

Solvent feedstock effect: the insights into the deactivation mechanism of Cu/SiO₂ catalysts for hydrogenation of dimethyl oxalate to ethylene glycol†

Chao Wen, Yuanyuan Cui, Wei-Lin Dai,* Songhai Xie and Kangnian Fan

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The variation of the supports on the Cu/SiO₂ catalyst plays an important role in the catalytic performance for hydrogenation of dimethyl oxalate. The loss of silica in the form of tetramethoxy-silane from the support under the reaction conditions is responsible for the deactivation of the Cu/SiO₂ catalyst.

The synthesis of ethylene glycol (EG) from syngas is more economic and energy efficient compared with the petrochemical route for EG production.¹ This synthesis process contains two steps. The first step for production of dimethyl oxalate (DMO) has been scaled up to industrial levels with a capacity of 10 000 tons per year in 2010.² The hydrogenation of DMO to EG is attracting significant interest from both academic and industrial researchers. Cu supported silica catalysts that exhibit excellent catalytic activity and high selectivity to EG have been extensively studied.³ However, these well-established silica-supported, copper-based catalysts still have a fatal problem, the short lifespan, which severely blocks their industrial application.

Numerous studies have been devoted to improve the poor catalytic performance and short lifespan of the Cu/SiO₂ catalysts. Modification with boron on the surface of the Cu/SiO₂ catalysts shows great enhancement in the catalytic stability on account of maintaining the balance of Cu⁰ and Cu⁺ distribution and the retarding surface transmigration of copper nanoparticles.⁴ A kind of Cu/SiO₂/Cordierite monolithic catalyst was also studied by Ma *et al.*,⁵ and their results showed that the regular channel structure and the uniform distribution of flow of the monolithic catalyst were responsible for the improved thermal stability.

The modulation of interaction between copper metal particles and the silica supports is generally used to promote copper dispersion or decrease the copper particle size, however, the deactivation mechanism of the Cu/SiO₂ catalyst in the DMO to EG process seems to be still undiscovered. Recently, Lin *et al.*⁶ studied the effect of the solvent on copper particles and found that the Cu/SiO₂ catalyst without any modification was more

stable in the DMO–ethanol feedstock than in the DMO–methanol feedstock. They suggested that the CO splitting from methanol and the oxidation of alcohols over Cu/SiO₂ could be the main causes for the aggregation of copper species. However, based on our present work, the variation of the silica supports in the DMO–methanol solution should not be overlooked and the tiny silica erosion under reaction conditions which further results in the agglomeration of copper particles could be another critical factor for the poor stability of the Cu/SiO₂ catalyst.

In our present work, a Cu/SiO₂ catalyst with 15 wt% copper loading is prepared by the ammonia-evaporation method without any modification. The catalytic performance for vapor-phase hydrogenation of DMO is studied in the DMO–MeOH stream and DMO–EtOH stream containing 15 wt% DMO in methanol and ethanol solution respectively. To further investigate the solvent feedstock effect, the catalyst is also exposed to the pure methanol stream alone under identical reaction conditions.

The long-time catalytic performance for vapor-phase hydrogenation of DMO is shown in Fig. 1. It is clear that the Cu/SiO₂ catalyst is more stable in the DMO–EtOH stream, even after 300 h of time on stream. Both the catalytic activity and selectivity remain unchanged. However, obvious deactivation occurs on the Cu/SiO₂ catalyst in the DMO–MeOH stream after running for 140 h. Conversion on the liquid hourly space velocity (LHSV) is also conducted to evaluate the catalytic behaviour (Fig. S1, ESI†), and the DMO conversion on LHSV in the DMO–MeOH and DMO–EtOH stream is almost the same in the first 8 h, however, a severe drop in the conversion could be observed at higher LHSV on the Cu/SiO₂ catalyst running in the DMO–MeOH stream for 100 h, whereas the conversion in the DMO–EtOH stream running for 8 h and 100 h seems to be unchanged. These results indicate that some of the active sites are definitely lost during the long-time catalytic testing in the DMO–MeOH stream.

