

Supplementary information

Superhydrophobic Materials as Efficient Catalysts for Hydrocarbon Selective Oxidation

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1. Experimental Section

Material Preparation

Tetraethyl orthosilicate (TEOS, 99%), cobaltous acetate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 99%), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%), cyclohexane (C_6H_{12} , 99.5%), n-butyl alcohol ($\text{C}_4\text{H}_9\text{OH}$, 99.5%), and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%) were obtained from Tianjin Kermel Chemical Reagent Development Center, China. Poly (oxyethylene) nonylphenol ether (NP-7, Industrial Grade) was purchased from Dalian chemical ctl., China. 3,3,3-trifluoro-propyltriethoxysilane (FPTES, 95%) was obtained from Zhejiang Chem-Tech Co., China and purified before use.

First, three kinds of solution (solution A, B, and C) were obtained. Solution A was composed of 15.05 g of Np-7, 35.05 g of cyclohexane, and 8.05 g of n-butyl alcohol; solution B was the metal ammonia complex water solution (0.13 g of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 5.35 g of H_2O , and 2.00 g of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (21%)); solution C was a mixture of 3.12 g of TEOS and 2.60 g of FPTES. Microemulsion was obtained with the blending of solutions A and B. To this microemulsion, solution C was added slowly under stirring. The stirring was continued for 13 h. It was then centrifugated, washed with hot ethanol to remove the surfactant and dried at 353 K for 12 h. The non-organic group containing Co-SiO₂ was synthesized without FPTES.

Characterization

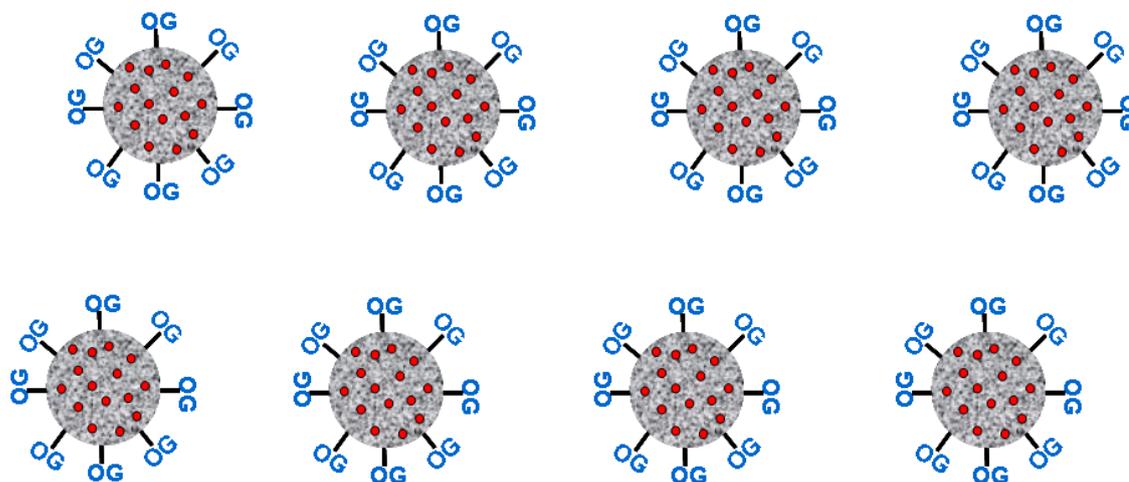
The microstructure of the materials was examined by transmission electron microscopy (TEM) on a FEI Tecnai G2 Spirit electron microscope at an accelerating voltage of 120 kV. The surface morphology was observed by scanning electron microscopy (SEM) on a FEI Quanta 200F. Fourier transform infrared (FT-IR) spectra were collected between 4000 and 400 cm^{-1} on a Bruker Tensor 27 FT-IR spectrometer in KBr media. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) were collected over a wavelength range from 800 to 190 nm on Shimadzu UV-2550 Spectrophotometer equipped with a diffuse reflectance attachment. The kinetics measurements of the ultraviolet-visible absorption spectra were carried out on the same instrument at the wavelength of 584.5 nm. The nuclear magnetic resonance spectra of ^{29}Si with magic-angle spinning (^{29}Si MAS NMR) were taken on a Bruker DRX-400 spectrometer with a spinning frequency of 4.7 kHz. Content of cobalt in the materials and the leaching cobalt in the products were analysed on Leeman PLASMA-SPEC-II and Shimadzu ICPS-8100 inductively coupled plasma atomic emission spectrometer (ICP-AES). We also measured the surface hydrophilicity/hydrophobicity of these materials deposited as a film on a glass substrate using contact angle measuring system JC 2000 C1. The amount of water droplet was 5 μL . The sorption experiment was performed at 273 K on a Micromeritics ASAP 2020 system to measure the adsorbed quantity of hydrophilic water (V_{water}) and hydrophobic benzene (V_{benzene}), respectively. Prior to the measurement, the samples were out gassed at 80 $^{\circ}\text{C}$ for at least 10 h. Hydrophobicity index (HI) were obtained according to the formula: $\text{HI} = V_{\text{benzene}}/V_{\text{Water}}$.

