

High activity and selectivity of Ag/SiO₂ catalyst for hydrogenation of dimethyl oxalate†

Anyuan Yin, Xiaoyang Guo, Weilin Dai* and Kangnian Fan

Received 25th March 2010, Accepted 16th April 2010

First published as an Advance Article on the web 12th May 2010

DOI: 10.1039/c0cc00581a

Ag/SiO₂ prepared by a sol–gel process is highly effective for selective gas-phase hydrogenation of dimethyl oxalate to corresponding alcohols. The catalysts are of great potential as industrially viable and novel catalysts for the production of methyl glycolate and ethylene glycol.

Methyl glycolate (MG), as an important fine chemical intermediate, has been widely applied in various fields.¹ Many catalytic and non-catalytic procedures have been developed for the synthesis of MG,² however the harsh reaction conditions and lower yields (lower than 70%) hindered its further application in industry.³ Therefore, the development of a more efficient and green catalytic synthetic procedure is still a challenging subject in the modern chemical industry.

Ethylene glycol (EG), due to its water solubility with arbitrary ratio, high boiling point and low freezing point, is extensively used as antifreeze, lubricant, plasticizer, surfactant and so on. Besides, it has also been widely applied in synthesizing polymer and polyester.⁴ Nowadays, ethylene oxidation is a universal industrial approach to produce EG. However, as crude oil resources shrink, synthesis of EG from syngas is attracting more and more interest.⁵ Alternative methods that proceed under mild reaction conditions with stable and easy-to-handle heterogeneous catalysts are therefore economically and environmentally benign.

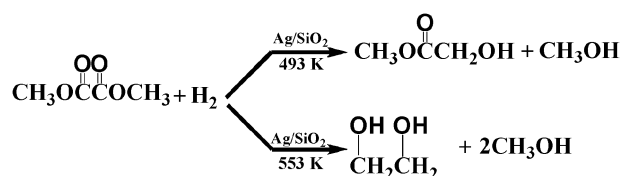
The hydrogenation of esters to alcohols is a conversion of industrial importance, being employed in the production of fatty alcohols, and being a potential route to EG *via* dimethyl oxalate (DMO).⁶ DMO has been the most widely examined substrate to feature in literature reports of ester hydrogenation,⁷ and so can be taken to represent a benchmark reaction in this type of catalysis. Furthermore, its hydrogenation to alcohol is of industrial interest.⁸ Our previous investigation showed that more than 95% yield of EG could be obtained over a copper-based catalyst,⁹ however, the hydrogenation intermediate MG could not be gained *via* the copper catalyst because the thermodynamic constant of the second hydrogenation step is two orders of magnitude larger than that of the first hydrogenation step. Hence, how to design an efficient catalyst that could control the hydrogenation production dynamically is still a great challenge.

Herein, we not only present a new strategy for highly efficient synthesis of MG and EG simply by regulating the

reaction temperature *via* hydrogenation of DMO but also design a highly efficient catalyst with high activity and stability. (Scheme 1)

Silver-based catalysts have long been extensively studied as oxidizing catalysts and have been applied industrially in the epoxidation of ethylene.¹⁰ However, the general lack of affinity of silver toward H₂ due to the filled d-band of silver has limited its further application in hydrogenation reactions.¹¹ Nagase *et al.* and Hohmeyer *et al.* have reported the selective hydrogenation of unsaturated aldehydes to the corresponding alcohols over silver catalysts supported on metal oxides,¹² showing that the activity and selectivity were only moderate. In this work, we report an Ag/SiO₂ catalyst, prepared by a novel synthetic method, exhibiting unprecedented catalytic activity and temperature controlled selectivity for the hydrogenation of DMO to the corresponding alcohols. To the best of our knowledge, this is the first report on the catalytic properties of a supported silver catalyst for the gas-phase selective hydrogenation of ester.

15Ag/SiO₂ catalyst with 15 wt% silver loadings was prepared by a new sol–gel procedure. The Ag/SiO₂ catalysts were prepared in three steps: (1) preparation of silver ammonium solution using silver lactate as the original silver precursor, (2) silica polymerization in the as-obtained silver solution, generating the as-synthesized mesostructure of silica and (3) deposition of silver on silica by calcinations to produce Ag/SiO₂ catalysts. The details for the preparation process can be found in the supporting information.† Fig. 1A shows a typical TEM image of a freshly reduced Ag/SiO₂ catalyst, from which it can be seen that the silver nanoparticles exhibit a spherical shape with an average size of 12 nm and are highly dispersed on the silica support. The highly dispersed silver particles might originate from the formation of Ag₆(Si₂O₇) species due to the stronger interaction between silver and the SiO₂ support, which pre-suppress the aggregation of silver nanoparticles. Fig. 1B shows the XRD patterns of the freshly calcined 15Ag/SiO₂ catalyst, reduced 15Ag/SiO₂-re catalyst and the 15Ag/SiO₂-po catalyst working for 250 h under reaction conditions. For calcined 15Ag/SiO₂ catalyst (graph a), besides a wide peak from amorphous silica, a strong peak



Scheme 1 Temperature controlled selective hydrogenation of DMO to MG and EG over 15Ag/SiO₂ catalyst.

