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Partial hydrogenation of dimethyl oxalate on Cu/SiO_2 catalyst modified by sodium silicate

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ARTICLE INFO	A B S T R A C T					
Keywords: Hydrogenation Dimethyl oxalate Methyl glycolate Cu/SiO ₂ Na ₂ SiO ₃	Cu/SiO ₂ catalyst modified with Na ₂ SiO ₃ was prepared by the ammonia evaporation impregnation method and applied in the partial hydrogenation of dimethyl oxalate (DMO) to methyl glycolate (MG). The addition of Na ₂ SiO ₃ led to a serious shrinkage of those accumulation pores in the catalyst, but hardly affect the structure of the mesopores bellow 8 nm. Moreover, the trace amount of Na ₂ SiO ₃ enhanced the formation of copper phyllosilicate, which resulted in a minor increment in Cu ⁺ species as well as a decrease of Cu ⁰ species. An unexpected high MG yield of about 83% and MG selectivity of 99.8% was achieved over the Cu/SiO ₂ catalyst modified with 0.5% Na ₂ SiO ₃ dopant could be key reason for the higher selectivity, because the larger pores can ensure the fast transfer of MG to the external surface. Thus, the further hydrogenation of MG can be prevented. Moreover, the decrement of Cu ⁰ species induced by doping of Na ₂ SiO ₃ could be another reason for the higher					

1. Introduction

Methyl glycolate (MG) is an excellent organic solvent and important fine chemical intermediate [1]. Due to its unique molecular structure with both hydroxyl and ester groups, MG can undergo reactions like carbonylation, oxidation, hydrolyzation etc. It has been widely applied in the manufacture of glycolic acid, DL-glycine and malonate ester [2]. Traditionally, MG can be synthesized via the coupling reaction of formaldehyde and methyl formate over various acid catalysts, however it is not pratically feasible in large scale production due to the low yield and environment contamination [3-7]. Recently, as one of the crucial step in the synthesis technology of ethylene glycol via syngas, hydrogenation of dimethyl oxalate (DMO) has drawn much attention from both scientific and industrial fields. The hydrogenation of DMO is a complex reaction comprising of several consecutive and parallel reactions, among which, the hydrogenation of only one of the carbonyls of dimethyl oxalate can produce methyl glycolate with higher selectivity. Therefore, production of MG via hydrogenation of dimethyl oxalate (DMO) is promising as an emerging C1 chemistry route owing to its higher yields, environment friendly and atomic economy [8,9].

Generally, Cu/SiO_2 catalysts are widely used for ethylene glycol (EG) production via DMO hydrogenation due to its high activity in the adsorption of C–O/C=O group and the lower activity in dissociating

the C–C bond[9–11]. Ammonia-evaporation method has been studied systematically in the preparation of Cu/SiO₂ catalysts, including the evaporation temperature [12], Cu loading [13], doping [14–17], morphology [18] and so on. Lin et.al [19] found that the unstable active centers was caused by methanol, and the CO splitting from methanol and the oxidation of alcohol over Cu/SiO₂ catalysts are the main reasons for sintering of copper, which resulted in deactivation. Yue and coworks [20] designed a Cu/SiO₂ -based monolithic catalyst for hydrogenation of DMO to EG. The catalyst is low cost, stable, and exhibits high activity in the reaction of hydrogenation of DMO, achieving a 100% conversion of DMO and more than 95% selectivity to EG. Cu-Au catalysts and silver-manganese nanocatalysts were also used in for ethylene glycol (EG) production via DMO hydrogenation [21–24].

selectivity to MG, since insufficient activated H₂ could be provided for the further hydrogenation of MG.

However, it is difficult to achieve excellent selectivity to MG on Cu/ SiO_2 catalyst at the conditions of high DMO conversion because the thermodynamic equilibrium constant of the MG hydrogenation to EG is two orders of magnitude larger than that of DMO hydrogenation to MG [1]. Therefore, the synthesis of MG via DMO needs a moderate reaction condition and a catalyst with relatively weak hydrogenation property. Previous reports showed that silver-based catalysts exhibited high catalytic performance for partial hydrogenation of DMO to MG at low temperature [25–27]. Besides, several bimetallic catalysts (such as CuAu, CuZr, AuAg alloy etc.) are also used for the synthesis of MG via

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the hydrogenation of DMO [15,28–30].

