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Selective synthesis of C_2–C_4 hydrocarbons from $CO + H_2$ on composite catalysts

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A copper–zinc–aluminum methanol synthesis catalyst has been prepared using a precipitated hydrotalcite-type precursor that decomposes to a mixture of the corresponding amorphous oxides at a low temperature. TPR studies show that such a mixture is easy to reduce giving a highly dispersed catalyst. When this is mixed with a zeolite, the resulting hybrid catalyst gives C_2–C_4 hydrocarbons with very high selectivity. This may be useful in obtaining LPG from synthesis gas.

Keywords: Cu–Zn–Al catalyst; hybrid catalyst; hydrotalcite; methanol synthesis; synthesis of C_2–C_4 hydrocarbons; zeolites

1. Introduction

Increased demand for energy and chemicals renewed the interest in catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen. Fischer–Tropsch (FT) synthesis generally yields a wide range of products from methane to heavy oil and wax. It is possible, in principle, to terminate the chain growth process in FT synthesis by containing the catalyst particles within the small pores of a support [1–3]. This would result in a sharp decrease in the production of hydrocarbons above a certain chain length. However, the product distribution on FT catalysts follows the Anderson–Schulz–Flory law and a fairly high yield of undesirable methane cannot be avoided. An alternative to this approach is to convert the primary products obtained in the synthesis gas reaction on a methanol synthesis catalyst [4–6] or on a FT catalyst [7,8], to secondary reaction products on a shape selective zeolite catalyst.

Attempts have been made to develop catalysts to produce C_2–C_4 hydrocarbons similar in composition to LPG from synthesis gas. This includes Fe–Mn–Cu

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catalysts reported by Kodama et al. [9] and supported molybdenum catalyst of Murchison [10]. These, however, did not have enough C_2–C_4 selectivity and the products contained a very large amount of undesirable methane. Fujimoto et al. [5] reported Pd/SiO_2 and zeolite composites that had remarkable C_2–C_4 selectivity. Pd/SiO_2 is a known low pressure methanol synthesis catalyst. The methanol formed initially gets converted to hydrocarbons on the zeolite. The same authors also used commercial Cu–Zn(c) (BASF S8-45) and Zn–Cr (BASF 85-10 reduced) catalysts mixed with various zeolites and obtained C_3–C_4 hydrocarbons in high yield [6]. In this paper, we report the studies on the selective synthesis of C_2–C_4 hydrocarbons from synthesis gas on composite catalysts consisting of a Cu–Zn–Al low pressure methanol synthesis catalyst and a zeolite.

2. Experimental

2.1. CATALYST PREPARATION

Cu–Zn–Al mixed oxides are well known catalysts used in methanol and CO shift conversion reaction at low temperature [11–14]. A hydrotalcite-like precursor $(CuZn)_6Al_2CO_3(OH)_{16}\cdot 4H_2O$ ternary phase was prepared by the following method. To 1 M solution of the nitrates of copper, zinc and aluminum (atomic ratio 38 : 38 : 24), an excess of 1 M solution of $NaHCO_3$ was added at 60°C. The initial and the final pH of the solution were about 2 and 8 respectively. The precipitate was washed thoroughly with distilled water so that the filtrate had less than 10 ppm sodium. It was then dried at 90°C overnight. The precursor (coded MT1) was calcined in air for 24 h at 360°C (coded MT2) and reduced in hydrogen (coded MT3) at a flow rate 25 ml/min g of the solid for 8 h at 360°C to obtain the methanol synthesis catalyst.

NaY having $SiO_2/Al_2O_3 = 2.89$, was purchased from Associated Cement Company. ZSM-5 having $SiO_2/Al_2O_3 = 70$ was prepared as reported earlier [15]. Template-free zeolites were treated with a 2 N solution of NH_4NO_3 several times till the filtrate had less than 10 ppm sodium. It was then calcined at 550°C overnight. The resulting HZSM-5 was exchanged with a 0.01 M solution of $MnSO_4$ for 72 h at 80°C. The amount of exchanged manganese was found to be 4.65 per cent by weight.

The hybrid catalysts were prepared by mixing the desired amounts of the reduced methanol synthesis catalysts MT3 and a zeolite, pressed to pellets under pressure. The pellets were broken to particles of 180–300 micron size to be used as catalysts.

