

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

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The CO₂ 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 Ga₂O₃ and Cr₂O₃ to Cu/ZnO catalyst gave much more enhanced yield on the formation of oxygenates. From the results, the promotional effect of Cr₂O₃ has been explained in terms of increase in the intrinsic activity of Cu while that of Ga₂O₃ 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 CO₂ has attained great importance in recent years from the view point of the global warming nature of CO₂. Among the methods of converting CO₂ directly into value added products, hydrogenation of CO₂ is perhaps the most simple route.¹ Cu/ZnO bas-

ed catalysts were found to be effective towards methanol synthesis either from CO or CO₂ hydrogenation.²⁻⁴ Several reports have been cited on the simultaneous production of methanol (MeOH), and dimethyl ether (DME) from CO₂ or CO hydrogenation over hybrid catalysts, *i.e.*, combination of methanol synthesis (MS) and methanol dehydration (MD) catalysts.⁵⁻⁷ The improvement of oxygenate yield over hy-

brid catalysts is attributed to lessening thermodynamic constraint of CO₂ conversion.⁶

Although addition of various promoters like Al₂O₃, Ga₂O₃, Cr₂O₃ and ZrO₂ etc. to Cu/ZnO based catalysts were reported in the literature,⁸⁻¹⁰ 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 CO₂ hydrogenation over several solid acid catalysts in combination with a suitable MS catalyst were reported,¹¹ 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 N₂O pulse chromatographic method and MD catalysts by NH₃ temperature programmed desorption (TPD). The activities of MS catalysts were tested by mixing it with equal weight of γ -alumina and the activities of MD catalysts were tested by mixing it with a Cr₂O₃ promoted CuO/ZnO catalyst. This work is an extension of the preliminary report which was given as a proceeding paper.¹²

Experimental

Cu/ZnO based catalysts with and without promoters were prepared by conventional coprecipitation using Na₂CO₃ 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 NH₄Y zeolite at 673 K for 24 h. The metal cation containing zeolites were prepared by ion-exchanging NaY zeolite or NH₄Y 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, NH₃ TPD and N₂O 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 H₂/Ar (5% H₂) mixture and simultaneously the temperature was increased at a rate of 10 K/min up to 873 K, where the flow of H₂/Ar mixture was continued for 1 h. For NH₃ 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 NH₃. The NH₃ flow was maintained for 3 h during which the adsorption of NH₃ on the catalyst took place. After the completion of NH₃ adsorption, NH₃ was replaced by He flow and was continued for 1 h at the same temperature in order to remove the physisorbed NH₃, 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 H₂ consumption on MS catalyst and the desorbed NH₃ 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 H₂/Ar (5% H₂) mixture at 523 K for 3 h, followed by cooling to 333 K under He flow prior to the N₂O pulse adsorption. Porapak T column was used to separate N₂O and N₂ gases coming out of the catalyst due to the interaction of N₂O with Cu metal as: 2Cu+N₂O → Cu₂O+N₂. By assuming the number of Cu atoms as 1.46 × 10¹⁹/m² in a monolayer, the Cu metal area was calculated. The details of this technique were described elsewhere.¹³

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 H₂/N₂ (10% H₂) mixture. The reactor was made of a stainless steel tube with an inner diameter of 4.5 mm. The hydrogenation of CO₂ was carried out in a temperature range of 523 K at a pressure of 30 kg/cm² and at a space velocity of 1800 mL/g_{cat}·h maintaining H₂/CO₂=3. Effluent gas from the reactor was analyzed by on-line gas chromatograph (Donam model DS 6200) using carbosphere column (connected to TCD) for CO₂ 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 γ -Al₂O₃ and tested for CO₂ hydrogenation. To find out the effect of solid acid on the yield of oxygenates, the solid acid was mixed with equal weight ratio of Cr₂O₃ 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 CO₂ hydrogenation in the literature,¹⁴⁻¹⁶ and then their catalytic activities were examined in the oxygenates synthesis as being mixed with γ -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 un-interacted CuO (T_{max}~620 K) and the other is due to interaction with ZnO (T_{max}~660 K), in addition to the presence of Cu(I) oxide in minor portion (T_{max}>773 K). The higher T_{max} of bulk CuO phase as shown in this figure was

