

Supporting Information

Rational design of carbon support to prepare ultrafine-iron-oxide catalyst for air oxidation of alcohols

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Experimental Section

Materials synthesis.

All chemicals used in the experiments were of analytical grade, and were used without further purification. Double-distilled water was used in all of the experiments. The mesoporous carbon (MC) was prepared using a modified hard-template method. Typically, phosphoric acid was dropped into an aqueous solution containing aluminium nitrate nonahydrate, citric acid (denoted as CA) and sucrose (denoted as SU) with specific mole ratio (see in Table S1). Then, a diluted aqueous ammonia (10 %) solution was used to adjust the pH value of the solution to 5.1. After that, the mixture was heated at 353 K till water and other volatiles were removed to obtain the as-synthesized precursor. The solid was first pretreated at 573 K in muffle for 10 minutes, and then calcined at 1073 K under argon atmosphere for 6 h. Lastly, the composite was treated with 4 M HCl or HNO₃ at 353 K for 6 h to remove the AlPO component. The resulting products were filtered, washed with deionized water, and dried at 373 K overnight.

Ordered mesoporous carbon (CMK-3) was prepared with SBA-15 as hard template and sucrose as the carbon source using a procedure reported by Ryoo et al.^[1] SBA-15 was prepared following the synthesis procedure reported by Zhao et al.^[2] Briefly, 1.0 g of SBA-15 silica was added to a solution containing 1.25 g of sucrose, 0.14 g of sulphuric acid and 5.0 g of distilled water. The mixture was kept in an oven at 80 °C for 6 h, then the temperature was increased to 160 °C and maintained for another 6 h. The heating procedure was repeated after the additional carbon precursor was added (0.8 g of sucrose, 0.09 g of H₂SO₄ and 5.0 g of H₂O), aiming to completely infiltrate internal pores of SBA-15. The carbon–silica composite was obtained after pyrolysis at 900 °C for 6 h under argon flow and successive washing in 10 wt% hydrofluoric acid aqueous solution to remove silica template. Other carbon materials, including carbon nanotube (CNT), Black Pearls 2000 (BP-2000) and active carbon (AC) were obtained commercially and treated with 4 M HNO₃ for 6 h before used as reference catalyst supports.

Supported iron oxide catalysts were prepared by the wet impregnation method. Carbon support was added into a water solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the resultant mixture was stirred for about 3 h at room temperature. After that, water was evaporated at 353 K and the resultant solid was calcined at 673 K for 6 h under an argon flow. The loading of iron oxide was calculated with Fe_2O_3 .

Catalytic test.

The aerobic oxidation of benzyl alcohol was carried out in a 50-mL two-neck flask at atmospheric pressure. Typically, 0.3 g catalyst was used as catalyst. After a suspension of catalyst in toluene (10 mL) was treated at 353K, 1.0 mmol benzyl alcohol was added into the reactor. The mixture was contacted with air and the reaction temperature was kept at 353 K. The products were taken via a sampling pipe and analyzed with a gas chromatograph equipped with a HP-5 column and FID detector. In the recycle experiment, the solid catalyst was separated by filtration after reaction and treated at 400 °C for 1 h before next cycle test.

Characterization.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). N_2 adsorption-desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 473 K for 20 h before measurements. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) model. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the Barret-Joyner-Halenda (BJH) model. XPS was performed on a Thermo ESCA LAB 250 system with $\text{MgK}\alpha$ source (1254.6 eV). Diffused reflectance of infrared Fourier transform (DRIFT) spectra were recorded on Thermo Nicolet 6700 FT-IR spectrometer. Transmission electron microscopy (TEM) images and the high-angle annular dark field STEM (HAADF-STEM) images were taken with a FEI Tecnai F20 EM with an accelerating voltage of 200 kV equipped with an energy-dispersive spectroscopy analyzer. Raman spectra were recorded on a Bruker RFS 100 Raman

spectrometer with an argon laser (514 nm) as an excitation source. Temperature programmed reduction (TPR) was performed on Tianjin Xianquan TP-5079 Adsorption analyzer. Before detection, the catalysts (50 mg) were firstly treated in Ar (99.99%) flow at 400 °C for 10 min. The zeta-potential curve was measured as a function of pH 2–8 on a Zeta PALS analyzer (Brookhaven Instruments Corporation, USA). The sample was suspended in aqueous 0.01 M NaCl solution, and 0.5 M NaOH and HCl solutions were used to adjust the pH. Boehm titration method was used to determine the amounts of surface groups. Carbon support (0.1 g) was placed in 10 mL of 0.05 M solution of the following: sodium hydroxide, sodium carbonate, sodium bicarbonate. The vials were sealed and shaken for 24 h and filtrated, and then a known quantity of hydrochloric acid was added to each filtrate. The excess acid left in the solution was titrated with NaOH on an Automatic Potentiometer titrator (LeiCi ZDT-4A). The amounts of acidic sites were calculated with the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups, NaHCO₃ neutralizes carboxylic groups, and Na₂CO₃ neutralizes carboxylic and lactonic groups.

Reference:

- [1] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki. *J. Am. Chem. Soc.* 2000, **122**, 10712.
- [2] D. Zhao, J. Feng, O. Huo, N. Melosh, G.H. Fredrickson, B.F. Chemlka and G.D. Stucky. *Science*, 1998, **279**, 548.

Table S1: Synthesis parameters and texture properties of MC and supported iron oxide catalysts.

