Gold nanoparticles on hydrotalcites as efficient catalysts for oxidant-free dehydrogenation of alcohols

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Electronic Supplementary Information

1. Experimental details

(1) Catalyst preparation

The hydrotalcite (HT) with a composition of $Mg_6Al_2(OH)_{16}CO_3$ was prepared by an established method.[1] XRD measurements confirmed the formation of the HT structure. The HT was calcined at 500 °C for 4 h before the loading of Au. The structure of HT was destroyed during the calcination, but it could be recovered in the subsequent impregnation or deposition-precipitation processes because of the "memory effect" of the Mg-Al HT.[1,2] Au catalysts were loaded on the HT by the impregnation or the deposition-precipitation (DP) method.[3] For the impregnation method, the support was immersed into the aqueous solution of $HAuCl_4$, and the mixture was stirred for 0.5 h, followed by drying at 65 °C. The powdery catalyst was finally reduced by H_2 at 250 °C. Cu/HT and Ag/HT were also prepared by the same procedure using $Cu(NO_3)_2$ and $AgNO_3$ as the precursors, respectively. For the DP method, the pH of the $HAuCl_4$ aqueous solution was first adjusted to 9.0, and then the powdery HT was added into the solution. After stirring at 80 °C for 1 h, the solid was recovered by filtration, followed by thorough washing to remove Cl^- ions. The powdery sample was dried at 120 °C overnight. The Au loadings were analyzed by the ICP technique.

(2) Catalyst characterization

XRD, TEM and XPS were used to characterize the structures and the physicochemical properties of catalysts. XRD was performed with a Panalytical X'pert Pro Super X-ray diffractometer with Cu K_α radiation (40 kV and 30 mA). TEM measurements were performed on a JEM 2100 electron microscope operated at an acceleration voltage of 200 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of the suspensions were applied on a copper grid coated with carbon. XPS measurements were carried out with a Quantum 2000 Scanning ESCA Microprob instrument (Physical Electronics) using Al-K_α radiation.

(3) Catalytic reaction

The dehydrogenation of alcohols was carried out using a batch-type reaction vessel with

a reflux condenser. Typically, the powdery catalyst (typically, 0.20 g) was added into the alcohol and solvent (*p*-xylene) placed in the reaction vessel, and then pure Ar gas was bubbled into the mixture. After purging with Ar gas (flow rate, 8 cm^3 min^{-1}) for 1 h to remove the remaining air in the reaction system, the mixture was heated to the reaction temperature with stirring. The flow rate of Ar was typically kept at 3 cm^3 min^{-1} during the reaction. After the reaction, the catalyst was separated by centrifugation, and the liquid products were analyzed by a gas chromatograph (Shimazu GC-14B) after the addition of an internal standard.