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, 200433, Shanghai, P.R. China. E-mail: wldai@fudan.edu.cn; Fax: +86 5566 5572; Tel: +86 5566 4678

† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c0cc00581a

positioned at $2\theta = 33.8^\circ$ corresponding to the $\text{Ag}_6(\text{Si}_2\text{O}_7)$ (JCPDS 85-0281) could be observed; no other silver-containing peaks were detected, implying that the silver particles are in a nano regime or exist in the form of silver silicate, which could be reduced to highly dispersed silver nanoparticles under the reducing conditions. This could be further proved by the TPR results (Fig. S1†). Silver supported catalysts with different loadings exhibited the same peak only with different intensities (Fig. S2†). The H_2 uptake per mol Ag calculated from the TPR result is almost constant. (Table S2†) After reduction at 573 K under 5% H_2/Ar atmosphere, the four peaks positioned at $2\theta = 38.2^\circ, 44.3^\circ, 64.5^\circ,$ and 77.6° ascribed to the (111), (200), (220), and (311) lattice planes of the metallic Ag appeared, which indicated that the silver silicate decomposed into silver nanoparticles with the average size of 10 nm as calculated according to the Scherrer equation. Although Ag particle size increased with the increase of the Ag loading, the textural structure (pore size distribution and N_2 adsorption and desorption) did not change much. (Table S1 and Figs. S3–S4†)

The catalytic performance of 15Ag/SiO₂ catalyst for the temperature controlled synthesis of MG and EG was investigated for the continuous gas-phase hydrogenation of DMO. Prior to the hydrogenation reaction, the 15Ag/SiO₂ catalyst was reduced in 5% H_2/Ar at 573 K for 4 h. Fig. 2 presents the results of the hydrogenation of DMO over 15Ag/SiO₂ catalyst at 493 K for 120 h and 553 K for 120 h respectively. The DMO conversion could be up to 100% and the selectivity to MG and EG could reach 92% and 96% respectively after 10 h on stream, with no further change observed over prolonged reaction time. After recovering, the catalyst could still keep high catalytic performance. The high activity and stability of the reduced 15Ag/SiO₂ catalyst in the gas-phase hydrogenation reaction are compatible to the XRD results that the particle size of silver was only slightly enlarged from 12 to 14 nm after 250 h on stream, indicating a confinement effect of the silica on the sintering of the silver particles during the hydrogenation reaction. In addition, the surface silver content and the chemical environment investigated by XPS (Fig. S5†) almost did not change, which is consistent with the excellent catalytic performance of the silver catalyst.

For comparison, the silver and silica were also tested for catalytic performance evaluation. The absence of silver or the silica does not cause measurable activities, which suggests a

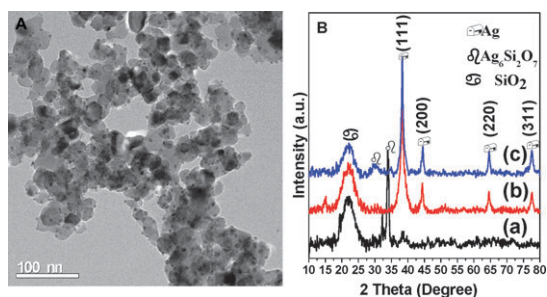


Fig. 1 (A) TEM image of freshly reduced 15Ag/SiO₂ catalyst and (B) XRD patterns of 15Ag/SiO₂: (a) calcined catalyst at 673 K; (b) reduced catalyst of (a) at 573 K in 5% H_2/Ar for 4 h; (c) post-reacted catalyst of (b) after running for 120 h at 473 K, then 553 K for 120 h.

