Electronic Supplementary Information

Extremely low loading of Ru species on hydroxypatite as an effective heterogeneous catalyst for olefin epoxidation

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Experimental section

Materials: All of the chemicals were used as reviewed. Ca(NO3)2.4H2O (99%, Acros), (NH4)2HPO4 (99+, Acros), conc. NH3 (Beijing Shiji), conc. HCl (Beijing Shiji) conc. HNO3 (Beijing Shiji), Organic solvents (Beijing Shiji), RuCl3.nH2O (35-40% Ru, Acros), RuCl3.nH2O (37% Ru, Shanghai Tuosi Chemical), commercial 5% Ru/C (Canan Technique Material (Hangzhou) Inc.) iso-butyraldehyde (98%, Alfa Aesar), mesitylene (98+%, Alfa Aesar), cyclohexene (99%, J&K), cis-cyclooctene (95%, Alfa Aesar), cyclododecene (97%, Alfa Aesar), 1-methyl cyclohexene (96%, J&K), 1-phenyl cyclohexene (97%, Alfa Aesar), trans-methyl stilbene (98%, Alfa Aesar), indene (95%, Innochem), norbornene (99%, Alfa Aesar), 1-hexene (97%, J&K), 1-decene (95%, J&K).

Synthesis of HAP: The preparation of HAP was synthesized according to the literature procedure. A solution of 15.767 g of Ca(NO3)2.4H2O in 60 mL DI water was adjusted to pH 11-12 with using concentrated NH3 solution. Thereafter, the solution was added more 50 mL DI water. A solution of 5.296 g of (NH4)2HPO4 in 60 mL DI water was also adjusted to pH 11-12 with using concentrated NH3 solution. Then, more 50 mL deionized water was added. After that, the phosphate solution was added dropwise into calcium nitrate solution for ca. 1 h. to produce a milky white precipitate which was then stirred overnight. The precipitate was filtered, washed with DI water (3×200 ml), dried at 60 °C under vacuum, and calcined at 500 °C for 3 h.

Synthesis of Ru species immobilized HAP (Ru/HAP): Ru metal doped on HAP was prepared with wetness impregnation method. In brief, the synthesized HAP (1.0 g) was dispersed in 400 mL DI water, and then 0.5 mL RuCl3.nH2O aqueous solution (1000 mg/L) was added under magnetically stirring at room temperature for 24 h. The obtained slurry was filtered, washed with DI water (3×200 mL) and then dried overnight at 60 °C under vacuum yielding Ru/HAP as the dark-grey powders.

Synthesis of Ru nanoparticles immobilized HAP (0.05 wt% Ru NP/HAP): The obtained 0.05 wt% Ru/HAP powders were calcined under H2 flow at 450 °C for 10 h with a heating rate of 5 °C/min.
Characterizations: All of the prepared catalysts were characterized with various techniques which consisted of XRD (D8 Advance, Bruker using Cu-Kα radiation with wavelength 1.5418 Å, 40 kV, 40 mA), ICP-AES (IPPE-9000, Shimadzu Plasma Atomic Emission Spectrometer), TEM (JEOL 2100F electron microscope), SEM (FESEM, JEOL-6701F electron microscope), BET (Quantachrome Instrument, Autosorb-1), XPS (ESCALab220i-XL electron spectrometer).

Epoxidation of Alkenes: The alkene epoxidation was carried out in round bottom glass and mesitylene was used as internal standard. Typically 5 mL of acetonitrile, 1 mmol of alkene, 5 mmol of iso-butyraldehyde and 20 mg of catalyst were mixed with stirring under O₂ bubbling. For reusability test, the catalyst was separated by centrifugation, washed with acetonitrile, then dried at 60 °C overnight. The starting materials and products were determined by GC (Shimadzu GC-2010-Plus) and GC-MS (Shimadzu GCMS-QP2010). The reactivity of the prepared catalysts was reported as % conversion of the reactant and % selectivity of the epoxide product.
Fig. S1 (a) TEM and (b) SEM images of synthesized HAP.

Fig. S2 XRD patterns of synthesized HAP and 0.05 wt% Ru/HAP and 0.05 wt% Ru NP/HAP.

Fig. S3 Bright field TEM images of fresh 0.05 wt% Ru/HAP.
Fig. S4 TEM images of 0.05 wt% Ru NP/HAP.

Fig. S5 XRD patterns of 0.05 wt% Ru/HAP after the 5th run in reusability test compared to fresh 0.05 wt% Ru/HAP.

Fig. S6 TEM images of 0.05 wt% Ru/HAP after the 5th run in reusability test compared to fresh 0.05 wt% Ru/HAP.
Scheme S1. Plausible mechanism of cyclohexene epoxidation using the 0.05 wt% Ru/HAP catalyst.

References.
