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Selective production of oxygenates from CO₂ hydrogenation over mesoporous silica supported Cu-Ga nanocomposite catalyst

Amol M. Hengne, Kushal D. Bhatte, Samy Ould-Chikh, Youssef Saih, Jean Marie Basset* and Kuo-Wei Huang*

Abstract: Carbon dioxide hydrogenation to oxygenates (methanol and dimethyl ether (DME)) was investigated over bifunctional supported copper catalysts promoted with gallium (Ga). Supported Cu-Ga nanocomposite catalysts were characterized by X-ray diffraction, transmission electron microscopy with energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy and H₂ temperature programmed reduction. In comparison with Cu-SBA-15 based catalysts, Ga promoted catalysts prepared by the urea deposition method (CuGa/SBA-15-UDP) was found active and selective for CO₂ hydrogenation to oxygenates. The use of Ga as the promoter showed increased acidic sites as confirmed by the NH₃-TPD, Pyridine-IR and 2,6-lutidine-IR studies. The favorable effect of Ga on CO₂ conversion and selectivity to oxygenate may come from the strong interaction of Ga with silica, which is responsible for the enhanced metal surface area, formation of nanocomposite and metal dispersion. Notably, incorporation of Ga to Cu/SiO₂ showed a several-fold higher rate for methanol formation (13.12 $\mu\text{mol/g}_{\text{Cu}}\cdot\text{sec}$) with a reasonable rate for the DME formation (2.15 $\mu\text{mol/g}_{\text{Cu}}\cdot\text{sec}$) as compared to those of Cu/SiO₂ catalysts.

Introduction

Methanol and dimethyl ether (DME) production from the selective hydrogenation of carbon dioxide could be a useful method for the utilization of less hazardous CO₂ as an alternative to toxic and reactive CO, which is extensively used nowadays at the industrial scale for the production of several chemicals and fuels.^[1] Moreover, selective conversion of CO₂ to value added products could be a green and economically viable strategy towards the mitigation of global warming.^[2] Both methanol and DME are currently considered as suitable starting components for various downstream processes. In particular, DME has been recently considered as a potential clean oxygenated additive to overcome the emission problems of the diesel engine. Furthermore, it is nontoxic and can be used to replace LPG for cooking, heating, electrical power generation, etc.^[3-5] Despite numerous studies devoted to the catalytic synthesis of DME, there are still various challenges to overcome before practical industrial applications.^[6,7] Two main routes are envisaged for the production of DME from CO₂, i) a two-step process, whereby methanol produced on a metallic catalyst in the first step is subsequently dehydrated over solid acid catalyst to make DME, and ii)

a single-step process which can be conducted in one reactor over bi-functional catalysts having both hydrogenating (metallic) and dehydrating (acid) functions.^[8-10]

The synthesis of methanol through hydrogenation of CO or CO₂ were mainly investigated over copper based catalysts in the presence of various modifiers (Zn, Zr, Ce, Al, Si, V, Ti, Ga, B, Cr, etc.).¹¹⁻¹⁹ Conversion of CO₂ to methanol and DME or *in situ* conversion of methanol to DME in one step may help to displace the equilibrium for CO₂ hydrogenation towards methanol production.^[20] As such, a great deal of research was devoted to the study of combinations of the well-known tri-component (CuZnAl) methanol synthesis catalyst with acidic zeolite (e.g. ZSM-5) as catalyst for this reaction.^[21] However, under typical hydrogenation conditions, this combination usually yields unstable catalysts as the microporous nature of ZSM-5 imposes severe diffusion limitations. Indeed, the use of acid catalysts during dehydration steps often leads to the formation of coke on the catalyst surface, which limits access to active sites and hence leads to a decrease in activity with time on stream.^[22] There is a need to develop efficient catalyst systems having desirable properties, e.g. high specific surface area, highly active site, dispersion, appropriate acid/basic sites distribution and smaller particle size in order to increase the activity and selectivity to oxygenates during CO₂ hydrogenation.^[23] Utilization of a suitable support could lead to the formation and stabilization of the active phase of the catalyst as well as tuning the interactions between the major component and the promoter.^[24]

Because of the high surface area and wide pore volume of SBA-15, one would expect a better catalytic performance of supported Cu-Ga mixed oxides during the production of oxygenates from CO₂ hydrogenation. Herein, we present the results dealing with the preparation, characterization, and catalytic activity of Cu-Ga mixed oxides supported on mesoporous silica (SBA-15) catalysts.

Results and Discussion

The results of surface area, pore volume and pore size determined using N₂ adsorption at (-196 °C) over supported Cu-Ga catalysts are summarized in Table 1. The specific surface area of SBA-15 is 722 m²/g, with an average pore size of 6.2 nm. After the deposition of Cu and/or Cu-Ga, the BET surface area decreased significantly. This was further confirmed with the linear decrease in the pore volume. All the catalysts showed type (IV) N₂ adsorption and desorption isotherms, and the results were consisted with the H₂ hysteresis loop, indicating that they all possess cylindrical pores having modified pore structures.^[25] The isotherms of Cu and/or Cu-Ga incorporated catalysts showed slightly sharp and destructed H₂ hysteresis loop as compared to the parent SBA-15, presumably because of the partially deformed ordered structures, as seen from the space between the pores

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of silica wall (Figure S1a-b). The obtained differences in pore size distribution by using N_2 desorption method could come from the high concentration of Cu-Ga in the channels of silica, but there is no obvious change found in the pore size distribution in the recovered catalysts. These observations suggest that the mesoporous nature of silica support was only altered to slightly smaller pore sizes with the UDP method (Figure S2a-b).

