

were observed as products. These products are exactly what can be expected from the reaction involving PPN<sup>+</sup> analogue (Table 6).

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## The CO<sub>2</sub> Hydrogenation toward the Mixture of Methanol and Dimethyl Ether: Investigation of Hybrid Catalysts

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Catalytic hydrogenation of carbon dioxide for the simultaneous synthesis of methanol and dimethyl ether (together called oxygenates) over a combination of methanol synthesis and methanol dehydration catalysts has been studied. Various methanol synthesis and methanol dehydration catalysts were examined for this reaction. The addition of promoters like Ga<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> to Cu/ZnO catalyst gave much more enhanced yield on the formation of oxygenates. From the results, the promotional effect of Cr<sub>2</sub>O<sub>3</sub> has been explained in terms of increase in the intrinsic activity of Cu while that of Ga<sub>2</sub>O<sub>3</sub> being increase in the dispersion of Cu. Among the methanol dehydration catalysts examined, the solid acids bearing high population of intermediate-strength acid sites were found to be very effective for the production of oxygenates. HY zeolite which contains strong acid sites produce small amount of hydrocarbons as by-products. However, CuNaY zeolite in which the presence of strong acid sites are minimum gives very high oxygenates yield without the formation of hydrocarbons.

### Introduction

The subject on the utilization of CO<sub>2</sub> has attained great importance in recent years from the view point of the global warming nature of CO<sub>2</sub>. Among the methods of converting CO<sub>2</sub> directly into value added products, hydrogenation of CO<sub>2</sub> is perhaps the most simple route.<sup>1</sup> Cu/ZnO bas-

ed catalysts were found to be effective towards methanol synthesis either from CO or CO<sub>2</sub> hydrogenation.<sup>2-4</sup> Several reports have been cited on the simultaneous production of methanol (MeOH), and dimethyl ether (DME) from CO<sub>2</sub> or CO hydrogenation over hybrid catalysts, i.e., combination of methanol synthesis (MS) and methanol dehydration (MD) catalysts.<sup>5-7</sup> The improvement of oxygenate yield over hy-

brid catalysts is attributed to lessening thermodynamic constraint of CO<sub>2</sub> conversion.<sup>6</sup>

Although addition of various promoters like Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> etc. to Cu/ZnO based catalysts were reported in the literature,<sup>8-10</sup> no insight investigation on the role of these catalysts in improving the yield of oxygenates was cited. The *in-situ* conversion of MeOH to DME from CO<sub>2</sub> hydrogenation over several solid acid catalysts in combination with a suitable MS catalyst were reported,<sup>11</sup> but no clear cut characteristics of these solid acid catalysts were available. The development of hybrid catalyst system is mainly dependent on the characteristics of MS catalysts as well as MD catalysts. The characteristic features of an MS catalyst are: highly active copper metal area, dispersion of copper and the easy reduction of copper oxide phase. On the other hand, the activity of an MD catalyst lies on the acid site population present in it. The present investigation is an attempt to answer these points.

For this purpose, selected Cu/ZnO based MS catalysts have been characterized by temperature programmed reduction (TPR) and Cu area measurement by N<sub>2</sub>O pulse chromatographic method and MD catalysts by NH<sub>3</sub> temperature programmed desorption (TPD). The activities of MS catalysts were tested by mixing it with equal weight of  $\gamma$ -alumina and the activities of MD catalysts were tested by mixing it with a Cr<sub>2</sub>O<sub>3</sub> promoted CuO/ZnO catalyst. This work is an extension of the preliminary report which was given as a proceeding paper.<sup>12</sup>

## Experimental

Cu/ZnO based catalysts with and without promoters were prepared by conventional coprecipitation using Na<sub>2</sub>CO<sub>3</sub> as a precipitating agent, followed by washing and filtering. The resulted precipitate was dried in air at 393 K for 12 h and then calcined at 623 K for 5 h. HY zeolite was prepared by calcining NH<sub>4</sub>Y zeolite at 673 K for 24 h. The metal cation containing zeolites were prepared by ion-exchanging NaY zeolite or NH<sub>4</sub>Y zeolite with aqueous solutions of metal nitrates at 353 K for 24 h, followed by drying at 393 K for 24 h and calcining at 773 K for 24 h.

