

Supporting Information

Disposed Battery Supported Ag Catalyst for Efficient Oxidation of Alcohols and Carbon Oxide

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Experimental

Pre-treatment of disposed battery

To obtain pure MnO₂, manganese dioxide powder mixture (20 g) from disposed battery was treated in hydrochloric acid (15-30 ml) by stirring at 70-80 °C for 4 h. The precipitation was filtered and the filtrate was then oxidized by NaClO solution (12%, 120-200 ml) at 45 °C for 6 h. The insoluble MnO₂ was separated and washed by dilute hydrochloric acid, dried in air at 100 °C overnight.

Preparation of Ag/MnO₂ and Ag/Mn₃O₄ catalysts

Silver was deposited on the as-obtained MnO₂ by in-situ reduction using NaBH₄ as reducing agent. In a typical synthesis of Ag-9/MnO₂, PVP (MW = 30 000, 100 mg) and 0.14 g of dried MnO₂ were dispersed homogeneously in 20 ml of deionized water under vigorous stirring at room temperature. AgNO₃ aqueous solution (4.4 mg/ml, 5 ml) was added dropwise into the suspension. Then 80 mg NaBH₄ was added to the mixture slowly, with stirring for 2 h under room temperature. The products were collected by filtration, washed with ethanol to remove any possible organic remnants, and were then heated at 373 K overnight. The as-fabricated catalyst is designated as Ag-9/MnO₂ (9 stands for the silver loading in weight percentage). The catalysts with different Ag loading were prepared by the same procedure just tuning the amount of AgNO₃ in the corresponding suspension. Before gas-phase alcohols oxidation test, Ag/MnO₂ catalysts was pre-activation, using WHSV = 20 h⁻¹ and O₂/ol = 0.6 at 280 °C in advance, and then Ag/MnO₂ was transformed into Ag/Mn₃O₄.

Characterizations

The catalysts were characterized by using X-ray diffraction (XRD, Rigaku Ultima IV diffractometer (Cu K radiation = 1.5406 Å), transmission electron microscopy (TEM, JEOL-JEM-2010 instrument at 200 kV) and high-resolution transmission electron microscope (HRTEM, JEOL-2010F instrument at 200 kV). Specific surface area was determined from N₂ adsorption isotherm at -196 °C using standard Brunauer-Emmett-Teller (BET) theory. Before the measurement, degassing was conducted at 200 °C for 2 h to remove possible moisture. X-ray photoelectron spectroscopy (XPS) were recorded on a VG EscaLab 220i spectrometer, using a standard Al Kα X-ray source (300 W) and an analyzer pass energy of 20 eV. All binding energies are referenced to the adventitious C1s line at 284.9 eV.

Reactivity tests

The gas-phase selective oxidation of alcohols on these catalysts with molecular oxygen was performed on a fixed-bed quartz tube reactor (700 mm length by 6 mm inner diameter) under atmospheric pressure as described previously.¹ Cyclohexanol was continuously fed using a high-performance liquid pump in parallel with O₂ (oxidant) and N₂ (diluted gas of 50 ml/min) feeding using calibrated mass flow controllers into the reactor heated to the desired reaction temperature. WHSV was calculated by dividing the mass flow rate of alcohol feedstock by the catalyst mass. The effluent was cooled using an ice-salt bath (-15 °C) to liquefy the condensable vapors for analysis using an Shimadzu-2014 GC gas chromatography-flame ionization detector (GC-FID) with a 60 m HP-5ms capillary column. The catalytic activity tests for CO oxidation were carried out in a continuous-flow fixed bed quartz tubular reactor at ambient pressure. The reactor was charged with 100 mg of the prepared catalyst. The reactant gases (1.0% CO, 16% O₂, balanced with nitrogen) passed through the reactor at a flow rate of 100 mL min⁻¹. The reactor effluent was analyzed by the gas chromatograph equipped with a TDX column.

