

Electronic Supporting Information

Cobalt immobilized on hydroxyapatite as a low-cost and highly effective heterogeneous catalyst for alkenes epoxidation under mild condition.

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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 (37%Ru, Shanghai Tuosi Chemical), CoSO₄·7H₂O (99.5%, Sinopharm Chemical Reagent Co.Ltd), FeSO₄·7H₂O (99~101%, Shantou Xi long Chemical Co., Ltd.), MnSO₄·H₂O (≥99%, Sinopharm Chemical Reagent Co.Ltd), Cu(OAc)₂·H₂O (Beijing shuanghuan huaxue shijichang), Pd(OAc)₂ (98%, Aldrich) iso-butylaldehyde (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 by simple chemical precipitation. A solution of Ca(NO₃)₂·4H₂O (66.8 mmol) 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 (NH₄)₂HPO₄ (40.1 mmol) 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 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 Co/HAP: Co metal doped on HAP was prepared with ion exchange method. In brief, the synthesized HAP (1.0 g) was stirred magnetically with 400 mL DI water. Then, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solution was prepared to be Co^{2+} precursor (0.4770 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 100 mL DI water resulting concentration of Co^{2+} about 1000 mg/L). After that, the desired amount of Co from aqueous $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ solution was pipetted in to HAP suspension (0.5, 10, 30 and 50 mL were pipetted to prepared 0.05, 1, 3 and 5 wt% of Co immobilized on HAP respectively) and it was further stirred at room temperature for 24 h. The obtained slurry was filtered, washed with deionized water (3×200 mL), and then dried overnight at 60 °C under vacuum, yielding the Co doped on HAP as the light pink powders. For other metals (Ru, Cu, Mn, Pd and Fe) immobilized on HAP, metal salts ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{Pd}(\text{OAc})_2$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)³⁻⁶ were used as precursors following the same procedure that mentioned above.

Characterizations: All of the prepared catalysts were characterized with various techniques which consisted of XRD (D8 Advance, Bruker using $\text{Cu-K}\alpha$ 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).

Epoxidation of Alkenes: The alkene epoxidation was operated in round bottom glass and mesitylene was used as internal standard. Typically 5 mL of acetonitrile or dichloromethane, 1 mmol of alkene, 5 mmol of *iso*-butyraldehyde and 20 mg of catalyst were mixed with stirring under O_2 bubbling. For reusability test, the catalyst was separated by centrifugation, washed with CH_2Cl_2 , then dried at 60 °C overnight. The starting materials and products were determined by GC (Shimadzu GC-2010-Plus) equipped with a flame ionization detector (FID) and a Rtx-5 capillary column (0.25 mm in diameter, 30 m in length) and GC-MS (Shimadzu GCMS-QP2010). The reactivity of the prepared catalysts was reported as % conversion of substrate and % selectivity of the epoxide product. Moreover, the BET surface area of the used 0.05 wt% Co/HAP was determined by N_2 adsorption-desorption isotherms. The up-scale of 5 mmol cyclohexene epoxidation in 25 mL CH_3CN , with 25 mmol *iso*-butyraldehyde was tested over 100 mg of 0.05 wt% Co/HAP under O_2 balloon at 30 °C for 4 h. After that, the catalyst was separated by centrifugation, washed with CH_3CN and dried at 80 °C overnight. The recovered catalyst was then determined by N_2 adsorption-desorption isotherm.