A home made pulse-reactor interfaced to a TCD equipped GC (Shimadzu Model 8A) through a 6-way sampling valve was used for TPR, NH<sub>3</sub> TPD and N<sub>2</sub>O pulse chromatographic method. In TPR studies of the MS catalysts, the catalyst was activated under He flow at 673 K for 1 h, cooled to 323 K followed by replacing He with H<sub>2</sub>/Ar (5% H<sub>2</sub>) mixture and simultaneously the temperature was increased at a rate of 10 K/min up to 873 K, where the flow of H<sub>2</sub>/Ar mixture was continued for 1 h. For NH<sub>3</sub> TPD studies of MD catalysts, the activated MD catalyst under He flow at 673 K for 1h was cooled to 373 K, where He flow was replaced by NH<sub>3</sub>. The NH<sub>3</sub> flow was maintained for 3 h during which the adsorption of NH<sub>3</sub> on the catalyst took place. After the completion of NH<sub>3</sub> adsorption, NH<sub>3</sub> was replaced by He flow and was continued for 1 h at the same temperature in order to remove the physisorbed NH<sub>3</sub>, followed by increasing the temperature at a rate of 7.6 K/min up to 873 K where He flow was maintained for further 1 h. Both H<sub>2</sub> consumption on MS catalyst and the desorbed NH<sub>3</sub> from MD catalyst was monitored by a TCD and the data

was recorded by a GC software (dsCHROM plus).

For the measurement of Cu metal area, the catalyst was reduced under H<sub>2</sub>/Ar (5% H<sub>2</sub>) mixture at 523 K for 3 h, followed by cooling to 333 K under He flow prior to the N<sub>2</sub>O pulse adsorption. Porapak T column was used to separate N<sub>2</sub>O and N<sub>2</sub> gases coming out of the catalyst due to the interaction of N<sub>2</sub>O with Cu metal as: 2Cu+N<sub>2</sub>O → Cu<sub>2</sub>O+N<sub>2</sub>. By assuming the number of Cu atoms as 1.46 × 10<sup>19</sup>/m<sup>2</sup> in a monolayer, the Cu metal area was calculated. The details of this technique were described elsewhere.<sup>13</sup>

Prior to the activity test, the hybrid catalyst, mixture of an MS catalyst and an MD catalyst in one to one weight ratio (size: 60-80 mesh), placed in a fixed bed micro reactor was reduced at 523 K in H<sub>2</sub>/N<sub>2</sub> (10% H<sub>2</sub>) mixture. The reactor was made of a stainless steel tube with an inner diameter of 4.5 mm. The hydrogenation of CO<sub>2</sub> was carried out in a temperature range of 523 K at a pressure of 30 kg/cm<sup>2</sup> and at a space velocity of 1800 mL/g<sub>cat</sub>·h maintaining H<sub>2</sub>/CO<sub>2</sub>=3. Effluent gas from the reactor was analyzed by on-line gas chromatograph (Donam model DS 6200) using carbosphere column (connected to TCD) for CO<sub>2</sub> and CO and Porapak T column (connected to FID) for MeOH, DME and hydrocarbons. The tubing from the reactor to the GC and the back pressure regulator, which was used for maintaining reaction pressure, were heated at 423 K so as to avoid any condensation of the products.

