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Short Communication

Highly efficient mesostructured Ag/SBA-15 catalysts for the chemoselective synthesis of methyl glycolate by dimethyl oxalate hydrogenation



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1. Introduction

Methyl glycolate (MG) is usually used as a raw material for the synthesis of polyglycolic acid and other important organic chemicals. Several approaches to MG production have been developed, but weaknesses of these methods such as severe reaction conditions or lower yields (<70%) markedly hinder their practical applications [1–4]. The chemoselective hydrogenation of dimethyl oxalate (DMO) has led to the development of a more efficient and greener catalytic procedure for the challenging feat of efficient MG synthesis [5–8]. Copper-based catalysts are usually preferred for ethylene glycol (EG) and ethanol (EtOH) syntheses by the DMO hydrogenation [9-14]. However, excellent selectivity for the mono-hydrogenation of DMO to MG is difficult to achieve using analogous copper catalyst systems mainly because of the high thermodynamic constant of the subsequent hydrogenation of MG to EG. Studies have shown that Au and Ag have superior catalytic capability over Cu for the chemoselective hydrogenation of DMO to MG [5–8]. From the viewpoint of practical application, developing Ag-based catalysts that match the urgent demands for catalytic efficiency, long-term stability, and easy handling is a challenge. Undoubtedly, probing into the relationship between the properties of Ag crystallites and the catalytic performance could significantly help advance the design and fabrication of Ag-based catalysts with promising features.

ABSTRACT

Ag/SBA-15 catalyst is found to exhibit excellent catalytic activity and long-term stability for the chemoselective hydrogenation of dimethyl oxalate to methyl glycolate. The size of Ag crystallites, which is markedly affected by the Ag loading levels and catalyst pretreatment conditions, is a key factor determining the reaction rate of the structure-sensitive hydrogenation but hardly influenced the product distribution. The best catalytic hydrogenation activity is obtained over the Ag/SBA-15 catalyst with an average Ag crystallite size of around 3.9 nm. © 2013 Elsevier B.V. All rights reserved.

Ordered mesoporous materials (OMMs) based silicas like MCM-41, SBA-15, and HMS with tunable and regular mesopores, easily accessible internal surface, and relatively high surface areas have been extensively used as carriers for preparing supported metal catalysts. These catalysts are efficient for many catalytic reactions in which hydrogen is required, such as photocatalysis, hydrogenation, oxidative dehydrogenation, hydrodesulfurization, and the Fischer-Tropsch synthesis [15-18]. The high surface area and uniform pore size distribution in OMMs allow better dispersion and stabilization of crystallites in oxide or metal phases with easily controlled sizes. Moreover, the narrow pore size distribution of OMMs is evidently beneficial for preventing the sintering effect of metal crystallites, which is important for catalyst stability. Different from previously reported silica or MCM-41 supported Ag catalysts [5,6], the Ag/SBA-15 designed in the present study is an attractive catalyst that displays excellent activity, selectivity, and stability for the DMO hydrogenation to MG, as well as crystallite size dependence that may help reveal the importance of nanocatalysis.

2. Experimental

2.1. Catalyst preparation

Mesoporous SBA-15 was synthesized according to literature [19]. Classic volumetric impregnation was adopted to fabricate Ag/SBA-15 catalysts. Typically, a specific amount of AgNO₃ was dissolved in deionized water with one drop of 37 wt.% HNO₃ solution. The calcined SBA-15 and AgNO₃ solution were quickly mixed and subjected to



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aging at room temperature for 10 h. Prior to calcination in air at 623 K for 4 h, the obtained powder was dried at 383 K in darkness. Before catalytic evaluation, the Ag/SBA-15 catalyst precursors were reduced at 623 K at different temperature ramping rates (2, 6, and 10 K/min) by 5% H₂–95% N₂ gas for 4 h, affording the catalysts denoted as x%Ag/SBA-15-2 K, x%Ag/SBA-15-6 K, and x%Ag/SBA-15-10 K (where x stands for Ag mass loading).

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) analysis was performed with a PANalytical X'pert Pro Super X-ray diffractometer using Cu K_α radiation $(\lambda = 0.15418 \text{ nm})$. Nitrogen adsorption–desorption isotherms were measured by static N₂ physisorption at 77.3 K with a Micromeritics TriStar II 3020 surface area and pore analyzer. Transmission electron microscopy (TEM) images were obtained on a Tecnai F30 apparatus operated at 300 kV. The metallic loadings of the samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Thermo Elemental IRIS Intrepid II XSP. The hydrogentemperature-program reduction (H₂-TPR) was performed on a Micromeritics Autochem II 2920 instrument. O2 chemisorption experiments were conducted on a Micromeritics Autochem 2020 instrument following a method described in previous literature [20]. Before O₂ chemisorption measurement at 443 K, the samples were reduced and then evacuated for 30 min at 623 K, thereafter cooled to 443 K. Metal dispersion was also estimated by the metal size according to $D = 1.17/d_{Ag}$, where d_{Ag} was calculated from the Ag diffraction at a $2\theta = 38.06^{\circ}$ using the Scherrer equation.