2.2. REACTION STUDIES

CO hydrogenation reactions were carried out at 300 psi in a fixed bed continuous flow microreactor (Autoclave Engineers BTR-Jr). One gram of the catalyst was loaded into the reactor and reduced at 360°C for 2 h in hydrogen at a flow rate of 50 ml/min after which the catalyst temperature was brought down to the reaction temperature. CO and H_2 gases (research grade, IOL) were used without further purification. Argon was used as an internal standard. The effluent gases were analysed by two on line gas chromatographs with FID and TCD detectors. The hydrocarbons were separated on a Porapak PS column (2 m × 1/8″) and CO, CO_2 and argon on a CTR-1 column (2 m × 1/4″). Data acquisition and peak integration were carried out by a SP 4270 integrator. Conversion was calculated as

$$\text{conversion} = \frac{[\mathrm{CO}]_r/[\mathrm{Ar}]_r - [\mathrm{CO}]_p/[\mathrm{Ar}]_p}{[\mathrm{CO}]_r/[\mathrm{Ar}]_r} \times 100\,,$$

where $[\mathrm{CO}]_r$ and $[\mathrm{Ar}]_r$ are the concentrations of CO and Ar in the reactant and $[\mathrm{CO}]_p$ and $[\mathrm{Ar}]_p$ are the respective concentrations in the product.

2.3. CATALYST CHARACTERIZATION

X-ray powder diffractograms were recorded on a Philips PW 1820 diffractometer using Cu K_α radiation with nickel filter.

TG analysis was carried out in nitrogen atmosphere in a Dupont thermal analyser upto 800°C using α-alumina as reference at a heating rate of 10°C/min.

Temperature programmed reduction (TPR) of hydrogen was studied in a conventional flow apparatus using TC detectors. A premixed gas containing 94% nitrogen and 6% hydrogen was used. Traces of oxygen and water were removed by passing the gas through heated copper turnings at 400°C and activated molecular sieves respectively.

About 50 mg of the sample (MT1) was loaded in a quartz reactor, heated in nitrogen at 360°C for 6 h and cooled down to room temperature. It was then reduced in 6% H_2 in nitrogen (flow rate 55 ml/min) at a heating rate of 10°C/min.

For TPD of hydrogen 200 mg of the methanol synthesis catalyst was reduced at 360°C in hydrogen at a flow rate of 25 ml/min for 2 h and then flushed with argon for 30 min. It was then cooled to room temperature in a flow of argon. Following the adsorption of hydrogen at room temperature, the TPD spectrum was recorded at an argon flow rate of 50 ml/min and heating rate of 20°C/min.

3. Results and discussion

The X-ray diffraction pattern of the MT1 sample matched well with that of crystalline hydrotalcite, $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$. The purity of the phase depends on the mode of addition of $NaHCO_3$ solution to the solution of the nitrates. After calcination for 24 h at 360°C, XRD showed two broad bands that were close to the

100 and 101 planes of ZnO. After reduction at 360°C, XRD showed two broad bands that could be assigned to ZnO and metallic zinc. The broadening of the lines indicates that the ZnO particles are of very small size. The copper and aluminum containing phases were X-ray amorphous.

Precipitation of the copper–zinc–aluminum catalyst precursor was studied by Gheradi et al. [14]. It was shown that pure hydrotalcite phase precipitates out when the molar ratio of Cu : Zn : Al in the solution is 38 : 38 : 24. Hence, this ratio was selected in our preparation. A change in the composition of the starting solution of the nitrates led to the precipitation of a mixture of hydrotalcite and malachite phases.

The thermogram of the precursor showed 31% weight loss at about 350°C and then a small loss near 700°C. In the synthesized sample with composition $(Cu_{2.46}Zn_{3.54})Al_2CO_3(OH)_{16}\cdot 4H_2O$, Cu^{2+} and Zn^{2+} have replaced Mg^{2+} randomly. The expected mass loss in the formation of a mixture of CuO, ZnO and Al_2O_3 is 30.84%, which matches well with the experimental mass loss. The hydrotalcite $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$ consists of alternate layers of $[Mg_6Al_2(OH)_{15}]^{3+}$ and $[CO_3H_2O]^{2-}$ sheets. A low temperature decomposition of such a phase is expected to give an amorphous oxidic mass. Crystallization of the individual oxides would require diffusion of the ions through large distance which is not likely at such low temperature. Reduction of this material may give rise to very finely dispersed copper. This appears to be the major advantage of using a hydrotalcite like precursor for the preparation of the Cu–Zn–Al low pressure methanol synthesis catalyst.