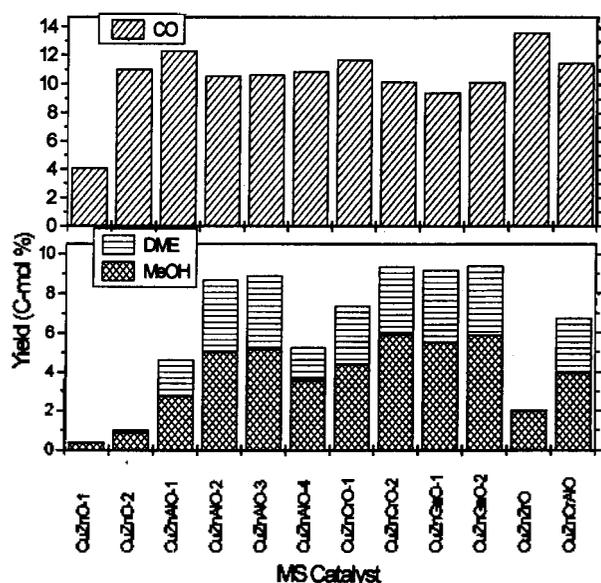


Figure 1. Catalytic activity of various MS catalysts mixed with γ -alumina in the CO_2 hydrogenation; catalyst=MS catalyst (0.5 g)+ γ -alumina (0.5 g), temperature=523 K, pressure=30 kg/cm², $\text{H}_2/\text{CO}_2=3$, flow rate=30 mL/min. MS catalysts (compositions of reduced forms, wt%): CuZnO-1 (Cu/ZnO=25.5/74.5), 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 N_2 adsorption and N_2O surface titration

Catalyst	BET surface area (m ² /g)	Cu area ^a (m ² /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

^a based on the catalyst mass of reduced form.

also reported.¹⁷ Even though the presence of ZnO is to increase the T_{max} slightly, its beneficial role as antisintering agent, to give uniform distribution of Cu etc., have been described by many others.¹⁸⁻²⁰ Lowering of T_{max} and also the presence of CuO phase in single environment is observed from the TPR patterns of Cr_2O_3 , Ga_2O_3 and Al_2O_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 ZrO_2 addition is observed from its TPR pattern. The increase of T_{max} due to ZnO addition to CuO/ Al_2O_3 catalysts is reported by Robinson and Mol.²¹ The variation between the T_{max} of CuO phase shown in this figure and that of reported value²¹ should be due to the difference in the method of preparation and the temperature programming rate.

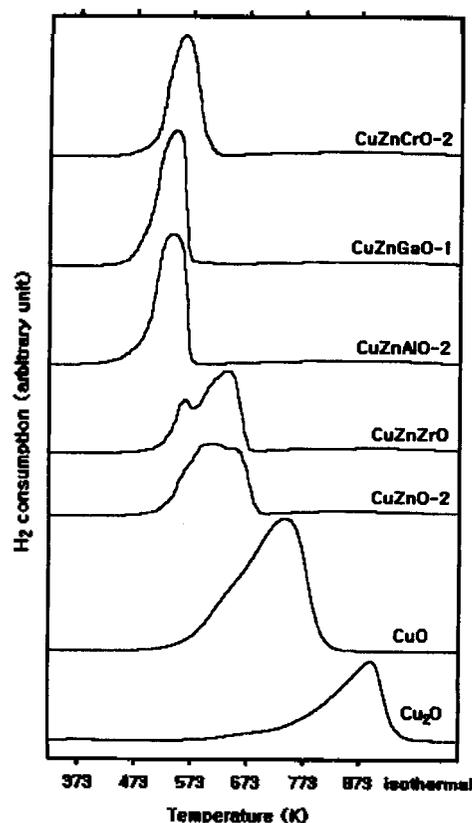


Figure 2. TPR patterns of methanol synthesis catalysts.

The N_2O 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.*¹³ Assuming that all the copper oxide was reduced during the reduction step adopted prior to the N_2O pulse adsorption, the particle size of Cu metal was calculated using the equation, $d_{\text{Cu}}=6000/(8.92(S_{\text{Cu}}))$, where d_{Cu} is the Cu particle size (assuming the presence of spherical particles), 8.92 is the density of the Cu metal in g/cm³ and S_{Cu} is the Cu metal area in m²/g_{Cu}. Bartley *et al.*²² have also applied this equation for calculating the Cu particle size from oxygen adsorption measurements. Parris and Klier²³ 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 N_2O uptake) to the total number of Cu atoms present in the catalyst as reported in the literature.^{24,25} 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/ Ga_2O_3 > Cu/ZnO/ Al_2O_3 > Cu/ZnO/ Cr_2O_3 > Cu/ZnO/ ZrO_2 > Cu/ZnO. Thus it is clear that Ga_2O_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, ZrO_2 followed by Cr_2O_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 γ -Al₂O₃^a

Catalyst	STY ^b (C mol·kg _{cat.} ⁻¹ ·h ⁻¹)		TOF for oxygenates ^c (h ⁻¹)	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

