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# Enhanced hydrogenation of dimethyl oxalate to ethylene glycol over indium promoted $\text{Cu}/\text{SiO}_2$

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#### 1. Introduction

The hydrogenation of dimethyl oxalate (DMO) has attracted attention because it can bridge the gap between synthesis gas and methyl glycolate (MG), ethylene glycol (EG) and ethanol, etc. [1–3]. EG is widely used as a solvent and anti-freezing agent, and in the production of polyester fiber, among many other applications [1]. As a versatile building block, synthesis gas can be readily produced from coal, natural gas and biomass, making the DMO-to-EG process more economically and technologically feasible [4].

 $H_3COOC-COOCH_3 + 2H_2 \rightarrow H_3COOC-CH_2OH + CH_3OH$ (1)

$$H_{3}COOC-CH_{2}OH + 2H_{2} \rightarrow HOH_{2}C-CH_{2}OH + CH_{3}OH$$
(2)

Various catalytic materials have been designed to facilitate the efficient hydrogenation of DMO to EG. The most widely used catalyst in industry is the well-established copper-chromium, which exhibits excellent activity and stability [5,6]. However, the hazardous Cr<sup>6+</sup> motivates exploration of other effective and yet more environmentally friendly alternatives. Silica supported copper catalysts have been found to be active in this process due to a unique Cu-O-Si structure that balances the concentration of surface Cu<sup>+</sup> and Cu<sup>0</sup> species. The former species facilitates the activation of

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#### ABSTRACT

Hydrogenation of dimethyl oxalate (DMO) on  $Cu/SiO_2$  catalysts is the final reaction step in a growing industrial syngas to ethylene glycol (StEG) process. In the present work, indium species are found to dramatically enhance the performance of a  $Cu/SiO_2$  catalyst prepared by urea-assisted gelation for the conversion of DMO to EG. Characterization reveals that indium species have negligible effect on the content of  $Cu^+$  species on the surface. Rather, the promotional effect likely originates from interactions between reduced indium species and  $Cu^0$  species though enhanced ability of the latter to activate H<sub>2</sub>.

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ester group in DMO, while the latter serves to activate and dissociate  $H_2$  molecules. Different preparation methods (*e.g.*, ammonia evaporation, sol-gel, precipitation-deposition, impregnation), silica supports (*e.g.*, MCM-41, SBA-15, HMS), and process variables (*e.g.*, pH, temperature) have been explored to prepare catalysts with high metallic dispersion and moderate interaction between copper and silica [4,7–12].

Such catalytic systems suffer from inherent issues such as susceptibility to Cu agglomeration due to its low Hüttig temperature, and loss of Cu<sup>+</sup> species by valence transition during the reaction [13]. These problems cause diminution of active sites, collapse of the synergistic effect between Cu<sup>0</sup> and Cu<sup>+</sup> species, and eventually the degradation of catalytic performance. One strategy to address these issues is through modification of the properties of silica supported copper catalyst with appropriate promoters. A variety of species (*e.g.*, Au, Ag, Ni, La, Zn, B<sub>2</sub>O<sub>3</sub>, etc.) have been found to improve the catalytic performance of silica supported copper catalysts by increasing the dispersion and/or enhancing the stability of Cu<sup>0</sup> and/or Cu<sup>+</sup> species [11,14–18]. The forms of promoters and their specific role in enhancing catalytic performance are a topic still under intense investigation.

Here we report the promotional effect of indium species on the performance of hydrogenation of DMO to EG on silica supported copper catalysts. The highly dispersed catalysts are synthesized in a simple, robust method with a low amount of the cheap, nontoxic promoter. The effect of weight hourly space velocity (WHSV)



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and pressure on the catalytic performance and the stability of catalysts are studied in detail. Various characterization methods are conducted to elucidate the role of indium species to establish the structure-performance correlation and reveal how the size distribution of promoter and the interaction between two metals modify the properties of main catalytic components.

#### 2. Experimental

#### 2.1. Materials

All the reagents are commercially available and used without further purification. Copper (II) nitrate trihydrate (99%, Acros Organics), Indium (III) nitrate hydrate (99.99%, Alfa Aesar), 40 wt% Ludox AS-40 colloidal silica (Sigma-Aldrich), dimethyl oxalate (99%, Sigma-Aldrich), concentrated nitric acid (68-70%, BDH), urea (99.7%, Fisher Chemical), ammonia aqueous solution (BDH, 28%) are used as received. H<sub>2</sub> (UHP), He (UHP), Ar (UHP), N<sub>2</sub>(UHP), and air (Zero grade) are supplied by Praxair. Deionized water (18 M $\Omega$ ) is obtained by using a Milli-Q water system with Barnant B-pure filter.