Catalytic oxidation of hydrocarbon

Catalytic reactions were performed in a 100 ml autoclave reactor with a teflon insert inside. Typically, 15.00 g of ethylbenzene and 0.05 g of catalyst were placed in the reactor, respectively. Then, after being sealed, the reactor was heated to the reaction temperature 120 $^{\circ}\text{C}$, while agitation was ensured by an external magnetic stirrer. Upon heating to the reaction temperature, the reactor was charged with 1.0 MPa of O_2 and O_2 was fed continuously to maintain constant pressure. The reaction

products were identified by Agilent 6890N GC/5973 MS detector and quantitated with an internal standard (1,2,4,5-tetramethylbenzene) method by Agilent 4890D GC equipped with PEG-20 M capillary column (50 m \times 0.32 mm \times 0.4 μ m). For the selective oxidation of cyclohexene and tetralin, reaction time was 90 min; reaction pressure was 0.3 MPa; reaction temperature was 80 and 100 $^{\circ}$ C, respectively. For cyclohexane oxidation, 0.12 g of catalyst was used and 0.12 g of tert-butyl hydroperoxide (TBHP, 65 wt%) was used as initiator. The reaction was carried out at 115 $^{\circ}$ C for 360 min. The reaction products were quantitated by Agilent 4890D GC equipped with OV-1701 column (30 m \times 0.25 mm \times 0.3 μ m) and titration. After the decomposition of cyclohexylhydroperoxide (CHHP) to cyclohexanol by adding triphenylphosphine to the reaction mixture, cyclohexanone and cyclohexanol were determined by the internal standard method using toluene as an internal standard. The concentration of CHHP was determined by iodometric titration, and the by-products acid and ester by acid-base titration. All the mass balances are above 92%.

