better catalytic behavior of Cu–$La_2Zr_2O_7$/HY (Table 1) can be related to the original preparation

Table 2
Evolution of SCu (m^2/g) in different conditions

Conditions	Cu–ZnO(CO_3)	Cu–$La_2Zr_2O_7$
MeOH synthesis catalyst		
H_2 (270°C) [a]	18	10
H_2 (400°C) [a]	10	9
$CO_2 + H_2$ (400°C) [a]	6	6
Composite catalyst		
$CO_2 + H_2$(400°C) [b]	< 1	5

[a] After 5 h.

[b] After reacting for 8 h.

technique which avoids the presence of Na and gives a good stability by forming a definite compound with a reasonable BET surface area [5].

Another aspect, observed in catalysts used for the reaction at 400°C, is the difference in coke formation. After the reaction the catalysts prepared by Na_2CO_3 were black whereas the samples obtained with the oxalate technique were always gray. It can been seen from the results of Table 4, that the preparation technique (related with the presence of Na) also affected the coke formation (expressed as organic carbon contents) which can be considered as a cause of the deactivation of catalytic activity of zeolite. Although no mechanism for the preferential coke formation of the composite catalysts can be proposed, it seems that not only the activity for methanol formation but also the acidic property of HY zeolite were influenced by Na in methanol synthesis catalyst. Table 5 shows the decrease of the catalytic activity to convert methanol into dimethylether at 300°C or into C_{2+} hydrocarbons at 350°C between before and after used for the reaction at 400°C. In both cases, the deactivation of Cu–ZnO(CO_3)/HY was remarkable (22.8% and 35.6%) by comparing the catalytic behaviors of 'before' and 'after' with Cu–ZnO(Oxa)/HY. It seems that this deactivation of zeolite activity is induced by the neutralization of the acidic site by Na and the coke formation.

Table 4
Carbon content of catalysts used

Catalyst	C-contents (%)
Cu–Zn(CO_3)/HY	0.9
Cu–ZnO(Oxa)/HY	0.2
Cu–ZnO–$La_2Zr_2O_7$(CO_3)/HY	3.1
Cu–ZnO–$La_2Zr_2O_7$(Oxa)/HY	0.1
Cu–$La_2Zr_2O_7$(Oxa)/HY	0.1

3.3. Influence of the addition of ZnO or ZrO_2 to Cu–$La_2Zr_2O_7$/HY catalysts

In Cu–$La_2Zr_2O_7$ catalysts prepared by oxalate technique, the addition of ZnO or ZrO_2 has a positive effect on the methanol formation at 250–300°C, whereas if the same catalyst is associated with HY zeolite, the additives lead to reduced activities at 250–300°C (Fig. 2). A comparable deactivation was also observed in Cu–ZrO_2/HY. On the other hand, at 400°C a promoting effect of ZnO and ZrO_2 in hydrocarbon formation expressed by the increases of C_{2+} yield was evidenced (Table 6). This effect

Table 3
Characteristics of composite catalysts

Catalyst	300°C (Before) [a]		300°C (After) [b]		400°C HC yield (%)
	Oxy [c] yield (%)	SCu (m^2/g)	Oxy [c] yield (%)	SCu (m^2/g)	
Cu–ZnO(CO_3)/HY	7.7	18	0.8	0.2	2.2
Cu–ZnO(Oxa)/HY	9.3	10	2.2	0.6	3.8
Cu–ZnO–$La_2Zr_2O_7$(CO_3)/HY	6.9	9	0.5	0.2	2.4
Cu–ZnO–$La_2Zr_2O_7$(Oxa)/HY	9.8	8	2.7	0.6	4.5

[a] Before used at 400°C.

[b] After used at 400°C.

[c] MeOH + Me_2O.

Table 5
Deactivation of zeolite in composite catalyst

Catalyst	into Me_2O [a] (300°C)	into C_{2+} [b] (350°C)
Cu-ZnO(CO₃)/HY		
Before	69.7	74.8
After	52.4	48.2
Ratio(After/Before)	22.8	35.6
Cu-ZnO(Oxa)/HY		
Before	68.4	69.0
After	62.4	50.5
Ratio(After/Before)	8.8	26.8

[a] $Me_2O/(MeOH+Me_2O)$ (%).
[b] $C_{2+}/(MeOH+Me_2O+C_{2+})$ (%).

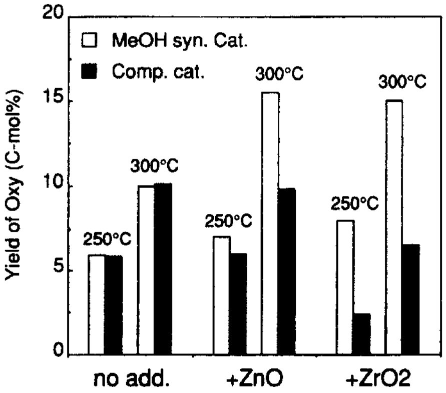

Fig. 2. Influence of the addition of ZnO and ZrO_2 on methanol synthesis catalyst and composite catalyst.

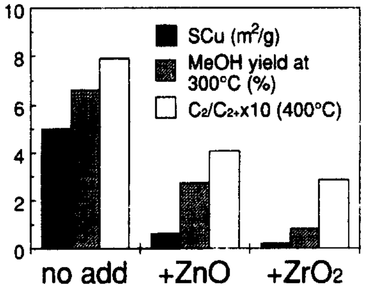

Fig. 3. Relation between SCu, MeOH yield and C_2/C_{2+} ratio.

can be explained by increase in methanol formation at high temperature (not directly related with SCu), but perhaps also by an additional isosynthesis reaction observed in the presence of CO and H_2 on ZrO_2 [9] and $La_2Zr_2O_7$ [10] but not over Cu–ZrO_2 and Cu–$La_2Zr_2O_7$ with CO_2–H_2. Table 6 also points out a product distribution that the promoted catalysts enhanced C_3 and C_4 hydrocarbon formation compared with non promoted one. This distribution can be related with the low SCu, as explained before, which lowers C_2/C_{2+} ratio by decreasing the hydrogenation of olefinic intermediates, favoring so the chain growth (Fig. 3).

4. Conclusion

Cu–$La_2Zr_2O_7$ methanol synthesis catalyst is an advantageous component for composite catalyst enabling the hydrogenation of CO_2 into lower hydrocarbons by the process including methanol synthesis and MTG reaction. The properties of the composite catalysts leading to a high performance can be attributed to the preparation techniques of Na free methanol synthesis catalyst with good thermal stability. From the comparison of Cu–ZnO(CO_3)/HY with Cu–$La_2Zr_2O_7$/HY, a solid–solid interaction between the components of the catalyst causes the sintering of Cu and the deactivation of the acidic sites of zeolite. These factors explained the catalytic behaviors of composite catalysts.

Table 6
Hydrogenation of CO_2 over composite catalysts at 400°C

Catalyst	Conversion of CO_2 (%)	Conversion to (C mol-%)			Ratio of HC (C mol-%)				
		HC	Oxy [a]	CO	C_1	C_2	C_3	C_4	C_{5+}
Cu–$La_2Zr_2O_7$/HY	37.9	4.1	0.3	33.5	20	63	14	3	0
Cu–ZnO–$La_2Zr_2O_7$/HY	37.1	5.0	0.4	31.7	8	37	34	16	5
Cu–ZrO_2–$La_2Zr_2O_7$/HY	37.2	6.7	0.2	30.3	9	26	38	18	9

[a] MeOH + Me_2O.

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