#### 2.2. Catalyst preparation

10 wt% Cu/SiO<sub>2</sub> catalyst is prepared by urea-assisted gelation. Briefly, 2.03 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 3.5 mL of ammonia aqueous solution is dissolved in 96.5 mL of DI water in a round-bottom flask. Subsequently, 3 g of urea is added before slowly dropping 12 g of 40 wt% Ludox AS-40 colloidal silica under stirring. The mixture is vigorously stirred and aged at 80 °C in water bath for 4 h. The obtained light blue precipitate is filtrated, washed three times with deionized water, dried overnight at 120 °C in an oven. Copperindium bimetallic catalysts are prepared by incipient wetness impregnation. For example, to prepare the sample with 0.5 wt% of In, 5 g of oven-dried10 wt% Cu/SiO<sub>2</sub> is mixed with 6.5 mL solution containing 0.0777 g indium nitrate. The slurry is dried at room temperature for 48 h and then at 120 °C for 12 h. Finally, all samples are calcined at 400 °C for 3 h in air to obtain calcined catalysts.

1 wt% In/SiO<sub>2</sub> is prepared with incipient wetness impregnation to determine if metallic indium species consume N<sub>2</sub>O during N<sub>2</sub>O titration process as urea assisted gelation does not work for depositing indium species on colloidal silica. 40 wt% Ludox AS-40 colloidal silica is first dried to remove water, grinded to fine particles and then mixed with a certain amount of aqueous solution containing indium nitrate. The slurry is dried at room temperature for 48 h and then at 120 °C for 12 h. Finally, the sample is calcined at 400 °C for 3 h in air.

#### 2.3. Catalyst characterization

Nitrogen adsorption-desorption isotherms at -196 °C are measured with a Micromeritics ASAP 2020 surface area and pore analyzer. Samples are degassed at 120 °C for 1.5 h to remove physically adsorbed impurities before each measurement. The specific surface areas are calculated following the Brunauer-Emmett-Teller (BET) method. Pore size distribution is calculated by Barrett-Joyner-Halenda method (BJH) method using the adsorption isotherm branch.

The actual metallic contents of catalysts are analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on a Perkin Elmer Avio 200 instrument. The surface area of copper on catalysts is measured by pulsed N<sub>2</sub>O titration method at 60 °C. The consumption of N<sub>2</sub>O is detected by TCD and the specific area of metallic copper is calculated from the total amount of N<sub>2</sub>O consumption assuming  $1.46\times10^{19}$  copper atoms/m². The result from  $N_2O$  titration on 1 wt%  $In/SiO_2$  shows that reduced indium species do not consume  $N_2O$ .

 $H_2$  temperature-programmed reduction ( $H_2$ -TPR) is performed on a Micromeritics Autochem II 2920 instrument. For  $H_2$ -TPR, 100 mg of an calcined catalyst is loaded into the U-shape quartz tube. The sample is reduced with 10%  $H_2$ /Ar flowing at 40 mL/min at a ramping rate of 10 °C/min from RT to 600 °C. A TCD detector is used to monitor the consumption of  $H_2$ .

The Fourier-transform infrared (FT-IR) spectra of calcined catalysts are collected on Perkin Elmer Spectrum 100 FT-IR spectrometer with 4 scans for each spectrum at room temperature. The spectrometer is equipped with a diamond internal reflection element (IRE) and operated in ATR mode. Sample powders are spread on the IRE and tightened by an alumina cylinder to ensure a close contact with IRE.

X-ray diffraction (XRD) patterns of catalysts are collected on a Rigaku SmartLab SE X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm) with a scanning angle (2 $\theta$ ) range of 10° to 90°. The tube voltage and current were 40 kV and 44 mA, respectively. The XRD patterns for calcined catalysts are scanned at a speed of 15°/min. For *in situ* XRD measurement, calcined catalysts are reduced in an *in situ* reactor with 20% H<sub>2</sub>-80% N<sub>2</sub> mixture (100 mL/min) at 350 °C for 2 h. XRD patterns are collected when the temperature is held at 350 °C or decreases to 190 °C at a scanning speed of 5°/min. The Cu crystallite size is calculated according to Scherrer equation using the full width at half-maximum (FWHM) of the Cu(1 1 1) diffraction peak at 2 $\theta$  = 43.2°.