2. Scheme of material structure



Scheme S1. Structure of the designed material

3. Characterization results

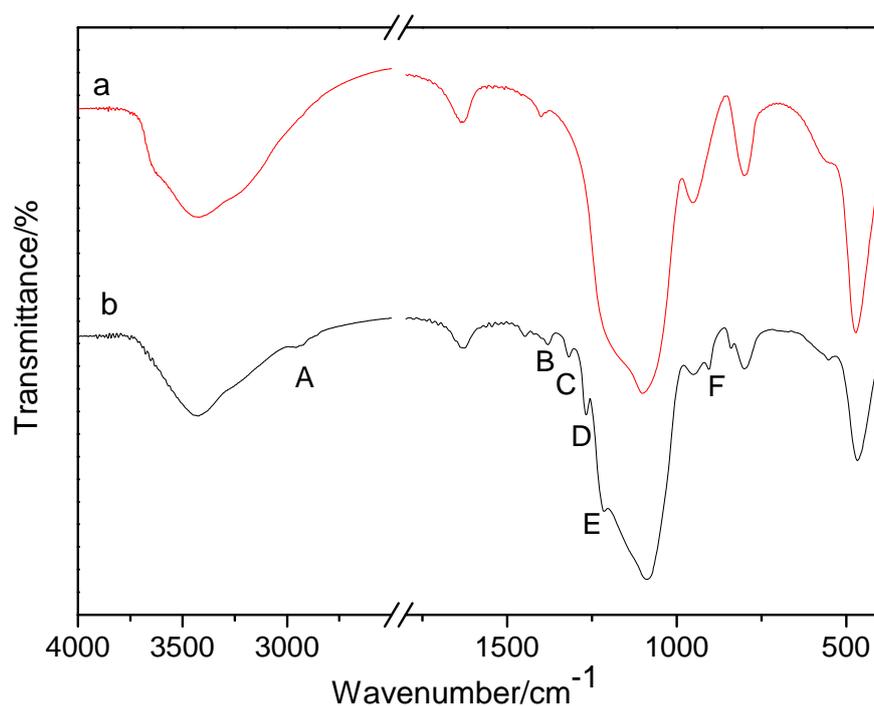


Fig. S1 FT-IR spectra of (a) Co-SiO₂, (b) FP-Co-SiO₂.

Typical bands associated with the formation of a condensed siloxane network were present in both cases (Si–O–Si bands around 1217, 1090, 800 and 470 cm⁻¹). For the spectrum of FP-Co-SiO₂ new absorption bands A-F correspond with the complicated vibration of organic group Si-CH₂CH₂CF₃. In addition, the absorption band at around 950 cm⁻¹ was assigned to Si–O vibration in Si–OH group. Compared with that of Co-SiO₂, the intensity of this band apparently decreased in the spectrum of FP-Co-SiO₂. This indicates that the amount of hydrophilic Si–OH on the surface remarkably decreased caused by the substitution of hydrophobic Si–CH₂CH₂CF₃.

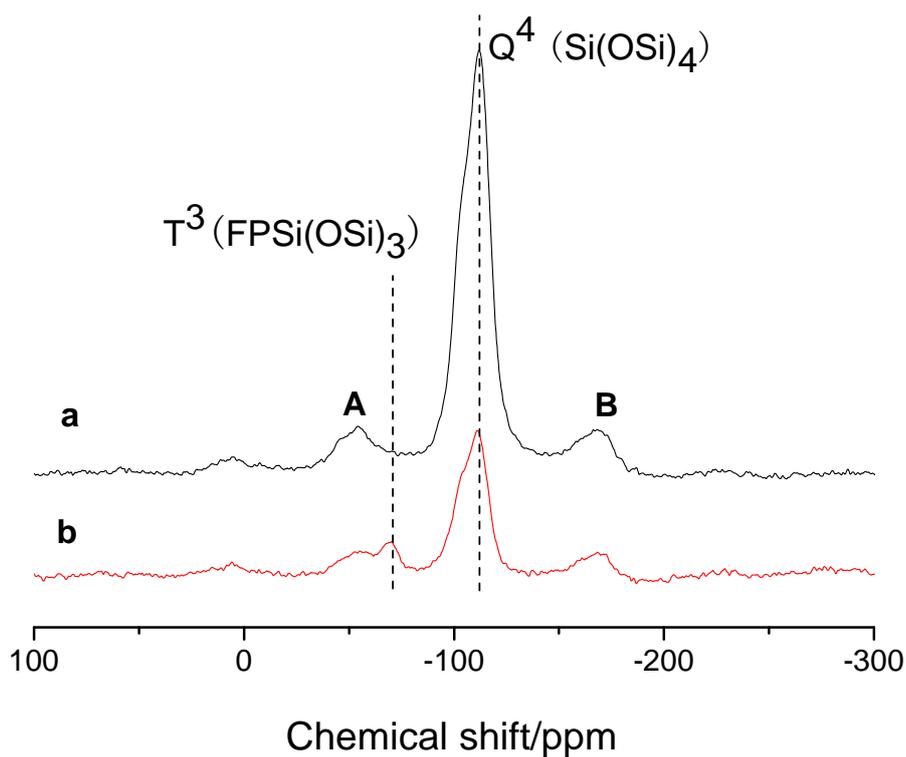


Fig. S2 ^{29}Si MAS-NMR spectra of (a) Co-SiO_2 and (b) FP-Co-SiO_2 .

