Direct Synthesis of Dimethyl Ether from Syn-gas over Cu-based Catalysts: Enhanced Selectivity in the Presence of MgO

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ABSTRACT

Direct synthesis of dimethyl ether (DME) from syn-gas was investigated over a series of hybrid catalytic systems containing Cu-based methanol synthesis component with varying amount of ZnO and MgO, and γ -Al₂O₃ as a methanol dehydration component. Methanol synthesis and methanol dehydration components were homogeneously mixed in 2:1 weight ratio to prepare the hybrid catalysts, which were characterized by Transmission electron microscopy, Scanning electron microscopy, BET surface area analyzer, Powder X-Ray diffraction, NH₃-Temperature programmed desorption and H₂-Temperature programmed reduction methods. Syn-gas to DME (STD) reaction was studied in an isothermal fixed bed reactor at 30 bar and 260 °C. The catalysis results revealed an improved effectiveness of the catalyst in the presence of 20 mol% MgO, enabling a significant enhancement in CO conversion from 19 to 37% and DME selectivity from 36 to 83%, when compared with the activity of a catalyst without MgO. By-products, CO₂ and C₁-C₂ hydrocarbons, selectivity were also decreased from 48 to 14% for CO₂ and from 8 to 2.5% for hydrocarbons. Catalyst performance, CO conversions and DME selectivity were evaluated by varying the reaction temperature, pressure, space velocity and H₂/CO ratio in syn-gas. XRD data revealed the formation of a well crystalline malachite structure for the catalysts containing up to 20 mol% MgO, but the crystallinity in the structure lost when 30% MgO was added, resulting in a decreased catalytic activity.

Keywords: Dimethyl ether, Cu/ZnO/MgO, hybrid catalysts, MgO effect, syngas, methanol dehydration, methanol synthesis.

1. INTRODUCTION

Dimethyl ether (DME) is gaining considerable attention worldwide as a cleaner fuel because of its environmentally benign fuel properties [1-2]. DME is a colorless gas (at STP) and can be liquefied at about 6 atm at 25 °C, which allows its usage on the same platform of current LPG storage and distribution technologies with minor modifications [3]. The cetane number of DME (55-60) is higher than diesel oil (~50). DME is also an excellent feedstock and intermediate for methyl acetate, dimethyl sulfate and light olefins [4].

Conventionally, DME is produced via a two-step process. The first step is the catalytic conversion of syn-gas to methanol and the second step is the dehydration of methanol over alumina or zeolite based acidic materials [5]. Methanol synthesis is a high temperature and high pressure process and is limited by thermodynamic constraints. Because of very low equilibrium of the conversion of syn-gas to methanol, direct conversion of syn-gas to DME (STD) has inherent thermodynamic advantage to achieve higher syn-gas conversion, and thus an overall economy of the process [6-8]. The key steps in the STD process are as follows:

Since direct conversion of syn-gas to DME also involves in situ methanol formation, the catalyst for the STD process must contain bifunctional sites for methanol synthesis and its subsequent dehydration. The most common hybrid catalysts containing bifunctional sites for direct conversion of syn-gas to DME are prepared either by physical mixing of both components or through co-precipitation of methanol synthesis catalyst and its subsequent impregnation on methanol dehydration catalyst [9-11]. In this process, DME selectivity strongly depends on the catalyst properties, such as acidity, nature of acid sites, pore size and crystallinity, and the reaction factors, such as temperature, pressure and space velocity of the feed stream. Under comparable operating conditions, the rate of methanol conversion and the selectivity of DME are governed by the physiochemical properties of the catalytic materials. Side reactions such as Fischer-Tropsch (FT), water gas shift, methanation and coke formation may cause lower DME selectivity in the STD process. Therefore, the catalyst must have the ability to suppress these side reactions to enhance DME selectivity.

Currently Cu-ZnO-Al₂O₃ catalyst, containing Cu and Zn in a ratio of 70:30, is used in industrial process for methanol synthesis [12-13]. It is known from the literature that the presence of Cu in metallic Cu⁰ form with high degree of dispersity is essential to achieve high selectivity for methanol formation [14]. Cu dispersion and its intrinsic activity are beneficially influenced by the homogeneous presence of ZnO in the catalyst. The latter component acts as a geometrical spacer between Cu nanoparticles [15] which helps to disperse Cu in course of catalyst preparation [12], and hence to achieve high surface area of Cu. High surface area of Cu per unit weight of catalyst is necessary to achieve high selectivity in methanol formation. Additionally strong metal-support interaction (SMSI) between ZnO and Cu is believed to affect the in situ formation of catalytically active sites. Recently, Behrens and co-workers have reported that ZnO promoted SMSI with Cu, which induced the formation of “methanol active copper”. Different models for this synergy have been discussed in the literature [16, 17-20]. The defect sites in the catalysts can also influence methanol formation [16].

Variation of reaction parameters during catalyst preparation may lead to the formation of different hydroxycarbonate precursor phases, most preferred being zincian-malachite (Cu,Zn)₂(OH)₂CO₃ [12]. It is well known that incorporation of Zn²⁺ into the crystal lattice of malachite favors aggregation of the CuO/ZnO nanostructuring upon calcination due to the favorable distribution of both the species in the crystal lattice of the precursor compound [21]. However, incorporation of Zn²⁺ into the malachite crystal lattice is also limited to <30% due to chemical constraints [22]. Small amount of Al₂O₃ acts as a structural promoter in the methanol synthesis catalyst [23-24], though Al³⁺ incorporation into the malachite structure can cause charge mismatch. Rather MgO can be an interesting replacement for Al³⁺ because of similar charge of Mg²⁺ and Zn²⁺, and only 2% less ionic radii of Mg²⁺ as compared to Cu²⁺. Thus, more Cu dispersion per unit weight of catalyst can be expected in the presence of MgO. Recent studies have shown that MgO has potential to serve as an effective structural promoter, demonstrating its ability to reduce the reaction temperature, and hence to (i) achieve high selectivity for the desired products by lowering by-products formation, (ii) inhibit premature catalyst sintering, (iii) improve conversion rates of substrates and (iv) increase active metal surface area [25-26]. Fitzpatrick et al. have reported that the activity of the Cu-ZnO catalyst for methanol synthesis improved significantly in the presence of MgO [27]. The presence of MgO in the catalyst also reduced by-products formation. Among several promoters (SiO₂, MnO, Al₂O₃, MgO) tested, the authors reported that the highest Cu surface area and methanol selectivity was achieved by the catalyst that contained 1.5 wt% MgO.

Subsequent dehydration of methanol to DME takes place in the presence of an acidic catalyst. Solid acid catalysts, such as HZSM-5, H-beta, SAPO's, γ-Al₂O₃, TiO₂, SiO₂-Al₂O₃ and Al₂O₃-TiO₂ have been used for the dehydration of methanol in the temperature range of 250-400 °C

[28-31]. Mao et al. have studied the activity of a bifunctional catalytic system, containing MgO modified HZSM-5 and Cu/ZnO/Al₂O₃ for direct conversion of syn-gas to DME [32]. The authors revealed that MgO helped in neutralizing the stronger acid sites to weaker sites. The strong acidic sites are reported to enhance DME degradation to lower hydrocarbons [10].

Although Mao et al. have reported the beneficial effect of MgO for methanol dehydration, the role of MgO in the bifunctional catalyst for the STD process is yet to be investigated. Therefore, it is worthy to study the effect of MgO on the properties of the hybrid Cu/ZnO/MgO- γ -Al₂O₃ catalyst and its catalytic effectiveness for direct conversion of syn-gas to DME. Additionally, we studied the combined effects of ZnO and MgO on the Cu-based hybrid ternary catalytic systems by changing the weight ratio of ZnO and MgO in the catalyst compositions.