2.3. Catalytic test

DMO hydrogenation reaction was carried out in continuous flow mode in a stainless steel tubular reactor equipped with a computercontrolled auto-sampling system. Typically, 200 mg of a catalyst precursor (40–60 meshes) was loaded into the center of the reactor, and both sides of the catalyst bed were packed with quartz powders (40–60 meshes). 0.02 g/mL DMO methanol solution was pumped into the catalyst bed with a Series III digital HPLC pump (Scientific Systems, Inc.). The products were analyzed by an on-line gas chromatograph (Agilent 7890A) equipped with a flame ionization detector and a capillary column (KB-Wax, 30 m). Turnover frequency (TOF) was calculated according to the following equation:

$$\text{TOF} = \frac{\text{C}_{\text{DMO}} \cdot \text{V} \cdot \text{X}_{\text{DMO}}}{\text{D} \cdot \text{N}_{\text{Ag}}}$$

where C_{DMO} is the DMO concentration in the DMO methanol solution, V is the flow rate of the DMO methanol solution, X_{DMO} is the DMO conversion measured, N_{Ag} is the total amount of Ag and D is the Ag dispersion obtained from O₂ chemisorption analyses. Through adjusting the LHSV_{DMO}, the DMO conversion was controlled to lower than 30% to provide appropriate data for the TOF calculation (Table S1).

3. Results and discussion

3.1. Texture characterization

The actual Ag loading determined by ICP-OES was slightly lower than the preset values, indicating that most of the Ag precursors were successfully loaded onto the pore surface of SBA-15 (Table 1). The surface area, pore volume, and average pore size (getting from Fig. S1) progressively decreased with increased Ag loading compared with the pure SBA-15, which could be mainly ascribed to the exacerbation of pore blocking by Ag crystallites.

The XRD patterns indicated that the structure of the well-ordered mesoporous SBA-15 did not significantly change after the immobilization

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Textural and physicochemical characteristics of SBA-15 and Ag/SBA-15 catalysts.

Catalyst	Metal loading (wt. %) ^a	S_{BET} (m ² /g)	V _{pore} (cm ³ /g)	D _{pore} (nm) ^b	Crystallite size (nm)	
					by XRD ^c	by TEM
SBA-15	_	833.4	1.07	5.56	_	_
5%Ag/SBA-15	4.3	439.5	0.58	5.05	3.0	2.8
7.5%Ag/SBA-15	6.9	439.1	0.63	5.23	3.1	3.0
10%Ag/SBA-15	9.3	410.6	0.58	5.24	3.6	3.9
12.5%Ag/SBA-15	12.2	397.4	0.55	4.99	15.2	n. m. ^d
15%Ag/SBA-15	13.8	287.8	0.39	4.86	26.0	n. m.

^a Metal loading was determined by ICP-OES.

^b Obtained from $P/P_0 = 0.99$.

^c Determined by the Scherrer equation from XRD patterns.

^d Not measured.

of Ag crystallites and subsequent treatments of high-temperature calcination and hydrogen reduction (Fig. S2). The Ag/SBA-15 catalysts showed a broad peak at 23° ascribed to amorphous silica and five other diffraction peaks that all corresponded to the characteristic diffraction of cubic Ag metallic crystals (Fig. 1). Different Ag loadings induced obvious variations in the intensity and sharpness of these diffractions. Using the Scherrer equation, the size of Ag crystallites were found to increase gradually from 3 to 26 nm with increased Ag loading from 5 wt.% to 15 wt.% (Table 1). The easy aggregation of Ag crystallites at high surface concentrations and the limited capability of SBA-15 to accommodate excess Ag atoms may be responsible for the large crystallite sizes at high Ag loadings. Anand et al. [21] found similar phenomena on Ag/SBA-15 synthesized by an impregnation method.

The ordered hexagonal and straight channels were clearly observed in the HRTEM images of SBA-15 (Fig. 2). In the case of 5%Ag/SBA-15-2 K and 10%Ag/SBA-15-2 K catalysts reduced at a low temperature ramping rate, spherical Ag crystallites were found to be homogeneously dispersed on the pore surface of SBA-15. The statistical values for the average crystallite size were consistent with the XRD results. As for the 10%Ag/SBA-15-6 K and 10%Ag/SBA-15-10 K catalysts reduced at an elevated temperature ramping rate, apparent aggregation of Ag crystallites occurred and the amount of large Ag crystallites was noticeable. However, the calcination of Ag/SBA-15 catalyst precursors in air did not induce the growth of Ag crystallites. The formation of surface Ag species and their interaction with SBA-15 surface could be responsible for the effect of reductive atmosphere and temperature on the size and shape of Ag crystallites.