Table 1. Textural properties of supported Cu-Ga catalysts.

Catalyst	Surface Area (m^2/g)	Pore volume (cc/g)	Pore Size (nm)	Particle Size (nm)*
SBA-15- Calcined	722	1.1	6.2	N/A
9Cu/SBA-15- IMP calcined	502	0.79	6.2	15
16Cu2Ga/SBA- 15-IMP Calcined	359	0.66	6.1	20
10Cu5Ga/SBA- 15-UDP Calcined	387	0.58	6.1	28
10Cu5Ga/SBA- 15-UDP Recovered	343	0.56	6.07	N/A

*Particle size (nm) calculated by N_2O method, N/A: Not applicable.

XRD patterns of calcined CuGa catalysts prepared by impregnation and urea deposition methods are shown in Figure 1a. The appearance of indexed diffraction lines at $2\theta = 35.7^\circ$, 38.8° , 48.1° , and 64.1° can be attributed to the presence of CuO crystalline phase [JCPDS file no. 80-1268]. The XRD patterns of all used 16Cu10Ga/SBA-15-IMP and 10Cu5Ga/SBA-15-UDP catalysts exhibited diffraction peaks characteristic of the inert carborundum, which is used to dilute the catalyst during the reaction (Figure 1b). Those catalyst samples recovered after the reaction showed peaks at $2\theta = 43.5^\circ$ (111), 50.6° (200) and 74.3° (220), indicative of the presence of metallic Cu in all used catalysts [JCPDS file no. 04-0836]. In all the samples no characteristic peaks of Ga oxides were observed indicating either amorphous nature of Ga oxides and/or being diffused in the bulk matrix of the silica support. The presence of a small peak at $2\theta = 36.50^\circ$ is likely due to the formation of Cu_2O . The latter might be formed via partial oxidation of metallic Cu while exposing the samples to air before XRD or during the preparation procedures as discussed in the XPS study. The estimated particle sizes of metallic Cu were found to be in the range of 10-20 nm based on the calculation from the Scherer equation using the intense peak at $2\theta = 43.5^\circ$, allowing us to correlate with the particle sizes obtained from the HRTEM study.

XPS of 16Cu10Ga/SBA-15-IMP and 10Cu5Ga/SBA-15-UDP catalyst samples after reaction exhibit an intense doublet at 932.8 and 952.4 eV (Figures S3 and S4), which can be attributed to the electron ejection from the $Cu2p_{3/2}$ and $Cu2p_{1/2}$ core shells of metallic Cu, respectively. The disappearance of satellite peaks, characteristic of Cu^{2+} species, suggests that most of the surface CuO has been reduced to the metallic form after the reaction.

Figure 1. XRD patterns for: (a) Calcined 16Cu10Ga/SBA-15-IMP and 10Cu5Ga/SBA-15-UDP catalysts, (b) Carborundum, Recovered 16Cu10Ga/SBA-15-IMP and 10Cu5Ga/SBA-15-UDP catalysts.

This observation is consistent with the TPR results (Figure 3), clearly indicating the almost complete reduction of CuO in all the catalysts under the hydrogenation conditions. Distinguishing Cu^0 from Cu^+ species based solely on their Cu 2p binding energies is not unambiguous. Nevertheless,

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judging from the asymmetric shape of Cu LMM Auger spectra, one could tentatively conclude that both Cu^+ and Cu^0 are present on the catalyst surface, as observed in 10Cu5Ga/SBA-15-UDP compare to impregnation 16Cu10Ga/SBA-15-IMP.^[26]

Similarly, the intense doublets at 1118.4, 1118.16 and 1145.2 eV represent the binding energy of $\text{Ga}2p_{3/2}$ and $\text{Ga}2p_{1/2}$ indicative of the Ga^{3+} oxidation state. HRTEM images of the 10Cu5Ga/SBA-15-UDP catalyst before and after reaction are shown in (Fig. 2). The SBA-15 support shows the characteristic hexagonal pore structure with particle sizes in the range of 100-300 nm (Figure S4a). Using the impregnation method to load Cu and Ga (16Cu10Ga/SBA-15-IMP) species appeared to cause partial destruction of the ordered mesoporous structure of the SBA-15 support.

Figure 2. HRTEM images 10Cu5Ga/SBA-15-UDP a) Calcined, b-c) Activated d) Reaction recovered.