Among three different acidic materials (γ -Al₂O₃, HZSM-5, SiO₂-Al₂O₃) used in the formulation of the hybrid catalysts, γ -Al₂O₃ was found to be most effective in combination with Cu/ZnO/MgO, which showed constant methanol conversion over a longer reaction time with high selectivity in DME. Thus, γ -Al₂O₃ was selected as a component for methanol dehydration in the hybrid catalyst. Furthermore, it is known that γ -Al₂O₃ can resist structural changes during methanol dehydration because of its high hydrothermal stability, and thus minimize the formation of undesired side products [33-34]. The focus of this study is to evaluate the structural and physicochemical properties of the catalysts as a function of MgO content and the effect of these catalytic properties on the conversion of syn-gas, and DME yield and selectivity.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Copper nitrate (Cu(NO₃)₂·2.5H₂O), zinc nitrate (Zn(NO₃)₂·XH₂O) were purchased from Alfa Aesar. Magnesium nitrate (Mg(NO₃)₂·6H₂O) and sodium carbonate were obtained from Acros India and Merck India, respectively. All chemicals were used as received.

CuO/ZnO/MgO was prepared by a co-precipitation method. A 1000 mL aqueous solution containing copper nitrate, zinc nitrate and/or magnesium nitrate salts of total molarity of 1.0 and a 500 mL aqueous solution of Na₂CO₃ of 0.5M were mixed in drop wise fashion in a 2 L jacketed reactor containing 500 mL of distilled water. The jacketed reactor (Figure S1) was stirred continuously at 350 rpm and 70 °C during mixing of the two solutions. The pH of the mixture was maintained at 7 during precipitation by controlling the flow rates of the two solutions. After complete precipitation, the precipitates were aged for 1 h at 70 °C. The precipitate was then filtered and washed several times with distilled water to remove residual sodium ions. Complete removal of

Na⁺ and other ions was confirmed by the conductivity measurement of the filtrate. The precipitate was washed until the conductivity of the filtrate was similar to that of distilled water. The washed solid was dried at 80 °C in a furnace for 12 h and subsequently calcined under air at 400 °C for 4 h. Other catalysts (Table 1) were prepared by following the similar procedure. The atomic percentage of each metal in the catalyst, as listed in Table 1, represents their theoretical values. Hereafter, the catalysts are represented by the presence of metal components wherein Cu, Zn and Mg are abbreviated as C, Z and M, respectively. The value in parenthesis represents the percentage of Mg in the catalyst. The hybrid catalysts were prepared by grinding as-synthesized CZM catalysts and γ -Al₂O₃ in 2:1 weight ratio in an analytical mill (IKA, Germany). The resultant powder was then pressed into pellets by using a KBr pelletizer. Henceforth, methanol synthesis catalysts, *e.g.* CZM, and methanol dehydration catalysts, *e.g.* γ -Al₂O₃ are abbreviated as MSC and MDC, respectively.

Table 1. Compositions of the as-synthesized CZM catalysts.

Catalysts	Cu (atom %)	Zn (atom %)	Mg (atom %)
CZM(0)	55	45	0
CZM(5)	55	40	5
CZM(10)	55	35	10
CZM(20)	55	25	20
CZM(30)	55	15	30

2.2. Instrumentation

Surface area measurement. Brunauer-Emmett-Teller (BET) surface area of the catalyst samples was determined by a multipoint N₂ adsorption-desorption method using Micromeritics ASAP 2020 analyzer. The pore volume was determined at a relative N₂ pressure (p/p₀) of 0.99. In each of the typical measurement, approximately 100 mg of calcined hybrid catalyst sample was taken in a glass reactor and degassed under helium at 300 °C for 3 h at a heating rate of 10°C/min.

Power X-ray Diffraction (XRD). The powder X-Ray diffraction patterns of the investigated catalysts were obtained from Philips X'Pert (40 kV, 30 mA) X-ray diffractometer equipped with Cu K α radiation source (λ = 1.542) and a nickel filter in the 2 θ range of 10°-70° at a scanning speed of 5°/min. Sample preparation for the X-ray analysis involved gentle grinding of the solid into a fine powder and packing of approximately 0.5-0.8 g of powder into an aluminium sample holder with light compression to make it flat and tight.

Temperature Programmed Desorption of Ammonia (NH₃-TPD). NH₃-TPD measurement of the catalyst samples was performed on Thermo Fischer Scientific TPD/R/O (1100 series) analyzer to determine the surface acidity. In each of the typical analysis, approximately 100

mg of the sample was loaded in a quartz cell and initially flushed with a He gas flow at 400 °C for 2 h, cooled to 150 °C and then saturated with ammonia at the same temperature for 30 minutes at a flow rate of 20 mL/min. After exposure to ammonia, the catalyst samples were subsequently purged with the He flow and the temperature was raised up to 800 °C at a linear heating rate of 10 °C/min for measuring desorbed NH₃ by using a thermal conductivity detector (TCD).

Temperature Programmed Reduction Study (TPR). TPR study of the catalyst samples was performed on the same instrument used for TPD studies to determine the reduction behavior of the materials. In this analysis, approximately 20 mg of each sample was loaded in a U-shaped glass cell and the sample was flushed with a Ar gas at a flow rate of 30 mL/min and at 150 °C for 2 h, following which the sample was cooled down to 50 °C at a rate of 10 °C/min. The sample was then heated up to 900 °C at a heating rate of 10 °C/min in the presence of a mixture of 5% H₂ in Ar.

Scanning Electron Microscopy (SEM). The surface morphology of the catalyst samples was characterized by VEGA LSU (TESCAN) SEM analyzer. The image was obtained at a magnification of 1100X and at 15 kV (kilovolt) using a secondary electron detector.

Transmission Electron Microscopy (TEM). TEM images and selected area electron diffraction (SAED) analyses were performed on a JEOL JEM 2010 transmission electron microscope operated at an accelerating voltage of 200 kV. Samples for TEM analyses were prepared by applying one drop dispersed solution of the sample onto the carbon coated Cu grid and allowing the solvent to slowly evaporate at room temperature.

Turn-over frequencies (TOFs). TOF values for all hydride catalysts were calculated from the rates of CO consumption measured from catalytic experiments. The number of active catalyst sites used for TOF calculation were measured from H₂-chemisorption study in which the adsorbate-free reduced catalyst sample was cooled down to 50 °C in a He stream and then saturated with H₂ gas for minimum 60 minutes. The sample was further cooled down to -195 °C by using liquid nitrogen, and residual H₂ was flushed out with a He flow. The temperature-programmed desorption experiment was carried out by ramping the temperature up to 350 °C at a heating rate of 2 °C/min.

2.3. Catalysis experiments

The catalytic effectiveness of all bifunctional hybrid catalysts were tested by using a high pressure fixed bed tubular reactor (Figure 1). Typically, 12 g of catalyst in the form of oxide pellet (450-600 microns) was placed in the middle of the reactor tube. The catalyst occupied about 10 cm length of the reactor and the remaining length of the tube was filled with inert glass beads from both sides to keep the catalyst bed fixed in the middle. The glass beds act as a preheating zone for the feed gases. As shown in figure 1, the test reactor set up is equipped with a gas feeding system,

tubular furnace, mass flow controllers (MFC), back pressure regulator, product recovery and separation system and a gas outflow measuring section.

Figure 1. Schematic diagram of a tubular reactor for bench scale conversion of syn-gas to DME.