Transmission electron microscopy (TEM) images are obtained on a Hitachi HT7800 transmission electron microscope operating at an acceleration voltage of 100 kV. Reduced catalyst powders are passivated with 0.5 vol%  $O_2$ /He (100 mL/min) at RT for 12 h. The passivated samples are first grinded to fine particles and then ultrasonically dispersed in ethanol at RT for 1 h. The solution is dipped onto carbon-coated copper grid (300 mesh) and evaporating the solvent before it is loaded into the chamber. More than 300 particles are counted for the distribution of particle size. The mean diameter of particles is calculated with the following formula:

$$\bar{d} = \frac{\sum d_i}{n}$$

where  $d_i$  is the diameter of the *i*-th particle and n is the total number of particles.

X-ray photoelectron spectroscopy measurements are performed using a Kratos AXIS Ultra DLD XPS system, with a monochromatic Al K $\alpha$  source, operated at 15 keV and 150 W and a hemispherical energy analyzer. The X-rays are incident at an angle of 45° with respect to the surface normal and analysis is performed at a pressure of 1x10<sup>-9</sup> mbar. High resolution core level spectra are measured with a pass energy of 40 eV and survey scans with a pass energy of 160 eV. The *in situ* reduction of the catalysts is performed in a reaction cell (Model

ES-009R01) directly attached to the XPS chamber, which allows the sample to be treated under  $H_2$  flow conditions. The reaction cell is evacuated and then the sample transferred back to the analysis chamber without exposure to the external atmosphere. Since the SiO<sub>2</sub> support is an insulator, a charge neutralizer is used to compensate the substrate charge during XPS measurements. Calcined catalysts are reduced at 350 °C in an *in situ* cell for 1.5 h. XPS analysis is conducted on the same instrument after the sample cooling down to RT. All spectra are corrected using 284.8 eV as a reference for C1s binding energy (BE). X. Yu et al./Journal of Catalysis xxx (xxxx) xxx

#### 2.4. Catalytic tests

Catalytic evaluation of vapor-phase DMO hydrogenation is conducted in a continuous flow mode using a stainless-steel tubular reactor. In a typical run, 0.8 g of calcined catalyst (40–60 mesh) is placed in the center of the reactor (9.4 mm internal diameter), and the top and bottom side of the catalyst bed are packed with adequate amount of quartz powder (20-40 and 40-60 meshes). The calcined catalyst is activated in a flow of 20% H<sub>2</sub>-80% N<sub>2</sub> stream (75 mL/min) controlled by mass flow controllers at 350 °C and ambient pressure for 4 h with a ramping rate of 2 °C/min. The system pressure is increased and precisely controlled at 2.5 MPa with a back-pressure regulator when the reactor is cooled to the target reaction temperature (190 °C). A 10 wt% DMO solution (in methanol) is pumped into the reactor using an ISCO pump (Teledyne ISCO). The products are collected after the reaction reaches steady state and analyzed on a gas chromatograph (Agilent 5890) equipped with a flame ionization detector and RTX-Wax capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu m$  ). The calculation of the conversion of DMO and selectivity to various products (methyl glycolate and ethylene glycol) follows formula below:

$$X_{DMO} = \frac{n_{DMO,in} - n_{DMO,out}}{n_{DMO,in}} \times 100$$
$$S_{MG} = \frac{n_{MG}}{n_{DMO,in} - n_{DMO,out}} \times 100$$

$$S_{EG} = \frac{n_{EG}}{n_{DMO,in} - n_{DMO,out}} \times 100$$

The selectivity to other products including ethanol, 1,2butanediol (1,2-BDO) and 1,2-propanediol (1,2-PDO) is negligible.

Turnover frequency (TOF,  $mol_{DMO}/(mol_{Cu on the surface} \times h)$  or  $h^{-1}$ ) of the reaction is measured when the DMO conversion is lower than 20% (T = 190 °C, P(H<sub>2</sub>) = 2.5 MPa, H<sub>2</sub>/DMO molar ratio = 95, WHSV = 4.8 h<sup>-1</sup>). The TOF value is calculated based on the number of surface Cu<sup>0</sup> atoms determined by N<sub>2</sub>O titration method.

#### 3. Results and discussion

#### 3.1. Catalytic performance

The hydrogenation performance DMO over silica supported copper and copper-indium catalysts was investigated in a fixed bed reactor. Fig. 1(a) shows the effect of weight percentage of In on the performance at 190 °C. Further increasing the amount of In above 0.5 wt% decreases both the conversion and EG selectivity, which may result from covering active sites by excess amount of indium species.