The TEM images of the reduced and spent catalysts are shown in Fig. 2. Obvious aggregation of the copper particles could be observed on the Cu/SiO₂ catalysts after reaction. The much bigger copper particle size (*ca.* 7.9 nm) of the catalyst running in the DMO–MeOH stream for 300 h than that of the catalyst running in the DMO–EtOH stream (*ca.* 6.0 nm) could be observed, indicating

Department of Chemistry and Shanghai Key Laboratory Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P. R. China.

E-mail: wldai@fudan.edu.cn; Fax: +86-21-55665572; Tel: +86-21-55664678

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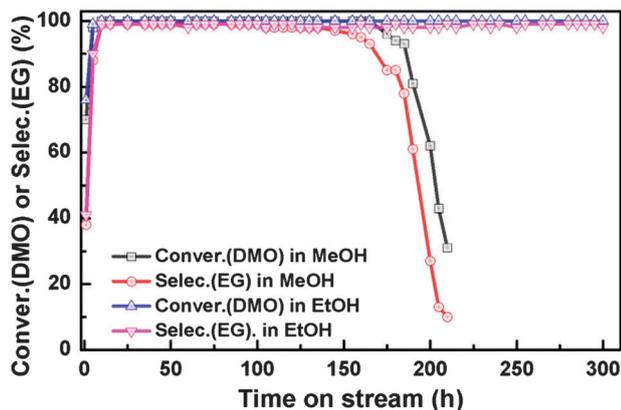


Fig. 1 Catalytic performance of the Cu/SiO₂ catalysts in the DMO–MeOH stream and DMO–EtOH stream. Reaction conditions: P_{H_2} = 3.0 MPa, T = 473 K, H_2/DMO = 150 (mol/mol), LHSV = 0.3 h⁻¹.

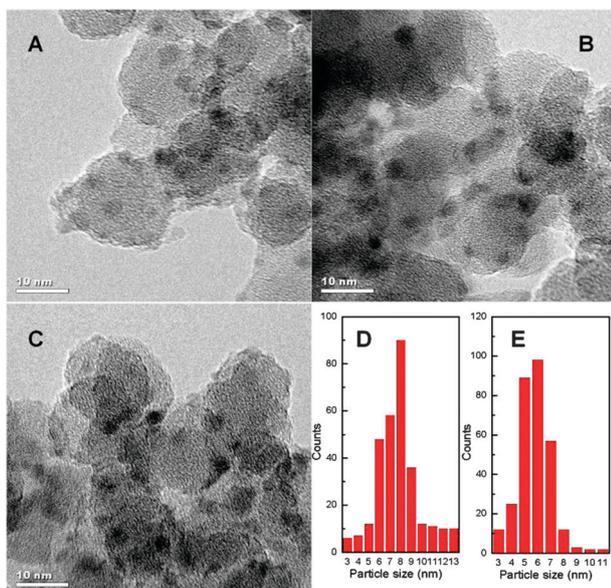


Fig. 2 TEM images of the reduced Cu/SiO₂ (A); Cu/SiO₂ after reaction in DMO–MeOH stream for 300 h (B) and in DMO–EtOH stream for 300 h (C); copper particle size distribution for Cu/SiO₂ after reaction in DMO–MeOH stream for 300 h (D) and in DMO–EtOH stream for 300 h (E).

that the ethanol solvent could better prevent the copper agglomeration during the reaction process compared with the methanol solvent. Interestingly, clear spherical silica particles could be observed in the freshly reduced and DMO–EtOH stream spent catalysts, whereas these spheres in the spent catalyst after 300 h reaction in the DMO–MeOH stream seem to be destroyed with an irregular shape, suggesting that the silica structure must be changed under the methanol containing stream.