In this case, the Cu-Ga nanocomposite particles have an average size between 20-40 nm and are present both on and outside the surface of the SBA-15 support (Figures S4b-d). Meanwhile, the UDP method yielded better dispersed (10Cu5Ga/SBA-15-UDP) supported Cu-Ga species with a relatively smaller average particle size between 5 to 20 nm (Fig. 2b-c), in good agreement with the value of 15 nm estimated from the XRD patterns of the used catalysts (*vide supra*). Moreover, the activated sample 10Cu5Ga/SBA-15-UDP has been further explored by using DF-STEM imaging and mapping of the elements by STEM-EELS (Figure 3). The images suggested that the Cu-Ga particles are well dispersed in the mesoporosity of SBA 15 support (Figure 3 a). The high magnification image showed several Cu-Ga nanocomposites

stack in the pores of SBA-15 (Figure 3 b). The Cu-Ga particles observed in 10Cu5Ga/SBA-15-UDP showed lattice fringes, which is mainly corresponding to Cu {111} and {220} planes, in agreement with XRD results. The elemental mapping demonstrate that Ga and Cu atoms tends to segregate (Figure 3 c). While the copper atoms tends to form nanoparticles (Figure 3 d), gallium atoms seems to form an amorphous phase inside the SBA-15 pores.

Figure 3. Dark field STEM image of Cu5Ga/SBA-15-UDP activated sample (a and b), c) segregation of Ga and Cu atoms highlighted by elemental mapping from STEM-EELS. Yellow square on image c) show the area where the EELS spectrum image was recorded. The inset in c) is a colored overlay of the EELS maps corresponding to Cu and Ga L-edge. Image d) shows metallic Cu nanoparticles left outside the SBA-15 support. The inset in image d) is a fast Fourier transform applied to the whole picture which show characteristic d-spacings attributed to {220} and {111} planes of Cu metal.

The metallic Cu is generally the active species (or at least involved in the activation of H_2) in the catalytic hydrogenation of CO_2 and one can thus expect a better activity to be observed when highly dispersed Cu species are prepared (at lower temperatures). Accordingly, H_2 -TPR experiments were performed in order to investigate the reducibility of Cu for all prepared catalysts (Figure 4). All samples exhibited a sharp reduction feature centered between 160 and 280 °C. These peaks are attributed to the consumption of H_2 during the reduction of CuO to the metallic Cu.^[27] In the case of 9Cu/SBA-15-IMP catalyst, such H_2 consumption reached its maximum at 267 °C, but the maximum H_2 consumption occurred at a lower temperature in the presence of Ga. These observations suggest that Ga may activate H_2 and hence improve the Cu reducibility.^[28, 40] Addition of gallium is expected to lead to a better reducibility and higher dispersion of supported copper oxide species (*Cf.* the results of XRD and HRTEM). The reduction of well dispersed Cu surface in

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10Cu5Ga/SBA-15-UDP indicated the sequential reduction pattern for copper oxide (Cu^{2+}) to metallic Cu (Cu^0) via Cupric oxide (Cu^+).

Figure 4. H_2 TPR study of copper and Cu-Ga oxide catalysts.

Figure 5. NH_3 TPD profiles of supported copper catalysts.

Acidity measurements (NH_3 -TPD) were also carried out (Figure 5). Monometallic Cu catalysts showed ammonia desorption peak at temperatures from 100–250 °C, indicative of the presence of weak acid sites and similar results were observed with 16Cu10Ga/SBA15-IMP. In contrast, Ga incorporated 10Cu5Ga/SBA15-UDP catalysts showed two NH_3 desorption peaks in both temperature ranges from 100–300 °C and 350–500 °C, suggesting that addition of Ga increases the acid strength compared to those of the monometallic Cu catalyst and Cu-Ga prepared by the impregnation method.

Figure 6. 2,6-lutidine desorption on 10Cu5Ga/SBA15-UDP; a) activated sample b) 200 °C c) 300 °C d) 400 °C.

In order to optimization of acidic sites and strength, the acidic characters of the catalysts were further established by IR using both pyridine and 2,6-lutidine as probe molecules (Figures S6–S11). The peaks at 1455 cm^{-1} and 1545 cm^{-1} are corresponding to the nature of Lewis and Bronsted acid sites, respectively. Pyridine adsorption followed by FTIR further confirmed the presence of Lewis acid sites on all catalysts.^[29–30]

On the other hand, 2,6-lutidine was used to identified weak and moderate Bronsted acid sites.^[31] SBA-15 supported monometallic Cu catalysts did not show any peak of Bronsted acid sites, but peaks at 1618 and 1583 cm^{-1} , corresponding to the weak Lewis acid sites using 2,6-lutidine. However, incorporation of Ga and Cu-Ga to silica exhibited Bronsted acid sites peaks at 1625 and 1645 cm^{-1} along with characteristic peaks of Lewis acid sites using both probe molecules (Figure 6). Estimation of acid sites were conducted at different temperatures from 100 to 400 °C, Cu (9Cu/SBA-15-IMP) and Cu-Ga (10Cu5Ga/SBA-15-UDP) containing catalysts did not showed measurable stability of acid sites above 300 °C, while some of acid sites were observed in 5Ga/SBA-15.

The combination of supported Cu-Ga (10Cu5Ga/SBA-15-UDP) catalyst showed both Lewis and Bronsted acid sites with a strong acid strength (178 $\mu\text{mol/g}$) at 200 °C, three times more than those of monometallic 9Cu/SBA15-IMP catalysts (200 °C) (Table 2 and Figures S6–S11). These observations clearly suggest that the higher acidic strength of SBA-15 supported Cu-Ga play an important role in the dehydration of methanol to DME.