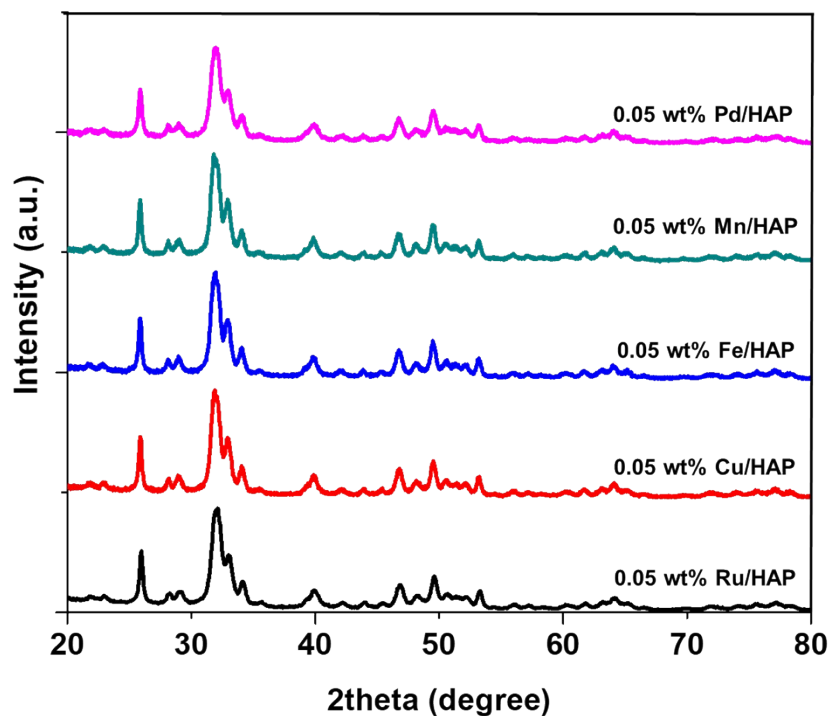


Fig. S1 XRD spectra of various metals supported HAP.

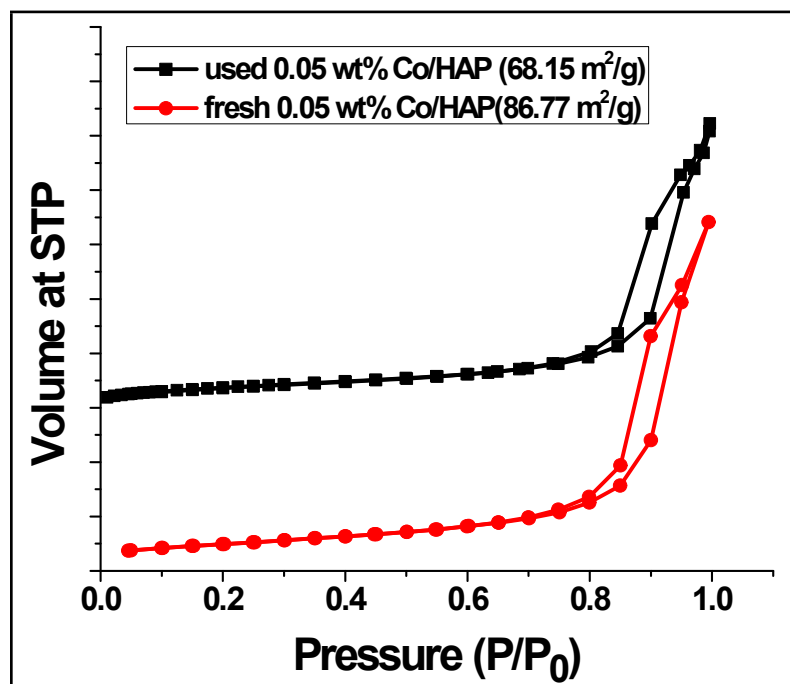


Fig. S2 N₂ adsorption-desorption isotherms of the fresh and used 0.05 wt% Co/HAP catalyst.