Before catalysis, the loaded catalyst in the reactor was first subjected to a one stage activation process in which the catalyst was reduced with a stream of pure H₂ at 300 °C for 5 h. H₂ and CO gases in 1.5:1 ratio were then fed into the reactor through separate mass flow controllers. As the feed stream passed through the inert beds, it was heated to achieve the desired temperature. Effluent stream leaving from the bottom of the reactor passed through a condenser to a product separator. Condensed liquid product stream was separated from the non-condensable gases in the separator. A back pressure regulator (BPR) was placed in the separator to regulate the system pressure. The gaseous effluents leaving the separator through the BPR passed through a wet gas meter, which measured the volumetric flow rate. Most of the reactions were performed under the operating reactor pressure of 30 bar with a space velocity of 2000 ml/g_{cat}.hr and at 260 °C. The experiments were also performed by varying the reaction temperature, pressure, space velocity and H₂/CO ratio in the range of 240-260 °C, 30-50 bar, 2000-4000 ml/g_{cat}.hr and 1-3, respectively. The gaseous products were analyzed by using an Agilent 7890A gas chromatograph equipped with a TCD detector for CO and CO₂ analysis and a FID detector for DME and hydrocarbons analysis. HP Plot-U column was used for analysis of methanol and DME. Haysep Q and Molsieve 13x columns were used for analysis of H₂ and CO/CO₂, respectively. CO conversions and the selectivity of the products were calculated in mol% by using the following equations.

$$\text{Conversion of CO (mol\%)} = \frac{(\text{inlet moles of CO} - \text{outlet moles of CO})}{\text{inlet moles of CO}} \times 100$$

$$Selectivity\ (mol\%) = \frac{n_i \times \text{moles of produced component}}{(\text{inlet moles of CO} - \text{outlet moles of CO})} \times 100$$

where n_i is the stoichiometric coefficient for each of the product produced.

3. RESULTS AND DISCUSSION

3.1. Surface Properties

The surface properties of all the catalyst samples containing MSC and MDC components and their catalytic activities (turnover frequency (TOF), CO conversions) are presented in Table 2. Surface area of the catalysts was calculated by applying the multipoint BET method whereas pore volume was calculated from BJH method using desorption branch of the isotherm. The surface area of the catalysts, determined from multipoint N₂ adsorption-desorption isotherm studies (Figure S2a), was found to increase linearly from 79.2 m²/g to 95.9 m²/g as the MgO content in the catalysts increased from 0 to 20%. The highest surface area of the CZM(20)- γ -Al₂O₃ catalyst can be attributed to the promoting behavior of MgO towards the nanostructuring of CuO domains. Noteworthy, CZM(30)- γ -Al₂O₃ catalyst, containing maximum MgO loading (30%), exhibited lowest surface area of 67.1 m²/g which may be due to inhibition in nanostructuring phenomenon by excess MgO during the calcination process. SEM images of the CZM(20)- γ -Al₂O₃ catalyst shows an uniform sponge like morphology (Figure S3d). When compared the surface area of the CZM(20)- γ -Al₂O₃ and CZM(0)- γ -Al₂O₃ catalysts, the surface area of the former catalyst is enhanced by 22% than the latter. Zander et al. have also reported higher surface area of 20% MgO loaded Cu based methanol synthesis catalyst [21], which is in well agreement with our observation. The N₂ adsorption-desorption isotherms, as shown in Figure S2, show a type IV isotherms for all MSC catalysts with an H1-type hysteresis loop, which is characteristic of mesoporous materials having interparticle pores of nanoscale dimensions. The pore size, shown in Table 2, was calculated by employing non local density functional theory (NLDFT) on the respective N₂ adsorption-desorption isotherms (Figure S2b).

As seen in Table 2, surface areas of all hybrid catalysts are lower than that of γ -Al₂O₃, MDC component in the catalyst. To study the effect of physical mixing of these two components, we performed surface area analysis of both the components separately. Surface areas of all MSC components were found to be in the range of 16-25 m²/g, whereas the surface area of MDC component (γ -Al₂O₃) is 230 m²/g. Thus, the observed surface areas of the hybrid catalysts (67-96 m²/g) are the average values of the surface areas of the MSC and MDC components. These calculations are shown in the supporting information.

Table 2. Textural and structural properties of the hybrid catalysts containing MSC and MDC components.

Catalyst	Surface area (m ² /g)	Pore size (nm)	Total pore volume (cm ³ /g)	Crystallite size from XRD (nm)	TOF × 10 ⁻² (s ⁻¹)	CO conversion (%)
CZM(0)- γ -Al ₂ O ₃	79.2	9.4	0.19	13.9	1.2	19.8
CZM(5)- γ -Al ₂ O ₃	80.2	9.5	0.19	12.7	2.8	25.5
CZM(10)- γ -Al ₂ O ₃	86.5	9.4	0.21	11.9	3.5	30.6
CZM(20)- γ -Al ₂ O ₃	95.9	8.1	0.22	8.6	8.3	46.2
CZM(30)- γ -Al ₂ O ₃	67.1	9.4	0.18	13.1	6.1	21.1
γ -Al ₂ O ₃	230.0	7.8	0.73	-	-	-

3.2. Crystalline Properties from X-Ray Diffraction

XRD patterns of the MSC catalysts before and after calcination are shown in Figures 2a and 2b, respectively. The results show the formation of single phase materials before calcination with a crystal structure similar to that of well crystalline phase of zincian malachite (Cu,Zn)₂(OH)₂CO₃ (ICSD: 72-75) which has been reported as a relevant precursor material [35]. Our findings also correspond to the literature reports describing rosasite or malachite as favored precursor phases for catalysts containing atomic Cu concentration of >20% [36]. Subsequent calcination of these malachite type of structures leads to the formation of small CuO crystallites and more uniformly dispersed Cu-Zn oxide phases which are believed to be ideal intermediates of final reduced catalysts [37-38]. The role of MgO in promoting the formation of malachite can clearly be understood after analyzing the pattern of CZM(0) catalyst as it precipitated out in the form of a mixed aurichalcite (ICSD: 17-743) and malachite type of structure. Aurichalcite material which usually exists in the form of large platelets with unfavorable meso-structure may get reduced at higher temperature [22]. Our TPR results (*vide infra*) agrees well with the literature observation. In the presence of MgO in the catalyst matrix, malachite structure was found to form predominantly (Figure 2a), which is considered as the relevant precursor for the preparation of active nanostructured Cu/ZnO [39].

Figure 2. XRD patterns of MSC catalyst before calcination (a) and after calcination (b). Figure 2(c) shows XRD pattern of the reduced form of CZM(20) catalyst after reaction.

When compared with different standard planes of malachite, *e.g.*, (120) , (220) , $(20\bar{1})$, a slight shift of peak associated with $(20\bar{1})$ plane at $2\theta = 31.23^\circ$ was observed for the prepared catalysts. A shift of 2θ from 31.23° to 32.33° , 32.44° , 32.5° and 32.75° was observed for CZM(0), CZM(5), CZM(10)

and CZM(20), respectively, which may be due to the assimilation of Mg^{2+} cations in the lattice of malachite, resulting in more Cu dispersion and high surface area. The maximum peak shift was observed for CZM(20). The observed peak shift of $(20\bar{1})$ plane for catalysts containing MgO is also in agreement with the study done by Zander et al. [21], where the authors reported a similar peak shift for $(20\bar{1})$ plane in malachite structure when Zn^{2+} or Mg^{2+} cations were incorporated into the catalyst matrix. Interestingly, CZM(30) catalyst containing the maximum amount of MgO did not show any crystalline peak, which suggests that an amorphous nature of this catalyst dominated by the presence of excess MgO. Perhaps, MgO formed a layer over the catalyst surface which might have encapsulated the active Cu-ZnO sites.

Upon calcination of all MSC catalysts at 400 °C, crystalline CuO was formed (Figure 2b) and some reflections of ZnO were observed. This interpretation is based on the standard XRD spectrum of pure CuO (JCPDS 80-1268), ZnO (JCPDS 36-1451) and MgO (JCPDS 89-7746), which are also included in Figure 2b, confirming only single species of Cu was formed after calcination. Reflections at $2\theta = 35.6^\circ$ and 38.9° can be assigned to $(\bar{1}11)$ and (111) plane of CuO and indexed to its monoclinic phase. Likewise, reflections at $2\theta = 31.9^\circ$ and 36.2° can be assigned to hexagonal phase of ZnO. However, after adding MgO, many ZnO reflection peaks were overlapped with those of CuO, suggesting a well dispersed mixture of CuO-ZnO is present in the catalysts when MgO was added. The absence of standard reflections for MgO at $2\theta = 37.5, 43.0$ and 62.6° might be attributed their amorphous nature.