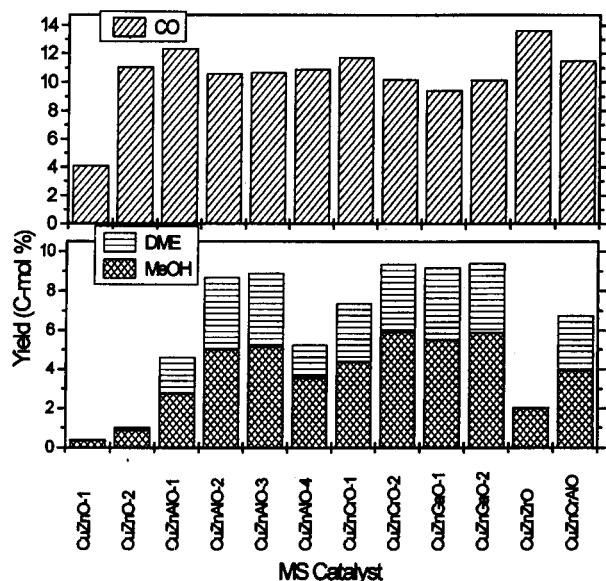
In order to know the effect of the promoters in MS catalysts on the activity, an MS catalyst was mixed with equal weight ratio of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and tested for CO<sub>2</sub> hydrogenation. To find out the effect of solid acid on the yield of oxygenates, the solid acid was mixed with equal weight ratio of Cr<sub>2</sub>O<sub>3</sub> promoted Cu/ZnO catalyst.

## Results and Discussion

In the primary stage of this work, various MS catalysts were prepared according to the compositions appeared to be effective for the methanol synthesis from CO<sub>2</sub> hydrogenation in the literature,<sup>14-16</sup> and then their catalytic activities were examined in the oxygenates synthesis as being mixed with  $\gamma$ -alumina. The results are shown in Figure 1. Among the examined catalysts, CuZnCrO-2, CuZnGaO-2, CuZnGaO-1, CuZnAlO-3 have been proven to be very active catalysts.

As representative MS catalysts, CuZnO-2, CuZnAlO-2, CuZnGaO-1, CuZnCrO-2 and CuZnZrO were chosen to investigate the details further. In all the catalysts, the Cu composition is maintained nearly 50% by weight. The remaining portion is mainly with ZnO. The composition of the promoter is fixed based on the activity results shown in Figure 1.

The physical characteristics of the representative catalysts are shown in Table 1. It is observed from the table that the BET surface area of the Cu/ZnO catalyst has been increased by the addition of promoters. The TPR patterns of these catalysts (Figure 2) indicate the presence of Cu(II) oxide in two different environments, one is due to uninteracted CuO (T<sub>max</sub>~620 K) and the other is due to interaction with ZnO (T<sub>max</sub>~660 K), in addition to the presence of Cu(I) oxide in minor portion (T<sub>max</sub> > 773 K). The higher T<sub>max</sub> of bulk CuO phase as shown in this figure was



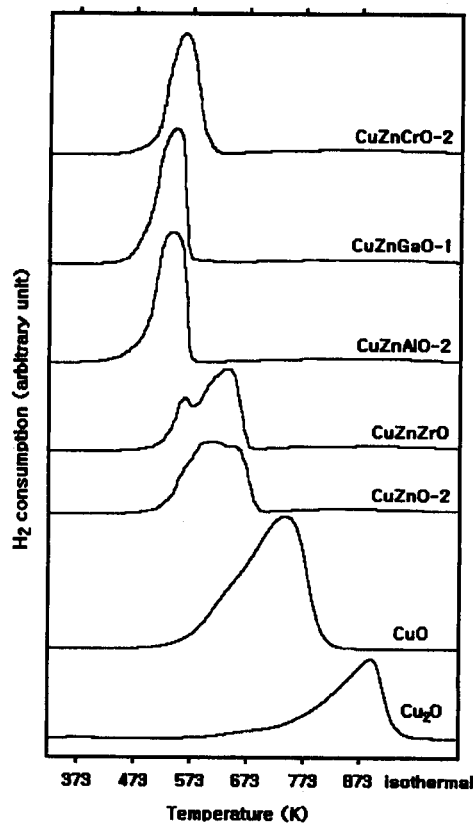
**Figure 1.** Catalytic activity of various MS catalysts mixed with  $\gamma$ -alumina in the  $\text{CO}_2$  hydrogenation; catalyst=MS catalyst (0.5 g)+ $\gamma$ -alumina (0.5 g), temperature=523 K, pressure=30 kg/cm<sup>2</sup>,  $\text{H}_2/\text{CO}_2=3$ , flow rate=30 mL/min. MS catalysts (compositions of reduced forms, wt%): CuZnO-1 (Cu/ZnO=25.5/74.5), CuZnO-2 (Cu/ZnO=50/50), CuZnAlO-1 (Cu/ZnO/ $\text{Al}_2\text{O}_3=29.4/70.4/10.2$ ), CuZnAlO-2 (Cu/ZnO/ $\text{Al}_2\text{O}_3=50/45/5$ ), CuZnAlO-3 (Cu/ZnO/ $\text{Al}_2\text{O}_3=52/45/3$ ), CuZnAlO-4 (Cu/ZnO/ $\text{Al}_2\text{O}_3=54.8/35.2/10$ ), CuZnCrO-1 (Cu/ZnO/ $\text{Cr}_2\text{O}_3=37.3/47.8/4.9$ ), CuZnCrO-2 (Cu/ZnO/ $\text{Cr}_2\text{O}_3=50/45/5$ ), CuZnGaO-1 (Cu/ZnO/ $\text{Ga}_2\text{O}_3=50/25/25$ ), CuZnGaO-2 (Cu/ZnO/ $\text{Ga}_2\text{O}_3=54.8/27.4/17.8$ ), CuZnZrO (Cu/ZnO/ $\text{ZrO}_2=50/40/10$ ), CuZnCrAlO (Cu/ZnO/ $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3=44.7/26.1/25.2/4$ ).