The effect of WHSV on the catalytic performance  $(10Cu/SiO_2)$ and  $10Cu0.5ln/SiO_2$ ) was investigated to measure the production capacity on different catalysts. Fig. 1(b and c) shows that the performance in terms of conversion and selectivity to EG decreases on both catalysts with the increasing WHSV due to the shortening of contact time of the reactant with catalysts [19]. However, the performance of  $10Cu0.5ln/SiO_2$  is superior to that obtained with  $10Cu/SiO_2$  catalyst under different WHSV, confirming the advantage of bimetallic catalyst in this case. The results show that incorporation of an appropriate amount of In can improve the performance of 10 wt% Cu/SiO\_2.

The effect of  $H_2$  pressure on the performance of catalysts was also examined. As shown in Fig. 1(d and e), the selectivity to EG increases with elevated  $H_2$  pressure, possibly arising from the increased concentration of surface absorbed  $H_2$  species [20]. However, the performance of hydrogenation of DMO on 10Cu0.5In/SiO<sub>2</sub> is much less influenced than that on 10Cu/SiO<sub>2</sub> in the low-pressure

range showing a potential to decrease the operating pressure in industry.

Turnover frequency is calculated according to the DMO conversion data (less than 20% at 190 °C) and the surface amount of Cu<sup>0</sup> sites determined by N<sub>2</sub>O titration method. As shown in Table 1, the TOF value has a volcano shape with respect to the increasing amount of In content. The value is larger on bimetallic catalysts when the In content is not higher than 1 wt%, reaching a maximum (70.3 ± 5.9 h<sup>-1</sup>) at 0.25 wt% In doping.

The comparison of stability is performed on  $10Cu0.5In/SiO_2$  and  $10Cu/SiO_2$  catalyst (Fig. 1(f)) over a 100 h run test. While both catalysts are stable, the activity of  $10Cu0.5In/SiO_2$  and its selectivity to EG are much higher than the monometallic Cu counterpart.

#### 3.2. Material characterizations

Various characterization methods have been conducted to reveal why an appropriate amount of indium species can promote the performance of Cu/SiO<sub>2</sub> in the hydrogenation of DMO to EG. The chemical compositions and textural properties of all catalysts are summarized in Table 1. ICP-OES proves the effectiveness of the preparation method which can deposit most of the copper and indium species onto the silica support. The N<sub>2</sub> physisorption measurement shows that all the calcined samples exhibit type IV isotherms with mesopore diameter of ~20 nm, as well as some microporosity (Fig. 2). The BET surface areas of samples with low In loading amount (0-1 wt%) are all close to each other. The exception is the material with 2 wt% loading of indium species which shows a 23% decrease in the BET surface area compare with monometallic Cu catalyst, possibly arising due to pore blockage by indium oxide particles at such high loading. Indeed, the introduction of indium species decreases the pore volume by about 10-15% when compared with the pore volume of monometallic Cu catalyst

H<sub>2</sub>-TPR was conducted to understand the reducibility of the catalvsts and to elucidate surface chemical information such as the distribution of metal species and the interaction between them. Fig. 3(A) shows the H<sub>2</sub>-TPR profiles of 10 wt% Cu/SiO<sub>2</sub> with different amounts of In. For 10 wt% Cu/SiO2, the peak centered at 192 °C is assigned to the collective reduction of Cu<sup>2+</sup> species to Cu<sup>0</sup>/Cu<sup>+</sup>. The reduction of bulk cupric oxide usually occurs at much higher temperatures of around 243–255 °C [11,18]. Thus, the low reduction temperature of 10 wt% Cu/SiO<sub>2</sub> indicates a high dispersion of copper species on silica, which is further supported by TEM measurements, and a weak interaction between certain amount of copper species (e.g. CuO) with SiO<sub>2</sub>. Interestingly, the reduction temperature gradually increases with the amount of indium species as listed in the inset except for the sample with 0.25 wt% In. The gradual shift of reduction temperature suggests the existence of an interaction between copper and indium species. Thus, the incorporation of In hinders the reduction of 10 wt% Cu/SiO<sub>2</sub>, which is similar to modification of copper catalysts with other promoters [11,17,18,21]. The growing peak with respect to increasing indium content at 270 °C is ascribed to the partial reduction of indium species, which is further confirmed by XPS (see below). As indium species are very difficult to be well dispersed on silica, the size distribution is broad with a certain amount of large grains [22,23]. The reduction behavior of indium species is highly dependent on the particle size, with small grains able to be reduced below 300 °C and large grains being reduced only at very high temperatures [23,24]. The reduction of indium species could also be initiated by the neighboring copper species when they are in close contact. We also cannot rule out that part of the reduction profile of indium species with small particle size may be overlapped with the reduction profile of copper species, given the low loading of indium species in this study.