Easy reducibility of the precursor is seen from the TPR spectrum (fig. 1). Reduc-

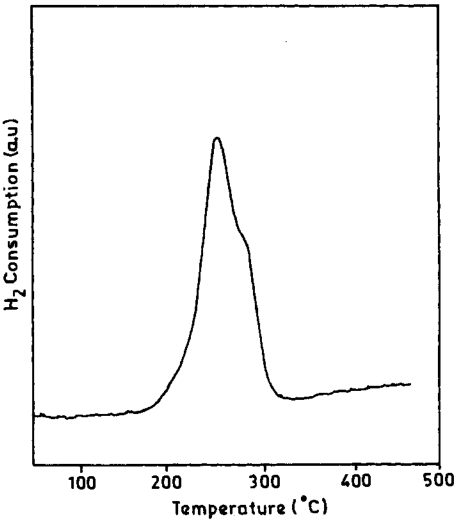

Fig. 1. TPR of calcined samples.

tion begins at 200°C and is complete at 275°C. The peak is at 255°C. It is essentially a single step reduction with a shoulder at 265°C. No further reduction was noticed even on heating upto 530°C.

TPD of hydrogen shows two peaks at 240 and 540°C. A small amount of hydrogen is weakly adsorbed but major part of it is adsorbed strongly and desorbs at a higher temperature.

3.1. METHANOL SYNTHESIS

Fig. 2 shows the results of methanol synthesis as a function of time on stream. At the beginning of the reaction, the product consisted of more than 80% methanol. After about 3 h, a nearly constant product composition was reached. The product contained C_1–C_5 hydrocarbons and nearly 50% methanol. No aromatic product was detected. From this, it is clear that methanol is formed first, which decomposes to aliphatic hydrocarbons on the acidic alumina. Ramarason et al. [16] also reported the similar behaviour on Cu/Zn/Al_2O_3 catalyst. Poisoning the acidic sites with ammonia gave methanol with 85% selectivity.

Conversion of methanol to hydrocarbons is enhanced very much by raising the temperature and at 300°C the product did not contain any methanol. The product pattern as well as CO conversion, however, is unaffected by increase of pressure, as seen from table 1. As expected, the product did not contain any olefin due to the

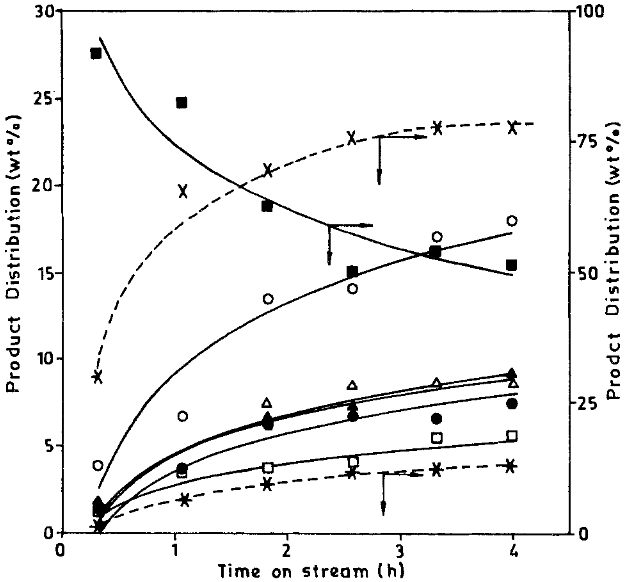

Fig. 2. Product composition in CO hydrogenation reaction on MT3 catalyst. (Temperature = 275°C; pressure = 300 psi; CO : H_2 = 1 : 3; W/F = 14.93 g-cat h/mol.) (■) CH_3OH; (×) CO converted; (○) CH_4; (□) C_2H_6; (△) C_3H_8; (▲) C_4H_{10}; (●) C_{5+}; (✳) CO converted to CO_2.

Table 1
Carbon monoxide hydrogenation over MT catalyst. (Pressure = 300 psi, CO : H_2 = 1 : 3, W/F = 14.93 g-cat h/mol, TOS = 4 h)

	Temperature (°C)			
	250	250[a]	275	300
conversion (mol%)				
CO	77.25	77.04	87.30	94.84
CO_2	12.76	11.82	16.53	19.57
CO	64.49	65.22	70.77	75.27
(conversion to hydrocarbon and oxygenates)				
product distribution (wt%)				
C_1	17.89	18.05	36.11	35.78
C_2	5.60	5.06	13.95	16.90
C_3	9.11	7.55	18.47	22.97
C_4	8.52	5.39	12.78	15.69
C_5	7.49	8.38	7.76	8.63
CH_3OH	51.35	54.99	6.16	–

[a] Pressure = 600 psi.

good hydrogenating activity of the MT3 catalyst. Since cyclization of the olefins at the acidic sites is the route to aromatics, no aromatics was found in the product. Although the C_2–C_4 hydrocarbons are formed in good yield at 300°C, the major problem with the MT3 catalyst is the formation of a large amount of methane that is difficult to separate from CO.