**Table 1.** Characteristics of methanol synthesis catalysts determined by  $\text{N}_2$  adsorption and  $\text{N}_2\text{O}$  surface titration

Catalyst	BET surface area (m <sup>2</sup> /g)	Cu area <sup>a</sup> (m <sup>2</sup> /g)	Cu Crystallite Size (nm)	Dispersion (%)
CuZnO-2	17.4	4.33	77.7	1.33
CuZnAlO-2	73.4	22.30	15.1	6.87
CuZnGaO-1	92.5	26.75	12.6	8.24
CuZnCrO-2	35.8	10.24	32.8	3.15
CuZnZrO	24.8	9.95	33.8	3.07

<sup>a</sup> based on the catalyst mass of reduced form.

also reported.<sup>17</sup> Even though the presence of ZnO is to increase the  $T_{\text{max}}$  slightly, its beneficial role as antisintering agent, to give uniform distribution of Cu etc., have been described by many others.<sup>18-20</sup> Lowering of  $T_{\text{max}}$  and also the presence of CuO phase in single environment is observed from the TPR patterns of  $\text{Cr}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  promoted Cu/ZnO catalysts. This indicates that the CuO exists as a homogeneous phase and that the addition of those promoters helps to reduce CuO phase easily. No significant promotional effect due to  $\text{ZrO}_2$  addition is observed from its TPR pattern. The increase of  $T_{\text{max}}$  due to ZnO addition to CuO/ $\text{Al}_2\text{O}_3$  catalysts is reported by Robinson and Mol.<sup>21</sup> The variation between the  $T_{\text{max}}$  of CuO phase shown in this figure and that of reported value<sup>21</sup> should be due to the difference in the method of preparation and the temperature programming rate.



**Figure 2.** TPR patterns of methanol synthesis catalysts.

The  $\text{N}_2\text{O}$  chemisorption results of the catalysts have been displayed in Table 1. The Cu metal area values were calculated according to the method described by Evans *et al.*<sup>13</sup> Assuming that all the copper oxide was reduced during the reduction step adopted prior to the  $\text{N}_2\text{O}$  pulse adsorption, the particle size of Cu metal was calculated using the equation,  $d_{\text{Cu}}=6000/(8.92(S_{\text{Cu}}))$ , where  $d_{\text{Cu}}$  is the Cu particle size (assuming the presence of spherical particles), 8.92 is the density of the Cu metal in g/cm<sup>3</sup> and  $S_{\text{Cu}}$  is the Cu metal area in m<sup>2</sup>/g<sub>Cu</sub>. Bartley *et al.*<sup>22</sup> have also applied this equation for calculating the Cu particle size from oxygen adsorption measurements. Parris and Klier<sup>23</sup> obtained a fairly good agreement between the average particle size obtained from X-ray line broadening and from oxygen chemisorption experiments. Dispersion of Cu was calculated as the ratio of number of surface Cu atoms (obtained from the  $\text{N}_2\text{O}$  uptake) to the total number of Cu atoms present in the catalyst as reported in the literature.<sup>24,25</sup> From the Table 1, it is observed that addition of promoters increased the Cu area, dispersion and decreased the Cu particle size. The Cu area values are found to be in the order: Cu/ZnO/ $\text{Ga}_2\text{O}_3$  > Cu/ZnO/ $\text{Al}_2\text{O}_3$  > Cu/ZnO/ $\text{Cr}_2\text{O}_3$  > Cu/ZnO/ $\text{ZrO}_2$  > Cu/ZnO. Thus it is clear that  $\text{Ga}_2\text{O}_3$  addition has an advantage in increasing the Cu metal area which is attributed due to the formation of more number of smaller Cu crystals. This is in line with the observed values of dispersion and the Cu crystallite size. Among the promoters,  $\text{ZrO}_2$  followed by  $\text{Cr}_2\text{O}_3$  roles are minimal either in increasing the Cu metal area or the dispersion of Cu, although their effect is clearly visible when compared to the unpromoted catalyst.