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**Fig. 1.** (a) Effect of In weight percentage on the performance of hydrogenation of DMO to EG on different catalysts, reaction condition:  $T = 190 \circ C$ ,  $P(H_2) = 2.5 \text{ MPa}$ ,  $H_2/DMO$  molar ratio = 95, WHSV = 0.5 h<sup>-1</sup>. (b, c) Effect of WHSV on the DMO hydrogenation performance for catalysts (b)  $10Cu/SiO_2$  and (c)  $10CuO.SIn/SiO_2$ , reaction condition.  $T = 190 \circ C$ ,  $P(H_2) = 2.5 \text{ MPa}$ ,  $H_2/DMO$  molar ratio = 95. (d, e) effect of  $H_2$  pressure on the DMO hydrogenation performance for catalysts (d)  $10Cu/SiO_2$  and (e)  $10CuO.SIn/SiO_2$ , reaction condition.  $T = 190 \circ C$ ,  $P(H_2) = 2.5 \text{ MPa}$ ,  $H_2/DMO$  molar ratio = 95. f. Stability of catalysts in DMO hydrogenation, reaction condition.  $T = 190 \circ C$ ,  $P(H_2) = 2.5 \text{ MPa}$ ,  $H_2/DMO$  molar ratio = 95. f. Stability of catalysts in DMO hydrogenation, reaction condition.  $T = 190 \circ C$ ,  $P(H_2) = 2.5 \text{ MPa}$ ,  $H_2/DMO$  molar ratio = 95, WHSV =  $1 h^{-1}$ .

Table 1
Physicochemical and catalytic properties of $\mathrm{Cu}/\mathrm{SiO}_2$ catalyst with different In loading amount.

Sample	Cu content, <sup>a</sup> (wt %)	In content, <sup>a</sup> (wt %)	$S_{BET}$ , $^{b}/m^{2}$ g $^{-1}$	$V_{p}$ , $c/cm^3 g^{-1}$	$S_{Cu}$ , $d/m^2 g^{-1}$	d <sub>p</sub> , <sup>e</sup> /nm	d <sub>p</sub> , <sup>f</sup> /nm	TOF, <sup>g</sup> /h <sup>-1</sup>
10Cu/SiO <sub>2</sub>	11.4	0	256	0.81	3.9	4.6	2.9	38.8 ± 4.6
10Cu0.25In/SiO <sub>2</sub>	10.6	0.30	242	0.74	4.5	4.2	3.3	70.3 ± 5.9
10Cu0.5In/SiO <sub>2</sub>	10.2	0.53	256	0.71	4.7	4.4	3.4	64.2 ± 2.4
10Cu1In/SiO <sub>2</sub>	10.5	1.04	244	0.73	4.3	4.2	3.4	54.3 ± 2.3
10Cu2In/SiO <sub>2</sub>	9.9	1.93	198	0.70	4.8	4.5	3.3	$14.6\pm0.3$

<sup>a</sup> Determined by ICP-OES analysis.

<sup>b</sup> BET specific surface area.

<sup>c</sup> Pore volume that obtained from  $P/P_0 = 0.99$ .

<sup>d</sup> Cu metallic surface area per gram of catalyst determined by N<sub>2</sub>O titration method.

<sup>e</sup> Average particle size determined by TEM images.

<sup>f</sup> Average particle size determined by Cu(1 1 1) peak from *in situ* XRD patterns at 190 °C.

<sup>g</sup> TOF value calculated according to surface number of Cu<sup>0</sup> atoms from N<sub>2</sub>O titration method.

XRD patterns of the calcined samples and the *in situ* reduced catalysts were collected to understand the existing phase and crystallite sizes within the catalysts. The XRD patterns of calcined samples (Figure S2(A)) do not exhibit noticeable peaks belonging to metal oxides implying their high dispersion and amorphous character. After *in situ* reduction at 350 °C, the peaks (Fig. 3(B)) at 43.5° and 74.4° can be ascribed to Cu<sup>0</sup>(1 1 1) and Cu<sup>0</sup>(2 2 0) [4,18,25]. The average particle size of Cu crystallite is calculated in terms of Scherrer equation and listed in Table 1. The crystallite sizes for all the samples are around 3 nm, which shows that the metallic species are well-dispersed after reduction.