The average crystallite size of the CuO phase in calcined catalyst was estimated by applying Scherrer's equation to the CuO peak at $2\theta = 38.9^\circ$ corresponding to (111) plane and these values are shown in Table 2. Among all the catalysts, CZM(20) exhibits low intensity broader peaks owing to the presence of small crystallites. The crystallite size of CuO increased in the CZM(30) catalyst which contained highest amount of MgO (30%). Such an increase in the size may result in a decrease of active Cu^0 sites in the reduced catalyst, which is believed to be the active sites for methanol synthesis [40].

XRD pattern of the reduced form of CZM(20)- γ - Al_2O_3 after reaction is shown in Figure 2c. It shows characteristic peaks for cubic metallic Cu (JCPDS 04-0836) at $2\theta = 43.5^\circ, 50.4^\circ$ and 74.2° , suggesting CuO in the catalyst was converted to active Cu after reaction. However, ZnO and MgO retained their oxidation state, as evidenced from their characteristic XRD peaks, which is important to maintain dispersion of metallic copper in the catalyst during methanol synthesis.

3.3 Acid Density from NH_3 -TPD Measurement

NH_3 is widely used as a molecular probe for measuring total acid density of acidic materials because of its selective interaction with both Brönsted and Lewis acid sites. In this experiment, NH_3 was first allowed to absorb on the surface of the hybrid catalysts and then NH_3 was desorbed from the acidic sites as the temperature of NH_3 -adsorbed material gradually increased. Usually, desorption of NH_3 at lower and higher temperatures are expected from weaker and stronger acidic sites [41]. NH_3 -TPD profile of all hybrid catalysts show three desorption peaks in the temperature range of 145-148 °C (T_1), 270-335 °C (T_2) and 519-600 °C (T_3) (Figure 3), presumably due to the presence of weak, medium and strong acid sites in the materials. The corresponding acid density values at each peak and their acid density percentage contribution towards total acidity are tabulated in Table 3. These data show that the total acidity of the catalysts decreased in the order of $\text{CZM}(0)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(5)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(10)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(20)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(30)\text{-}\gamma\text{-Al}_2\text{O}_3$, whereas medium acidity at T_2 decreased in the order of $\text{CZM}(20)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(30)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(10)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(5)\text{-}\gamma\text{-Al}_2\text{O}_3 > \text{CZM}(0)\text{-}\gamma\text{-Al}_2\text{O}_3$. On the other hand, acid density at T_3 showed decreasing trend as the amount of MgO in the catalysts increased. However, due to the opposite trends of medium and strong acidity values of the catalysts, the total acidity values show a slight decreasing trend as a function of MgO content, which could be primarily dominated by the basicity of MgO .

Figure 3. NH_3 -TPD profiles of the hybrid catalysts after calcination.

MgO altered the nature of acidic sites in the catalyst. It is because of strong basic property of MgO which primarily targeted the stronger acidic sites, thus ultimately reduced or modified the stronger acid sites to the moderate or weaker sites. As shown in Table 3, the value of moderate acidic sites increased from 32% in CZM(0)- γ -Al₂O₃ to 45% in CZM(20)- γ -Al₂O₃, but decreased to 36% in the catalyst containing 30% MgO. The moderate acid density of CZM(20)- γ -Al₂O₃ catalyst is about 42% higher than the CZM(0)- γ -Al₂O₃. It is believed that moderate acidic sites catalyze methanol dehydration to DME, whereas stronger acid sites enhance the formation of undesired hydrocarbons and coke [42]. Thus, CZM(20)- γ -Al₂O₃ catalyst is expected to show higher selectivity towards DME formation. It is important to note that the extent of modification of all the hybrid catalysts containing the same amount of γ -Al₂O₃ is largely dependent on the amount of MgO.

Table 3. NH₃-desorption properties of the hybrid catalysts.

Catalyst	Acid density (mmol of NH ₃ /g of catalyst)					Total
	Weak (T1) (%)	Medium (T2) (%)	Strong (T3) (%)			
CZM(0)- γ -Al ₂ O ₃	0.37 (47.6)	0.25 (31.6)	0.16 (20.8)			0.78
CZM(5)- γ -Al ₂ O ₃	0.35 (45.7)	0.27 (36.2)	0.14 (18.1)			0.76
CZM(10)- γ -Al ₂ O ₃	0.34 (45.5)	0.29 (39.4)	0.12 (15.1)			0.75
CZM(20)- γ -Al ₂ O ₃	0.31 (41.2)	0.33 (44.7)	0.1 (14.1)			0.74
CZM(30)- γ -Al ₂ O ₃	0.38 (52.7)	0.26 (36.1)	0.08 (11.3)			0.72
γ -Al ₂ O ₃	0.77 (44.3)	0.6 (38.5)	0.37 (21.2)			1.74

3.4. Reduction Behavior of Catalysts

The catalytic performance of the bifunctional hybrid catalyst depends on the reducibility of copper as well as their acidity [4,43]. Figure 4 illustrates the degree of copper reduction of the CZM- γ -Al₂O₃ catalysts. Based on the results obtained from XRD analysis of the calcined catalyst samples (Figure 2), it is confirmed that Cu is present in the form of CuO only. The TPR pattern of the CZM(0)- γ -Al₂O₃ catalyst shows two distinct peaks at 263 and 428 °C, suggesting that CuO in the catalyst undergoes reduction to metallic Cu in two stages i.e. Cu²⁺→Cu⁺→Cu⁰ [44]. This result also shows that CZM(0)- γ -Al₂O₃ possess non-uniformly dispersed active Cu⁰ sites. On the other hand, the TPR pattern of the catalysts containing MgO i.e. CZM(5)- γ -Al₂O₃, CZM(10)- γ -Al₂O₃, CZM(20)- γ -Al₂O₃ and CZM(30)- γ -Al₂O₃ showed a single broad reduction peak, suggesting one-stage reduction behavior of CuO to metallic copper [45]. This interpretation agrees well with the XRD spectrum of used CZM(20)- γ -Al₂O₃ showing the presence of metallic Cu (Figure 2c). The presence of MgO in the catalysts might have facilitated the fast reduction of CuO, resulting in

broadening of the reduction peak. This reduction behavior may also be attributed to the promoting effect of MgO in favoring the nanostructuring of CuO and its easy availability on the catalyst surface.

Figure 4. H₂-TPR profiles of the hybrid catalysts after calcination.

Additionally, reduction peak of the catalysts containing CZM(5), CZM(10) and CZM(20) shifted considerably towards lower reduction temperatures as the amount of MgO increased, indicating an accessibility of more CuO to the reducing gas from the catalysts surface, owing to the structural modification of the catalyst by MgO. The observed reduction temperature of all MgO incorporated CZM- γ -Al₂O₃ catalysts is lower than that of reported reduction temperature (336 °C) of Al₂O₃ (3.3 wt%) incorporated Cu-ZnO (abbreviated as CZA) bifunctional catalyst [45]. Lower reduction temperatures facilitate easy conversion of CuO to metallic copper without changing the structural integrity of the catalyst. Thus, MgO is a better additive for making the catalyst more active by lowering the reduction temperature significantly. It is also seen from Figure 4 that CZM(30)- γ -Al₂O₃, containing maximum amount of MgO, shows reduction peak at comparatively higher temperature (299 °C) than those of other CZM- γ -Al₂O₃ materials, which may be attributed to the presence of excess non-reducible MgO. Furthermore, higher reduction temperature of

CZM(30)- γ -Al₂O₃ than that of CZM(0)- γ -Al₂O₃ (263 °C) could attribute to the fact that excess MgO might have blocked the accessibility of the reducing gas to CuO. The higher crystallite size of the CZM(30)- γ -Al₂O₃ (13.1 nm, Table 2) than those of other MgO containing CZM- γ -Al₂O₃ materials could also contribute to its higher reduction temperature as observed by Agrell et al [46]. The authors reported that large crystallites tend to be reduced more slowly than the smaller ones due to the relatively lower surface area exposed to H₂ [46]. Since the catalysts containing CZM(0), CZM(5) and CZM(30) components have higher crystallite size and insufficient amount of ZnO as a geometrical spacer as compared to CZM(10) and CZM(20) analogues, early deactivation for the former materials may be expected because CuO particles might not be well dispersed and present in agglomerated form.