1 G. F. Zhao, H. Y. Hu, M. M. Deng, M. Ling and Y. Lu, *ChemCatChem*, 2011, **3**, 1629.

Supplementary Figures

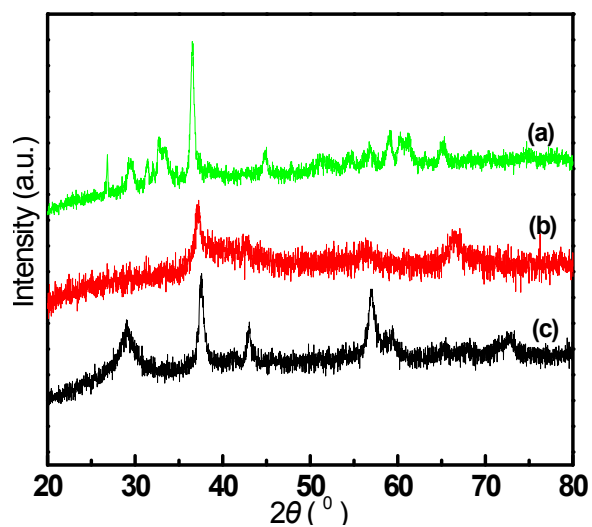


Fig. S1 The XRD patterns of the (a) MnO_x , (b) before calcination MnO_2 , (c) after calcination MnO_2 at 400°C .

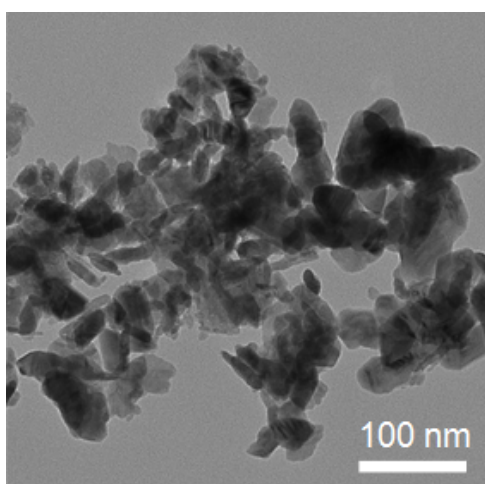


Fig. S2 TEM images of pure MnO_2

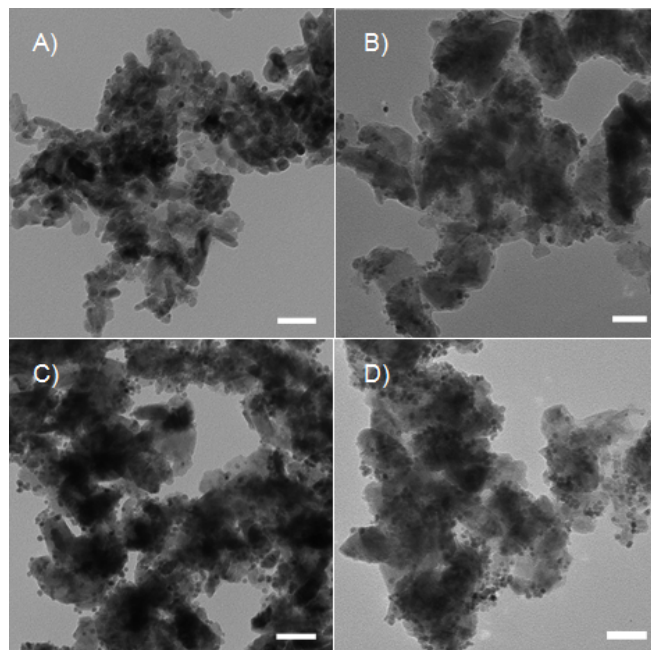


Fig. S3 TEM images of (A) Ag-3/MnO₂, (B) Ag-5/MnO₂, (C) Ag-7/MnO₂, and (D) Ag-11/MnO₂, scar bar 50 nm.