Recently, Dai et al. [31] reported a copper-based hydroxyapatite (HAP) supported (Cu/HAP) catalysts with excellent catalytic performance for the synthesis of MG with a yield of 70%. The author pointed out that the relatively lower hydrogen activation ability was one of the important reasons for the high selectivity to MG. Sun et al. [32] reported a sputtering (SP) Cu/SiO₂ catalysts with a selectivity of more than 87% via freezing Cu in a zero-valence state. The author pointed out that the regulation of Cu chemical properties by changing the electron structure is a feasible strategy to control the hydrogenation products.

As reported by the previous work, copper phyllosilicates, which is responsible for the formation of Cu⁺, can be formed during the preparation of Cu/SiO₂ catalysts by ammonia evaporation (AE) method [33]. Under the ammonia conditions, Cu^{2+} complex can react with the silanol groups of the silica surface via hydrolytic adsorption to form \equiv SiOCu^{II} monomer, which is difficult to be reduced to metallic copper due to the strong interaction between the copper species and SiO₂. In this paper, Na₂SiO₃ was applied to modify the surface characteristic of the Cu/SiO₂ catalyst to modulate its hydrogen activation ability. The SiO_4^{4-} group derived from the hydrolysis of Na₂SiO₃ was found to be able to enhance the formation of copper phyllosilicates. Thus, the amount of exposed metallic copper decreased in the final reduced catalysts and the hydrogen activation ability of the catalyst can be modulated. Fortunately, the Cu/SiO₂ decorated with sodium silicate in the present work displays an un-expectative catalytic performance with a high yield of MG ($Y_{MG} = 83\%$). Moreover, the effect of the copper valence state distribution on the hydrogenation of DMO to MG was evaluated to clarify the formation mechanism of MG.

2. Experimental

2.1. Catalyst preparation

Cu/SiO₂ powder was prepared by the ammonia-evaporation (AE) method which has been described in detail in our previous reports [13,20]. Na₂SiO₃-modified Cu/SiO₂ catalyst was prepared by the impregnation method through immersing uncalcined Cu/SiO₂ powder in sodium silicate solution, stirred for 4 h, subsequently evaporated at 353 K using vacuum rotary, and then dried at 393 K for 4 h, calcined at 673 K in flowing air for 4 h. The final calcined sample was designed as xSS-Cu/SiO₂, where SS and x represented Na₂SiO₃ and its mass content to the catalyst, respectively.

2.2. Catalyst characterization

Fourier-transform infrared radiation (FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 in the range of 4000–400 cm⁻¹. The samples were finely grounded, dispersed in KBr, and pelletized. The spectral resolution was 4 cm⁻¹, and 32 scans were recorded for each spectrum.

Transmission electron microscopy (TEM) images were obtained using a Philips TECNAI G2 F20 system electron micro-scope at 100 kV equipped with a field emission gun.

Temperature-programmed reduction (TPR) was carried out on a Micromeritics Autochem II 2920. Catalyst of 50 mg was loaded into a quartz tube and dried in an argon stream at 393 K for 1 h before the reduction. The catalyst was then heated in 30 ml/min of 5%H₂-Ar at a heating rate of 10 K/min up to 973 K. The amount of H₂ consumption was monitored by a thermal conductivity detector (TCD).

Powder X-ray diffraction (XRD) analysis of the catalysts were performed using a Rigaku C/max-2500 diffractometer employing the graphite filtered Cu K α radiation ($\lambda = 1.5406$ Å) at room temperature. Data points were acquired by step scanning with a rate of 12°/min from $2\theta = 10^{\circ}$ to $2\theta = 90^{\circ}$.

X-ray photoelectron spectroscopy (XPS) analysis of the catalysts

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were carried out on a Perkin-Elmer PHI 1600 ESCA system operated at a pass energy of 187.85 eV for survey spectra with an Mg $K\alpha$ X-ray source (E = 1253.6 eV).

