Aerobic oxidation of alcohols over hydrotalcite-supported gold nanoparticles: the promotional effect of transition metal cations

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Electronic Supplementary Information (ESI)

1. Experimental details

(1) Catalyst preparation

The hydrotalcite (HT) precursor with a composition of $Mg_4Al_2(OH)_{12}CO_3$ was prepared by a homogeneous precipitation method using urea hydrolysis.[1] Transition metal-containing HT (M-HT, M = Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) supports were prepared by adopting the "memory effect"of HT.[2] In a typical procedure, a thermally decomposed HT mass (1.0 g calcined at 500 ^{o}C for 6h) was reconstructed into the layered hydrotalcite structure along with M^{n+} cations by contacting with aqueous M^{n+} nitrate solution (0.5 mmol M^{n+}/g HT precursor) in the presence of atmospheric CO_2 (as a source of interlayer CO_3^{2-} anion) under stirring at room temperature for 12 h. The M-HT samples were washed and dried at 110 ^{o}C for 10 h before the loading of Au.

The MgCr-HT with a composition of $Mg_6Cr_2(OH)_{16}CO_3$ was prepared by a modified coprecipitation method. In a typical procedure, a mixed aqueous solution of Mg^{2+} and Cr^{3+} nitrates (with Mg/Cr molar ratio of 3.0) were added dropwise to an aqueous Na_2CO_3 solution at 70 ◦C under vigorous stirring. The pH of the solution was adjusted to 10.5 ± 0.1 by adding aqueous NaOH solution, and the resulting gel-like material was transferred to an autoclave and aged at 160 ◦C for 48 h. The resultant slurry was separated by filtration, followed by washing with distilled water (till the pH of filtrate close to 7) and drying at 110 ◦C for 20 h.

The Au/HT and Au/M-HT catalysts were prepared by a sequential deposition-reduction approach,[3] with some modifications. Typically, the obtained M-HT (1.0 g) was then added to 50 mL of an aqueous solution of $HAuCl_4$ (1 mM, theoretical Au laoding is 1 wt%). After stirring for 2 min, 0.2 mL of aqueous NaOH (0.5 M) was added and the resulting mixture was stirred at room temperature for 12 h. The obtained slurry was filtered, washed with deionized water, and dried at RT in vacuo. The solid was subsequently treated with aqueous $NaBH_4$ (three-fold excess) solution at room temperature for 2 h, then filtered, washed and dried to yield the Au/M-HT catalyst. For Au/Cr-HT catalyst, a part amount of solid sample was not treated with $NaBH_4$ to get the unreduced Au/Cr-HT sample.

Reference catalysts Au/TiO_2 and Au/CeO_2 were prepared by the traditional deposition-precipitation (DP) method[4], Titania P25 and self-made CeO_2 nanorod were used as supports. In a typical preparation, aqueous $HAuCl_4$ solution was heated up to 70 ^{o}C. The Au concentration in the solution corresponds to the theoretical Au loading of 2 wt% in the case of a complete DP. The pH of the solution was adjusted to 8.0 by a dropwise addition of 0.5 M NaOH aqueous solution. Then 1.0 g of support was added with vigorous stirring at 70 ^{0}C for 2 h; during the stirring, the pH value was maintained by NaOH solution. After cooling to room temperature, the suspension was filtered and washed thoroughly with deionized water. The solid was dried at 110 ^{0}C overnight and calcined in air at 300 ^{o}C for 4 h.

Reference catalysts Au/$Ga_3Al_3O_9$[5] and Au/Cr_2O_3 were prepared by the homogeneous DP method using urea as the precipitation agent as developed by Louis et al.[6] and the theoretical Au loading was 1 wt% in the case of a 100% DP.