**Table 2.** Comparison of activities of MS catalysts in combination with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>a</sup>

Catalyst	STY <sup>b</sup> (C mol·kg <sub>cat.</sub> <sup>-1</sup> ·h <sup>-1</sup> )		TOF for oxygenates <sup>c</sup> (h <sup>-1</sup> )	DME selectivity in oxygenates (%)
	CO	Oxygenates		
CuZnO-2	2.05	0.19	4.11	15.4
CuZnAlO-2	1.97	1.62	6.92	42.3
CuZnGaO-1	1.75	1.71	6.06	39.9
CuZnCrO-2	1.90	1.74	15.84	36.7
CuZnZrO	2.53	0.39	3.64	4.30

<sup>a</sup> Reaction Conditions: catalyst=MS catalyst (0.5 g)+ $\gamma$ -alumina (0.5 g), temperature=523 K, pressure=30 kg/cm<sup>2</sup>, H<sub>2</sub>/CO<sub>2</sub>=3, flow rate=30 mL/min. <sup>b</sup> based on the total mass of hybrid catalysts packed in the reactor. <sup>c</sup> based on the no. of Cu atom exposed on the surface.

Table 2 shows the catalytic activity data for the formation of CO and oxygenates over hybrid catalysts (0.5 g of MS catalyst+0.5 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). From the data, it is clear that while ZrO<sub>2</sub> addition promotes the CO formation mainly, other promoters are responsible for the formation of oxygenates.

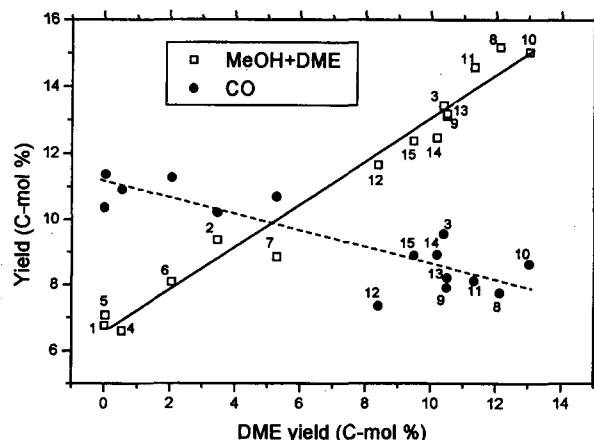
Turnover frequency (TOF) value, which is the number of moles of oxygenates produced per the number of moles of surface Cu per second has been calculated from the rate of formation of oxygenates and Cu-dispersion values, and are presented in Table 2. It is interesting to note that the rate of oxygenates produced are nearly same over Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> promoted catalysts. The order of rate of oxygenates formation over different MS catalysts are found to be: Cu/ZnO < Cu/ZnO/ZrO<sub>2</sub> << Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> ~ Cu/ZnO/Ga<sub>2</sub>O<sub>3</sub> ~ Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub>. It is interesting to observe that even though the number of surface Cu atoms over Ga<sub>2</sub>O<sub>3</sub> promoted catalyst are very high compared to other promoted catalysts, the rate of formation of oxygenates over this catalyst is only comparable to the other promoted catalysts. The TOF values indicate the beneficial role of Cr<sub>2</sub>O<sub>3</sub> addition. The TOF values over different MS catalysts are in the order: Cu/ZnO/ZrO<sub>2</sub> ~ Cu/ZnO < Cu/ZnO/Ga<sub>2</sub>O<sub>3</sub> << Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> << Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub>. Thus, Cr<sub>2</sub>O<sub>3</sub> addition to Cu/ZnO catalyst enhances the TOF *i.e.*, intrinsic activity.

