Supporting Information

High Activity and Selectivity of Ag/SiO_2 Catalyst for Hydrogenation of Dimethyloxalate

An-Yuan Yin, Xiao-Yang Guo, Wei-Lin Dai*, Kang-Nian Fan

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

I. Catalyst preparation

Silver supported silica catalysts were synthesized by sol-gel method. A typical procedure for fabricating Ag/SiO_2 catalyst was as follows. A defined amount of silver lactate was dissolved in deionized water. The amount of silver lactate was adjusted to yield 5, 10, 15, 20 wt.% of Ag in the final catalyst. This mixture was then added to a 25% ammonia solution under stirring for 2 h at 313 K. Subsequently, a defined amount of tetraethoxylsilicate (TEOS) was added to the reaction mixture. The solvent was then evaporated in a water bath at 363 K until a gel was obtained. Thereafter, the gel was vacuum dried at 393 K for 12 h. The resulting solid was calcinated at 673 K for 2 h in flowing air. The final calcined sample was designed as $x Ag/SiO_2$ where x denotes silver loading.

For comparison, catalyst containing 15% silver was prepared by impregnation of silica (Aerosil 200, Degussa) with an aqueous solution of silver lactate. Impregnation was followed by drying (313 K, 12 h), calcinations at 673 K for 2 h in flowing air. The catalyst was denoted as $15Ag/SiO_2$-im.

II. Procedure for the gas-phase hydrogenation reaction

The catalytic performance evaluation was conducted with a fixed-bed microreactor. Typically, 2.0 g of catalyst (40-60 meshes) sample was packed into a stainless steel tubular reactor with the thermocouple inserted into the catalyst bed for better control of the actual pretreatment and reaction temperature. Catalyst activation was performed at 573 K for 4 h. After cooling to the reaction temperature, 15 wt.% DMO in methanol and H_2 were fed into the reactor at a H_2/DMO molar ratio of 100 and a system pressure of 2.5 MPa. The room temperature liquid hour space velocity (LHSV) was set at 0.2 h^{-1}. The products were analyzed by GC equipped with FID.

III. Characterization of the catalysts

Specific surface areas of the samples are measured by nitrogen adsorption at 77 K (Micromeritics Tristar ASAP 3000), using the BET method. The X-ray powder diffraction (XRD) of the catalysts was carried out on a German Bruker D8 Advance X-ray diffractometer using nickel filtered Cu Kα radiation at 40 kV and 20 mA. A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li)

detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. Temperature programmed reduction (TPR) profiles were obtained on a Tianjin XQ TP5080 autoadsorption apparatus. 20 mg of the calcined catalyst was outgassed at 473 K under Ar flow for 2 h. After cooling to room temperature under Ar flow, the in-line gas was switched to 5% H_2/Ar, and the sample was heated to 673 K at a ramping rate of 10 K/min. The H_2 consumption was monitored by a TCD detector. XPS spectra are recorded under ultra high vacuum ($<10^{-6}$ Pa) at a pass energy of 93.90 eV on a Perkin-Elmer PHI 5000C ESCA system equipped with a dual X-ray source by using Mg anode and a hemispherical energy analyzer. All the energies are calibrated with contaminant carbon (C 1s=284.6 eV) as a reference.

Table S1. Physico-chemical parameters of Ag/SiO_2 catalyst

Catalyst	BET $m^2 \cdot g^{-1}$	D_{pore} nm	V_{pore} $cm^3 \cdot g^{-1}$	d_{Ag} [a] nm	$X_{Ag/Si}$ [b] mol/mol
5Ag/SiO_2	233	12.1	0.87	10.3	0.024
10Ag/SiO_2	158	10.8	0.54	10.2	0.033
15Ag/SiO_2	122	13.0	0.52	12.4	0.046
20Ag/SiO_2	113	13.3	0.48	14.5	0.045
15Ag/SiO_2-im	132	12.6	0.52	31.4	0.072

[a] Calculated according to the full width at half-maximum of Ag (111) reflection using Scherrer equation.[b] Calculated from the XPS results after reduction.

Table S2. Relative H_2 uptake per mol Ag of Ag/SiO_2 catalyst

catalyst	H_2 uptake (mol H_2 per mol Ag)[a]
$5Ag/SiO_2$	0.38
$10Ag/SiO_2$	0.45
$15Ag/SiO_2$	0.48
$20Ag/SiO_2$	0.41
$15Ag/SiO_2$-im	0.50

[a]: calculated by H_2 uptake based on TCD by a run with CuO as reference compound.