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Table 2 Acidic Strength of Cu, Ga and Cu-Ga catalysts using (pyridine and 2,6-lutidine) IR study

Catalyst	Lewis acid strength ($\mu\text{mol/g}^*$)	Bronsted acid strength ($\mu\text{mol/g}^{\#}$)	Total Acid strength ($\mu\text{mol/g}^{\#}$)
9Cu/SBA-15- IMP calcined	60	<0.01	60
5Ga/SBA-15- UDP Calcined	85	63	148
10Cu5Ga/SBA-15- UDP Calcined	140	38	178

*Acid strength calculated from pyridine as a probe molecule measured at 200 °C

[#]Acid strength calculated from 2,6-lutidine as a probe molecule measured at 200 °C

The results of the catalytic hydrogenation of CO₂ using different copper catalysts at 250 °C, 25 bar and a weight hourly space velocity around 30000 h⁻¹ are summarized in Table 2. The major products were methanol (MeOH) and dimethyl ether (DME). Only traces of carbon monoxide (CO) could be detected in the outlet stream under the present operating conditions. All catalytic data were taken when the catalyst reached a steady state.

Table 3 Catalytic performance for CO₂ hydrogenation over supported

Catalyst	Carbon Balance, %	Conversion, %	Selectivity, %		
			CH ₃ OH	CO	DME
10Cu5Ga/SBA-15UDP	99.95	3	71	<0.01	29
4Cu2Ga/SBA-15UDP	99.95	2	73	<0.01	27
10Cu/SBA-15IMP	100	0.045	99.9	<0.01	<0.01
16Cu10Ga/SBA-15IMP	99.96	1	78	<0.01	22
17Cu13Zn/SBA-15IMP	99.98	1	99.9	<0.01	<0.01

copper catalysts

Reaction conditions: T = 250 °C, P = 25 bar, Gas Flow (CO₂/Ar/H₂) = 5/5/15 ml/min, GHSV 30000 h⁻¹, CO₂/H₂ = 1:3, Time, 24h

Initially, copper in combination with Zn catalyst (17Cu13Zn/SBA-15 Imp), which is prepared by using

impregnation method, showed almost 99% selectivity to methanol. Monometallic 10Cu/SBA-15 catalyst showed very low conversion (around 0.05 %) with no formation of DME whereas introduction of Ga using impregnation (16Cu10Ga/SBA-15Imp) significantly improves the conversion to reach 1 %. Moreover, we detect the formation of DME with selectivity 22%. When using urea deposition-precipitation method to add Ga (10Cu5Ga/SBA-15UDP) showed increase in conversion up to 3% with both methanol and DME selectivity 71% and 29% respectively. Under the present operating conditions, the conversion of CO₂ is generally low. This could be due to the low residence times used in the present investigation. The effect of contact time on product activity and selectivity is further discussed below.

The results of the catalytic hydrogenation of CO₂ using different copper catalysts at 250 °C, 25 bar and a weight hourly space velocity around 30000 h⁻¹ are summarized in Figure 7. The major products were methanol (MeOH) and DME. Only traces of carbon monoxide (CO) could be detected in the outlet stream. All catalytic data were taken when the catalyst performance reached a steady state. The effect of Ga on the catalytic performance was assessed in terms of the formation rate of oxygenates. The monometallic Cu catalyst (Cu-SBA-15) showed a low methanol formation rate of 0.69 $\mu\text{mol/g}_{\text{Cu}}\cdot\text{sec}$ without any detectable DME formation. Interestingly, Ga promoted Cu catalysts prepared by impregnation (16Cu10Ga/SBA-15-IMP) and urea deposition method (10Cu5Ga/SBA-15-UDP) showed eight to ten times increase in the methanol formation rate (7.19-13.12 $\mu\text{mol/g}_{\text{Cu}}\cdot\text{sec}$), with the formation rate of DME between 0.084 and 2.15 $\mu\text{mol/g}_{\text{Cu}}\cdot\text{sec}$. The lower activity of 16Cu10Ga/SBA-15-IMP compared to those of 10Cu5Ga/SBA-15-UDP are likely a result of the increase in particle sizes and agglomeration of particles during the preparation of Cu-Ga nanocomposites by wet impregnation method (Figure S5).

Figure 7. Formation rate of methanol and DME. Reaction conditions: T = 250 °C, P = 25 bar, Gas Flow (CO₂/Ar/H₂) = 5/5/15 ml/min, GHSV 30000 h⁻¹, CO₂/H₂ = 1:3, Time, 24h.

