Electronic Supplementary Information

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

Pagasukon Mekrattanachai,[a, b] Jian Liu,[a, b] Zhaohua Li,[a, b] Changyan Cao*[a, b] and Weiguo Song*[a, b]

[a] Beijing National Laboratory for Molecular Sciences, Laboratory of Molecular Nanostructures and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 (China)

[b] University of Chinese Academy of Sciences, Beijing 100049 (China)

E-mail: cycao@iccas.ac.cn, wsong@iccas.ac.cn

Experimental section

Materials: All of the chemicals were used as revieved. $Ca(NO_3)_2.4H_2O$ (99%, Acros), (NH4)2HPO4 (99+%, Acros), conc. NH_3 (Beijing Shiji), conc. HCl (Beijing Shiji) conc. HNO_3 (Beijing Shiji), Organic solvents (Beijing Shiji), $RuCl_3$.nH2O (35-40% Ru, Acros), $RuCl_3.nH_2O$ (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.[19] A solution of 15.767 g of $Ca(NO)_3.4H_2O$ in 60 mL DI water was adjusted to pH 11-12 with using concentrated NH_3 solution. Thereafter, the solution was added more 50 mL DI water. A solution of 5.296 g of $(NH_4)_2HPO_4$ in 60 ml DI water was also adjusted to pH 11-12 with using concentrated NH_3 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.[19] In brief, the synthesized HAP (1.0 g) was dispersed in 400 mL DI water, and then 0.5 mL $RuCl_3$.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 H_2 flow at 450 °C for 10 h with a heating rate of 5 °C/min.[1-2]

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 acetronitrile, 1 mmol of alkene, 5 mmol of iso-butyrlaldehyde and 20 mg of catalyst were mixed with stirring under O_2 bubbling. For reusability test, the catalyst was separated by centrifugation, washed with acetronitrile, 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.

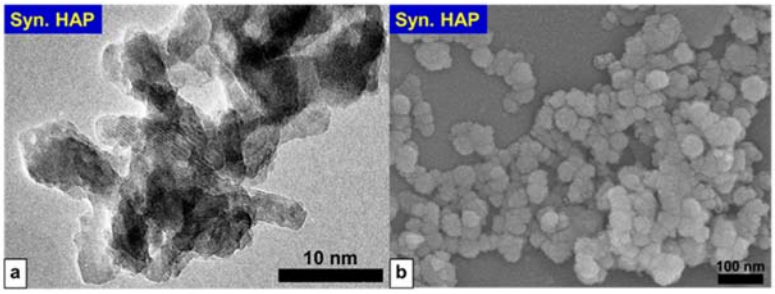


Fig. S1 (a) TEM and (b) SEM images of synthesized HAP.

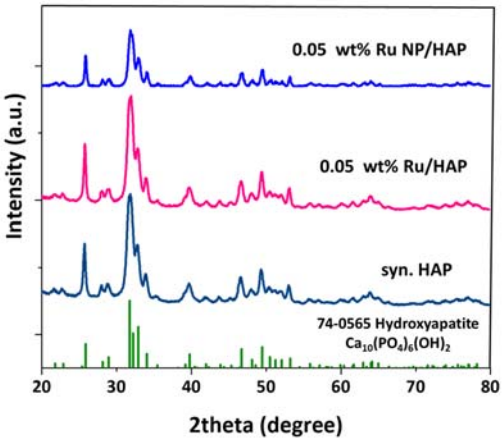


Fig. S2 XRD patterns of synthesized HAP and 0.05 wt% Ru/HAP and 0.05 wt% Ru NP/HAP.

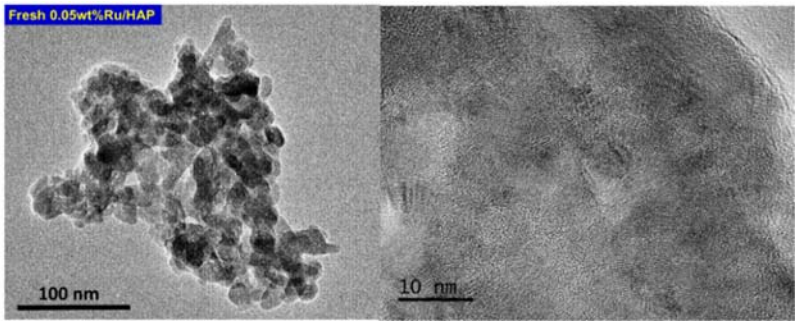


Fig. S3 Bright field TEM images of fresh 0.05 wt% Ru/HAP.

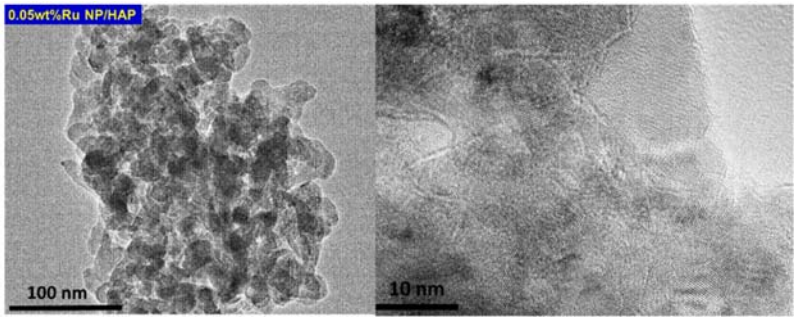


Fig. S4 TEM images of 0.05 wt% Ru NP/HAP.