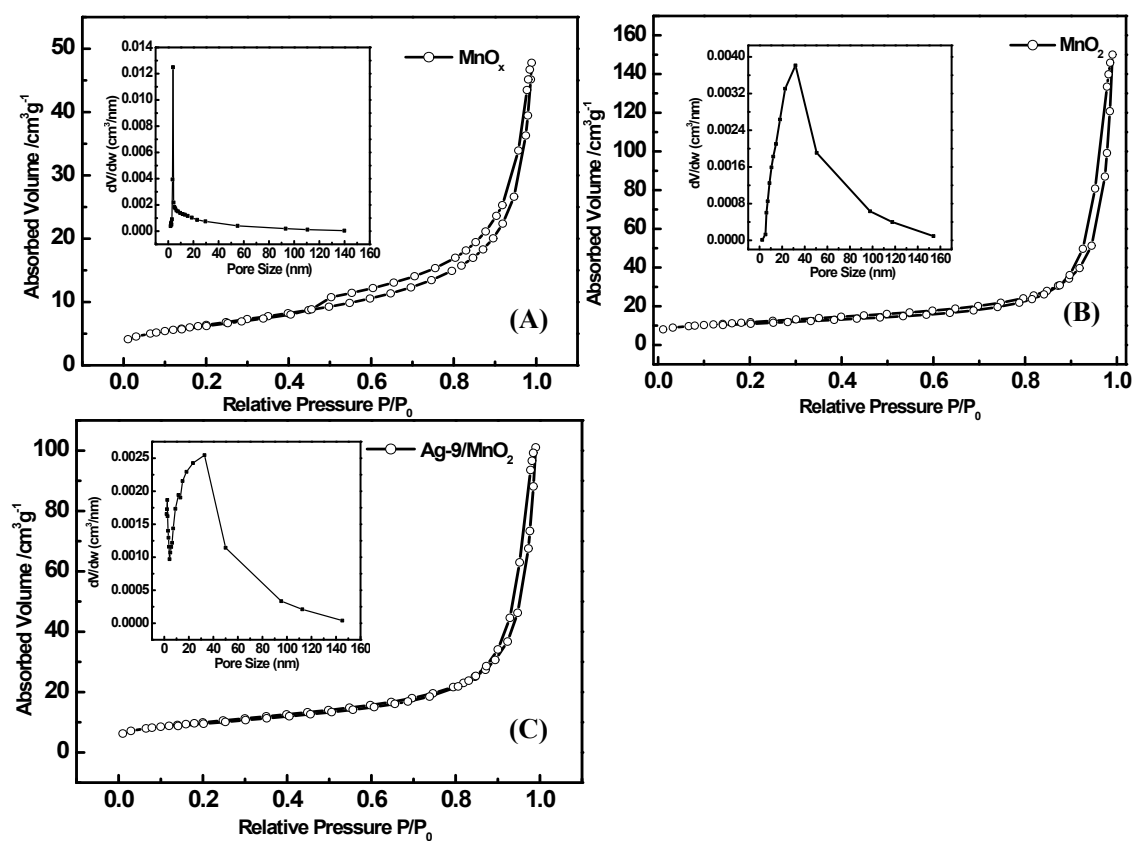


Fig. S4 N₂ adsorption - desorption isotherms and pore size distribution curves of (A) MnO_x, (B) MnO₂ and (C) Ag-9/MnO₂ catalysts.

Table S1. Oxidation of various alcohols over the pre-activated Ag-9/Mn₃O₄ catalysts.

Substrate	O ₂ /ol ratio (mol/mol)	Temperature (°C)	Conversion (%)	Selectivity (%)
1-phenylethanol	0.8	250	95	92
2-phenylethanol	0.8	280	23	70
1-octanol	0.6	270	40	87
2-octanol	0.6	250	34	75
benzylalcohol	0.6	230	92	98
1,2-propanediol	1.6	270	54	74

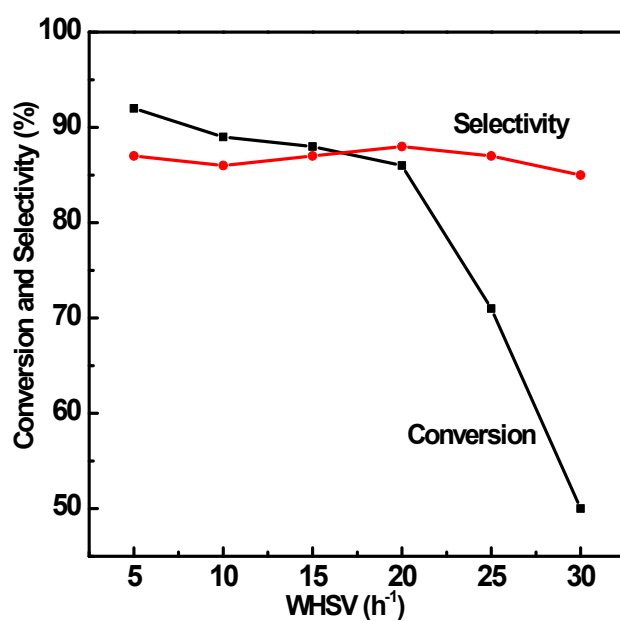


Fig. S5 WHSV with O₂/ol = 0.6 on the pre-activated Ag-9/Mn₃O₄ catalyst for the gas-phase oxidation of cyclohexanol at 280 °C.