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The weak basic urea used as the precipitation agent in the homogeneous phase helped to avoid agglomeration of primary particles to offer uniform sizes and shapes (Table T1).^[32] Addition of Ga to Cu/SBA-15 catalysts seemed to promote the catalytic formation of methanol and DME. The formation of DME upon addition of Ga (Figure 7), can be attributed to the dehydration of methanol in the presence of Bronsted acid sites as demonstrated in the FT-IR study (Figures S7 and S9). Indeed, the introduction of Ga via UDP yielded an even more active catalyst. The results of XRD, H₂-TPR, N₂O titration and HRTEM are consistent with the fact that the introduction of Ga via UDP preparation method would improve both reducibility and dispersion of the supported Cu species. Accordingly, one can ascribe the better catalytic performance of 10Cu5Ga/SBA-15-UDP to better reducibility and higher dispersion of supported Cu species. While the exact mechanism of the Ga promotion is still unclear, literature studies on analogous Pd/ β -Ga₂O₃ catalysts suggested that the enhancement of the activity may come from gallia surface, where carbon dioxide is chemisorbed to form carbonate species along with the dissociative absorption of H₂ on gallium.^[33] In addition, it has also been shown that Ga allows the formation of Bronsted and Lewis acid sites in combination of silica,^[34] which subsequently dehydrate the formed methanol to dimethyl ether.

It has been demonstrated from previous studies that the intrinsic activity of Cu, measured as turnover frequency (TOF), depends on the Cu particle sizes. To get further insight into the effect of Ga addition on the intrinsic activity of supported Cu metallic species during the hydrogenation of CO₂ at 250 °C and 25 bar, the TOF (s⁻¹) vs. Cu particle size (nm) as well as TOF (s⁻¹) vs. Cu surface area (m²/g) were determined (Figure 8).

Figure 8. the Relationship between TOF of CH₃OH Vs a) Cu surface area, b) Cu- particle size. Reaction conditions: T= 250 °C, P = 25 bar, Gas Flow (CO₂/Ar/H₂)= 5/5/15 ml/min, GHSV 30000 h⁻¹, CO₂/H₂ = 1:3, Time, 24h.

Interestingly, the TOF of methanol decreases linearly with increasing the average Cu particle sizes, while increasing Cu metal surface area favors the increase in TOF of methanol. These results suggest that the addition of Ga may promote the formation of smaller Cu particles and thus increase the metal surface area for a higher TOF for methanol formation.^[35-36]

We hypothesize that the Ga present on the surface could act as a strong anchoring site for the supported Cu species leading to higher dispersion upon reduction. Therefore, the excellent catalytic performance of our Cu-Ga catalysts supported on mesoporous silica can be rationalized by the high surface area of support and uniform pore size distribution.

Effect of temperature

Figure 9 shows the CO₂ conversion obtained under different temperatures ranging from 200 to 250 °C with a constant pressure (25 bar) and the same contact time (WHSV 30000 h⁻¹). As expected, the CO₂ conversion increased from 0.75 to 3% with increasing temperature from 200 to 250 °C. Meanwhile, the selectivity to methanol was decreased from 87 to 71% with a concomitant increase in the selectivity to DME. If one assumes that the formation of DME proceeds through a sequential mechanism whereby hydrogenation of CO₂ leads first to the formation of methanol, one can conclude that the dehydration of methanol to DME has a much higher activation energy, and hence a lower selectivity is observed at lower temperatures.

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Figure 9. Effect of temperature on CO₂ hydrogenation and oxygenate selectivity over 10Cu₅Ga/SBA-15-UDP. Reaction conditions: T = 200–250 °C, P = 25 bar, Gas Flow (CO₂/Ar/H₂) = 5/5/15 ml/min, GHSV 30000 h⁻¹, CO₂/H₂ = 1:3, Time, 24h.

Under the present operating conditions, no CO formation was detected. This is expected due to the endothermic nature of the RWGS reaction, which is usually thermodynamically limited at low temperatures.^[37] In fact, when the temperature was further increased to 300 °C (25 bar and 30000 h⁻¹), CO was formed as a main product (selectivity around 60%; Figures S10).

Effect of contact time

Figure 10. Effect of contact time on CO₂ hydrogenation and oxygenate selectivity over 10Cu₅Ga/SBA-15-UDP. Reaction conditions: T = 250 °C, P = 25 bar, Gas Flow (CO₂/Ar/H₂) = 5/5/15 ml/min, CO₂/H₂ = 1:3, Time, 24h.

The hydrogenation of CO₂ over 10Cu₅Ga/SBA-15-UDP was studied by varying the contact time using the catalyst from the same batch with various feed flows (Figure 10). The conversion was found to increase linearly when increasing the contact time. Using low contact time, and the selectivity to methanol is high whereas the selectivity to DME is relatively low. Further increasing the contact time leads to a decrease

in the selectivity of MeOH with a concomitant increase in the selectivity of DME. These observations suggest that the reaction may proceed via a sequential mechanism whereby CO₂ is first hydrogenated to MeOH and dehydrated later to DME. Under the present operating conditions, no CO formation was detected. The catalyst was further examined at a higher catalyst loading (five times) at 200–250 °C (Figures S11&S12). It was found that the conversion of CO₂ was increased from 2% to 11% with increasing the reaction temperature from 200 to 250 °C.

However, the selectivity to oxygenates (methanol and DME) was lowered from 78% to 45% with CO formation from 22–55% from temperature 200 to 250 °C. It was clearly demonstrated that with a low catalyst loading and contact time highly selective production of oxygenates can be achieved (99%).