The specific surface area of metallic copper was measured by the adsorption and decomposition of N₂O using the pulse titration method described in the literature [1,2]. Briefly, 100 mg of catalyst sample was reduced in 5% H₂-Ar at 623 K for 4 h and cooled to 363 K. Then 15% N₂O-Ar was introduced at a rate of 30 ml/min for 2 h, ensuring that surface Cu atoms were completely oxidized according to the reaction $2Cu(s) + N_2O \rightarrow Cu_2O(s) + N_2$. The quantity of chemisorbed N₂O was measured by a hydrogen pulse chromatographic technique on a Micromeritics Autochem II 2920 equipped with a TCD. Hydrogen pulse reduction of surface Cu₂O to metallic copper was conducted at 623 K to ensure that the chemisorbed N₂O on the copper surface immediately reacted with hydrogen gas introduced from the pulse loop. Hydrogen pulse-dosing was repeated until the pulse area no longer changed. The consumed amount of hydrogen was the value obtained by subtracting the small area of the first few pulses from the area of the other pulses. The specific area of metallic copper was calculated from the total amount of hydrogen consumption with 1.46×10^{19} copper atoms per m^2 [3,5].

Textual properties of the catalyst were determined by the mercury intrusion porosimetry (MIP) test using a Micromeritics Autopore IV.

2.3. Catalytic activity test

The catalytic performance was carried out in a continuous flow unit equipped with a stainless-steel tube reactor placed vertically inside a furnace with a temperature controller. The catalyst (40-60 meshes) was packed in the center of the tube reactor. The reaction was carried out after the catalyst was reduced in pure hydrogen atmosphere at 623 K for 4 h. The reactant (20 wt. % DMO (99.9% purity) in methanol (AR purity) solution) was injected from the top of the reactor through a high-pressure pump (Lab Alliance Series II pump) with a system pressure of 2.5 MPa. The reaction was performed at 473 K, with the weight liquid hourly space velocity (WLHSV) of 1.5 $g_{DMO} g_{cat}^{-1} h^{-1}$ (for short h^{-1}). The products collected in a condenser were analyzed on an Agilent Micro GC 6820 with an HP-INNOWAX capillary column (Hewlett-Packard Company, 30 m × 0.32 mm × 0.50 µm) equipped with a flame ionization detector (FID). To ensure repeatability, 4-6 separate GC samples were taken and the results were averaged for each experimental data point, and uncertainties were typically within 3%.

3. Results and discussion

3.1. Effect of Na₂SiO₃ on structure properties of the catalysts

The physicochemical properties of the catalysts modified with/ without Na₂SiO₃ were listed in Table 1. According to the data measured by N₂ physisorption, the specific surface area (S_{BET}) and the average pore diameter of the catalysts only showed neglect changes with the increment of Na₂SiO₃. However, when come to the results obtained by MIP method, the pore volume declined dramatically from 0.46 to $0.27 \text{ cm}^3/\text{g}$ and the average pore diameter increased nearly doubled from 16 to 30 nm with increasing of Na₂SiO₃. It has been reported that for the Cu/SiO₂ catalyst, the pore about 3 nm belonged to the pores between the layers of the copper phyllosilicate, and the pores about 15 nm were attributed to the accumulation pore [11]. Because we could only detect the pore structure larger than 10 nm by MIP method, above results suggested that addition of Na2SiO3 changed the structure of large pore and had little influence on the mesoporous between 2 nm and 8 nm. This suggestion can be also well illustrated by their pore size distribution curves shown in Fig. 1 This could be attributed to the condensation polymerization of silicate ions (SiO_4^{4-}) derived from the hydrolysis of Na2SiO3, which were anchored on the surface of the catalyst during the preparation procedure. As a result, it led to the

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Table 1

The textural properties and chemical compositions of Cu/SiO2 catalysts with different content of Na2SiO3

Catalysts	S _{BET} (m ² / g)	V _{pore} ^a (cm ³ / g)	d _{pore} ^a (nm)	V _{pore} ^b (cm ³ / g)	d _{pore} ^b (nm)	Cu dispersion ^c (%)	$S_{Cu 0}^{c} (m^2 g^{-1})$	$S_{Cu+}{}^{d} (m^2 g^{-1})$	X _{Cu0} ^e	$STY_{MG}^{f}(g_{MG} L^{-1}h^{-1-1})$
$\begin{array}{c} \text{Cu/SiO}_2\\ 0.25 \ \text{SS-Cu/SiO}_2\\ 0.5 \ \text{SS-Cu/SiO}_2 \end{array}$	413	0.98	9.5	0.46	16	8.8	11	9.4	0.539	10.3
	400	1	10	0.34	24	8.6	10.8	10.2	0.513	654
	388	1.07	11	0.27	30	8.2	10.3	10.3	0.498	1033

Pore volume and average pore diameter determined by BET.