(2) Catalyst characterization

XRD was performed on a Bruker Endeavour D4 with Cu K_α radiation (40 kV and 30 mA). SEM micrograph and EDX analysis were taken using a FEI Quanta 200F scanning electron microscope equipped with an energy-dispersive X-ray spectrometer at an acceleration voltage of 20 kV. TEM micrographs were acquired on a FEI Tecnai 20 electron microscope at an acceleration voltage of 200 kV with a LaB_6 filament. The average size of Au was calculated by counting ~200 Au particles. The BET surface areas were recorded on a Tristar 3000 automated gas adsorption system. The samples were degassed at 150 ^{o}C for 3 h prior to analysis. XPS was performed on a K-alpha machine (Thermo Scientific, UK) and the CasaXPS program for fitting. A monochromated Al K_α ($h\nu$ = 1486.6 eV) was used as X-ray source, and the system background pressure was less than 2×10^{-8} mbar. There is no Na (1s = 1072 eV), B (1s = 192 eV) and Cl ($2p_{3/2}$ = 199 eV) signals in the spectrum of Au/MgCr-HT catalyst. The gold loading of the catalysts was determined by ICP-OES after an aliquot of the sample was dissolved in a mixture of HCl and HNO_3. Basicity measurements were carried out by suspending 10mg of catalyst in 3 mL freshly distilled water and stirring for 0.5 h. The pH of the upper clear liquid of the sedimented suspension was measured by an Inolab 730 pH meter.

The temperature programmed surface reaction (TPSR) experiments were carried out as follows:[5] After the catalyst (50 mg) was activated at 200 ^{o}C for 2 h under He stream (50 ml/min), it was cooled down to room temperature and isopropanol vapor was introduced for adsorption at RT for 0.5 h. After the catalyst was swept with He for 60 min, the temperature was increased linearly with rate of 10 ^{o}C/min in He and the signals of H_2 (M/e = 2), acetone (M/e = 43 and M/e = 58), and propylene (M/e = 41) were recorded by online mass spectrometry (quadrupole mass spectrometer, Balzers TPG-300) simultaneously.

(3) Catalyst reaction

The aerobic oxidation of alcohols was carried out using a 25 mL two-necked round-bottle flask with a reflux condenser. Typically, the reactor was charged with 50 mg of catalyst, 1 mmol of benzyl alcohol, 0.5 mmol of *n*-dodecane (internal standard) and 10 mL of toluene. Molecular oxygen was bubbled through the reaction mixture (flow rate = 20 mL/min). The resulting mixture was then heated at 373 K for 0.5 h and cooled to room temperature. After the reaction, the catalyst was separated by centrifugation and washed with toluene. Recycled catalyst can be reused in the next run under the same conditions. The reaction products were qualitatively analyzed by a Shimadzu QP5050 GC-MS (CP-Sil 8CB, 50 m × 0.32 mm, d_f = 0.15 µm), and quantitatively analyzed by a Shimadzu GC-FID (RXI 5ms, 30 m × 0.25 mm, d_f = 0.5 µm) using an internal standard technique. In all cases, the carbon balances were in the range of 100 ± 3%.

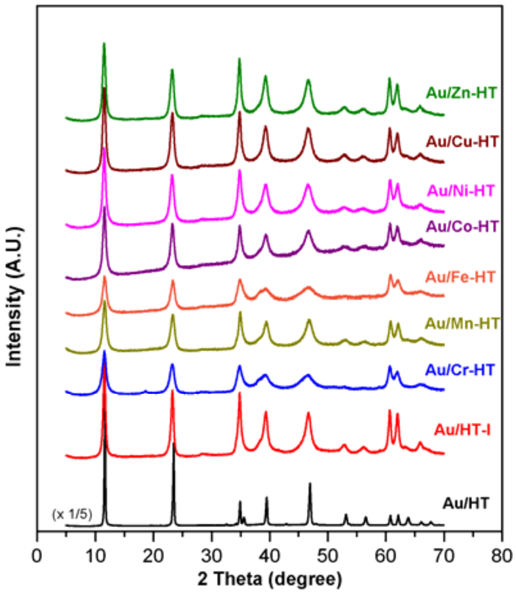


Fig. S1 XRD patterns of various Au/M-HT catalysts.

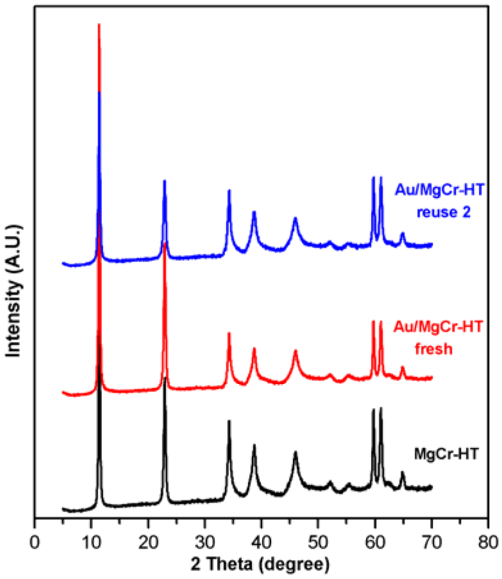


Fig. S2 XRD patterns of MgCr-HT support, fresh Au/MgCr-HT catalyst and recycled catalyst after second reuse.