Effect of total (CO₂ and H₂) pressure

As stated in the literature, high pressures are necessary for selective hydrogenation of CO₂ to methanol.^[38–39] The CO₂ conversion was about ≤0.5% at the reaction pressure of 1 bar (Figure 11).

Figure 11. Effect of H₂ pressure on CO₂ hydrogenation and oxygenate selectivity over 10Cu₅Ga/SBA-15-UDP. Reaction conditions: T = 250 °C, P = 1, 10 and 25 bar, Gas Flow (CO₂/Ar/H₂) = 5/5/15 ml/min, GHSV 30000 h⁻¹, CO₂/H₂ = 1:3, Time, 24h.

When the pressure was increased to 25 bar, an increase in CO₂ conversion to 0.5–3% was observed. The improvement of selectivity to DME from 15 to 29% was also achieved with increasing pressure from 1 to 25 bar.

Time on stream activity

Considering the interesting results obtained with the 10Cu₅Ga/SBA-15-UDP catalyst, a time on stream test was conducted while keeping all other parameters constant (Figure 6). The catalyst maintained a very high productivity for the methanol formation at 13.12 μmol/g·sec along with a DME formation rate of 2.15 μmol/g·sec over 50 h (Figure 12). Our

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catalysts showed stable performance during time on stream stability test presumably due to the high surface area of the SBA-15 support with availability of the pores and the formation of stable Cu-Ga nanocomposite to effectively avoid the thermal agglomeration under the hydrogenation conditions. Ga acts as a promoter and stabilizer, and can create the appropriate acidic sites and enhance the acidic strength in combination with silica, to favor the dehydration of methanol to DME.

Figure 12. Time on stream activity for formation rate of oxygenate over 10Cu5Ga/SBA-15-UDP. Reaction conditions: $T = 250\text{ }^{\circ}\text{C}$, $P = 25\text{ bar}$, Gas Flow ($\text{CO}_2/\text{Ar}/\text{H}_2$) = 5/5/15 ml/min, GHSV 30000 h^{-1} , $\text{CO}_2/\text{H}_2 = 1:3$, Time, 50h.

As a result, Cu-Ga nanocomposite supported on SBA-15 plays a vital role to maintain the consistent activity and productivity to oxygenates during time on stream.

Conclusion

In the single step oxygenates synthesis from CO_2 hydrogenation, the Cu-Ga catalysts are highly active and selective for the methanol and DME production because of increasing acidic sites (Bronsted and Lewis), i.e. metal (Cu) surface area and Cu particle size. The presence of Ga indeed enhances both the rate of methanol formation and the product selectivity of DME (30-40%) as compared to those of supported Cu catalysts. These Cu-Ga catalysts also showed excellent performance in the stability test for up to 50 h with constant selectivity for the formation of oxygenates (99%).

Experimental Section

Materials

High purity gases (Hydrogen 99.9995%, CO_2 , argon 99.9999%) were purchased from Specialty Gases Center of Abdullah Hashim Industrial Gases & Equipment Co. Ltd. (Saudi Arabia). Copper nitrate, gallium nitrate, zinc nitrate, amphiphilic triblock copolymer [poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)], tetraethyl

orthosilicate (TEOS) and Urea were purchased from Aldrich and used directly.

Catalyst preparation

SBA15

Mesoporous silica SBA-15 was prepared according to the literature.^[40] 2.0g of amphiphilic triblock copolymer (P123) was dissolved in 15.0 ml of water and mixed with 60.0 g of 2M $\text{HCl}_{(\text{aq})}$, and to this solution, 4.250 g of tetraethyl ortho-silicate (TEOS) were slowly added under constant stirring. The resulting mixture was stirred for additional 24h at $40\text{ }^{\circ}\text{C}$ and then aged in a Teflon bottle at $100\text{ }^{\circ}\text{C}$ for 48h. The solid precipitate was filtered and washed with deionized water until a neutral pH was reached. The solid was dried in open air and finally calcined in static air at $550\text{ }^{\circ}\text{C}$ for 24 h to decompose the triblock copolymer.

Impregnation method IMP-A

Supported Cu, Ga and Zn catalysts were prepared by the wet impregnation method. The synthesis was performed by suspending 0.50 g of SBA-15 in the aqueous medium with specific amounts of the respective metal precursors such as Cu nitrate, Zn nitrate and Ga nitrate. The suspension was stirred for 8 h at room temperature and filtered. The resulting solid was dried at $120\text{ }^{\circ}\text{C}$ for 12 h and calcined at $450\text{ }^{\circ}\text{C}$ for 8 h.

Urea Deposition Co-precipitation UDP-B

To an aqueous suspension of specific amount of the Cu nitrate, Ga nitrate, urea, 0.50 g of calcined SBA-15 was slowly added and then the mixture was stirred and heated at $90\text{ }^{\circ}\text{C}$ for 8 h. The resulting precipitate was filtered, dried in static air at $120\text{ }^{\circ}\text{C}$ for 12 h, and finally calcined at $450\text{ }^{\circ}\text{C}$ for 8 h.