For Co-SiO_2 , distinct resonances characteristic of the silica network [$\text{Q}^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 2-4$] are observed, and Q^4 species are the main components. For FP-Co-SiO_2 , besides Q^4 signal, resonances characterizing the organosiloxane network [$\text{T}^3 = \text{FPSi}(\text{OSi})_3$] are observed. The appearance of T^3 organosilane signals between -60 and -80 ppm are characteristic of fully cross-linked organosiloxane species, demonstrating the successful immobilization of the organic groups in the material. Signal A and B are spinning sidebands.

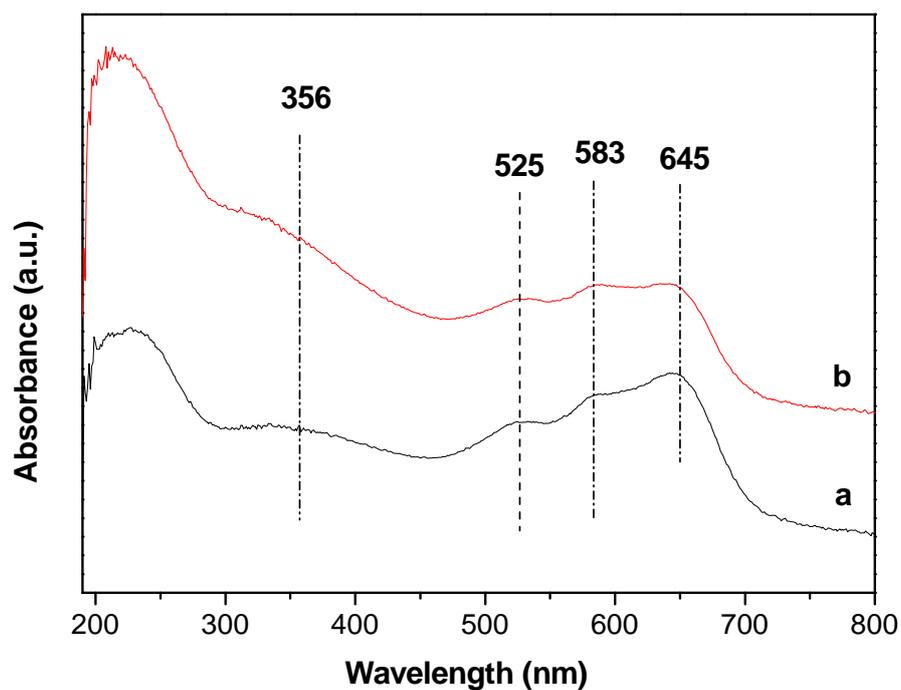


Fig. S3 UV-Vis DRS of (a) Co-SiO₂, (b) FP-Co-SiO₂.