2. TEM micrographs and particle size distributions for some typical supported Au catalysts prepared by the impregnation method
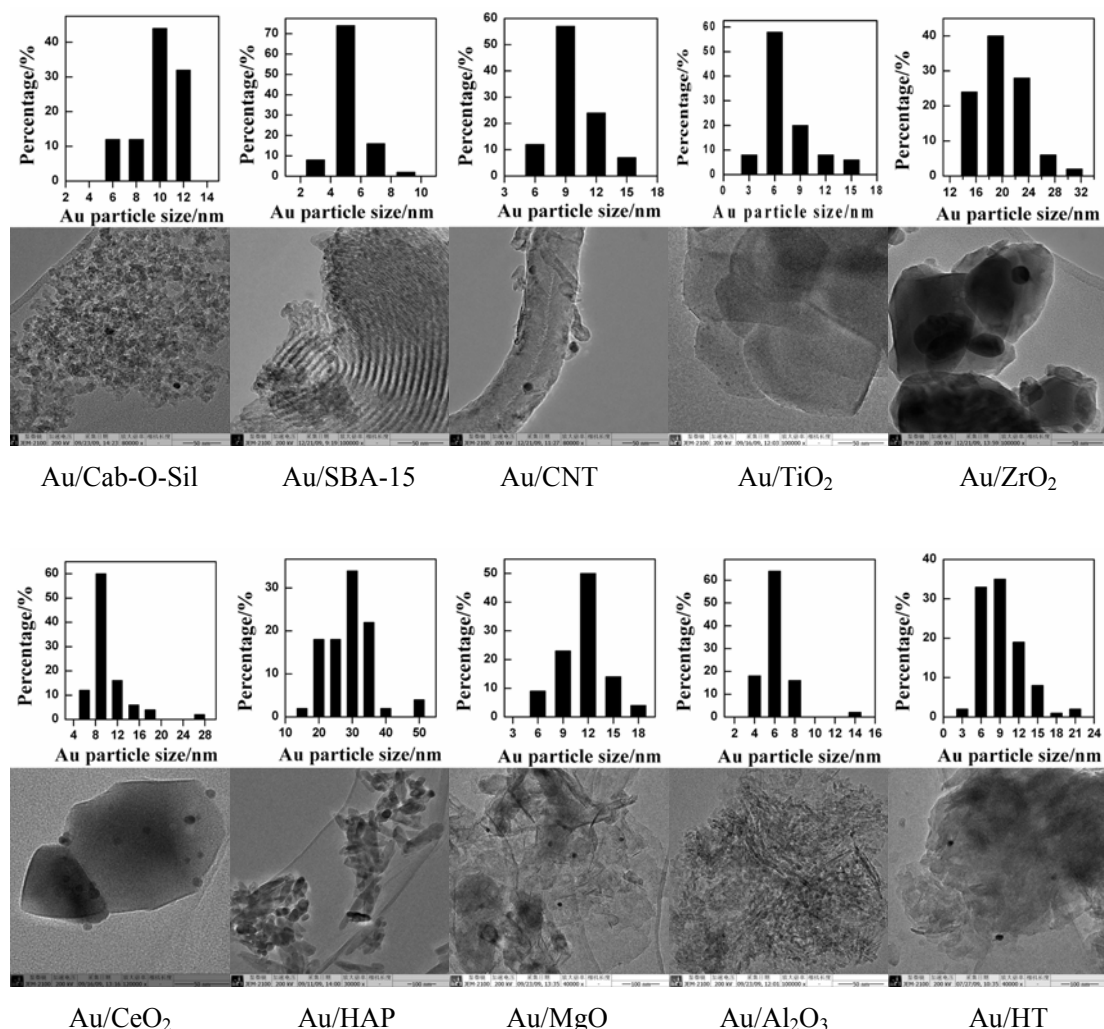

Au/Cab-O-Sil   Au/SBA-15   Au/CNT   Au/TiO$_2$ Au/ZrO$_2$

Au/CeO$_2$ Au/HAP   Au/MgO   Au/Al$_2$O$_3$ Au/HT

Fig. S1 TEM micrographs and particle size distributions for some typical supported Au catalysts prepared by the impregnation method.

3. Recycling uses of the 0.06 wt% Au/HT catalyst prepared by the DP method for the dehydrogenation of benzyl alcohol
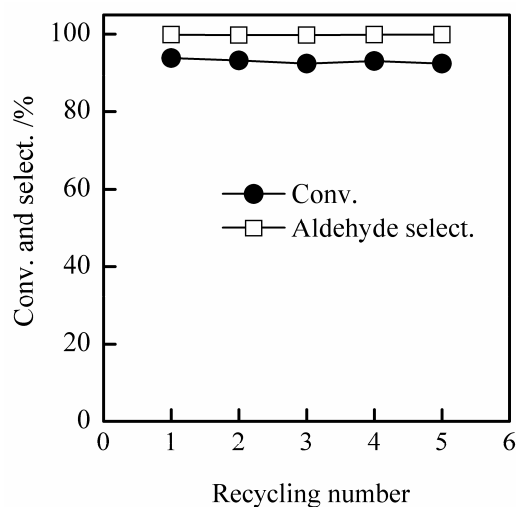

Fig. S2 Recycling uses of the 0.06 wt% Au/HT catalyst prepared by the DP method for the dehydrogenation of benzyl alcohol. Reaction conditions: catalyst, 0.20 g; T = 120 °C; benzyl alcohol, 1.0 mmol; p-xylene, 5.0 cm^3; Ar, 3 cm^3 min^{-1}; time, 6 h.

References

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3   M. Haruta, *Catal. Today*, 1997, **36**, 153.