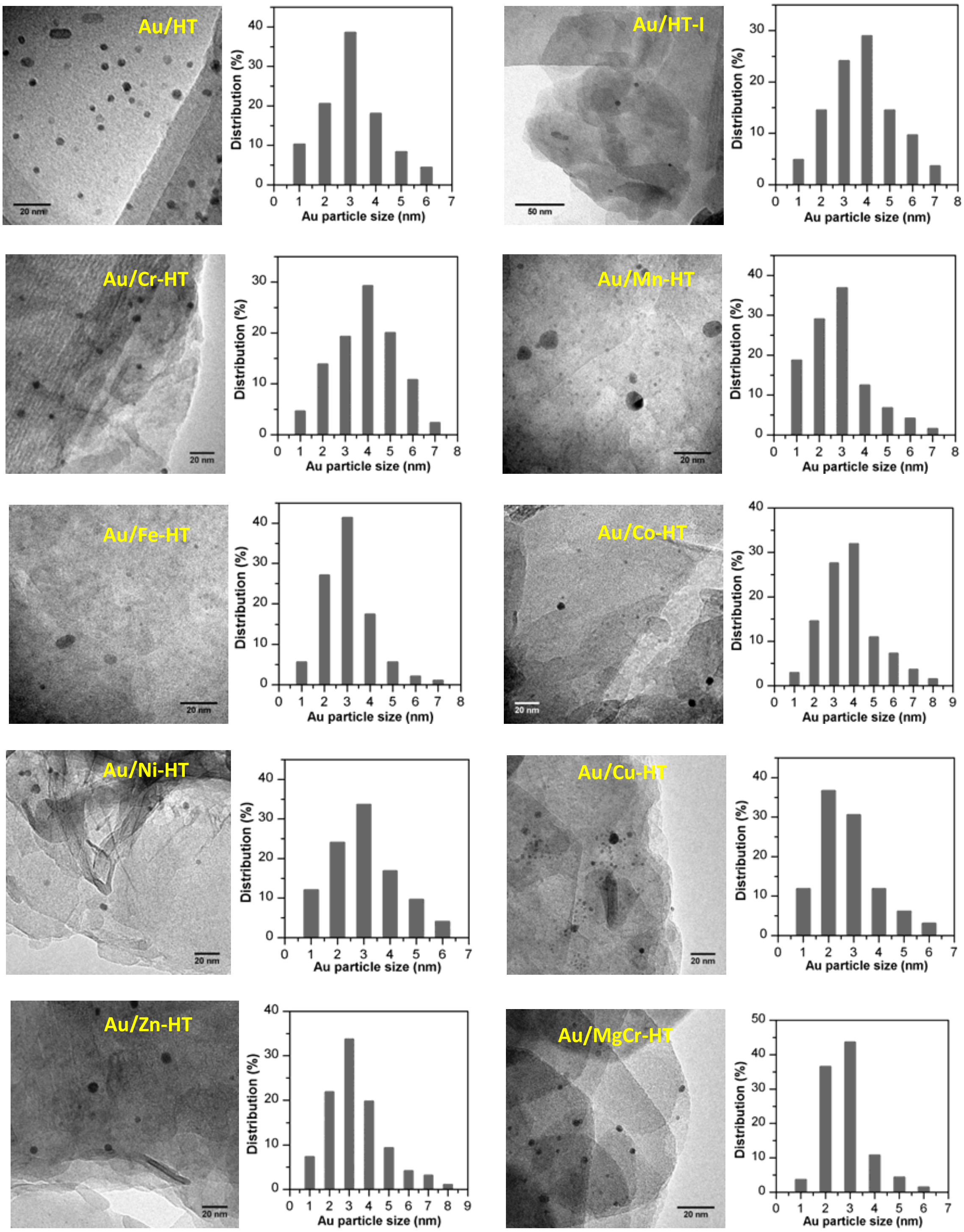


Fig. S3 TEM images and Au particle size distributions for various Au/M-HT catalysts.