Catalyst testing

All catalytic tests were conducted in gas phase using a fixed bed isothermal flow reactor purchased from Process Integral Development and engineering Technology (PI&D Eng. & Tech.). In a typical experiment, 0.50-0.250g of the as prepared catalysts (vide supra) diluted with inert carborundum (0.950-0.750g) were loaded into a stainless-steel (SS-316) reactor (length 30 cm and 9 mm *i.d.*). The SS tube is equipped with a 20 μm mesh size porous plate made from Hastelloy C, which is used to hold the catalyst inside the reactor. The catalyst was then reduced at $250\text{ }^{\circ}\text{C}$ in a flow of 5% H_2/Ar (5 mL/min @ *NTP*) for 12 h and later cooled to room temperature. The reactor was then heated to $250\text{ }^{\circ}\text{C}$ (50 $^{\circ}\text{C}/\text{min}$) under a mixture of gases (5mL/min@NTP) CO_2 , (15mL/min@NTP) H_2 and (5mL/min@NTP) Ar (1:3:1) having total feed flow (25 mL/min @ *NTP*). The pressure (1 to 25 barg) inside the reactor was controlled using an automated micrometric valve.

On-line gas analysis of the products was performed on a Varian 450 GC gas chromatograph. A sample from the reactor outlet stream was automatically injected on three parallel

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channels referred to here as channel A, channel B and channel C. In Channel A, the sample (1ml @ STP) was injected on a set of three packed columns, "Hayesep" Q (CP81073), "Hayesep" T (CP81072), and "Molsieve" 13X (CP81073) connected in series. A set of 10-way and 6-way Valco valves were used to allow automatic injection of the sample, backflushing of Hayesep T, and bypassing of Molsieve 13X columns. This channel was equipped with a TCD detector (He as reference gas) and used to monitor the amounts of CO and CO₂. Channel B uses a set of two capillary columns, CP-Wax 52 CB (CP8553) as a pre-column and Al₂O₃ MAPD (CP7432) connected in series. This channel was used to monitor methane, ethane, and ethylene. Meanwhile, channel C uses a CP-wax 52CB column (CP7668) to separate oxygenates. Each one of these two channels was equipped with a Flame Ionization Detector (FID). A 10-way Valco valve was used to allow simultaneous injection of the gas samples on both Channels A (500 µl @ STP was injected) and B (250 µl @ STP was injected). Estimation of CO₂ conversion was determined directly from the carbon balance, based on the product concentrations for which the sensitivity is higher. The formation rate of methanol is defined in micromoles of methanol produced per gram of Cu in the catalyst per second. Turn over frequency (TOF) is expressed as the number of methanol molecules produced per surface copper atom of the reduced catalyst per second.

Characterization methods

Surface area measurements were carried out using N₂ adsorption/desorption isotherms at 77 K on a Micromeritics@ ASAP2420. Prior to measurements, the catalyst samples were degassed in vacuum for 2 h at 250 °C and then surface areas of the samples were analyzed by using the multipoint BET analysis method in the P/P₀ = 0.05–0.30 pressure range. X-ray diffraction (XRD) patterns of all samples were collected using Bruker D8 Advanced A25 diffractometer with Cu K radiations, which is operated at 40 kV and 40 mA. The data sets were acquired in the step scan mode in the range of 20–80°, using a step interval of 0.05 and a counting time of 10°/min.

The TEM specimens were prepared by placing 1 µL of solution on carbon coated copper grids. The grids were then plasma cleaned for 50 seconds to reduce hydrocarbon contamination (Solarus, model 950). HRTEM images were obtained with a Tecnai T12 operated at 120 kV. Dark-field scanning transmission electron microscopy (DF-STEM) was performed on a Titan G 60–300 ST electron microscope at an accelerating voltage of 300 kV using a Gatan STEM detector (model 806). The elemental compositions of the samples were characterized based on the acquisition of spectra from electron energy loss spectroscopy (EELS). A small camera length of 38 mm was selected for imaging and elemental mapping in order to enhance the signal to noise ratio of the EELS spectra. Maps were recorded by using a beam current of 0.5 nA and a dwell time of 50 µs/pixel. The Cu and Ga L-edges were selected to build the chemical maps.

A special care was taken with the definition of the energy window and background for Ga L-edges in order to avoid the overlap with the Cu L₁-edge. H₂ Temperature programmed measurements (TPR) were carried out using an Altamira Instrument (AMI-200lp) equipped with a TCD detector to measure the H₂ uptake. The catalyst sample (about 0.0250g) was kept in a U-shaped quartz tube and pretreated under Ar flow (50 ml/min) for 2h at 250 °C in order to remove moisture and other surface impurities present on the sample. Further, the sample was allowed to cool down at room temperature under flow of Ar and then the gas was replaced by a mixture of 5% H₂/Ar for the TPR experiment. Finally, the temperature was raised from 50 °C to 750 °C (10 °C/min) under a flow of 5% H₂/Ar flow (50 ml/min). The X-ray photoelectron spectroscopy (XPS) of catalyst samples were carried out using Kratos AMICUS/ESCA 3400 spectrometer, using a monochromatic Mg Kα X-ray source operating at 120W and a pass energy of 20 eV under an operating pressure of 10⁻⁶ mbar. The binding energies of Cu2p and Ga2p core levels are referenced to the C 1s core level at 285.6 eV.