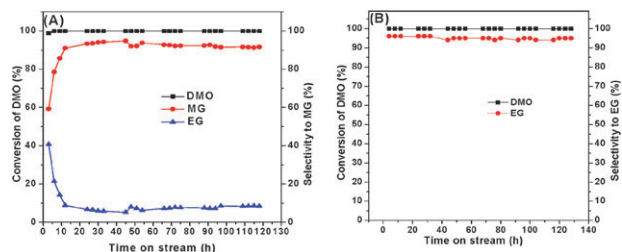


Fig. 2 The performance of the catalytic hydrogenation of DMO over 15Ag/SiO₂ catalyst. (A) Conversion of DMO and MG selectivity vs. time on stream. (B) Conversion of DMO and EG selectivity vs. time on stream. Reaction conditions: catalyst (2 g), 493 K for A and 553 K for B, 2.5 MPa, LHSV = 0.2 h⁻¹, and $\text{H}_2/\text{DMO} = 100$ (mol mol⁻¹).

synergetic effect of the silver and silica. The reaction was also carried out at lower temperature, but no satisfactory yields were obtained. To optimise the silver loading, a series of Ag/SiO₂ catalysts with Ag loading from 5 to 20 wt% were synthesized and tested for hydrogenation activity. The highest activity and selectivity to MG and EG could be obtained over 15Ag/SiO₂ catalyst; higher silver content would not increase the hydrogenation activity which might be a result of the saturation of silver on the surface of silica. Taking XPS results into consideration (Fig. 3), higher silver dispersion on the surface would be beneficial to obtain high yield of MG and EG, however, larger silver nanoparticles would greatly decrease the yield of MG. The intrinsic origin needs to be investigated in future work.

The highly efficient silver catalyst is also tolerant for the hydrogenation of various alcohols, esters and unsaturated aldehydes, which showed that the silver catalyst prepared by a sol-gel method was still active in chemoselective hydrogenation of both C=C bond and C=O bond. Table 1 presents the results for the synthesis of various alcohols and unsaturated aldehydes under continuous gas-phase conditions.

In summary, we have demonstrated a facile and efficient one pot route for the fabrication of MG and EG over the Ag/SiO₂ catalyst embedded with highly dispersed silver particles by a sol-gel method. The catalytic study revealed the remarkable stability, activity and selectivity in the gas-phase continuous hydrogenation of DMO. Therefore, this process has the

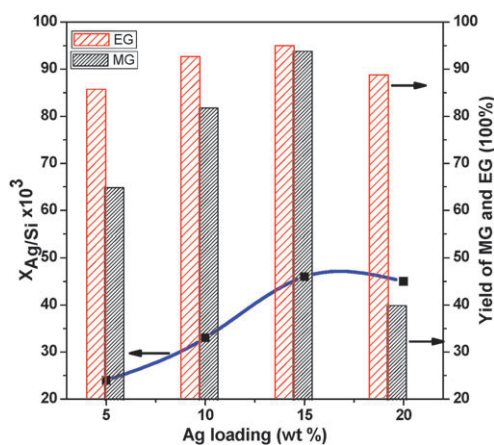


Fig. 3 Surface Ag dispersion ($X_{\text{Ag/Si}}$) calculated by XPS results and yield of MG and EG vs. the Ag loading.

Table 1 Selective hydrogenation reactions over fresh 15Ag/SiO₂ catalyst^a

Entry	t/h	T/K	P/MPa	Conversion/%	Selectivity/%
Dimethyl oxalate	12	493	2.5	100	92 ^b
Dimethyl oxalate	12	553	2.5	100	96 ^c
Dimethyl maleate	12	473	5.0	99	84 ^d
Dimethyl glutarate	12	373	0.1	62	100 ^e
Crotonaldehyde	9.5	413	2.0	96	40 ^f
Acetone	12	493	4.0	41	100 ^g

^a Reaction conditions: catalyst (1 g), H₂/substrate = 100 (mol mol⁻¹).

^b MG. ^c EG. ^d Dimethyl succinate. ^e Pentylene glycol. ^f Crotonyl alcohol. ^g Isopropanol.

potential to enable a more sustainable MG and EG synthesis in industry.

This work is financially supported by the Major State Basic Resource Development Program (Grant No. 2003CB615807), NSFC (Project 20973042), the Research Fund for the Doctoral Program of Higher Education (20090071110011), and the Natural Science Foundation of Shanghai Science & Technology Committee (08DZ2270500).

