

Electronic Supplementary Information

Three dimensional Ag/KCC-1 catalyst with hierarchical fibrous framework for the hydrogenation of dimethyl oxalate

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1. Experimental

1.1 Materials

Tetraethyl orthosilicate (TEOS), cyclohexane, pentanol, ethyl acetate, urea, MCM-41, SAB-15 and nitric acid (HNO₃) were purchased from Tianjin Kermel Chemical Co., Ltd. Cetylpyridinium bromide (CPB) was purchased from Aladdin. Silver nitrate (AgNO₃) was purchased from Tianjin Guangfu Technology Development Co., Ltd. All the reagents were used without further purification.

1.2 Preparation of KCC-1

The hydrothermal route for the synthesis of KCC-1 was as follows. CPB (6.6667 g) and urea (4 g) was dissolved in deionized water (200 mL) followed by the drop-wise addition of a stirred solution of TEOS (16 mL) and pentanol (10 mL) in cyclohexane (200 mL). The mixture was vigorously stirred for 2 h at room temperature, and the resulting microemulsion solution was transferred into Teflon-sealed hydrothermal reactors and heated at 120 °C for 5 h. After completion of the reaction, the mixture was cooled to the room temperature, then followed by filtering and washing with deionized water and ethyl acetate several times. Finally the residue was dried overnight in a vacuum drying oven and calcined at 400 °C in air for 4 h to obtain KCC-1.

1.3 Preparation of Ag nanocatalyst

Ag/KCC-1 catalysts were synthesized using the classic volumetric impregnation method. Typically, a defined amount of AgNO₃ was dissolved in deionized water with one drop of 10 wt.% HNO₃ solution. Then, AgNO₃ solution and KCC-1 were mixed together and subjected to aging without light in room temperature for 20 h. The

obtained powder was dried at 110 °C for 6 h and calcined in air at 400 °C for 4 h. The final calcined sample was designed as xAg/KCC-1 where x denotes silver loading. For comparison, 15Ag/SBA-15 and 15Ag/MCM-41 were obtained using the same method above.

1.4 Catalytic performance test

Gas-phase catalytic hydrogenation of dimethyl oxalate (DMO) was carried out in continuous flow mode in a stainless-steel fixed-bed reactor with an internal diameter of 8 mm. About 0.4 g catalyst (40–60 mesh) were placed in the reactor. The reaction test was carried out after the reduction of catalyst under hydrogen at 300 °C for 4 h at a temperature rate of 2 °C·min⁻¹. The reactant (10wt.% DMO, 99.9% purity, in methanol solution) was injected from the top of the reactor using a high-pressure pump with a system pressure of 3MPa. Catalytic performance was tested at 200 °C and the DMO weight liquid hourly space velocity (LHSV) varied from 0.5 to 5 h⁻¹. The reaction products collected in the condenser were analyzed using a gas chromatography (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). More than three samples were taken under the same experimental conditions and the results were averaged to ensure repeatability. DMO conversions were determined by the change of DMO weight before and after the reaction (equation 1). The selectivity of methyl glycolate (MG), ethylene glycol (EG) and ethanol were calculated using the following equation (equation 2). Turnover frequency (TOF) was calculated as per mol of consumed reactant per accessible Ag atom per hour (equation 3). Through adjusting the LHSV, the DMO conversion was controlled to lower than 30% for the convenience to calculate accurately the TOF of various catalysts.

$$\text{Conversion}(\%) = \frac{\text{mol of DMO put into the reactor} - \text{mol of DMO in the product}}{\text{mol of DMO put into the reactor}} \times 100\% \quad (1)$$

$$\text{Selectivity}(\%) = \frac{\text{mol of MG or EG in the product}}{\text{mol of DMO put into the reactor} - \text{mol of DMO in the product}} \times 100\% \quad (2)$$

$$\text{TOF} = \frac{w \cdot V \cdot C_{\text{DMO}}}{D \cdot N_{\text{Ag}}} \quad (3)$$

w: DMO concentration in the DMO methanol solution (mol/L);

V : flow rate of DMO methanol solution (L/h);

C_{DMO}: DMO conversion;

N_{Ag}: total amount of Ag (mol);

D: Ag dispersion obtained from H₂-O₂ chemisorption analyses.

1.5 Catalyst characterization

Textual properties of the samples were determined by a nitrogen-adsorption method using a Micromeritics Tristar II 3000 Analyser at 77 K. Pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method from the desorption branches of the adsorption isotherms, and the specific surface areas were calculated from the isotherms using the Brunauer-Emmett-Teller (BET) method.

Mercury intrusion porosimetry (MIP) was performed with Micromeritics AutoPore IV 9500. The Pore Sizer is a 225MPa mercury intrusion porosimeter, which determined pore sizes in the range of 5.5 nm to 250 μm . The apparatus had two low-pressure chambers and one high-pressure chamber. A measurement was conducted in two stages: a manual low pressure run from 0 to 0.170 MPa and an automated high pressure run from 0.170 to 225 MPa. Data was collected and handled by a computer acting as a control module.

