Electronic Supplementary Information

The base-free and selective oxidative transformation of 1,3-propanediol into methyl esters by different Au/CeO_2 catalysts

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Catalyst preparation

Single-crystalline CeO_2 nanopolyhedra, nanorods, and nanocubes were synthesized by a modified hydrothermal method following the reported procedure.[33] Typically, $Ce(NO_3)_3·6H_2O$ (99.5%; 4.5 mmol) was dissolved in aqueous NaOH solution (90 ml; 98%) of appropriate concentration (C_{NaOH}; see below). The prepared solution was then transferred into a Teflon-lined stainless steel autoclave and maintained at different temperatures (T) for 24 h. After cooling, the resulting solid product in the reaction solution was collected by filtration and then thoroughly washed by deionized (DI) water for three times. The final product was dried in vacuo at 70 ^oC overnight. The dried powders were calcined in air at 400 ^oC for 4 h. The values of C_{NaOH} and T were adjusted according to the target crystal shapes (rod: C_{NaOH} = 6 M, T = 100 ^oC; cube: C_{NaOH} = 6 M, T = 180 ^oC; polyhedron: C_{NaOH} = 0.1 M, T = 180 ^oC).

The deposition of Au onto the ceria substrate was conducted using a deposition/precipitation (DP) method.[S1] In brief, the CeO_2 power (2 g) was slurried in DI water (100 ml) whilst stirring and adding in the aqueous urea solution (50 ml; 1 M).

$HAuCl_4 \cdot 3H_2O$ (99.99%; 0.116 mmol) was dissolved in DI water (50 ml) and then dropwisely added to the above solution. The resulting precipitate was aged at room temperature for 1 h, then filtered and washed several times by DI water. The material was dried in vacuo at 70 ^{o}C overnight and then calcined in air at 400 ^{o}C for 4 h.

Catalyst Characterization

The specific surface area was determined by nitrogen adsorption on an ASAP 2020 (Micromeritics) at liquid nitrogen temperature applying the BET theory. The samples were degassed at 300 ^{o}C until a stable vacuum of ca. 5 mTorr was reached. Transmission electron microscopy (TEM) data were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. The X-ray diffraction (XRD) patterns were recorded at room temperature on a Bruker D8-advance X-ray diffractometer employing monochromatizaed CuKα radiation (40 kV, 40 mA). Hydrogen temperature programmed reduction (H_2-TPR) was carried out on Autochem II 2920 (Micromeritics, USA). A total of 100 mg catalyst was filled in quartz reactor. The catalyst powders were pretreated in O_2 flowing (20 ml/min) at 400 ^{o}C for 2 h and the test was performed with a 10% H_2/Ar gas mixture (20 ml/min) from room temperature to 850 ^{o}C (20 ^{o}C/min). The temperature-programmed desorption of ammonia and carbon dioxide (NH_3- and CO_2-TPD) experiments were carried out on Autochem II 2920 (Micromeritics, USA).[S2] The samples were pretreated in O_2 flowing (20 ml/min) at 400 ^{o}C for 1 h. After cooled to 50 ^{o}C, the sample was exposed to 10% NH_3/Ar mixture or 10% CO_2/Ar mixture flow (20 ml/min) for 1 h. Then the sample was flushed in Ar flow at 50 ^{o}C for removal of physically adsorbed CO_2 or NH_3. A CO_2-TPD (or NH_3-TPD) profile of the sample was recorded by increasing the temperature from 50 ^{o}C to 400 ^{o}C at a heating rate of 10 ^{o}C/min under 20 ml/min of Ar flow. The desorbed NH_3 or CO_2 was detected with a mass spectrometer (FISONS Instruments).

Procedure for catalytic oxidation

The oxidation experiments were carried out in a 50 ml steel autoclave (Jiangsu

Dantu Co. Ltd). The autoclave was charged with 210 mg of 1,3-propanediol (2.7 mmol) and 5.1 g of methanol (159 mmol). Then the 1 wt% Au/CeO_2 catalyst was added (0.48 g, 0.024 mmol Au) and the autoclave was sealed and pressurized to 21 atm with molecular oxygen. The mixture was stirred (900 rpm) and heated to 125 ^{o}C. At regular intervals, the autoclave was cooled to -10 ^{o}C, and a sample was taken out.

Product analysis

The reaction mixtures were analyzed by a Varian gas chromatograph 450-GC (USA), equipped with a flame ionization detector and a CP-Wax 58 (FFAP) CB (25 m x 0.25 mm x 0.2 μm; Chrompack Inc., USA) column and a Thermo Fisher GC-MS (Trace GC Ultra-ITQ 1100, the column was Thermo TR-Wax MS of 30 m in length, an inner diameter of 0.25 mm and an inner film of 0.25 μm). Reference samples were used to confirm the products whenever possible. Quantifiable product data were obtained from GC, and were calculated on the basis of an internal standard (butanol).

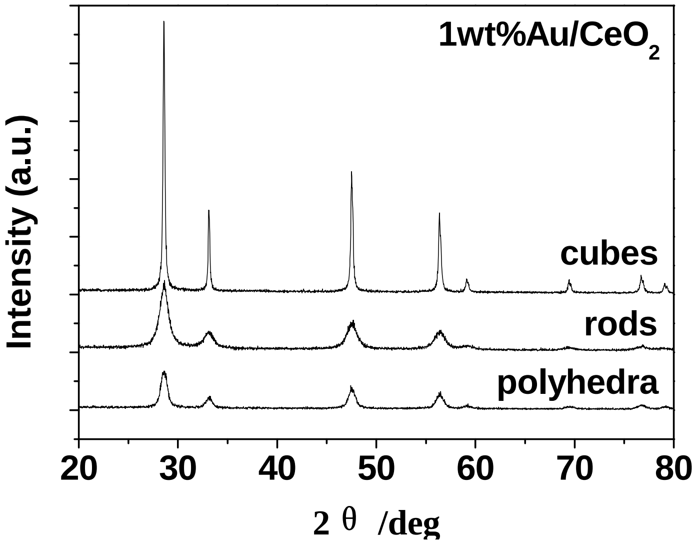

Fig. S1 XRD spectra of 1 wt% Au on CeO_2 nanorods, -polyhedra and -cubes calcined at 400 ^{o}C in air.

References

S1 S. Tsubota, M. Haruta, D. Cunningham and Y. Bando, *Preparation of Catalysts VI*, 1991, 227

S2 G. M. Zhao, J. H. Shi, G. Liu, Y. Liu, Z. L. Wang, W. X. Zhang and M. J. Jia, *J. Mol. Catal. A*, 2010, **372**, 32.