The Cu/SiO₂ catalysts present a kind of mesoporous structure with type IV nitrogen sorption isotherms, and the mesopore distributions seem to be constant even when the Cu/SiO₂ catalysts are exposed to different solvent streams (Fig. S2, ESI[†]). However, certain amounts of the micropores are also detected which could provide more refined information for the variation of the catalyst structure during the reaction process. Both the fresh Cu/SiO₂ and

the catalyst spent in the DMO–EtOH stream showed the microporous structure with a pore width of about 1.4 nm, however, in the catalyst after reaction in the DMO–MeOH stream, the pore distribution peak showed an obvious shift to 1.6 nm, meanwhile, the peak intensity decreased too (Fig. S3, ESI[†]). The increase in the microporous width and the decrease in the intensity of micropore distribution demonstrate that the microporous structures in the Cu/SiO₂ catalyst were destroyed during the reaction in the DMO–MeOH stream and the support structures of the catalysts are definitely changed. Our observations are consistent with Kim's studies, in which the higher KOH modification temperature resulted in a higher degree of damage to the SWNTs and the migration of micropore distribution to the larger pore width.⁷

In order to find out how methanol impacts on the silica supports, the product solution is carefully analyzed using GC-MS. Surprisingly, a tiny amount of tetramethoxysilane (TMOS) is detected (Fig. S3, ESI[†]). It is important to note that the TMOS is ever present in the DMO–MeOH stream product yet the amount is so small and usually goes undetected by the usual GC measurement. This result indicates that the TMOS, which is widely used as a silica source to synthesize SiO₂,⁸ could be generated from methanol and silica during the hydrogenation process. Thus some of the silica in the Cu/SiO₂ catalyst could be leached away in the form of TMOS, which may further lead to the aggregation of copper species. For a closer look, the mass loss rate and the accumulative amount of SiO₂ are shown in Fig. 3. When the Cu/SiO₂ catalyst is exposed to the methanol stream under the reaction conditions, the silica loss rate is slow at the beginning and becomes higher gradually with the time on stream. Importantly, after 150 h of running in the DMO–methanol stream, 0.05 g of silica (*ca.* 6.5 wt% of the support) is leached away from the catalyst, furthermore, after 300 h of time on stream, 0.14 g of the support in the catalysts is lost. The silica loss rate for the Cu/SiO₂ catalyst in the DMO–methanol stream is higher than that

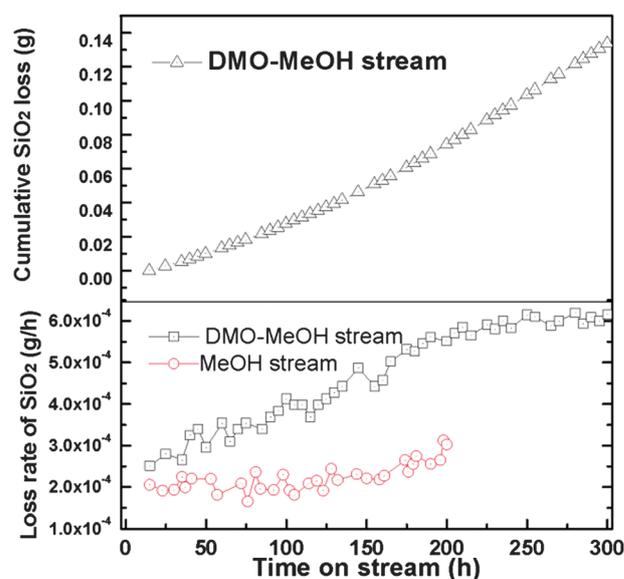


Fig. 3 Mass loss rate and the accumulative loss amount of SiO₂ of the Cu/SiO₂ in DMO–MeOH stream or MeOH stream. Reaction conditions: P_{H_2} = 3.0 MPa, T = 473 K, H_2/DMO = 150 (mol/mol), LHSV = 0.3 h⁻¹.