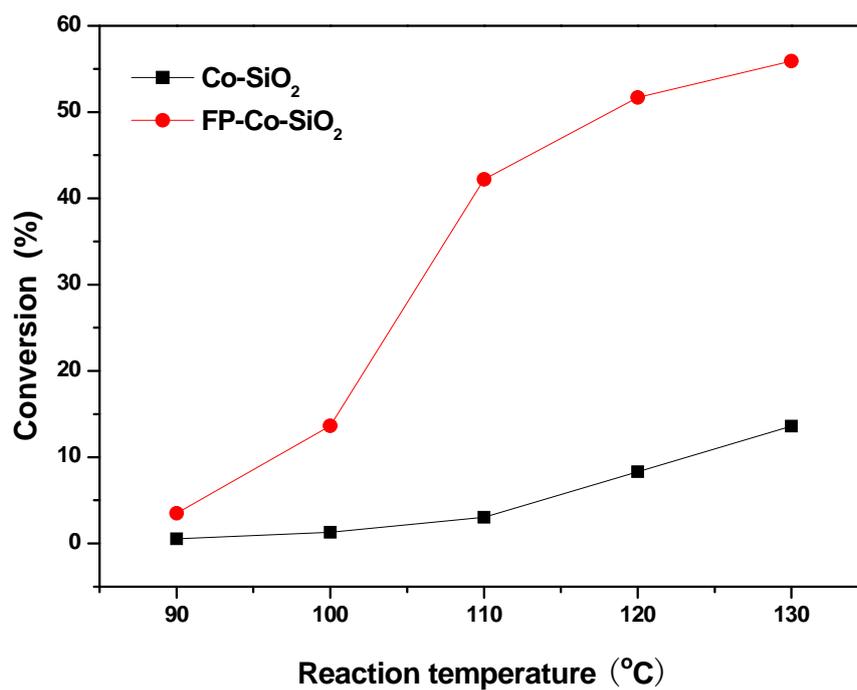


Fig. S4 Catalytic activities of Co-SiO₂ and FP-Co-SiO₂ on selective oxidation of ethylbenzene. (Reaction was carried out with 0.05 g of catalyst in 15 g of ethylbenzene for 420 min under 1.0 MPa O₂.)

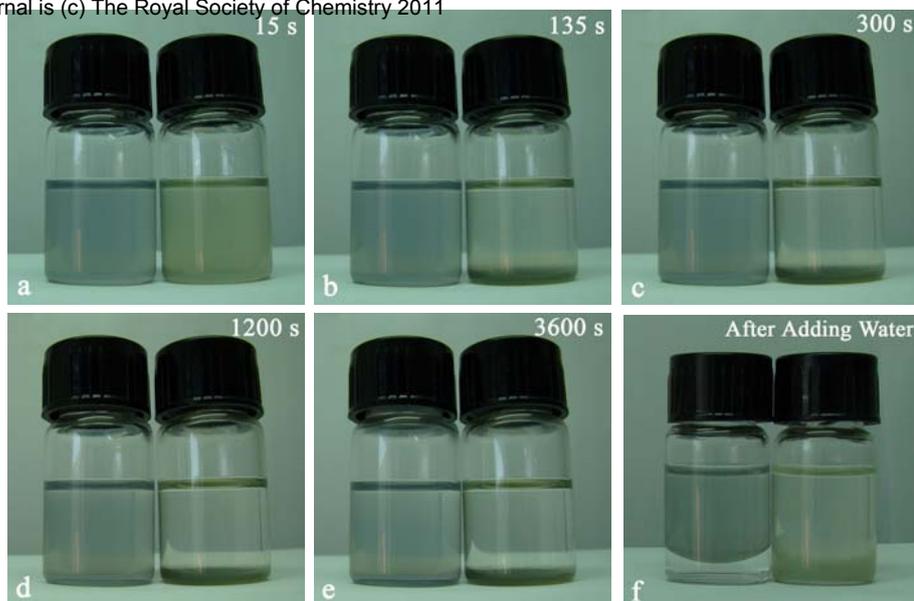


Fig. S5 Distribution comparison results of Co-SiO₂ (right) and FP-Co-SiO₂ (left) in ethylbenzene (a), (b), (c), (d), (e), and mixed liquid (f, ethylbenzene (upper phase) and water (lower phase)).