Transmission electron microscope (TEM) was conducted using a Philips TECNAI G2 F20 system electron micro-scope at 100 kV equipped with a field emission gun. The sample powder was dispersed in ethanol under ultrasonic and drops of the suspension were applied on a micro grid, followed by drying in air. 200 particles were counted to evaluate the particle size distribution.

Scanning electron microscope (SEM) was used to observe the surface morphology of the KCC-1 by employing a Hitachi S4800 field-emission microscope at 10.0 kV.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Rigaku C/max-2500 diffractometer, employing the graphite-filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. The particle size of silver was calculated with the X-ray-broadening technique using the Scherrer's equation. Data points were acquired by step scanning with a rate of $8^\circ/\text{min}$ from $2\theta = 10^\circ$ to $2\theta = 90^\circ$.

The elemental analysis of silver in all samples was performed on an inductively coupled plasma optical emission spectroscopy (ICP-OES) (VISTA-MPX, Varian). ~ 50 mg of the sample was dissolved in HF aqueous solution, and excessive amounts of boric acids solution were added to form complex with HF.

Ag active surface area and the mean particle size was determined by $\text{H}_2\text{-O}_2$ pulse chemisorption (Micromeritics AutoChem II 2920). After the catalyst was reduced at 300°C for 2 h under 10% H_2/Ar flow, it was cooled down to 170°C under the He atmosphere, and then 5% O_2/He pulses were injected until the eluted peak area of consecutive pulses was constant, followed by flushing with Ar, then the introduction of 10% H_2/Ar pulses. The stoichiometries of $\text{Ag}/\text{O}_2 = 2$, $\text{Ag}/\text{H}_2 = 1$ were assumed.¹ And the crystallite size could be estimated from the expression $d \text{ (nm)} = 1.17/D$ on the basis of these dispersion (D) data.

2. The gas-phase hydrogenation of DMO

The hydrogenation of DMO upon silver-based catalyst consists of two important reactions (equation 4 and 5): one carbonyl of DMO is first hydrogenated and lead to the formation of MG, which is the desired product in this study. Then the carbonyl of MG can be further hydrogenated to produce EG at appropriate conditions.

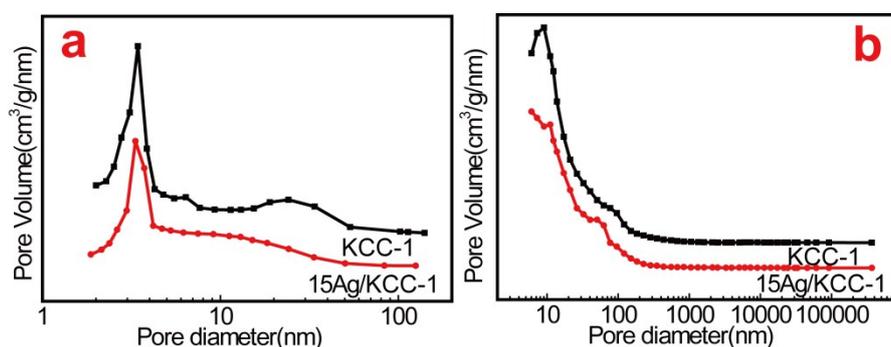
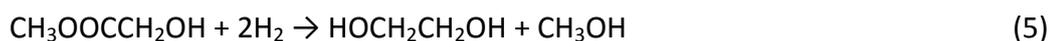
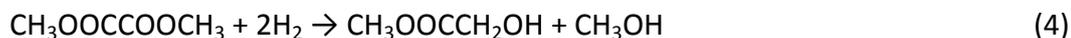


Fig. S1 (a) BJH pore size distribution spectrum, (b) MIP pore size distribution curves of KCC-1 and 15Ag/KCC-1 catalyst.

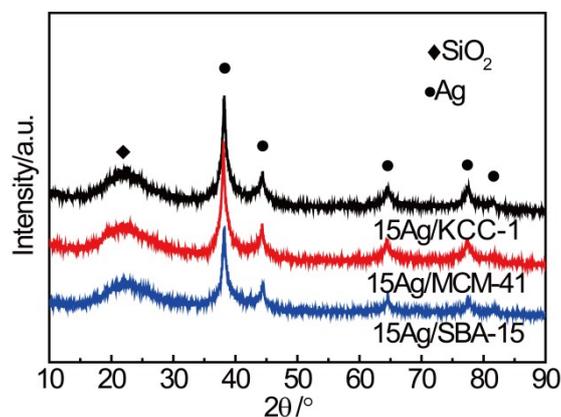


Fig. S2 Wide-angle XRD pattern of 15Ag/KCC-1, 15Ag/SBA-15, 15Ag/MCM-41 catalysts after reduction by hydrogen at 300 °C for 4h.

Notes and references

- 1 D. E. Strohmayer, G. L. Geoffroy and M. A. Vannice, *Applied Catalysis*, 1983, **7**, 189-198.