ATR-FTIR was utilized to reveal structural information for the calcined samples shown in Fig. 3(C). The band at 1118 cm<sup>-1</sup> is ascribed to asymmetric stretching vibration band ( $v_{SiO}$ ) of SiO<sub>2</sub>. The deformation band ( $\delta_{OH}$ ) of OH at 670 cm<sup>-1</sup> and asymmetric

stretching vibration band ( $v_{SiO}$ ) of Si–O at 1045 cm<sup>-1</sup> in the FTIR spectra prove the existence of cupric phyllosilicate (Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub>, Figure S1), suggesting the existence of Cu<sup>+</sup> during the reduction [11,26]. The relative content of cupric phyllosilicate in each sample can be estimated using the intensity ratio of the deformation band ( $\delta_{OH}$ ) of cupric phyllosilicate at 670 cm<sup>-1</sup> and the symmetric stretching vibration band ( $v_{SiO}$ ) of silica at 800 cm<sup>-1</sup>, denoted as  $I_{670}/I_{800}$  [27]. However, the  $I_{670}/I_{800}$  ratio only gives a qualitative estimation of the corresponding IR bands are not known. Nevertheless, cupric phyllosilicate exists in all the catalyst samples.

TEM images (Fig. 3(D), Figure S4) of reduced catalysts were obtained to reveal the distribution of particle sizes in the catalysts. The histograms of particle size (inset) exhibit a very narrow distribution with the mean particle diameter about 4 nm for all

4



Fig. 2. (A) N<sub>2</sub> adsorption-desorption isotherms and (B) BJH pore size distribution of the calcined catalysts of different copper loadings. a. 10Cu/SiO<sub>2</sub>, b. 10Cu0.25In/SiO<sub>2</sub>, c. 10Cu0.5In/SiO<sub>2</sub>, d. 10Cu1In/SiO<sub>2</sub>, e. 10Cu2In/SiO<sub>2</sub>.



Fig. 3. (A) H<sub>2</sub>-TPR profiles, a. 10Cu/SiO<sub>2</sub>, b.10Cu0.25ln/SiO<sub>2</sub>, c. 10Cu0.5ln/SiO<sub>2</sub>, d. 10Cu1ln/SiO<sub>2</sub>, e. 10Cu2ln/SiO<sub>2</sub>. (B) *in situ* XRD patterns of 350 °C reduced sample at 190 °C, a. blank XRD reactor, b. 10Cu/SiO<sub>2</sub>, c. 10Cu0.25ln/SiO<sub>2</sub>, d. 10Cu0.5ln/SiO<sub>2</sub>, e. 10Cu1ln/SiO<sub>2</sub>, f. 10Cu2ln/SiO<sub>2</sub>. (C) FT-IR spectra of calcined samples, a. 10Cu/SiO<sub>2</sub>, b.10Cu0.25ln/SiO<sub>2</sub>, b.10Cu0.25ln/SiO<sub>2</sub>, c. 10Cu0.5ln/SiO<sub>2</sub>, d. 10Cu1ln/SiO<sub>2</sub>, f. SiO<sub>2</sub>. (D) TEM images of reduced 10Cu0.5ln/SiO<sub>2</sub> catalysts.

the samples. Thus, copper species are highly dispersed on silica, which is consistent with the results of  $H_2$ -TPR and *in situ* XRD measurements.

Surface properties of reduced catalysts were investigated by XPS and with X-ray induced Auger electron spectroscopy (XAES). Figure S4 shows the Cu 2p XPS spectra of calcined samples. The peak at around 936 eV is assigned to Cu<sup>2+</sup> which is confirmed by the characteristic satellite peak of Cu<sup>2+</sup> species at 945 eV. No peaks belonging to Cu<sup>0</sup> or Cu<sup>+</sup> are observed suggesting that copper exists as Cu<sup>2+</sup> species in the calcined sample. After reduction, only two peaks at 932.1 and 951.9 eV are observed (Fig. 4(A)), attributed to Cu 2p3/2 and Cu 2p1/2, respectively [9,11]. Furthermore, the satellite peak and the peak with Cu 2p binding energy of 936 eV assigned to Cu<sup>2+</sup> species are absent. These results show that Cu<sup>2+</sup> species on the surface are reduced to Cu<sup>0</sup> and/or Cu<sup>+</sup> species which is consistent with H<sub>2</sub>-TPR result. The binding energy for Cu 2p3/2 in 10Cu0.5ln/SiO<sub>2</sub> is lower (0.4 eV) than that in 10Cu/SiO<sub>2</sub> indicating an electron transfer from reduced ln species to copper species. This

is reasonable since the Pauling electronegativity of copper (1.90) is higher than that of indium (1.78). Thus, an interaction between a certain amount of copper and reduced indium species, possibly by alloying, may exist in the bimetallic samples.