The observed reduction behavior of the hybrid catalysts can also be explained on the basis of amount of promoter (MgO) and co-promoter (ZnO) present in the CZM components. Since all the CZM materials contained the same amount of CuO, the degree of possible CuO-ZnO, CuO-MgO and ZnO-MgO interactions in the materials, which play an important role for the overall synergy, depends on the amount of MgO and ZnO. It is known that industrially applied Cu/ZnO catalyst, which can be considered as a model system, contains Cu and Zn in an optimum ratio of about 70:30 (~2.33) in the zincian malachite phase [22]. When compared Cu to Zn ratio for all CZM materials in our hybrid catalysts, these values for CZM(0) (1.22), CZM(5) (1.38) and CZM(10) (1.57) are much lower than the reported optimum value of 2.33. Noteworthy, CZM(30) has significantly higher Cu: Zn value of 3.66, because of less amount of ZnO, which suggests that the degree of CuO-ZnO interaction in it is less than those of other CZM materials. On the other hand, Cu:Zn value of the CZM(20) (2.2) matches well with the reported value of the model system, suggesting that ZnO and MgO are present in an optimum ratio in the CZM(20), and hence this material showed reduction peak at lowest temperature.

Assuming that Cu is only present as CuO in the catalysts, as observed from the XRD patterns, the stoichiometry of H₂ to CuO for complete reduction of CuO to Cu⁰ should be equal to unity according to equation (1). The TPR data of all hybrid catalysts indeed show the ratio of H₂ to Cu is close to unity (Table 4), which illustrates complete reduction of CuO at the reduction temperature.

Table 4. TPR data of the hybrid catalysts containing calcined CZM materials.

Catalyst	$T_{\max}$ (°C)	H ₂ consumption	
		(mmol H ₂ g ⁻¹)	H ₂ /Cu
CZM(0)	263	0.59	0.99
CZM(5)	258	0.42	0.99
CZM(10)	248	0.51	1.02
CZM(20)	232	0.77	1.03
CZM(30)	299	0.46	1.02
CZA ^a	336	n.a	n.a

^aCu-ZnO (Ref 45); n.a. = not available.

3.5. Morphology from SEM and HRTEM

The surface morphology of the hybrid catalysts containing CZM materials was characterized by SEM technique. Low resolution SEM images of all catalysts (Figure S3), show the formation of spherical particles which are self aggregated to larger particles. Due to the formation of self-assembled larger particles, the catalysts containing CZM(0), CZM(5) and CZM(30) show non-uniform size distribution, whereas the catalysts containing CZM(10) and CZM(20) components have uniform dispersion and size. The magnified SEM image of CZM(20) (Figure S3f) shows a “urchin like” morphology, revealing the presence of spherical granule-type particles. SEM image of CZM(30) (Figure S3e) shows the particles are distorted and irregular, presumably due to the presence of excess MgO [47].

Selected catalyst samples were subjected to HRTEM analysis: calcined CZM(0)-the catalyst with no MgO, calcined CZM(20)-the catalyst with optimum MgO and the reduced form of CZM(20) after reaction. The TEM images show that the particle sizes are in the range of 11-25 nm. TEM investigation of the calcined and the reduced catalysts showed that the general microstructure of CZM(0) (Figure 5a) and CZM(20) (Figure 5b) is similar and characterized by the presence of spherical assembly of CuO nanoparticles separated by differently sized crystallites of ZnO and/or MgO particles indicating the uniformly distributed nanoparticulate microstructures. This nanostructure is preserved (Figure 5c) even after the reduction. The presence of larger CuO particles in CZM(0) as compared to CZM(20) is consistent with difference in surface areas of the two catalysts (Table 2). This result indicates that the CuO particles are geometrically dispersed in a better way in the presence of MgO. SAED patterns of the catalysts revealed the formation of well crystalline materials. The presence of (111) plane of monoclinic CuO and (100) (110) and (002) planes of hexagonal wurtzite phase of ZnO have been identified as major phases in the SAED

pattern of CZM(0) (Figure 5d), whereas in CZM(20) (Figure 5e), in addition to these planes of CuO and ZnO, (220) plane of cubic MgO crystallites are clearly seen. Indexing of the SAED pattern was done by calculating d -spacing values from the magnified electron diffraction patterns and matching it with the standard values obtained from XRD analysis. The SAED image of the reduced form of CZM(20) material (Figure 5f) shows the characteristic phases for metallic Cu and ZnO, suggesting that the reduced form is still in its original non-decomposed active form in the matrix. The high resolution TEM images thus support the arrangement of well dispersed CuO and MgO nanoparticles in the ZnO matrix.

Figure 5. TEM images for calcined CZM(0) (a), CZM(20)(b), used CZM(20) and (c). (d), (e), and (f) are SAED patterns for CZM(0), CZM(20) and used CZM(20). Magnified TEM image of CZM(20) is shown in (g).

3.6. Specific Heat

It is well known that syn-gas to DME conversion process is highly exothermic (equation 1), which may cause a thermal sintering of active catalytic sites and hence catalyst deactivation, if heat of the reaction is not dissipated properly. Such exothermal behavior can be controlled by adding high heat retention materials such as oxides of boron, beryllium, lithium and magnesium to the catalytic system [48]. This practice is used in well-known FCC (fluid catalytic cracking) reaction in which mixing of high heat capacity material with zeolite catalyst helps to control the reaction temperature as well as to increase the efficiency and product selectivity of the overall catalytic system.

In the present work, we investigated the role of MgO in controlling the exothermicity of the reaction for which we theoretically calculated the specific heat capacity for all hybrid catalysts. This calculation was done by using the literature heat capacity values of each individual components of the catalyst system [49]. Considering the reduced state of the catalyst as Cu^0 , the calculated heat capacity values of the catalysts is plotted as a function of their MgO content (Figure 6). The plot shows an increase in specific heat capacity of the catalysts with an increase in MgO content. Thus, the temperature of the reaction is better controlled when more MgO is present in the catalyst, which makes the catalyst more stable towards thermal sintering and hence increases catalyst lifespan. Moreover, the ability to control the desired temperature of the reaction has beneficial effect in improving DME selectivity as DME is known to degrade to hydrocarbons at higher temperatures.

Figure 6. Calculated specific heat capacity of the reduced form of the hybrid catalysts as a function of MgO content in the catalysts composition.