^b Pore volume and average pore diameter are determined by MIP.

Cu dispersion and the Cu⁰ surface area are determined by N₂O titration.

^d Surface area of Cu⁺ is calculated by $S_{Cu}^{0} / X_{Cu}^{0} \times (1 - X_{Cu}^{0})$. ^e Peaks area ratio between Cu⁰ and (Cu⁰ + Cu⁺) by deconvolution of Cu LMM XAES.

^f STY represents the space time yield, grams of product per liter of catalyst per hour.



Fig. 1. Pore size distribution of Cu/SiO2 catalysts with different content of Na2SiO3 determined by mercury intrusion method.

serious shrinkage of those accumulation pores. It suggested that trace amount of Na2SiO3 could change the catalyst structure by shrinking the accumulation mesopores (Scheme 1).

3.2. Effect of Na_2SiO_3 on the chemical state of copper

Fourier-transform IR (FTIR) spectroscopy was used to investigate the structural evolution of the catalysts and the effect of Na₂SiO₃. As shown in Fig. 2, the formation of copper phyllosilicate in all calcined samples was confirmed by the appearance of the δ_{OH} bands at 1040 and 670 cm^{-1} [34]. While, the bands at 938 and 690 cm^{-1} were owed to the frequencies of the δ_{OH} bands for copper hydroxide. Furthermore, the relative amount of copper phyllosilicate can be evaluated by considering the integrated intensity of the δ_{OH} band at 670 cm⁻¹ normalized to the integrated intensity of the symmetric δ_{SiO} band of amorphous silica at 800 cm⁻¹, which are named I_{670}/I_{800} [35,36]. Inset in



Scheme 1. Diagram for the effect of Na₂SiO₃ dipping on the catalyst and DMO hydrogenation.



Fig. 2. FTIR spectra of calcined Cu/SiO₂ catalysts with different content of Na₂SiO₂.

Fig. 1 clearly shows that the relative amount of copper phyllosilicate was improved with increasing Na₂SiO₃. The reaction between SiO₄⁴ and Cu²⁺ to form copper phyllosilicate could be the reason for the increment. It could also be illustrated from the TEM images of calcined samples shown in Fig. 3.

It has been reported that the presence of copper phyllosilicate can enhance the metal-support interactions significantly, which are vital for the high activity and stability in hydrogenation of DMO [11,33,34]. This could be proved by the H₂-TPR profiles. As shown in Fig. 4, the temperature of main reduction peak rose apparently with the increase of the Na₂SiO₃ content. It indicated that trace Na₂SiO₃ will make the copper species more difficult to be reduced, which should be ascribed to the strengthened interaction between the copper species and the surface



Fig. 3. TEM images of (A) calcined Cu/SiO₂ monolithic catalyst and (B) calcined 0.25 SS-Cu/SiO₂ monolithic catalyst and (C) calcined 0.5 SS-Cu/SiO₂ monolithic catalyst.



Fig. 4. H₂-TPR profiles of Cu/SiO₂ catalysts with different content of Na₂SiO₃.

dopants.

In our previous work, it was found that the cooperative effect between Cu⁺ and Cu⁰ was responsible for the high catalytic activity for hydrogenation of DMO to ethanol [37,38]. The Cu⁺ species is formed upon the reduction of the copper phyllosilicate under the experimental conditions (e.g. 623 K), since the further reduction of Cu⁺ to Cu⁰ requires a temperature higher than 873 K [19]. While the Cu⁰ species is formed upon the reduction of the CuO in the calcined catalyst. As shown in Fig. 5, the change of copper species was exhibited by the XRD patterns of the calcined and reduced catalysts. The broad peak at 22° was attributed to amorphous silica. Moreover, the characteristic peaks of CuO at 35.4° and 38.6° (JCPDS05-0661) cannot be found for all the samples (Fig. 5A), indicating that the copper species was highly dispersed in these catalysts. Strong diffraction peaks of the reduced catalysts (Fig. 5B) at 36.4° can be ascribed to the characteristic of the Cu₂O (111) plane, which become stronger with the introduction of Na_2SiO_3 . The formation of Si-O-Cu is due to that $[Cu(NH_3)_4]^{2+}$ can exchange ions with Si-OH on surface of silica sol. [39] It implied that Na₂SiO₃ could prompt the formation of Cu⁺ species in Cu/SiO₂ catalysts. Additionally, the characteristic diffraction peaks at 43.3° for Cu⁰ was not detected in all the samples, probably due to its higher dispersion.