Knozinger and Co-workers<sup>26,27</sup> have proposed that the formation of ether takes place between the adsorbed alcohol on a acidic site and adsorbed alcoxide on a basic site. In order to understand the effect of acidic catalysts on the yield of oxygenates, particularly for the production of DME, many kinds of solid acids were examined for the oxygenates synthesis as they were mixed with the effective

**Table 4.** Acid-site distribution of solid acids investigated by NH<sub>3</sub> TPD

Solid-Acid	Acidity <sup>a</sup> (mmol <sub>NH3</sub> /g <sub>cat.</sub> )						
	Total	373-473 K	473-573 K	573-673 K	673-773 K	773-873 K	>873 K
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.74	0.07	0.19	0.10	0.12	0.18	0.10
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	1.43	0.25	0.35	0.22	0.23	0.24	0.15
NaY	0.77	0.43	0.33	0.01	0	0	0
Cu <sub>72</sub> Na <sub>28</sub> Y	3.33	0.60	1.62	0.85	0.15	0.07	0.03
Na <sub>44</sub> H <sub>56</sub> Y	1.93	0.50	0.95	0.34	0.07	0.04	0.03
HY	2.31	0.38	0.94	0.53	0.20	0.14	0.13

<sup>a</sup> no. sites that indicate different acid strength in terms of desorption temperature (K).



**Figure 3.** The dependence of the yields of CO and oxygenates on the activity of DME formation in the CO<sub>2</sub> hydrogenation; 250 °C, CuZnCrO-2 (0.5 g)+MDC (0.5 g), pressure=30 kg/cm<sup>2</sup>, flow rate=30 mL/min. MD catalysts: 1 (none), 2 ( $\gamma$ -alumina), 3 (silica-alumina), 4 (NaY), 5 (K<sub>80</sub>Na<sub>20</sub>Y), 6 (Mg<sub>57</sub>Na<sub>43</sub>Y), 7 (Ca<sub>49</sub>Na<sub>51</sub>Y), 8 (Cu<sub>72</sub>Na<sub>28</sub>Y), 9 (Zn<sub>70</sub>Na<sub>30</sub>Y), 10 (HY), 11 (Na<sub>44</sub>H<sub>56</sub>Y), 12 (Mg<sub>33</sub>-H<sub>67</sub>Y), 13 (Ca<sub>15</sub>H<sub>85</sub>Y), 14 (Cu<sub>80</sub>H<sub>20</sub>Y), 15 (Zn<sub>73</sub>H<sub>27</sub>Y).

**Table 3.** Nature of acid-sites present on zeolites

Sample	pK <sub>a</sub>	Nature of acid sites
NaY	> +4.0	Weak
Cu <sub>72</sub> Na <sub>28</sub> Y	≥ -5.6	Weak and Intermediate
Na <sub>44</sub> H <sub>56</sub> Y	≥ -5.6	Weak and Intermediate
Cu <sub>72</sub> Na <sub>28</sub> Y	≥ -5.6	Weak and Intermediate
HY	≥ -8.2	Weak, Intermediate and Strong

MS catalyst, CuZnCrO-2. From the reaction results, the dependence of the yield of oxygenates and CO on the activity of DME formation are shown in Figure 3. The combination of an MS catalyst with a highly active MD catalyst creates a strong driving force for CO<sub>2</sub> conversion to oxygenates thereby the yield of total oxygenates is improved while the yield of CO is decreased.