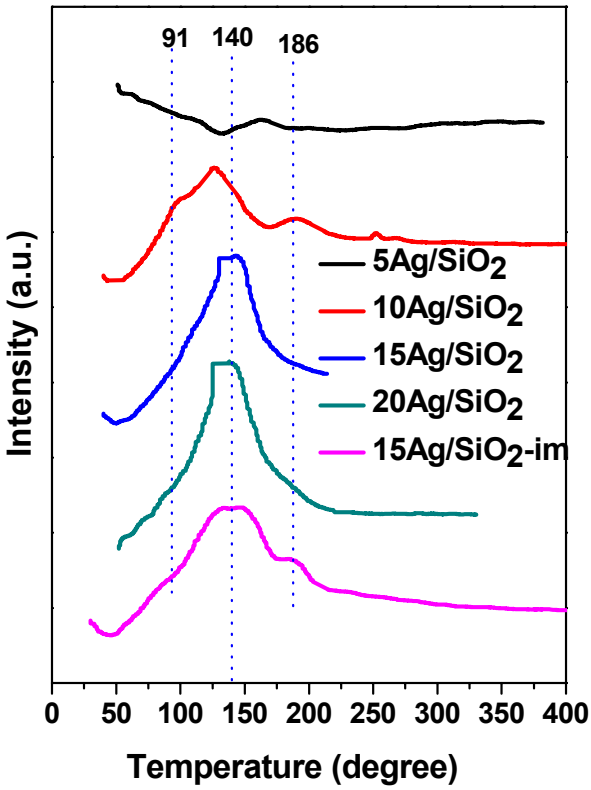

Figure S1. TPR profile of silver catalysts

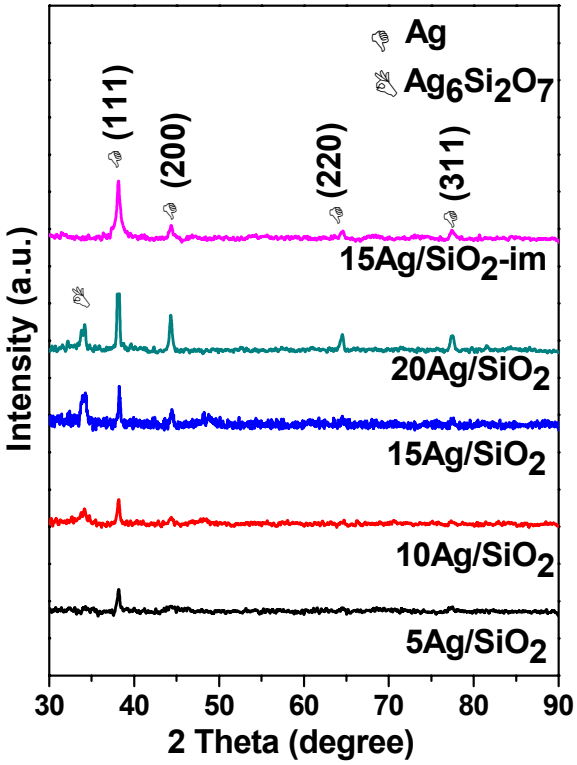

Figure S2. XRD pattern of different silver catalysts

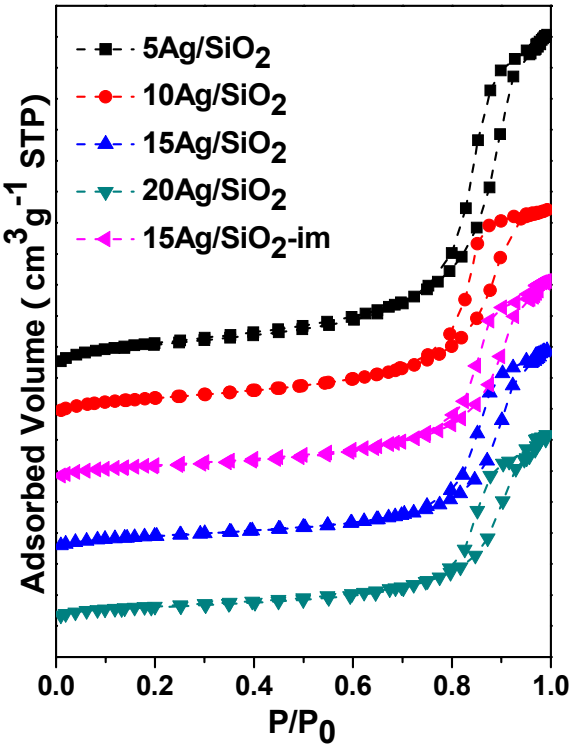

Figure S3. N_2 adsorption-desorption isotherm of silver catalysts.