XPS analysis was conducted to further discriminate the chemical states of copper species in the catalysts. As shown in Fig.6A, two intensive photoelectron peaks at 933.7 eV (with a satellite peak at 944 eV) and 953.3 eV were ascribed to the Cu 2p3/2 and 2p1/2 binding energy (BE), and no obvious variation was found when doping Na₂SiO₃



Fig. 5. XRD patterns of the calcined (A) and reduced (B) Cu/SiO_2 catalysts with different content of Na_2SiO_3 .

into the catalyst. Fig. 6B showed that the Cu 2p satellite peak at about 944 eV in the XPS patterns disappeared after reduction, suggesting that Na_2SiO_3 hardly affect the reduction of Cu^{2+} to Cu^+ or Cu^0 for all samples. It is well known that Cu^0 and Cu^+ species cannot be accurately confirmed since the binding energy of them overlap in Cu 2p XPS spectra, but they could be distinguished by their different kinetic energies in the Cu LMM XAES spectra. As shown in Fig. 6C, the broad and asymmetric Cu LMM XAES spectra indicated that Cu^+ and Cu^0 may coexist in a stable state on the catalyst surface. Deconvolution of the original spectra can generate peaks of 916.8 eV and 913.5 eV, which were attributed to Cu^0 and Cu^+ , respectively (Fig. 5C). As listed in

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Fig. 6. Cu2p X-ray photoelectron spectrum of (A) calcined and (B) reduced Cu/SiO₂ catalysts with different content of Na₂SiO₃. (C) Cu LMM XAES spectra of various catalysts.

Table 1, the $Cu^0/(Cu^0 + Cu^+)$ intensity ratio derived by fitting the Cu LMM peak decreased from 0.539 to 0.498 when increasing the content of Na_2SiO_3 from 0 to 0.5 wt.%. The decrease of the ratio could be related to the increase of the copper phyllosilicate in calcined catalysts.

In order to determine quantitatively the role of Na₂SiO₃ on tuning the copper valence state distribution, N₂O titration were applied to measure the surface area of Cu⁰ in the catalysts. It was found that the both the Cu⁰ surface areas and dispersion presented a slightly decline (Table 1), as a result of the introduction of Na₂SiO₃ into the catalysts. On the contrary, the Cu⁺ surface areas (obtained by S_{Cu}⁺ = S_{Cu}⁰/X_{Cu}⁰×(1- X_{Cu}⁰)) increase from 9.4 to 10.3 m²/g with the increase of Na₂SiO₃ content. Evidently, appropriate amount of Na₂SiO₃ had a positive influence on the formation of Cu⁺ species, leading to the decrease of Cu⁰/(Cu⁰ + Cu⁺).

3.3. Catalytic performance in the hydrogenation of DMO

Vapor-phase hydrogenation of DMO is known to involve several continuous reactions, including DMO hydrogenation to MG, MG hydrogenation to ethylene glycol (EG), and deep hydrogenation of EG to ethanol [29]. Fig. 7 presented the catalytic performance of partial hydrogenation of DMO over various catalysts. When $0.5 \text{ wt.}\% \text{ Na}_2\text{SiO}_3$ was introduced into the Cu/SiO₂ catalyst, the conversion of DMO decrease from 100% to 84%. It has been reported that the Cu⁰ species activates H₂ and the Cu⁺ species adsorbs the carbonyl group [6]. Our previous kinetic study has revealed that the dissociation adsorption of

Fig. 7. Correlation of the catalytic performance of the Cu/SiO₂ catalysts modified by Na₂SiO₃ with the Cu⁰ surface areas. Reaction conditions: T = 473 K, P = 2.5 MPa, H₂/DMO = 80 (mol/mol), Weight liquid hourly space velocity (WLHSV) = 1.5 h⁻¹.