Among the examined MD catalysts, some catalysts were selected for the detail investigation. In order to find out the nature of acid sites, Hammett indicators have been used. Table 3 shows the nature acid sites present on modified Y-zeolites. The acid-site distributions of selected solid acids have been investigated by TPD of NH<sub>3</sub>. The acid-site distribution in various temperature ranges of these catalysts are shown in Table 4.

For the sake of convenience, the above data has been di-

**Table 5.** Comparison of activities of various MD catalysts<sup>a</sup>

Catalyst	STY <sup>b</sup> (C mol·kg <sub>cat.</sub> <sup>-1</sup> ·h <sup>-1</sup> )			DME selectivity in oxygenates (%)
	CO	Oxygenates	Hydrocarbons	
γ-Al <sub>2</sub> O <sub>3</sub>	1.90	1.74	—	36.7
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	1.77	2.49	—	77.3
NaY	2.03	1.22	—	8.0
Cu <sub>72</sub> Na <sub>28</sub> Y	1.44	2.82	—	79.8
HY	1.60	2.79	0.10	86.6
Na <sub>44</sub> H <sub>56</sub> Y	1.51	2.71	—	77.8

<sup>a</sup> Reaction Conditions: Catalyst=Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> (0.5 g)+MD catalyst (0.5 g) temperature=523 K, pressure=30 kg/cm<sup>2</sup>, H<sub>2</sub>/CO<sub>2</sub>=3, flow rate=30 mL/min. <sup>b</sup> based on the total mass of hybrid catalysts packed in the reactor.

vided into three groups, i.e., as weak acids in the temperature range of 373-573 K, moderate acid sites in the temperature range of 573-673 K and as strong acid sites in the temperatures beyond 673 K. The total acidity of the solid acids are found to be in the order: CuNaY > HY > NaHY > Si-Al > NaY-γ-Al<sub>2</sub>O<sub>3</sub>. Among the solid acids, NaY and NaHY possess low number of acid sites and NaY contains only weak acid sites. In case of γ-alumina, in spite of the fact that it contains low number of total acid sites, all these are spread all over the regions. The zeolite CuNaY shows the most abundant amount of moderate acid sites. A similar trend of the pattern is observed in the case of NaHY but the overall acid sites on it are not so high as compared to those present on CuNaY and HY. The acid sites are evenly spread in all the regions in case of silica-alumina. The catalytic activities of these solid acids in combination with CuZnCr-2 are shown in Table 5.

The presence of almost only weak acid sites on NaY makes it inferior compared to all other MD catalysts in producing DME. Even though the total number of acid sites on γ-Al<sub>2</sub>O<sub>3</sub> are low, the presence of fairly good number of moderate and strong acid sites on it is the responsible factor in yielding little amount of DME. The presence of strong acid sites on HY are responsible in yielding low amounts of hydrocarbons, which are light alkanes (mainly C<sub>2</sub>-C<sub>4</sub>). Although the strong acid sites on silica-alumina are outnumbered those present on HY, the overall acid sites on silica-alumina are lower than those present on HY and this might be the reason for silica-alumina in not yielding the hydrocarbons. The presence of weak and moderate acid sites on CuNaY makes it an effective catalyst for DME synthesis.

### Conclusions

The following are the conclusions drawn out of this investigation.

1. Addition of Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> to Cu/ZnO permits easy reduction of CuO phase. However no such effect is observed in the case of ZrO<sub>2</sub> promoted catalyst.

2. Among all the promoters to Cu/ZnO, the role of Ga<sub>2</sub>O<sub>3</sub> in enhancing the number of active sites is clearly observed.

3. Although Cr<sub>2</sub>O<sub>3</sub> addition to Cu/ZnO can not create more number of active sites compared to Ga<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> promoted catalysts, its role is highly remarkable in increasing the intrinsic activity i.e., specific activity per site.

4. Among all the MD catalysts, CuNaY seems to be a

better dehydration catalyst and it is attributed to the presence of more number of moderate acid sites.

5. The presence of too much weak acid sites on NaY makes it inferior compared to all the MD catalysts in producing substantial quantities of DME.

6. From this work, it is concluded that Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub>+CuNaY is the best hybrid catalytic system in producing oxygenates from CO<sub>2</sub> hydrogenation.

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