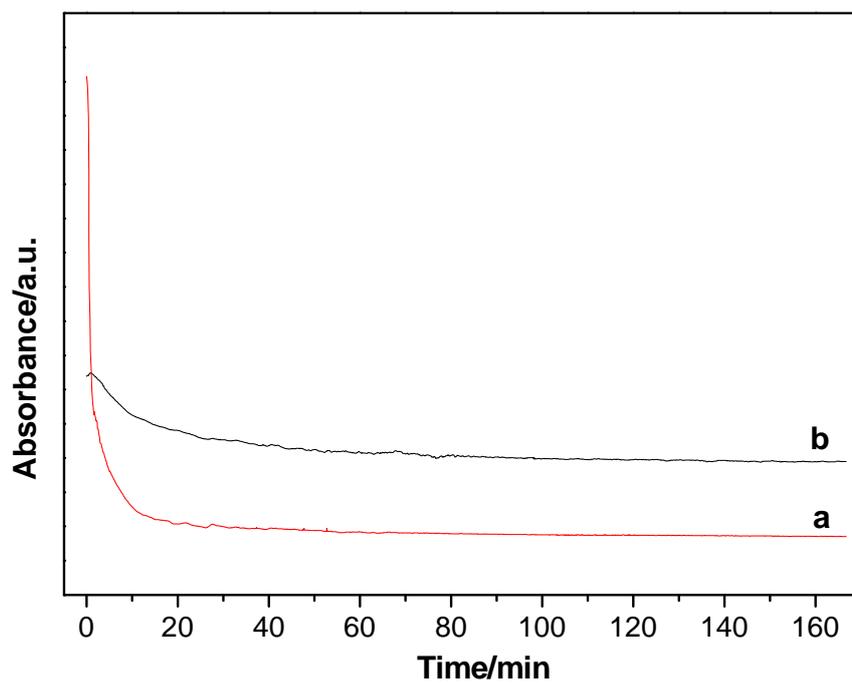


Fig. S6 Kinetic measurements curves of (a) Co-SiO₂ and (b) FP-Co-SiO₂ based on UV-Vis absorption at 584.5 nm.

Table S1 Comparison of the adsorbed quantity of water and benzene

| Material | Quantity Adsorbed of water (cm ³ /g STP) | Quantity Adsorbed of benzene (cm ³ /g STP) | HI ^a |
|------------------------|--|--|-----------------|
| Co-SiO ₂ | 111.27 | 8.20 | 0.07 |
| FP-Co-SiO ₂ | 69.01 | 90.44 | 1.31 |

^a Hydrophobicity index (HI) = $V_{\text{benzene}}/V_{\text{Water}}$

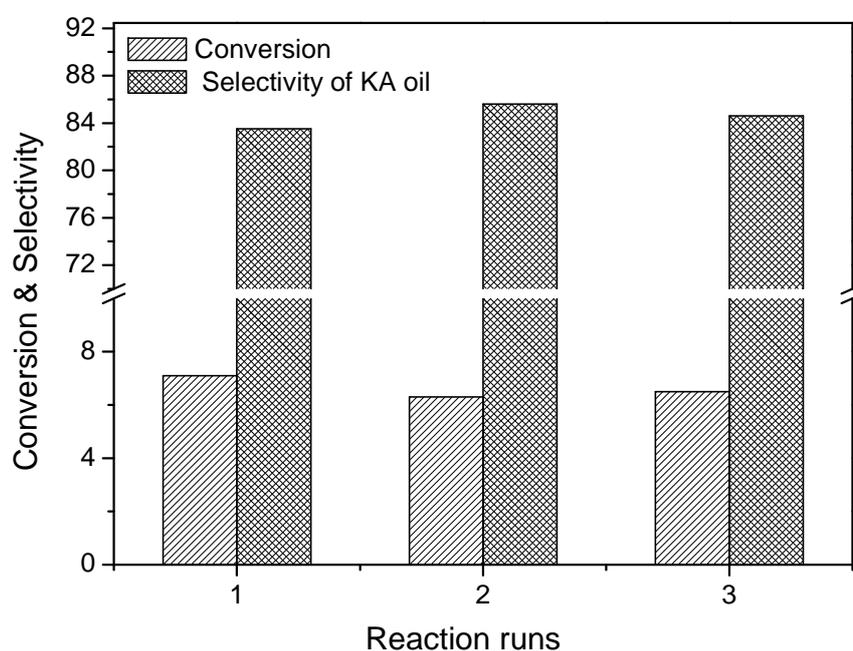


Fig. S7 Reusability of FP-Co-SiO₂ in cyclohexane oxidation. (KA oil: cyclohexanol and cyclohexanone)