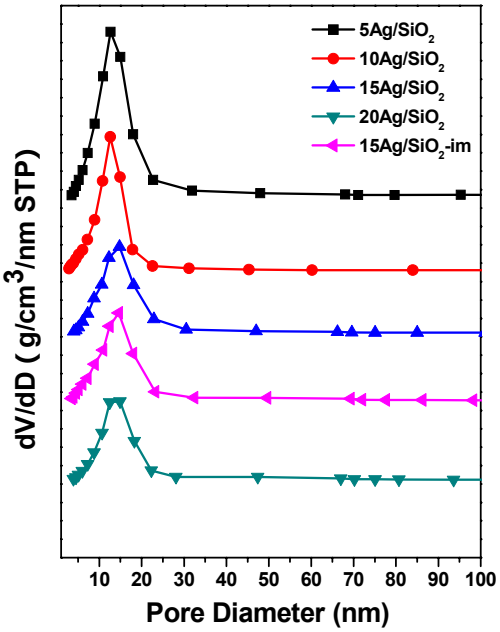

Figure S4. BJH pore size distribution of silver catalysts.

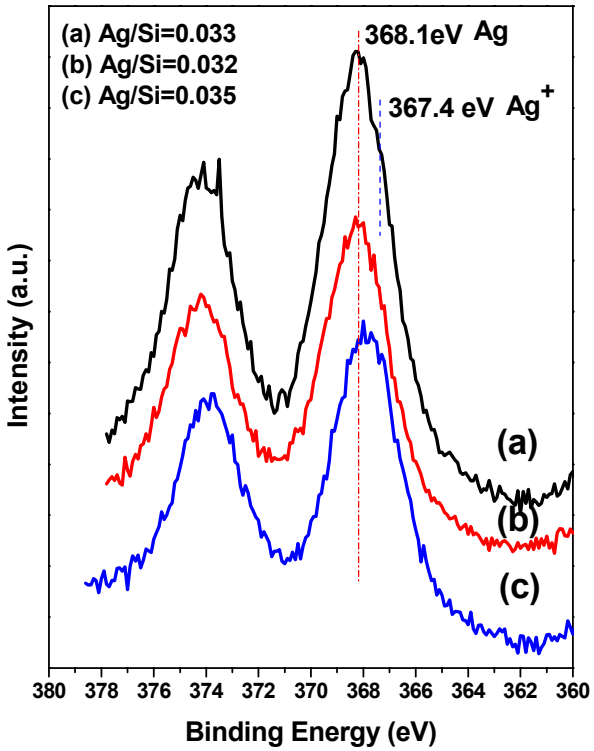

Figure S5. XPS results of 15Ag/SiO_2 catalyst: (a) calcined catalyst at 673 K; (b) reduced catalyst of (a) at 573 K in 5% H_2/Ar for 4 h; (c) post-reacted catalyst of (b) catalyst after running for 250 h under reaction conditions.

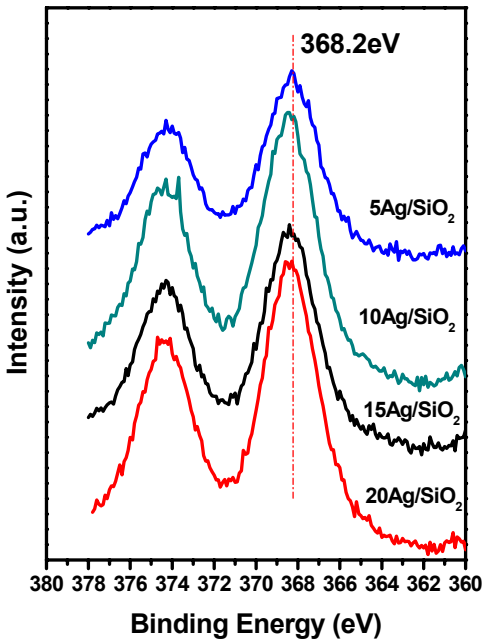

Figure S6. XPS spectra of the calcined samples with different silver loadings.