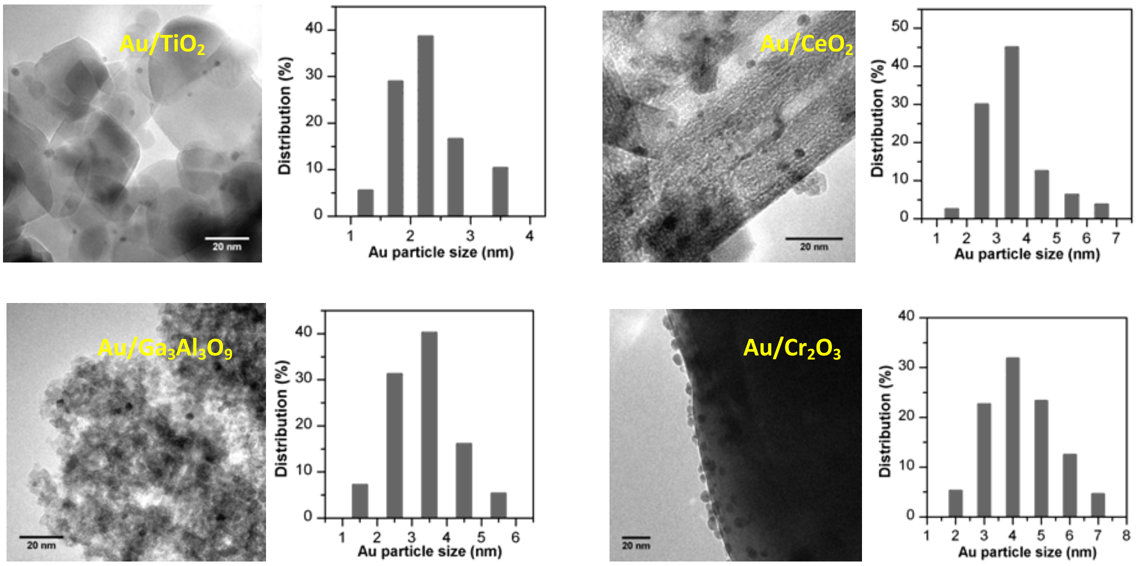


Fig. S4 TEM images and Au particle size distributions for the reference Au catalysts.

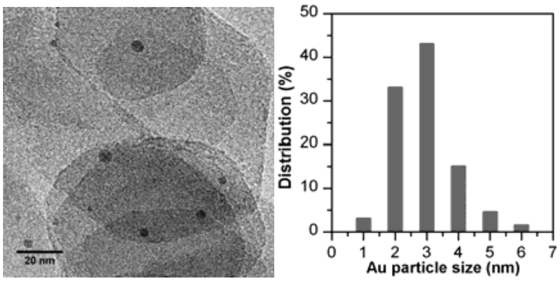


Fig. S5 TEM image and Au particle size distribution for the recovered Au/MgCr-HT catalyst after second reuse.

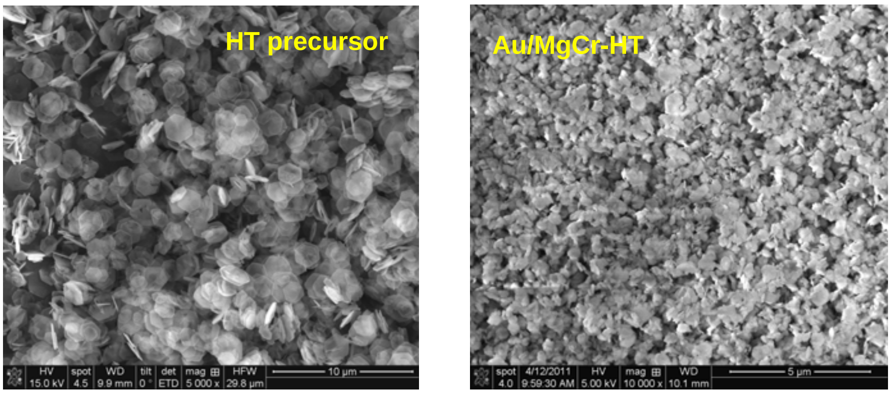


Fig. S6 SEM images for HT precursor and Au/MgCr-HT catalyst.