in the pure methanol stream. Based on Ono's research,⁹ the silica can react with dimethyl carbonate, which could be thought as the methoxy group source, to synthesize TMOS *via* gas-phase reaction over the alkali hydroxide supported catalyst. Thus, in the vapor-phase hydrogenation of DMO, the methoxy group derived from the DMO molecule, which contains double ester groups, could also be thought as the methoxyl group donor and help the formation of TMOS. Particularly, in the methanol solvent, the transesterification effect between DMO and methanol may enhance the concentration of CH_3O^- and leads to a higher TMOS formation rate.¹⁰ Also, the reaction between SiO_2 and methanol to generate TMOS under both supercritical and gas-phase conditions was evidenced by Chibiryaev *et al.*¹¹ However, in the case of the DMO–EtOH stream, neither TMOS nor tetraethoxysilane (TEOS) was detected in the DMO–EtOH stream product mixture. Although methanol is a product of DMO hydrogenation and the formation of TMOS seems to be possible, the concentration of CH_3O^- seems to be limited and both the generation amount and the rate of TMOS seem to be negligible. Chibiryaev *et al.* also confirmed the impossibility of formation of TEOS from silica and ethanol.¹¹ In addition, it can be roughly estimated that the synthesis of TEOS *via* silica and ethanol requires more energy compared with the synthesis of TMOS *via* silica and methanol by the bond enthalpy calculations.¹² Meanwhile, a study on the thermal decomposition of TMOS and TEOS by Lin *et al.*¹³ shows that TMOS is 2400 times more stable than TEOS at 800 K. Thus, TMOS is more favourably generated under the hydrogenation of DMO, and the Cu/SiO₂ catalyst is more stable in the DMO–EtOH stream than in the DMO–MeOH one.

The physicochemical properties of the catalysts are shown in Table S1 (ESI[†]). An obvious increase in the Cu loading could be observed in the catalyst after reaction in the DMO–MeOH stream, confirming again the loss of silica species during the reaction process. The decrease in the specific surface area and copper dispersion could be observed from the spent Cu/SiO₂ catalyst. It is interesting to find that the catalyst spent in the DMO–EtOH stream shows a lower decreasing value than that in the DMO–MeOH stream. The variation of the supports usually causes the changes in the specific surface area, which could further induce copper aggregation and result in the small copper surface area, the latter is considered as the crucial factor for the poor activity in the hydrogenation of DMO.¹⁴ The increased copper particle size (7.2 nm) after 300 h reaction in the DMO–MeOH stream as well as the catalytic activity loss should be ascribed to the erosion of the SiO₂ support in the form of TMOS. To further study the influence of the variation of the supports on the reduction behaviour of the Cu/SiO₂ catalyst, the TPR measurement was conducted and the results are shown in Fig. S6 (ESI[†]). The fresh Cu/SiO₂ catalyst shows only one peak at 525 K assigned to the well-dispersed copper oxide,^{3a} which is consistent with the XRD results. The Cu/SiO₂ catalyst spent in the DMO–MeOH stream also shows a single reduction peak, but the reduction peak shifts to a higher temperature of *ca.* 575 K, indicating that the crystalline copper species with large particle size are dominant.^{3a} For the Cu/SiO₂ catalyst spent in the DMO–EtOH stream, there are two distinct peaks which are assigned to the well-dispersed and crystalline copper species respectively. These results strongly suggest that

using ethanol as solvent could avoid the silica erosion effect caused by methanol, and the higher content of well dispersed copper particles could be afforded compared with the catalyst spent in the DMO–MeOH stream even after 300 h of time on stream.

Although the solvent feedstock effect on the hydrogenation of DMO has been carefully studied by Lin and co workers,⁶ their research mainly focussed on the aggregation of the copper particles caused by the CO splitting and the oxidation of alcohols on the copper surface. Based on the present study, the variation of the support under the methanol steam, which further leads to a decrease in the specific surface area and copper surface area, undoubtedly has significant influence on the deactivation of the Cu/SiO₂ in the DMO–MeOH stream. The loss of the silica in the form of TMOS evidenced by the GC-MS could be considered as a crucial factor for the copper aggregation.

In summary, the poor catalytic performance of the Cu/SiO₂ catalyst in hydrogenation of DMO with methanol as solvent is disclosed. The Cu/SiO₂ catalyst is more stable in the DMO–EtOH stream than in the DMO–MeOH one. The loss of the silica from the Cu/SiO₂ in the form of TMOS plays an important role in the decrease in copper surface area and the aggregation of copper particle size, which will lead to poor stability. As far as we know, this is the first report to study the solvent effect on the Cu/SiO₂ catalyst. Our study illustrates the deactivation mechanism of the Cu/SiO₂ catalyst and the erosion of the silica support, thus has extremely important practical significance in its large-scale industrial application.

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