Notes and references

- 1 Y. Sun, H. Wang, J. H. Shen, H. C. Liu and Z. M. Liu, *Catal. Commun.*, 2009, **10**, 678–681.
- 2 Q. Xu, *Coord. Chem. Rev.*, 2002, **231**, 83–108.
- 3 (a) D. He, W. Huang, J. Y. Liu and Q. Zhu, *Catal. Today*, 1999, **51**, 127–134; (b) D. He, W. Huang, J. Liu and Q. Zhu, *J. Mol. Catal. A: Chem.*, 1999, **145**, 335–228; (c) W. Huang, D. He, J. Liu and Q. Zhu, *Appl. Catal., A*, 2000, **199**, 93–98; (d) F. E. Celik, H. Lawrence and A. T. Bell, *J. Mol. Catal. A: Chem.*, 2008, **288**, 87–96.
- 4 G. H. Xu, Y. C. Li, Z. H. Li and H. J. Wang, *Ind. Eng. Chem. Res.*, 1995, **34**, 2371–2378.
- 5 X. G. Zhao, X. L. Lv, H. G. Zhao, Y. Q. Zhu and W. D. Xiao, *Chin. J. Catal.*, 2004, **27**, 125–128.
- 6 T. Turek, D. L. Trimm and N. W. Cant, *Catal. Rev. Sci. Eng.*, 1994, **36**, 645–683.
- 7 (a) R. A. Grey, G. P. Pez and A. Wallo, *J. Am. Chem. Soc.*, 1981, **103**, 7536–7542; (b) K. Nomura, H. Ogura and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2001, **166**, 345–349; (c) K. Nomura, H. Ogura and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2002, **178**, 105–114; (d) M. C. van Engelen, H. T. Teunissen, J. G. De Vries and C. J. Elsevier, *J. Mol. Catal. A: Chem.*, 2003, **206**, 185–192; (e) H. T. Teunissen and C. J. Elsevier, *Chem. Commun.*, 1997, 667–668; (f) H. T. Teunissen and C. J. Elsevier, *Chem. Commun.*, 1998, 1367–1368.
- 8 (a) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti and P. Frediani, *J. Mol. Catal.*, 1984, **22**, 353–362; (b) U. Matteoli, G. Menchi, M. Bianchi and F. Piacenti, *J. Mol. Catal.*, 1988, **44**, 347–355; (c) U. Matteoli, G. Menchi, M. Bianchi, F. Piacenti, S. Ianelli and M. Nardelli, *J. Organomet. Chem.*, 1995, **498**, 177–186; (d) U. Matteoli, G. Menchi, M. Bianchi, P. Frediani and F. Piacenti, *J. Mol. Catal.*, 1985, **29**, 269–270.
- 9 (a) A. Y. Yin, X. Y. Guo, W. L. Dai, H. X. Li and K. N. Fan, *Appl. Catal., A*, 2008, **349**, 91–99; (b) A. Y. Yin, X. Y. Guo, W. L. Dai and K. N. Fan, *Acta Chim. Sin.*, 2009, **67**, 1731–1736; (c) A. Y. Yin, X. Y. Guo, W. L. Dai and K. N. Fan, *J. Phys. Chem. C*, 2009, **113**, 11003–11013.
- 10 (a) D. J. Guo and H. L. Li, *Carbon*, 2005, **43**, 1259–1264; (b) J. Q. Lu, J. J. Bravo-Suarez, A. Takahashi, M. Haruta and S. T. Oyama, *J. Catal.*, 2005, **232**, 85–95.
- 11 R. J. Mikovsky, M. Boudart and H. S. Taylor, *J. Am. Chem. Soc.*, 1954, **76**, 3814–3819.
- 12 (a) Y. Nagase, H. Hattori and K. Tanabe, *Chem. Lett.*, 1983, 1615–1618; (b) Y. Nagase, H. Muramatu and T. Sato, *Chem. Lett.*, 1988, 1695–1698; (c) Y. Nagase, H. Muramatu, Y. Nakamura, Y. Yazawa and T. Imamoto, *Chem. Lett.*, 1992, 927–928; (d) P. Claus and H. Hofmeister, *J. Phys. Chem. B*, 1999, **103**, 2766–2775; (e) A. Sarkany and Z. Revay, *Appl. Catal., A*, 2003, **243**, 347–355; (f) Y. Y. Chen, C. A. Wang, H. Y. Liu, J. S. Qiu and X. H. Bao, *Chem. Commun.*, 2005, 5298–5300; (g) M. Steffan, A. Jakob, P. Claus and H. Lang, *Catal. Commun.*, 2009, **10**, 437–441; (h) C. E. Volckmar, M. Bron, U. Bentrup, A. Martin and P. Claus, *J. Catal.*, 2009, **261**, 1–8; (i) J. Hohmeyer, E. V. Kondratenko, M. Bron, J. Kroehnert, F. C. Jentoft, R. Schloegl and P. Claus, *J. Catal.*, 2010, **269**, 5–14.