Copper surface area and dispersion were measured by a nitrous oxide decomposition method using Altamira Instrument (AMI-200lp). In a typical experiment, 0.030g of the catalyst sample were first reduced under 5% H₂/Ar at 250 °C for 2 h followed by purging with He for 30 min and cooling to 60 °C. The catalysts were then exposed to 10% N₂O/He for 1h, in order to oxidize surface copper atoms to Cu₂O. Finally, the samples were cooled to room temperature and subjected to temperature programmed reduction (TPR) from 50 °C to 350 °C (10 °C/min) using 5% H₂/Ar flow to reduce Cu₂O back to metallic Cu. Cu surface area and dispersion were calculated from Cu surface area and dispersion were calculated from the amount of H₂ consumed during the TPR step by assuming that copper crystallites are spherical.^[41-42] Equation 1 is used to calculate Cu surface area

$$Cu\ S.A. \left(\frac{m^2}{g} \right) = \frac{[100(mol\ H_2)(SF)(N_A)]}{[(SD_{Cu})(W_{Cu})]} \quad (1)$$

Where mol H₂ = amount of H₂ consumed during the TPR step per unit mass of the catalyst (mol H₂/g_{cat}), SF = stoichiometric factor = 2, N_A = Avogadro's number = 6.022 × 10²³ atoms/mol, SD_{Cu} = copper surface density = 1.47 × 10¹⁹ atoms/m², W_{Cu} = Cu concentration evaluated from elemental analysis (wt. %). Copper dispersion is the surface copper to the total copper concentration in the catalyst. Cu dispersion (%) was estimated using equation 2.

$$\%D_{Cu} = [10^4 (mol\ H_2)(SF)(At.Wt.Cu)]/W_{Cu} \quad (2)$$

Where At.Wt.Cu = Atomic weight of Cu = 63.54.

The surface acidity of different catalysts were assessed using Temperature Programmed Desorption of NH₃ (NH₃-TPD). All experiments were performed using the same Altamira instrument described above. The catalyst sample (0.025g)

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was placed in a U-shaped quartz tube and the whole system was purged with Ar (25 mL/min @STP) for 15 minutes. Prior to each NH₃-TPD experiment, all catalyst samples were heated under a flow of H₂ (50 mL/min) up to 250 °C and then kept at the same temperature for another 1h. After cooling to 50 °C, the catalyst was then exposed to a stream of 1% NH₃/He (25 mL/min @ STP) for 1h. Weakly (or “reversibly”) adsorbed ammonia was subsequently removed by purging the catalyst under He for ca. 1h. The purging step was monitored by a Hiden HPR 20 Quadrupole Mass Spectrometer (QMS), and the amount of “reversibly” adsorbed ammonia was generally observed to decrease with time to finally reach negligible levels within 1 hour. Finally, TPD of NH₃ was carried out by heating the sample from 50 to 750 °C at a rate of 10 °C/min under a flow of He. The ammonia desorption was monitored by the QMS using the NH⁺ fragment (m/e=15) of NH₃. The response of the QMS was calibrated using pulses of known volume of NH₃.

The acid sites and strength of Cu-Ga catalytic system were also investigated by FTIR using two different probe molecules namely pyridine and 2,6-lutidine. Pyridine is commonly used as a basic probe molecule with a pK_b = 7.4 for the determination of Lewis and Bronsted acid sites. It does not interact with the weak acid sites due to the relatively lower basicity. The use of 2,6-lutidine, with a pK_b = 8.8, is thus used to detect the weak and moderate Bronsted acid sites. Infrared spectra were recorded with a Nicolet Magna FTIR spectrometer (4 cm⁻¹ resolution and 32 scans). The catalyst samples were activated under vacuum (10 μbar) at 400 °C for 6 hours. The activated catalysts were then molded on a self-supported wafer of 0.020g, prepared under a hydraulic pellet machine with a thickness of 0.5 mm. The catalyst-molded wafer was mounted on a Pyrex sample holder in an IR cell followed by the introduction of 2,6-lutidine or pyridine over the sample cell to allow the adsorption on the wafer under vacuum. Both probe molecules were degassed by three cycles of freeze-pump-thaw process. The catalyst wafer was evacuated at 110 °C for 1.5 h to remove the physisorbed probe molecule after adsorption. The cell was then evacuated at 200 °C, 300 °C and 400 °C for 1.5 h, respectively, and the cell was cooled down to room temperature and the spectra were taken. Quantification of the acid sites was done by using the modified Beer Lambert's law (eqn. 3) using the literature methods.^[43-44]

$$C_{sw} = \frac{AS}{me} \quad (3)$$

Where, C_{sw} (mol/g) is the concentration of Lewis or Bronsted acid sites in reference to a unit weight of the dry sample, A (cm⁻¹) is the integrated absorbance, S (cm²) is cross sectional area of the sample wafer, m(g) is the weight of the dry sample and e is the integrated molar extinction coefficient.

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Keywords: CO₂ hydrogenation • Copper gallium • Mesoporous silica • Bronsted acid sites • Oxygenates

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