3.2. SYNGAS CONVERSION ON MT3 + ZEOLITE COMPOSITES

Table 2 shows the results of syngas conversion on the various MT3 + zeolite composite catalysts taken in the weight ratio 1 : 1. The results on the pure MT3 catalyst are also included in the table for comparison. The product did not contain any unsaturated hydrocarbons. Although the amount of MT3 catalyst in the composites was half of that present in the pure catalyst, CO conversion has not decreased to the same extent (except in the case of the composite containing NH_4ZSM-5). The higher than expected conversion of CO on the composite catalysts is because of the ability of the acidic zeolites to convert methanol to hydrocarbons. On these catalysts, the conversion of CO to hydrocarbons takes place in two steps:

$$CO + H_2 \rightarrow CH_3OH \rightarrow \text{hydrocarbons}.$$

Under the conditions of the reaction, conversion of methanol to hydrocarbons on the zeolite is the rate determining step. A zeolite with good catalytic activity for this reaction will increase the reaction rate and hence conversion. When a catalyst con-

Table 2
CO conversion and product distribution on various composite catalysts. (Temperature = 275°C, pressure = 300 psi, W/F = 14.93 g-cat h/mol, CO : H = 1 : 1, TOS = 4 h)

	MT3 [a]	MT3 + HY	MT3 + MnZSM-5 [a]	MT3 + MnZSM-5	MT3 + MnZSM-5 [b]	MT3 + HZSM-5	MT3 + NH_4ZSM-5
conversion (mol%)							
CO	87.30	56.03	66.55	37.10	27.59	51.99	22.50
CO_2	16.53	20.61	14.24	13.12	8.28	23.38	0.82
CO	70.11	35.42	52.31	23.98	19.21	28.61	21.68
(converted to hydrocarbons and oxygenates)							
product distribution (wt%)							
C_1	36.11	18.87	28.49	6.92	7.46	4.80	2.16
C_2	13.95	13.05	15.36	16.62	24.71	22.22	2.43
C_3	18.47	16.30	18.74	30.36	19.07	33.01	5.46
C_4	12.78	28.39	20.44	15.57	15.41	3.16	0.36
C_5	7.76	12.24	13.53	8.52	10.11	7.61	0.14
C_{6+}	–	6.20	3.44	16.07	22.02	7.59	1.69
CH_3OH	10.93	4.94	–	2.15	–	11.56	87.73

[a] CO : H = 1 : 3.
[b] MT3 : zeolite = 1 : 3.

taining MT3 and MnZSM-5 in the ratio 1 : 3 was used, the conversion was much lower and the product did not contain any methanol. Here, methanol formed was immediately converted to the hydrocarbons and the step of the reaction occurring on the MT3 catalyst was rate determining.

The amount of methane in the product was found to increase sharply by increasing the CO : H_2 ratio. It can be seen from table 2 that the amount of methane formed is much lower when HZSM-5 or MnZSM-5 was used in the composites. Further, MnZSM-5 containing catalysts showed better selectivity for C_2–C_4 hydrocarbons. This prompted us to study the MT3 + MnZSM-5 composite catalyst more thoroughly.

Fig. 3 shows the product pattern of CO + H_2 reaction on the MT3 + MnZSM-5 composite catalyst as a function of temperature. At 250°C, methanol is the major product. As the temperature is raised, the amount of methanol decreases due to its conversion to hydrocarbons. The C_2–C_4 selectivity is obtained at 275°C. The highest amount of methane and carbon dioxide in the product increases with temperature. The latter is formed by water–gas shift reaction that dominates at higher temperature.

Fujimoto et al. [6] noticed a large amount of aromatics to be formed by carrying out the synthesis gas reaction on Pd/SiO_2 + ZSM-5 composite catalyst, whereas no aromatic product was formed in our reactions. It is known that methanol decomposition on the acidic zeolites gives olefins that undergo cyclization to the