Therefore, a series of Ag/SBA-15 catalysts with different Ag crystallite sizes were prepared by changing the temperature ramping rate during reduction. Initially, the Ag⁺ ions in AgNO₃ solution were adsorbed on the pore surface of SBA-15 by strong electrostatic adsorption. Calcination



Fig. 1. Wide-angle XRD patterns of (a) 5%Ag/SBA-15-2 K, (b) 7.5%Ag/SBA-15-2 K, (c) 10%Ag/SBA-15-2 K, (d) 12.5%Ag/SBA-15-2 K, and (e) 15%Ag/SBA-15-2 K.



Fig. 2. TEM images of (a) SBA-15, (b) 5%Ag/SBA-15-2 K, (c) 10%Ag/SBA-15-2 K, (d) 15%Ag/SBA-15-2 K, (e) 10%Ag/SBA-15-6 K, and (f) 10%Ag/SBA-15-10 K.

in air decomposed the weakly absorbed Ag precursors and formed highly dispersed Ag₂O clusters strongly anchored on the SBA-15 surface by the bond of Si - O - Ag, thereby strongly inhibiting the surface mass transfer and formation of large Ag crystallites. Under the atmosphere of hydrogen, the positively charged Ag species to metallic Ag atoms may significantly reduce the strength of the metal-support interaction and the Ag clusters were apt to move and coagulate because of the low melting points of nano-Ag and the weak interaction with the supports. High temperature and rapid temperature ramping inevitably led to the quick growth of Ag crystallites. Kazuma et al. [22] reported a similar finding after sintering Ag crystallites on graphene sheets. For a catalyst with an extremely high Ag loading such as 15 wt.%, even a low ramping rate for hydrogen reduction cannot afford highly dispersed Ag crystallites because of the too high surface concentration of Ag atoms. In this case, many worm-like Ag wires located in the straight channels of SBA-15 emerged in 15%Ag/SBA-15-2 K.

3.2. Effect of Ag loading

The performances of a series of Ag/SBA-15 catalysts with different Ag loadings for the DMO hydrogenation are shown in Fig. 3. It was not strange that pure SBA-15 completely did not catalyze the hydrogenation of DMO, suggesting that the active metal Ag played a vital role in the catalysis of DMO hydrogenation. Increased Ag loading from 5 wt.% to 10 wt.% considerably improved DMO conversion, whereas the selectivity to MG was almost unchanged (>94%). However, further increased Ag loading to 12.5 wt.% and 15 wt.% significantly decreased the hydrogenation activity. Extra high Ag loading did not promote the catalytic hydrogenation of DMO but instead considerably suppressed the activity that may be due to the variations in the actual size of Ag crystallites and the amount of Ag active sites.

3.3. H₂-TPR

The H_2 -TPR profiles of 5%Ag/SBA-15 and 10%Ag/SBA-15 catalysts gave one reduction peak centered at ca. 408 K and 417 K, respectively,

which was ascribed to the transformation of Ag⁺ to Ag⁰ (Fig. 4). When the silver loading was increased to 15 wt.%, a large reduction peak appeared at a low temperature of 401 K, although the 417 K peak still emerged on the shoulder of 401 K peak. The reducibility of Ag⁺ species is generally affected by both the interaction between metal and support and crystallite size. On the basis of TEM, XRD and O₂ chemisorption analyses, most of the Ag crystallites on 5%Ag/SBA-15 and 10%Ag/SBA-15 catalysts might be confined in the nanochannels of SBA-15 and possess small sizes. These Ag species were believed to strongly interact with the internal surface of SBA-15. They were relatively difficult to be reduced by hydrogen as compared to unsupported Ag₂O particles which usually showed a reduction peak at ca. 400 K [23]. However, high Ag loading in the 15%Ag/SBA-15 catalyst could not favor the efficient dispersion of Ag on the internal surface of SBA-15 and lead to the formation of many large Ag crystallites on the external surface. Therefore, the 401 K



Fig. 3. DMO hydrogenation performance over x%Ag/SBA-15-2 K as a function of Ag loading. Reaction conditions: Temperature = 473 K, $LHSV_{(DMO)} = 0.6 h^{-1}$, $P(H_2) = 3.0 MPa$, $H_2/DMO = 100$.



Fig. 4. H₂-TPR profiles of Ag/SBA-15 catalysts with different Ag loadings. (a) 5%Ag/SBA-15; (b) 10%Ag/SBA-15; (c) 15%Ag/SBA-15.

peak should be due to the reduction of these large Ag crystallites located on the external surface of SBA-15.