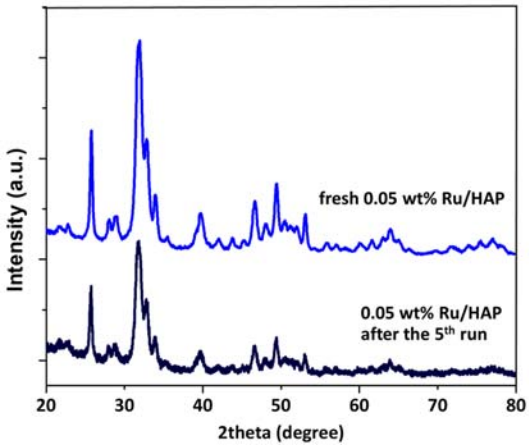


Fig. S5 XRD patterns of 0.05 wt% Ru/HAP after the 5th run in reusability test compared to fresh 0.05 wt% Ru/HAP.

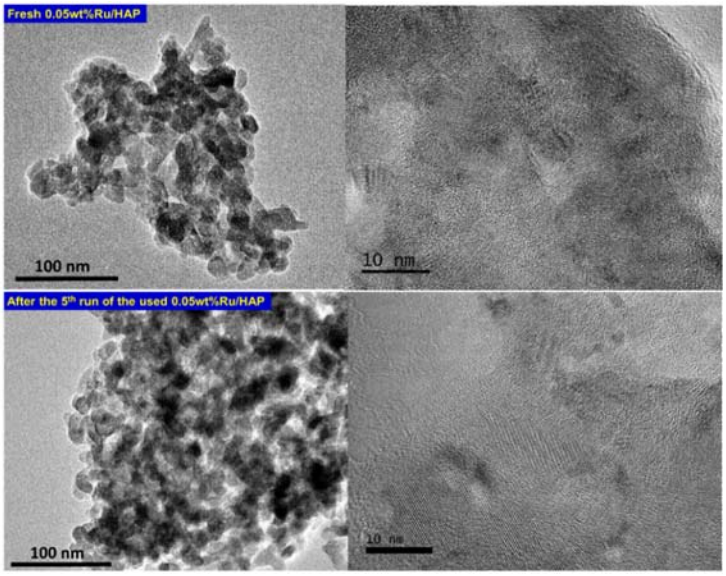
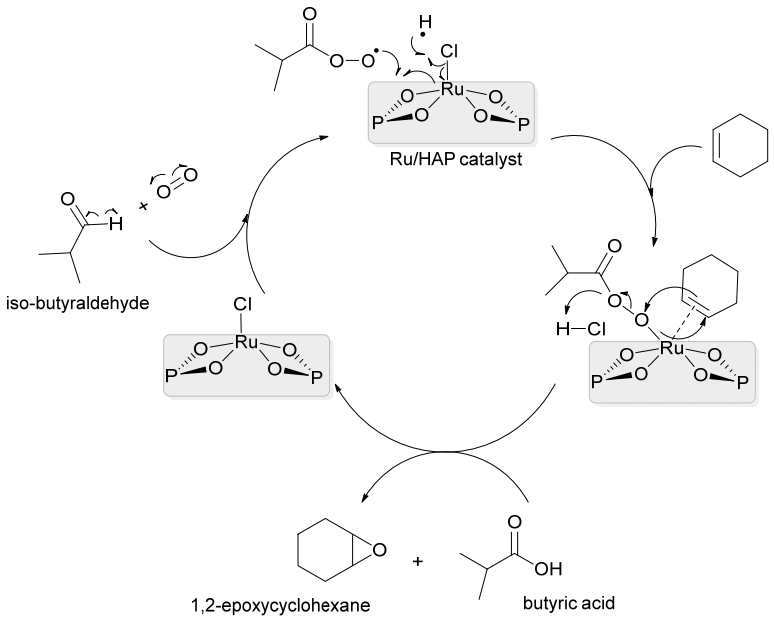


Fig. S6 TEM images of 0.05 wt% Ru/HAP after the 5th run in reusability test compared to fresh 0.05 wt% Ru/HAP.



Scheme S1. Plausible mechanism of cyclohexene epoxidation using the 0.05 wt% Ru/HAP catalyst.

References.

1. Y. V. Larichev, *J. Phys. Chem. C.* 2011, **115**, 631-635.

2. J. Ftouni, A. M. Murillo, A. Goryachev, J. P. Hofmann, E. J. M. Hensen, L. Lu, C. J. Kiely, P. C. A. Bruijnincx, B. M. Weckhuysen, *ACS. Catal*. 2016, **6**, 5462-5472.