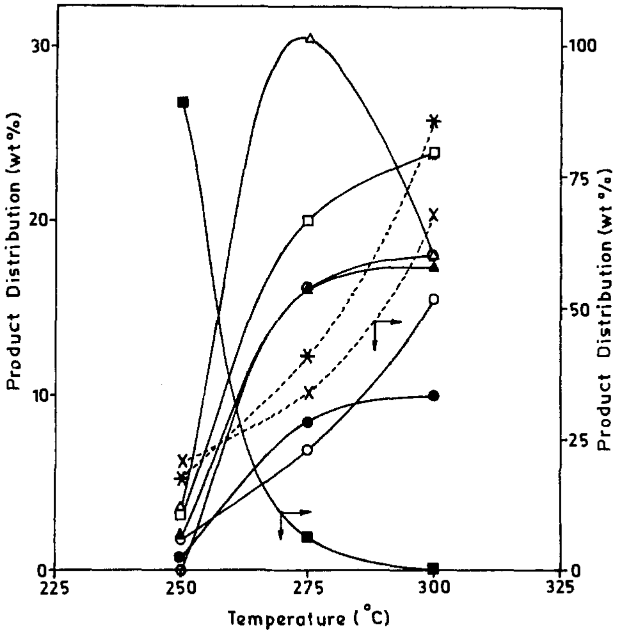

Fig. 3. Product distribution during $CO + H_2$ reaction on MT3 + MnZSM-5 catalyst. (Pressure = 300 psi; $CO : H_2 = 1 : 1$; $W/F = 14.93$ g-cat h/mol.) (■) CH_3OH; (×) CO converted; (○) CH_4; (□) C_2H_6; (△) C_3H_8; (▲) C_4H_{10}; (●) C_5; (⬡) C_{6+}; (⁎) CO converted to CO_2.

aromatics. It is likely that the olefins undergo rapid hydrogenation on the MT3 catalyst thus preventing the formation of aromatics.

It is believed that methanol conversion on acidic catalysts proceeds through the formation of CH_3^+ carbonium ion. Methylene insertion leads to the chain growth and various carbonium ions are formed that give rise to the olefins. CH_3^+ being the least stable, it will quickly change to $C_2H_5^+$ thus reducing the methane formation. The relative rate of formation of these carbonium ions of various chain lengths determines the selectivity for the C_2–C_4 olefins. In the case of the MT3 + zeolite composite catalysts, rapid hydrogenation of these olefins is responsible for the high C_2–C_4 paraffin selectivity.

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References

[1] C.D. Chang and R.F. Socha, US Patent 4,472,535 (1985).
[2] F.A.P. Cavalcanti, A.Yu. Stakheev and W.H.M. Sachtler, J. Catal. 134 (1992) 226.

[3] A. Shamsi, V.U.S. Rao, R.J. Gormley, R.T. Obevmyer, R.R. Schel and J.M. Stencel, Appl. Catal. 27 (1986) 55.

[4] C.D. Chang, Catal. Rev.-Sci. Eng. 25 (1983) 1.

[5] K. Fujimoto, H. Saima and H. Tominaga, J. Catal. 94 (1985) 16.

[6] K. Fujimoto, H. Saima and H. Tominaga, Ind. Eng. Chem. Res. 27 (1988) 920.

[7] P.D. Caeser, J.A. Brennan, W.E. Garwood and J. Ciric, J. Catal. 56 (1979) 274.

[8] C.D. Chang, C.T-W. Chu and R.F. Socha, J. Catal. 86 (1984) 289.

[9] S. Kodama, K. Tarama, A. Mishima, K. Fujita and M. Yasuda, Kogyo Kagaku Zasshi 48 (11) (1945) 3.

[10] C.B. Murchison, in: *Chemistry and Uses of Molybdenum*, eds. H.F. Barry and P.C.H. Mitchell (Climax, Michigan, 1982) p. 197.

[11] R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn, J.B. Bulko and T.P. Kobylinski, J. Catal. 56 (1979) 407.

[12] K. Klier, Adv. Catal. 31 (1982) 242.

[13] Ph. Courty and Ch. Marchilly, in: *Preparation of Catalysts III*, Studies in Surface Science and Catalysis, Vol. 16, eds. G. Poncelet, P. Grange and P.A. Jacobs (Elsevier, Amsterdam, 1983) p. 485.

[14] P. Gheradi, O. Ruggeri, F. Trifirò, A. Vaccari, G. Del Piero, G. Manara and B. Notari, in: *Preparation of Catalysts III*, Studies in Surface Science and Catalysis, Vol. 16, eds. G. Poncelet, P. Grange and P.A. Jacobs (Elsevier, Amsterdam, 1983) p. 723.

[15] C.V.V. Satayanarayana and D.K. Chakrabarty, Appl. Catal. 66 (1990) 1.

[16] E. Ramaroson, R. Kieffer and A. Koemmeann, Appl. Catal. 4 (1982) 281.