3.4. Effect of pretreatment

The pretreatment conditions for the Ag/SBA-15 catalyst precursors were also found to influence the catalytic performances remarkably. Fig. 5 shows that a slow temperature ramping rate of 2 K/min produced an excellent 10%Ag/SBA-15-2 K catalyst with DMO conversion (99.5%) and MG selectivity (95%). By contrast, 10%Ag/SBA-15-6 K and 10%Ag/SBA-15-10 K catalysts activated at higher temperature ramping rates had increasingly inferior hydrogenation activities but retained high MG selectivity (~99%). Combining the results of the effect of pretreatment conditions on the Ag crystallite size from TEM observation (Fig. 2) and the textural factors for the Ag/SBA-15 catalysts with different Ag loadings (Table 1), it is supposed that Ag crystallite size may provide more active sites and then enhance the rate of catalytic hydrogenation.

The mean sizes of the interesting worm-like Ag rods filling the channels of SBA-15 formed at a high temperature ramping rate were also calculated using the Scherrer equation (Fig. S3). These catalysts with obviously coagulated Ag crystallites displayed poor performance in the hydrogenation of DMO to MG (Fig. 4). However, the inaccessibility of these Ag rods for the DMO substrate could not be excluded to understand the effect of metal crystallite size.



Fig. 5. DMO hydrogenation performance over 10%Ag/SBA-15 reduced with different temperature ramping rates. The reaction conditions are the same as in Fig. 3.

3.5. Effect of Ag crystallite size

To better understand the essence of the effect of Ag crystallite size on catalytic behavior, the TOF values for different catalysts are also calculated using the metal dispersion from O₂ chemisorption (Table S1). Variations in TOF in the DMO hydrogenation as a function of the Ag crystallite size are shown in Fig. 6. All Ag/SBA-15 catalysts exhibited excellent selectivity to MG; thus, the Ag crystallite size only influenced the catalytic activity rather than the selectivity. Ag crystallites smaller than 3 nm displayed a low TOF of ca. 13 h^{-1} , which increased to $34 h^{-1}$ when the mean Ag crystallite size was 3.6 nm. Further increased Ag crystallite size resulted in a gradual decline in TOF, indicating that in addition to the simple relationship between the amount of surface metal atoms and the catalytic hydrogenation activity, some complicated correlations on the formation of catalytic sites with high efficiency for the chemoselective hydrogenation of DMO also existed. The dependence of TOF on the average size of Ag crystallites suggested that DMO hydrogenation was a structuresensitive reaction. In our previous work, a bimetallic Au-Ag catalyst showed a synergistic effect in which the Au sites helped activate the substrate ester molecules whereas the Ag sites contributed to activating the H₂ molecules by chemisorption [9]. Ag catalysts requiring special sites to serve as Au sites help activate the substrate ester molecules. Special low-coordinated Ag atoms are believed to be the active site for the chemoselective hydrogenation of DMO, and their surface concentration may reach the maximum when the average size of Ag crystallites is close to 3.9 nm.

3.6. Long-term performance

The catalyst 10%Ag/SBA-15-2 K with the best activity was subjected to a comprehensive catalytic evaluation for the DMO hydrogenation. The DMO liquid hourly space velocity (LHSV) markedly affected the catalytic performances similar to other kinetic factors such as reaction temperature and pressure (Fig. S4). At a DMO LHSV of 0.6 h⁻¹, the best performance was reached at 473 K. Moreover, the catalytic behavior of the 10%Ag/SBA-15-2 K catalyst was stable for no less than 100 h (Fig. S5). The XRD characterization on the recycled catalyst confirmed that the long-term reaction did not obviously enlarge the size of Ag crystallites (Fig. S5 inlet). Therefore, the Ag/SBA-15 catalyst fabricated by optimal synthesis and treatment methods is potential for the MG production by chemoselective hydrogenation of DMO.



Fig. 6. TOF and product selectivity for the hydrogenation of DMO as a function of average Ag crystallite size.

4. Conclusion

A series of Ag/SBA-15 catalysts with different sizes of Ag crystallites have been fabricated by an incipient wetness impregnation method and optimal reductive pretreatments. The Ag loading and temperature ramping rate for hydrogen reduction are found to influence the morphological features of Ag crystallites. The coagulation of Ag crystallites mainly induced by the thermal mass transfer of Ag clusters in the metallic state markedly suppresses the catalytic activity. In addition to the correlation between the amount of surface Ag atoms and catalytic hydrogenation activity, the 10%Ag/SBA-15-2 K catalyst with Ag crystallite size of ca. 3.9 nm performed the highest TOF for the DMO hydrogenation to MG.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.06.022.

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