3.7. Catalytic Activity

As discussed under experimental section, the effectiveness of the hybrid catalysts for the conversion of CO in H_2 and CO gas feed (H_2 : CO = 1.5) were tested on a fixed bed tubular reactor. Detailed experimental conditions and quantification of CO conversions and products and by-products selectivity are discussed in the experimental section. The results of the catalysis experiments are summarized in Figure 7. Among all the hybrid catalysts containing CZM(0) – CZM(30) as MSC counterpart and $\gamma\text{-Al}_2\text{O}_3$ as MDC, the catalyst containing CZM(0) show the lowest activity in terms of DME selectivity (36%), CO conversion (19%) and by-products

selectivity (48% for CO₂ and 8% for C₁ and C₂ hydrocarbons). Both CO conversions and DME selectivity improved from 28 to 37% and from 50 to 83%, respectively, when MgO incorporation in the catalysts increased from 5 to 20 wt%. The formation of CO₂ and C₁-C₂ by-products were also decreased as MgO incorporation in the catalysts increased. Additionally, MgO incorporated catalysts completely dehydrated methanol that was formed as an intermediate, as methanol was not detected in the product. The catalyst containing CZM(20) (20 wt% MgO) as MSC counterpart showed maximum activity, enabling highest DME yield (34%) and least by-product (5% CO₂). When compared the activity of the catalysts containing CZM(0) and CZM(20), the latter catalyst achieved about 27% higher DME yield than the former. However, the catalyst containing CZM(30) (30 mol% MgO) as MSC component showed lower activity, in terms of both CO conversion (20%) and DME selectivity (70%), when compared with the catalyst containing CZM(20). Mass balance for all hybrid catalyzed reactions was found out to be in the range of 96-100%.

This observed trend in activity of the catalysts can be explained by the change of surface and physico-chemical properties of the catalysts with an increase in MgO content that might alter the reaction kinetics of the STD process. As discussed under catalysts characterization section, the higher activity of MgO containing catalysts, especially CZM(20), can directly be related to its optimum Cu:Zn value of 70:30 (2.3). At this optimum Cu to Zn value, MgO believed to act as an efficient structural promoter, resulting in the formation of an active malachite precursor phase, which has reflected to its reduction profile. The lower activity of the CZM(5) and CZM(10) containing catalysts, possessing similar structure, can be explained by the formation of less uniformly dispersed CuO phase along with higher crystallite size particles upon calcination, whereas CZM(20) produced more uniformly dispersed porous CuO phase with lowest crystallite size, resulting in high surface area (Table 2). The lower activity of the catalyst without any MgO is presumably dominated by its aurichalcite structure which is considered to be less active for syn-gas to DME reaction. The decreased activity of the catalyst containing CZM(30) could be attributed to the presence of excess MgO in it and hence less ZnO-CuO interaction, resulting in lower reduction activity as seen from TPR experimental data.

Figure 7. The hybrid (CZM- γ -Al₂O₃) catalyzed conversion of CO and selectivity of the products. Reaction conditions: 30 bar, 260°C, 2000 1 WHSV and H₂/CO ratio=1.5.

TOF values for all hybrid catalysts were calculated from the rates of CO consumption measured from experiments presented in Figure 7 and the number of active Cu catalytic sites which were measured using H₂ chemisorption method [50]. These results are tabulated in Table 2 and also plotted as a function of MgO variation in the catalysts (Figure 8). The results show maximum TOF ($8.3 \times 10^{-2} \text{ s}^{-1}$) and CO conversion (46%) for CZM(20)- γ -Al₂O₃ catalyzed reaction which contained optimal amount of MgO (20%). When compared the activity of our investigated catalysts with a reported catalyst, CuO/ZnO/ γ -Al₂O₃, showing TOFs in the range of $8 - 28 \times 10^{-2} \text{ s}^{-1}$ for the conversion of syn-gas to DME, the activity of our CZM(20)- γ -Al₂O₃ catalyst is comparable in the lower range with the reported TOF values [51]. In the reported system, TOF values were calculated based on Cu sites that were obtained from N₂O titration method [52]. Additionally, the latter catalyst (CZM(20)- γ -Al₂O₃) produced DME with high selectivity than the reported one.

Figure 8. Correlation of TOF values (rate of CO conversion/active Cu atoms/s) with MgO content in the catalytic systems.

The observed activity of the hybrid catalysts can also be explained from the measured acidity and reducibility data. As discussed under NH₃-TPD result, weak, medium and strong acid sites and the total acidity of the catalysts changed in the presence of different amount of MgO promoter. It is evident from the literature that weak and medium acid sites facilitated DME formation, whereas strong acid sites accelerated DME degradation to by-products such as CO₂ and hydrocarbons [29, 52-53]. In this context, the present results showing maximum DME yield and least by-products formation by the catalyst containing 20% MgO also correlated well with its observed acidic properties of being the one which contained highest amount medium acid sites and least strong acid sites. These observations are also in accordance with the results obtained by Mao et al [32]. The authors reported the formation of high amount of by-products using catalysts that contained high amount of strong acid sites. However, CZM(30) catalyst, despite having less stronger acidic sites than CZM(20), showed lower selectivity in DME. This might be due to the more basic nature of CZM(30) as it contained highest amount of MgO.

Furthermore, for methanol dehydration to DME, basic sites of the catalysts are required along with Lewis acidic γ -Al₂O₃. Mao et al. have also reported the importance of basic sites in the catalyst composition [32].

S_A and S_B correspond to acid and base sites. According to the mechanism, bimolecular reaction of methanol conversion involved a weakly adsorbed CH_3OH on a basic site (S_B) through hydrogen bonding and a strongly adsorbed CH_3OH on an acidic site (S_A) through a coordination bond. While CH_3OH on the acidic site can polarize the C-O bond to make hydroxyl a better leaving group, the weakly adsorbed CH_3OH on the basic site enhances the nucleophilicity of oxygen such that this CH_3OH can be considered as an incipient alkoxide ion (eq 4), which can influence a nucleophilic displacement of a positively polarized carbon atom of the alcohol adsorbed to the acidic site to form DME (eq 5) [54-55].

Assuming our STD process follows the similar methanol dehydration mechanism, MgO is believed to serve the basic sites to progress the reaction. Therefore the mechanism adapted here can reasonably explain our experimental results elucidating the positive effect of MgO in CZM(20) by providing the reasonable basic nature to the catalyst system which resulted in increased DME selectivity and decreased the byproducts selectivity.

It is noted from the catalysis results that among all the catalysts containing the same amount of $\gamma\text{-Al}_2\text{O}_3$, only CZM(0) catalyzed reaction showed unconverted methanol in the product (Figure 7). As methanol was completely converted in the presence of MgO , the role of MgO in enhancing the dehydration activity of $\gamma\text{-Al}_2\text{O}_3$ is evident. To further analyze the role of MgO in reaction kinetics, we considered the following reaction scheme for the conversion of syn-gas to DME.

Scheme 1. Proposed reaction scheme for the conversion of syn-gas to DME.

Based upon the catalytic results obtained, we can propose that reactions 1 and 2 of Scheme 1 are favored by the presence of MgO, and hence the formation of by-products via reactions 3,4 and 5 are minimized. There are two competitive pathways for CO₂ formation, one via water gas shift (WGSR) and other via methanol degradation. It is believed that faster methanol dehydration in the presence of MgO slowed down CO₂ formation via methanol degradation. Additionally, favored hydrogenation of CO₂, formed from WGSR [56], by the Cu/ZnO/MgO/ γ -Al₂O₃ catalyst [35,57-58] reverses the equilibrium of reaction 4 towards methanol side, which results in the formation of more methanol intermediate and hence higher selectivity in DME via methanol dehydration and less selectivity in CO₂. It is also possible that the WGSR was suppressed by the investigated catalysts.

Mass transport calculation was carried out for the best catalyst, which in the present study is CZM(20)- γ -Al₂O₃ (see supplementary information). The Mears criterion [59]

$$\frac{-r'_A \rho_b Rn}{k_c C_{Ab}} < 0.15$$

gave $2.34 \times 10^{-6} < 0.15$ indicating no diffusion limitations. As far as heat transfer limitation is concerned, our catalytic system totally complies with the criterion because during the reaction, the temperature difference between the internal catalyst bed and the external wall of the reactor was less than 2°C suggesting the capability of the catalyst to qualify for the heat transfer criterion as well.