DMO is the rate-determining step for the hydrogenation of DMO to EG upon Cu/SiO₂ prepared by ammonia evaporation (AE) method [40]. However, it is worth noting that the conversion of DMO presented a decrease instead of increase trend although the surface area of Cu^+ is slightly improved by the addition of Na₂SiO₃. Meanwhile, the activation of H₂ on Cu⁰ sites should not be the key reason for the lower activity of Na₂SiO₃-modified Cu/SiO₂ catalysts, since there is only a minor decrease in the surface area of Cu⁰ species. According to the texture properties of the catalysts, the obvious decrease of the accumulation pore in the regime of pore diameter at 8–16 nm (Fig. 1b) could be the reason. It indicates that the active sites in the accumulation pores could be responsible for DMO hydrogenation. The loss of accumulation pores could decrease the accessibility of the active sites by DMO molecular, resulting in lower DMO conversion. As for the product distribution, a high EG selectivity of 92.2% was obtained over the Cu/SiO₂ catalyst, accompanied by the generation of only trace amount of MG $(S_{MG} = 0.8\%)$. However, barely any other product except MG was produced over the 0.5 SS-Cu/SiO₂ catalyst and the MG selectivity reached 99.8%. According to the structure properties of the catalyst, the loss of some smaller accumulation pores could be key reason for the higher selectivity, because the larger pore can ensure the fast transfer of MG to the external surface. Thus, the further hydrogenation of MG can be prevented. Some previous studies [29,31] showed that catalyst deactivation is obvious when conversion of DMO is much lower. It indicated that the presence of large amount of MG could affect the stability of copper-based catalyst. In this work, the catalyst activity did not show a dramatic decline when the conversion of DMO is lower than 90% with the increase of the WLHSV (in Fig.S1). The presence of sodium silicate should play an important role in stabilizing the catalyst activity, which is deserved a further study. In addition, the decrease of the Cu⁰ surface area could be another possible reason for the higher selectivity of MG over Na2SiO3-modified Cu/SiO2 catalysts. The insufficient Cu⁰ species prohibits the further hydrogenation of MG to EG due to the lack of enough activated hydrogen. Anyway, Na2SiO3.modified Cu/SiO₂ catalyst gave a high MG yield of above 83% at nearly 100% selectivity at $1.5 h^{-1}$. And the space time yields (STY) of MG over the 0.5 SS-Cu/SiO₂ catalyst were 100 times more than the Cu/SiO₂ catalyst (Table 1). These results may provide an inspiration on fabricating effective catalyst for the partial hydrogenation of DMO to MG.

4. Conclusions

In summary, we have demonstrated a simple method to modify the Cu/SiO_2 catalyst with Na_2SiO_3 for achieving high yields of MG via hydrogenation of DMO. According to the structure properties of the catalysts, the modification of Cu/SiO_2 catalyst by Na_2SiO_3 led to a serious shrinkage of those smaller accumulation pores in the catalyst, but hardly affect the structure of the mesopores bellow 8 nm. This could

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be attributed to the condensation polymerization of silicate ions (SiO_4^{4-}) derived from the hydrolysis of Na₂SiO₃ during the preparation. Moreover, the trace amount of Na₂SiO₃ enhanced the formation of copper phyllosilicate, resulting in a decrease of Cu⁰ species in the reduced catalyst. The disappearance of some smaller accumulation pores led to an increase of the proportion of larger accumulation mesopores, which will contribute to the rapid diffusion of MG. Thus, the deep hydrogenation of MG can be prevented. Moreover, lower amount of Cu⁰ species could also benefit the chemosynthesis of MG by supplying insufficient activated H₂ for its further hydrogenation. An unexpected MG yield of about 83% and selectivity of 99.8% were achieved on the 0.5SS-Cu/SiO₂ catalyst due to the relative higher proportion of larger mesopores and lower hydrogen activation ability, showing a prospective future of the catalyst in industrial applications.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2019.08.048.

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