As the difference in Cu 2p3/2 and Cu 2p1/2 binding energies between Cu<sup>+</sup> and Cu<sup>0</sup> are negligible, Cu LMM XAES was recorded to discriminate these peaks [9–11]. Two peaks with Auger kinetic energy of 914 eV and 917 eV are observed for the reduced catalysts (Fig. 4(B)), confirming the simultaneous existence of Cu<sup>0</sup> and Cu<sup>+</sup> species on these catalysts [11–14,28]. Deconvolution results (Table S1) show that the near-surface content of Cu<sup>+</sup> species for all samples with various In loading amounts is almost the same. The high content of Cu<sup>+</sup> species further confirms the assumption of well-dispersed copper species on silica and the existence of interaction between copper species and SiO<sub>2</sub> as indicated by H<sub>2</sub>-TPR and TEM.

Fig. 4(C) shows In 3d XPS spectra of calcined and reduced  $10Cu_{0.5In}/SiO_2$ . The peaks at approx. 446 eV and 453.6 eV are



Fig. 4. (A) Cu 2p XPS spectra and (B) Cu LMM XAES spectra of reduced catalysts, a. 10Cu/SiO<sub>2</sub>, b. 10Cu0.25In /SiO<sub>2</sub>, c. 10Cu0.5In/SiO<sub>2</sub>, d. 10Cu1In /SiO<sub>2</sub>, e. 10Cu2In/SiO<sub>2</sub>, (C) In 3d XPS spectra of calcined and reduced bimetallic samples, a. 10Cu0.25In/SiO<sub>2</sub>, b. 10Cu0. 5In/SiO<sub>2</sub>, c. 10Cu1In /SiO<sub>2</sub>, d. 10Cu2In/SiO<sub>2</sub>, i. calcined samples, ii. reduced samples.

assigned to In 3d5/2 and In 3d3/2, indicating that the indium species in the calcined sample are in oxide form [23,29]. However, two new peaks located at 444.1 eV and 451.7 eV attributed to metallic indium species emerge after reduction [30–33]. The result shows that indium species are partially reduced to metallic form after reduction consistent with the analysis in H<sub>2</sub>-TPR test.

#### 3.3. Discussion

High metal dispersion is generally acknowledged to enhance the hydrogenation activity of Cu/SiO<sub>2</sub> catalysts by promoting the formation of Cu<sup>+</sup> species for the cooperation between Cu<sup>0</sup> and Cu<sup>+</sup> sites [34,35]. It is proposed that Cu<sup>0</sup> species adsorb and dissociate hydrogen molecules, while the Cu<sup>+</sup> species stabilize the methoxy and acyl species from the activated ester molecules [11,15,18]. An excellent hydrogenation performance could be achieved *via* the synergetic effect of balanced Cu<sup>0</sup> and Cu<sup>+</sup> sites on the surface, which can explain the superior performance of 10Cu/SiO<sub>2</sub> in our case. The amount of Cu<sup>+</sup> sites has been proposed previously to be directly related to the selectivity to EG and the effect of promoters is usually ascribed to the increase in the content of Cu<sup>+</sup> species [11,15,18]. However, XPS results show that the near-surface amount of Cu<sup>+</sup> for the catalysts in our case (at least prior to reaction) is roughly the same. Furthermore, N<sub>2</sub>O titration results reveal that doping indium species (0.25-2 wt%) can slightly increase the surface amount of Cu<sup>0</sup> sites which might be another evidence for the existence of the interaction between copper species and indium species. However, the performance of bimetallic samples with low loading of indium species (10Cu0.25In/SiO2 and 10Cu0.5In/SiO<sub>2</sub>) are significantly improved over that of 10Cu/ SiO<sub>2</sub>. We propose that the increased performance of these In promoted samples might be attributed to the enhanced ability of adsorption and activation of H<sub>2</sub> on bimetallic surface sites.