^a Reaction Conditions: catalyst=MS catalyst (0.5 g)+ γ -alumina (0.5 g), temperature=523 K, pressure=30 kg/cm², H₂/CO₂=3, flow rate=30 mL/min. ^b based on the total mass of hybrid catalysts packed in the reactor. ^c 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 γ -Al₂O₃). From the data, it is clear that while ZrO₂ 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 Al₂O₃, Ga₂O₃ and Cr₂O₃ promoted catalysts. The order of rate of oxygenates formation over different MS catalysts are found to be: Cu/ZnO < Cu/ZnO/ZrO₂ << Cu/ZnO/Al₂O₃ ~ Cu/ZnO/Ga₂O₃ ~ Cu/ZnO/Cr₂O₃. It is interesting to observe that even though the number of surface Cu atoms over Ga₂O₃ 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 Cr₂O₃ addition. The TOF values over different MS catalysts are in the order: Cu/ZnO/ZrO₂ ~ Cu/ZnO < Cu/ZnO/Ga₂O₃ << Cu/ZnO/Al₂O₃ << Cu/ZnO/Cr₂O₃. Thus, Cr₂O₃ addition to Cu/ZnO catalyst enhances the TOF *i.e.*, intrinsic activity.

Knozinger and Co-workers^{26,27} 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 NH₃ TPD

Solid-Acid	Acidity ^a (mmol _{NH3} /g _{cat.})						
	Total	373-473 K	473-573 K	573-673 K	673-773 K	773-873 K	>873 K
γ -Al ₂ O ₃	0.74	0.07	0.19	0.10	0.12	0.18	0.10
SiO ₂ -Al ₂ O ₃	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 ₇₂ Na ₂₈ Y	3.33	0.60	1.62	0.85	0.15	0.07	0.03
Na ₄₄ H ₅₆ 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

^a no. sites that indicate different acid strength in terms of desorption temperature (K).

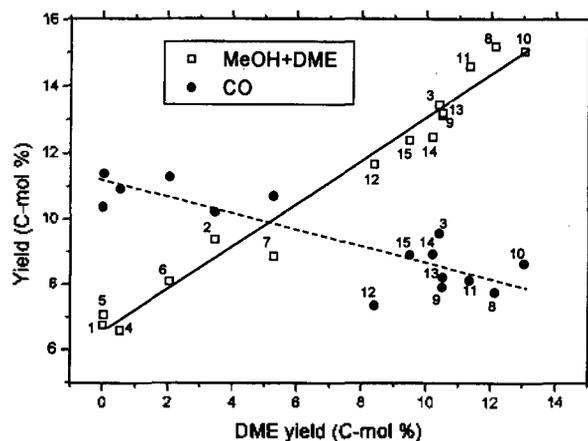


Figure 3. The dependence of the yields of CO and oxygenates on the activity of DME formation in the CO₂ hydrogenation; 250 °C, CuZnCrO-2 (0.5 g)+MDC (0.5 g), pressure=30 kg/cm², flow rate=30 mL/min. MD catalysts: 1 (none), 2 (γ -alumina), 3 (silica-alumina), 4 (NaY), 5 (K₈₀Na₂₀Y), 6 (Mg₅₇Na₄₃Y), 7 (Ca₄₅Na₅₅Y), 8 (Cu₇₂Na₂₈Y), 9 (Zn₇₀Na₃₀Y), 10 (HY), 11 (Na₄₄H₅₆Y), 12 (Mg₃₃-H₆₇Y), 13 (Ca₁₅H₈₅Y), 14 (Cu₈₀H₂₀Y), 15 (Zn₇₃H₂₇Y).

Table 3. Nature of acid-sites present on zeolites

Sample	pK _a	Nature of acid sites
NaY	> +4.0	Weak
Cu ₇₂ Na ₂₈ Y	≥ -5.6	Weak and Intermediate
Na ₄₄ H ₅₆ Y	≥ -5.6	Weak and Intermediate
Cu ₇₂ Na ₂₈ 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 CO₂ 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 NH₃. 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^a

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

^a Reaction Conditions: Catalyst=Cu/ZnO/Cr₂O₃ (0.5 g)+MD catalyst (0.5 g) temperature=523 K, pressure=30 kg/cm², H₂/CO₂=3, flow rate=30 mL/min. ^b 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-Al₂O₃. 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-Al₂O₃ 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 C₂-C₄). 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 Al₂O₃, Cr₂O₃ and Ga₂O₃ to Cu/ZnO permits easy reduction of CuO phase. However no such effect is observed in the case of ZrO₂ promoted catalyst.

2. Among all the promoters to Cu/ZnO, the role of Ga₂O₃ in enhancing the number of active sites is clearly observed.

3. Although Cr₂O₃ addition to Cu/ZnO can not create more number of active sites compared to Ga₂O₃ and Al₂O₃ 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/Cr₂O₃+CuNaY is the best hybrid catalytic system in producing oxygenates from CO₂ hydrogenation.

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