Effect of reaction temperature and pressure. In order to determine the influence of different reaction parameters such as reaction temperature, pressure, space velocity and H₂/CO ratio, CZM(20)- γ -Al₂O₃ was chosen as a model catalyst because of its optimal activity in CO conversion and DME yield. For a better interpretation and evaluation of results, equilibrium CO conversions and DME selectivity were calculated by using Aspen Plus® model (V7.1, Aspen Technology Inc.). The calculated values along with experimental results for temperature and pressure variations are shown in Figure 9. Under experimental conditions of H₂/CO ratio of 1.5 and space velocity of 2000ml/g_{cat}.h, the results show an increase in CO conversions as the reaction temperatures and pressures increased from 240 to 280 °C and 30 to 50 bar (Figure 9a), although this increase is more predominant under experimental conditions. From the trend of change, it is reasonable to predict that the experimental conversions could be equivalent to that of equilibrium values at higher temperatures, although this

Figure 9. Temperature and pressure dependence on CZM(20)- γ -Al₂O₃ catalyzed CO conversions (a) and DME selectivity (b,c), where eq= equilibrium (dashed lines) and exp= experimental (solid lines). Reaction conditions: H₂/CO ratio=1.5, Space velocity= 2000ml/g_{cat}.h.

study was not performed at above 280 °C to prevent an irreversible deactivation of MSC component of the catalyst, owing to sintering effects of copper particles. Furthermore, CO conversions at higher temperatures could be limited by thermodynamic equilibrium conversion [41]. In case of DME selectivity, the results show that the experimental DME selectivity at high pressures (>40 bar) are higher than those of equilibrium values. When compared as a function of temperature raise, the

experimental selectivity values were found to increase from 240 to 260 °C and then decreased at 280 °C (Figure 9c).

Influence of H₂/CO ratio. The effect of H₂/CO ratios on the conversions of CO was studied by varying H₂/CO ratio in the range of 1-3 at fixed temperature (260 °C), pressure (30 bar) and space velocity (2000 ml/g_{cat}.h). The results (Figure 10a) show about 20% increase in CO conversions with an increase in H₂/CO ratio from 1 to 3. The yields of by-products (CO₂, C₁-C₄ hydrocarbons) were also increased with an increase in H₂/CO ratios, resulting in a decrease in DME selectivity. As discussed Scheme 1, higher CO₂ by-product formation at higher H₂/CO value may be associated with enhanced WGSR activity (scheme 1, reaction 3 & 6) by water formed from reactions 2 and 5 (Scheme 1), owing to higher CO conversions and higher C1-C2 hydrocarbons formation.

Figure 10. The effect of (a) H₂/CO ratio and (b) space velocity on CZM(20)- γ -Al₂O₃ catalyzed CO conversions and products selectivity. Reaction conditions: T= 260 °C, pressure =30 bar and H₂/CO ratio=1.5.

Influence of space velocity. The influence of space velocity on CO conversions was studied by varying space velocity in the range of 2000-4000 ml/g_{cat}.h at fixed H₂/CO ratio of 1.5 in the feed gas. As shown in Figure 10b, an increase in space velocity from 2000 to 4000 ml/g_{cat}.h caused a significant increase in by-products formation as well as decrease in methanol dehydration, resulting in a drop of DME selectivity by as much as 60% and an increase in unconverted methanol in the product. The effect is more pronounced in the range of space velocity of 3000-4000 ml/g_{cat}.h. However, CO conversions varied a little (about 10%) in the entire range of space velocity. The observed results at higher space velocity could attribute to the higher rate of methanol formation

than its dehydration, resulting in methanol accumulation in the product stream. Consequently, reverse equilibrium of reaction 1 (Scheme 1) could favor CO conversion via reaction 5, and hence the formation of more C1-C2 hydrocarbons and CO₂ via reactions 5 and 6 of Scheme 1 occurred. A similar trend was also noted in a previous report in which the authors reported almost constant conversion of CO and lower DME selectivity when the space velocity was increased by 3 folds [60]. This trend of CO conversion and DME selectivity as a function of space velocity has also been demonstrated in other literature reports [61-62].

CONCLUSIONS

The synthesis of five hybrid bifunctional catalysts consisting of CZM materials (C = Cu, Z = Zn, M = Mg) of varying amount of MgO as a promoter and their characterizations by XRD, SEM, TEM, NH₃-TPD and H₂-TPR methods are reported. The characterization data suggests that the surface properties, pore diameter, morphology and crystallinity, the nature of acidic sites and reducibility of the catalysts depend on the amount MgO presence. It is observed that MgO (up to 20%) enhances the formation of crystalline malachite structure as an active catalyst precursor for syn-gas to DME (STD) conversion process. Non-crystalline material with high degree of amorphous nature is formed when 30% MgO was added during CZM material synthesis. As-synthesized CZM materials act as methanol synthesis catalysts (MSC), which were homogeneously mixed with γ -Al₂O₃ as methanol dehydration catalyst (MDC) in 2:1 weight ratio to prepare hybrid catalysts. The catalytic effectiveness of the hybrid bifunctional catalysts has been tested for direct conversions of syn-gas (a mixture of H₂ and CO gas of ratio 1.5) on a fixed bed tubular reactor. CO conversions, DME and by-products (CO₂, C₁-C₂ hydrocarbons) selectivity were determined to measure the effectiveness of the hybrid catalysts. The results show maximum effectiveness of the catalyst containing 20% MgO, in terms of high CO conversion (37%), high DME selectivity (83%) and low by-products selectivity (14%). It is explained that uniformly dispersed and accessible malachite crystallite structure of catalyst precursor, medium acidic sites, low pore diameter, optimum Cu to Zn ratio of 2.3 and favored heat capacity in controlling heat rise of the exothermic reaction are the reasons for higher activity of the catalyst containing 20% MgO. CZM(20)- γ -Al₂O₃ was used as a model catalyst for studying CO conversions in syn-gas as a function of reaction temperature, pressure, space velocity and H₂/CO ratio. The results show a significant variation of products distribution in the eluent due to variation of reaction parameters. Higher temperature (>260 °C), H₂/CO ratio (>1.5) and space velocity (>2000 ml/g_{cat}.h) resulted in the formation of more by-products and hence decreased DME selectivity.

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REFERENCES

- [1] S. H. Lima, A. M. S. Forrester, L. A. Palacio, A. C. Faro Jr., *App. Catal. A: Gen.* 488 (2014) 19.
- [2] X. L. Meng, R. Z. Chu, B. Qin, E. W. Yue, T. T. Chen, X. Ywei, *Energy sourc. A: Recovery util. environ. effects* 37 (2015) 870.
- [3] DME Handbook, Japan DME Forum, 2007.
- [4] S. W. Kang, J. W. Bae, K.W. Jun, H. S. Potdar, *Catal. Commun.* 9 (2008) 2035.
- [5] C. Arcoumanis, C. Bae, R. Crookes, E. Kinoshita, *Fuel* 87 (2008) 1014.
- [6] M. R. Rahimpour, A. K. Mostafazadeh, M. M. Barmaki, *Fuel Process. Technol.* 89 (2008) 1396.
- [7] M. Farniaei, M. Abbasi, A. Rasoolzadeh, M. R. Rahimpour, *J. Nat. Gas Chem.* 14 (2013) 158.
- [8] R. Phienluphon, K. Pinkaew, G. Yang, J. Lie, Q. Wei, Y. Yoneyama, T. Vitidsant, N. Tsubaki, *Chem. Eng. J.* 270 (2015) 605.
- [9] K. G. Mbuyi, M. S. Scurrrell, D. Hildebrandt, D. Glasse, *Top. Catal.* 55 (2012) 771.
- [10] Y. Wang, W. Wang, Y. Chen, J. Ma, R. Li, *Chem. Eng. J.* 250 (2014) 248.
- [11] J. H. Kim, M. J. Park, S. J. Kim, O.S. Joo, K. D. Jung, *Appl. Catal. A: Gen.* 264 (2004) 37.
- [12] M. Behrens, *J.Catal.* 267 (2009) 24.
- [13] F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro, F. Frusteri, *J. Catal.* 249 (2007) 185.
- [14] D. Wallet, D. Stirling, F. S. Stone, F. S. Spencer, *Faraday Discuss.* 87 (1989) 107.
- [15] I. Kasatkin, P. Kurr, B. Kniep, A. Trunschke, R. Schlögl, *Angew. Chem. Int. Ed.* 46 (2007) 7324.