Indeed, the estimated TOF value of bimetallic catalysts (10Cu0.2In/SiO<sub>2</sub> and 10Cu0.5In/SiO<sub>2</sub>) based on Cu<sup>0</sup> content, are much higher than the TOF of 10Cu/SiO<sub>2</sub> which indicates the nature of the active sites are significantly different. Thus, a new active phase attributed to the modification of Cu<sup>0</sup> crystallites with In<sup>0</sup> species is created on the surface. Wang et al. find that when the accessible metallic Cu surface area is below a certain value (approximately  $20 \text{ m}^2/\text{g}$  in their case), the catalytic activity of hydrogenation of DMO on silica supported copper catalysts linearly increases with increasing Cu<sup>0</sup> surface area. This was attributed to insufficient H<sub>2</sub> decomposition on Cu<sup>0</sup> limiting the reaction rates [36]. Considering that in the present case, the majority of copper species are Cu<sup>+</sup> and that the surface area of Cu<sup>0</sup> for all the samples is very low, it is likely that the incorporation of In<sup>0</sup> with Cu<sup>0</sup> clusters forms bimetallic sites that promote dissociation of H<sub>2</sub>. The TOF value of 10Cu2In/SiO<sub>2</sub> is much smaller than the TOF value of 10Cu/SiO<sub>2</sub> even though they have similar Cu<sup>+</sup> content and the bimetallic catalyst has ~22% higher amount of Cu<sup>0</sup> sites. It is generally accepted that the dispersion of supported metal oxides decreases with increased metal oxide loading. The absolute amount of unreduced In<sub>2</sub>O<sub>3</sub> species tends to increase with the incremental amount of indium species on the catalysts. Indeed, indium species are difficult to disperse on silica [22,23] and only small In<sub>2</sub>O<sub>3</sub> particles and/or In<sub>2</sub>O<sub>3</sub> particles close to Cu<sup>0</sup> sites can be reduced. Moreover, the generation of an excess amount of In<sup>0</sup> species on bimetallic catalysts with high loading of indium might also be a factor for deteriorating catalytic activity. This significant decrease in TOF from overpromotion of In is likely a result of disruption of the balance between Cu<sup>0</sup> and Cu<sup>+</sup> sites on the surface by In<sub>2</sub>O<sub>3</sub> species and/or excess In<sup>0</sup> species (*e.g.* covering sites with high activity and separating metallic sites from Cu<sup>+</sup> sites). Thus, incorporating only an appropriate amount of indium species offer-



**Fig. 5.** Schematic illustration of promotional effect of indium species on 10 wt% Cu/ SiO<sub>2</sub> in the hydrogenation of DMO to EG.

ing a balance between the amount of  $In^0$  species and  $In_2O_3$  species can improve the intrinsic activity of  $10Cu/SiO_2$ .

The detailed reaction pathways in the hydrogenation of DMO on Cu/SiO<sub>2</sub> catalysts are given in Fig. S5. Fig. 5 depicts the role of indium species in the hydrogenation of DMO to EG. The reduction of cupric phyllosilicate (Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub>) and copper oxide (CuO) can yield Cu<sup>+</sup> and Cu<sup>0</sup> sites, respectively. The reduction of indium species can be initiated by In<sub>2</sub>O<sub>3</sub> particles with small crystallite size and the intimate contact with neighboring Cu<sup>0</sup> species. The reduced indium species interacts with the Cu<sup>0</sup>, possibly by alloying, to form a new type of metallic sites. These sites enhance the adsorption and activation of H<sub>2</sub>, resulting in the efficient refilling of activated H<sub>2</sub> species consumed in the reaction and thus enhancing the number of turnover.

#### 4. Conclusions

Silica supported Cu-In bimetallic catalysts are successfully prepared *via* urea-assisted gelation followed by incipient wetness impregnation. The incorporation of a low amount (less than 1 wt % in this study) of cheap, nontoxic indium species dramatically enhances the intrinsic activity of Cu/SiO<sub>2</sub> for the conversion of DMO to EG. Two types of indium species, In<sup>0</sup> and In<sup>3+</sup>, are observed after reduction *via* XPS. An interaction among copper species and indium species are confirmed by H<sub>2</sub>-TPR, N<sub>2</sub>O titration and XPS. However, the surface content of Cu<sup>+</sup> which is related to the activation of ester group is not significantly affected by indium species. Instead, In<sup>0</sup> species might be alloyed with Cu<sup>0</sup> species to form a new type of metallic sites with enhanced ability to dissociate H<sub>2</sub> which might account for the observed increase in the intrinsic activity of bimetallic catalysts.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

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