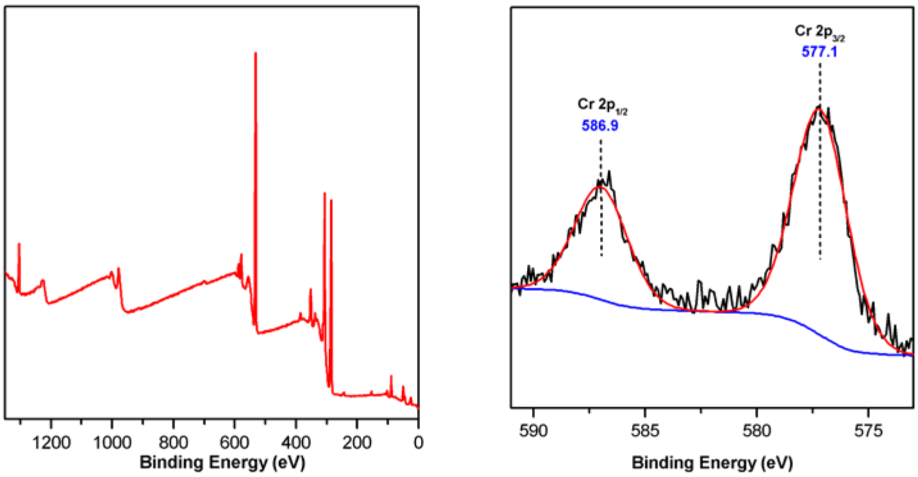
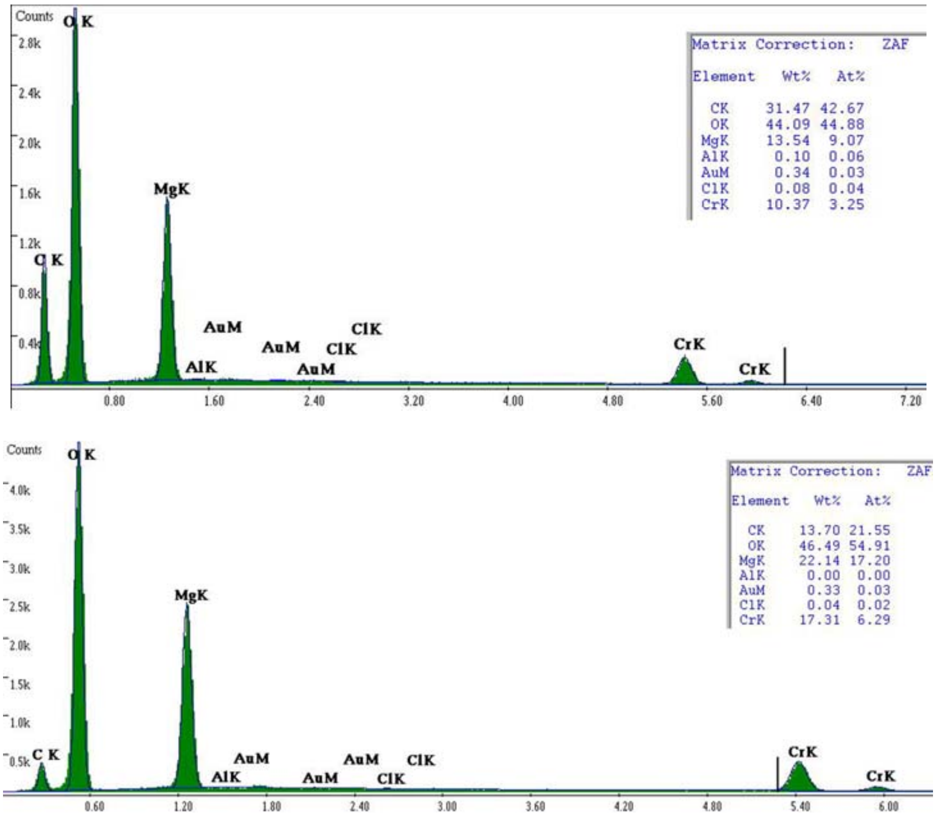


Fig. S7 XPS spectrum for Au/MgCr-HT catalyst and the Cr 2p peak.



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Matrix Correction:    ZAF

Element    Wt%    At%

  CK     31.47  42.67
  OK     44.09  44.88
  MgK    13.54   9.07
  AlK     0.10   0.06
  AuM     0.34   0.03
  ClK     0.08   0.04
  CrK    10.37   3.25
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Matrix Correction:    ZAF

Element    Wt%    At%

  CK     13.70  21.55
  OK     46.49  54.91
  MgK    22.14  17.20
  AlK     0.00   0.00
  AuM     0.33   0.03
  ClK     0.04   0.02
  CrK    17.31   6.29
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Fig. S8 EDX results for fresh Au/MgCr-HT (top, Mg/Cr = 2.79) and recovered Au/MgCr-HT after second reuse (down, Mg/Cr = 2.73).

References

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