- [16] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. L. Kniep, M. Tovar, R.W. Fischer, J. K. Nørskov, R. Schlögl, *Science* 336 (2012) 893.
- [17] J. C. Frost, *Nature* 334 (1988) 577.
- [18] N. Y. Topsoe, H. Topsoe, *Top. Catal.* 8 (1999) 267.
- [19] J. D. Grunwaldt, A. M. Molenbroek, N. Y. Topsoe, H. Topsoe, B.S. Clausen, *J. Catal.* 194 (2000) 452.
- [20] T. Ressler, B. L. Kniep, I. Kasatkin, R. Schlögl, *Angew. Chem. Int. Ed.* 44 (2005) 4704.
- [21] S. Zander, PhD dissertation, the Technical University of Berlin, 2013.
- [22] M. Behrens, F. Z. Girgsdies, *Anorg. Allg. Chem.* 636 (2010) 919.
- [23] M. V. Twigg, M. S. Spencer, *Top. Catal.* 22 (2003) 191.
- [24] M. Kurtz, N. Bauer, C. Buscher, H. Wilmer, O. Hinrichsen, R. Becker, S. Rabe, K. Merz, M. Driess, R.A. Fischer, M. Muhler, *Catal. Lett.* 92 (2004) 49.
- [25] R. Yang, Y. Zhang, Y. Iwama and N. Tsubaki, *Appl. Catal. A: Gen.* 288 (2005) 126.
- [26] B. Hu, K. Fujimoto, *Appl. Catal. B: Environ.* 95 (2010) 208.
- [27] T. Fitzpatrick, T. Hicks, *Advances in methanol synthesis*, March 2010.
- [28] F. Yaripour, F. Baghaei, I. Schmidt, J. Perregaard, *Catal. Commun.* 6 (2005) 542.
- [29] J. Wang, P. A. Chernavskii, A. Y. Khodakov, Y. Wang, *J. Catal.* 286 (2012) 51.
- [30] Y. Fu, T. Hong, J. Chen, A. Auroux, J. Shen, *Thermochim. Acta* 434 (2005) 22.
- [31] S. Jiang, Y. K. Hwang, S. H. Jhung, J. S. Chang, J.S. Hwang, T. X. Cai, *Chem. Lett.* 33 (2004) 148.
- [32] D. Mao, W. Yang, J. Xia, B. Zhang, Q. Song, Q. Chen, *J. Catal.* 230 (2005) 140.
- [33] P. P. Morajkar, J. B. Fernandes, *Catal. Commun.* 11 (2010) 414.
- [34] (a) F. Yaripour, F. Baghaei, I. Schmidt, J. Perregaard, *Catal. Commun.* 6 (2005) 147; (b) S. Dutta, S. De, A. K. Patra, M. Sasidharan, A. Bhaumik, B. Saha, *Appl. Catal. A: Gen.* 409-410 (2011) 133; (c) S. K. Das, M. K. Bhunia, A. Bhaumik, *Dalton Trans.* 39 (2010) 4382.
- [35] J. C. J. Bart, R. P. A Sneed, *Catal. Today* 2 (1987) 1.
- [36] B. Bems, M. Schur, A. Dassenoy, H. Junkes, D. Herein, R. Schlögl, *Chem. Eur. J.* 9 (2003) 2039.
- [37] K. Klier, *Adv. Catal.* 31 (1982) 243.
- [38] I. M. Cabrera, M. L. Granados, J. L. G. Fierro, *Catal. Lett.* 84 (2002) 153.
- [39] R. G. Herman, K. Klier, G. W. Simmons, B. P. Finn, J. B. Bulko, T. P. Kobylinski, *J. Catal.* 56 (1979) 437. [40] P. B. Rasmussen, M. Kazuta, Y. Chorkendorff, *Surf. Sci.* 318 (1994) 267.
- [41] M. Stiefel, R. Ahmad, U. Almond and M. Doring, *Fuel Process. Technol.* 92 (2011) 1466.
- [42] J. W. Bae, S. H. Kang, K. W. Jun, Y. J. Lee, *Ind. Eng. Chem.* 15 (2009) 566.

- [43] J. W. Bae, S. H. Kang, K. W. Jun, Y. J. Lee, *Appl. Catal. B: Environ.* 90 (2009) 426.
- [44] B. Lindström, L. J. Pettersson, P. G. Menon, *Appl. Catal. A: Gen.* 234 (2002) 111.
- [45] S. H. Kang, J. W. Bae, S. H. Kim, G. M. Dhar, K. W. Jun, *Energy Fuels* 24 (2010) 804.
- [46] J. Agrell, H. Birgersson, M. Boutonnet, I. M. Cabrera, R. Navarro, J. Fierro, *J. Catal.* 219 (2003) 389.
- [47] X. M. Liu, G. Q. Lu, Z. F. Yan, *Appl. Catal. A: Gen.* 279 (2005) 241.
- [48] C. M. T. Hayward, B. K. Speronello, W. R. Gustafson, G. S. Koerner, *European Patent* 0224992 (1986).
- [49] W. M. Haynes, *CRC Handbook of Chemistry and Physics*, 91st edition, CRC press, Taylor & Francis group, 2010-2011.
- [50] M. B. Fichtl, J. Schumann, I. Kasatkin, N. Jacobsen, M. Behrens, R. Schlögl, M. Muhler, O. Hinrichsen, *Angew. Chem. Int. Ed.* 53 (2014) 7043-7047.
- [51] J. W. Jung, Y. J. Lee, S. H. Um, P. J. Yoo, D. H. Lee, K. W. Jun, J. W. Bae, *Appl. Catal. B: Environ.* 126 (2012) 1-8.
- [52] K. W. Jun, M. H. Jung, K. S. R. Rao, M. J. Choi, K. W. Lee, *Stud. Surf. Sci. Catal.* 114 (1998) 447.
- [53] R. Montesano, A. Narvaez, D. Chadwick, *Appl. Catal. A: Gen.* 482 (2014) 69.
- [54] K. Kochloeft, W. Meye, *J. Catal.* 28 (1973), 69.
- [55] H. Knözinger, D. Dautzenberg, *J. Catal.* 33 (1974) 142.
- [56] T. Shishido, M. Yamamoto, I. Atake, D. Li, Y. Tian, H. Morioka, M. Honda, T. Sano, K. J. Takehira, *Mol. Catal. A: Chem.* 253 (2006) 270.
- [57] K. M. V. Bussche, G.F. Froment, *J. Catal.* 161 (1996) 1.
- [58] B. Denise, R. P. A. Sneed, *Appl. Catal.* 28 (1986) 235.
- [59] S. T. Oyama, X. Zhang, J. Lu, Y. Gu, T. Fujitani, *J. Catal.* 257 (2008) 1-4.
- [60] Z. Chen, H. Zhang, W. yang, D. Fang, *World Acad Sci Eng Technol.* 68 (2010).
- [61] S. Allahyari, M. Haghighi, A. Ebadi, *Chem. Eng. J.* 262 (2015) 1175-1186.
- [62] D. Mao, J. Xia, B. Zhang, G. Lu, *Energy Convers. Manage.* 51 (2010) 1134-1139.