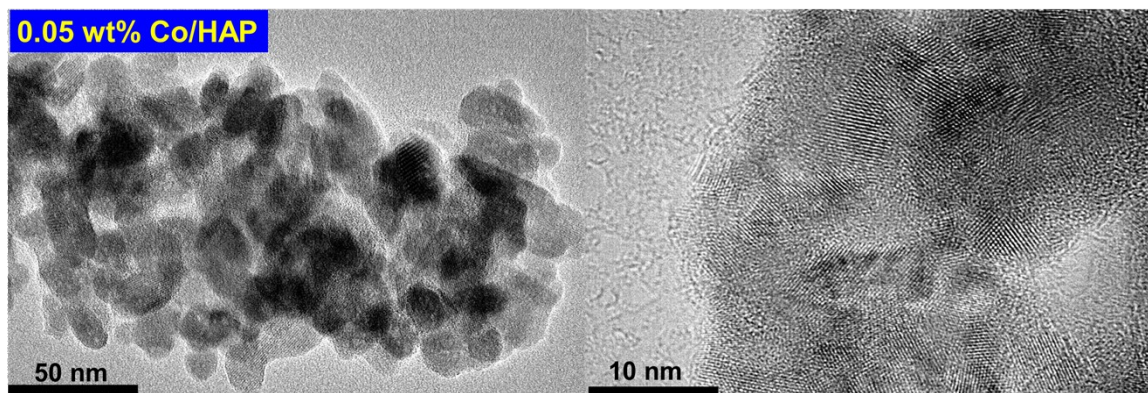
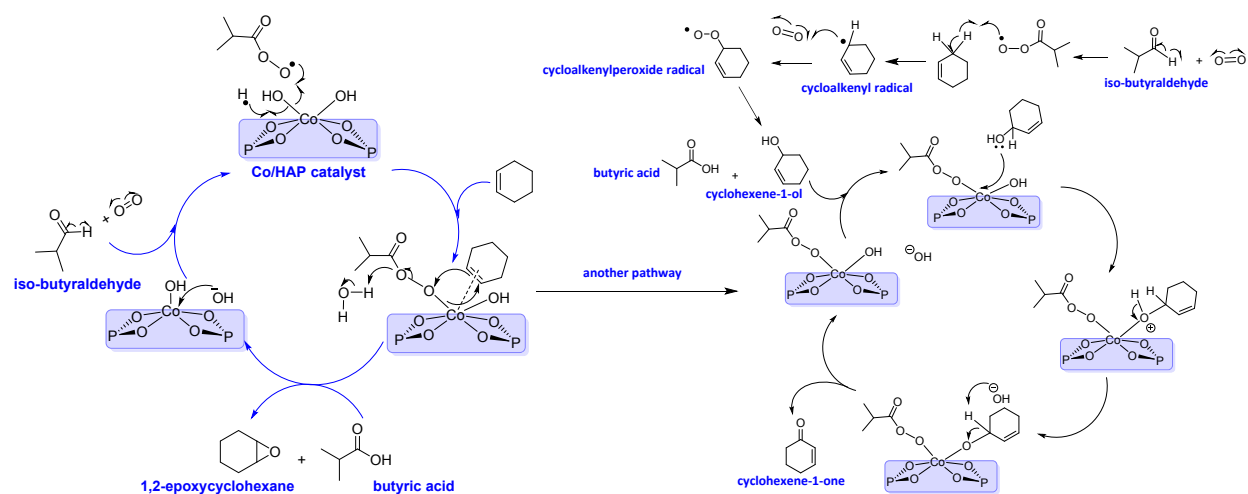


Fig. S3 TEM images of 0.05 wt% Co/HAP catalyst.



Scheme S1. A plausible mechanism for cyclohexene epoxidation over 0.05 wt% Co/HAP catalyst.

Table S1. The content of various metals and higher Co loading immobilized on HAP from ICP-AES analysis.

Catalyst	wt% metal from ICP-AES
0.05 wt% Co/HAP	0.02
0.05 wt% Ru/HAP	0.06
0.05 wt% Fe/HAP	0.09
0.05 wt% Mn/HAP	0.04
0.05 wt% Cu/HAP	0.06
0.05 wt% Pd/HAP	0.07
1 wt% Co/HAP	0.75
3 wt% Co/HAP	1.28
5% wt% Co/HAP	1.58

Table S2. Solvent effect in epoxidation of cyclohexene using 0.05 wt% Co/HAP as catalyst.

Solvent	Conv.%	Sel.%
CH₂Cl₂	100	95
CH ₃ CN	83	93
THF	13	33
MeOH	46	13
EtOAc	79	89
heptane	45	78
toluene	92	92

Reaction conditions: 0.05 wt% Co/HAP (20 mg), cyclohexene (1 mmol) solvent (5 mL), iso-butylaldehyde (5 mmol), 30 °C, O₂ balloon, 2 h. reaction time.