Sample	Composition of starting mixture (mol ratio) ^a	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size ^b (nm)
	CA: SU: Al: P			
MC-1	0.5:0.5:1:1	1392	1.67	6.5
MC-2	0.5:1.5:1:1	985	0.99	3.8
MC-3	0.5:2.5:1:1	954	0.72	2.9
5wt%FeO _x /MC-1	—	1047	1.49	5.3
5wt%FeO _x /MC-2	—	814	0.84	4.0
5wt%FeO _x /MC-3	—	555	0.46	3.2

^a Composition of starting mixture containing citric acid, sucrose, aluminium nitrate nonahydrate and phosphoric acid were denoted as CA, SU, Al and P, separately. ^bAverage pore diameters calculated from desorption branches using the BJH model.

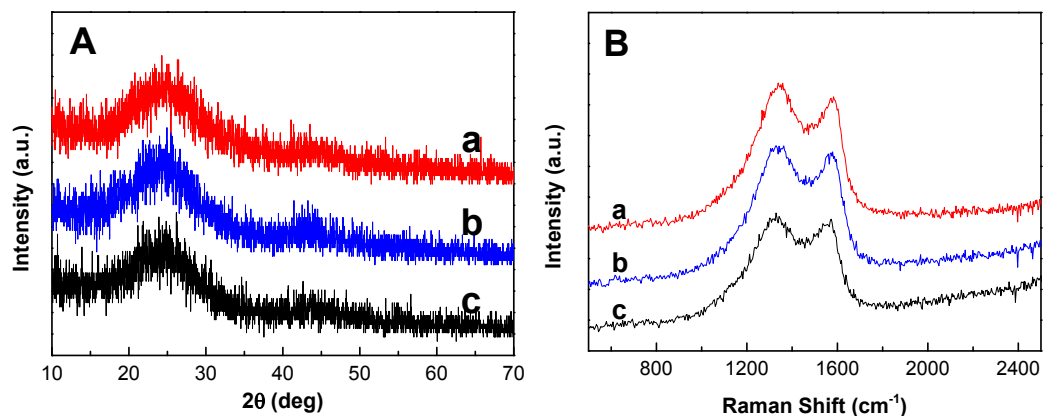


Fig. S1 XRD patterns (A) and Raman spectra (B) of carbon support: (a) MC-1; (b) MC-2 and (c) MC-3.

Table S2: Boehm titration results of different carbon supports.

Samples	Content (mmolg ⁻¹)			
	Carboxylic	Lactonic	Phenolic	Acidic
MC-1	0.92	0.91	1.40	3.23
MC-2	1.08	0.82	1.39	3.29
MC-3	1.01	0.78	1.17	2.96
H-CMK-3	0.24	0.34	0.89	1.47
H-AC	0.17	0.18	0.66	1.01
H-CNT	0.01	0.04	0.15	0.20

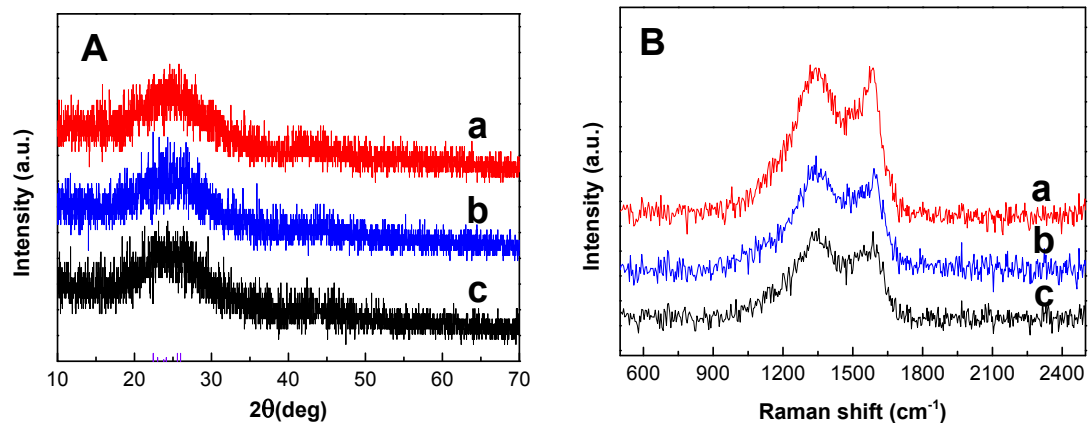


Fig. S2 XRD patterns (A) and Raman spectra (B) of the supported iron oxide catalysts: (a) 5wt%FeO_x/MC-1; (b) 5wt%FeO_x/MC-2 and (c) 5wt%FeO_x/MC-3.

Table S3: A comparative list of the metal catalyzed oxidation of benzyl alcohol to benzaldehyde: the reaction conditions, the selectivity and activity (TOF).

Catalyst	Temp. (°C)	Press. (atm)	Oxidant	Select. (%)	TOF (h ⁻¹)	Ref.
5wt% FeO _x /MC	80	1	air	>99	6.10 ^a	This work
15wt% MnO _x /C	80	1	air	>99	1.06	<i>Chin. J. Catal.</i> 2010, 31 , 1025
13wt%Co ₃ O ₄ /AC	80	1	O ₂	>99	0.97	<i>Chem. Eur. J.</i> 2011, 17 , 7112
1% Pt/C	60	1.5	O ₂	95	30	<i>J. Catal.</i> 2006, 244 , 113
1wt. %Au/AC	80	1.5	O ₂	89	23	<i>Catal. Commun.</i> 2008, 9 , 2395
1wt. %Au/AC	80	1.5	O ₂ ^b	26	78	<i>Appl. Catal. A.</i>
1% Pd/AC	60	1.5	O ₂ ^b	58	15	2009, 364 , 221

^a TOF calculated after 30 min of reaction. ^b This reaction was carried out under basic conditions (NaOH).

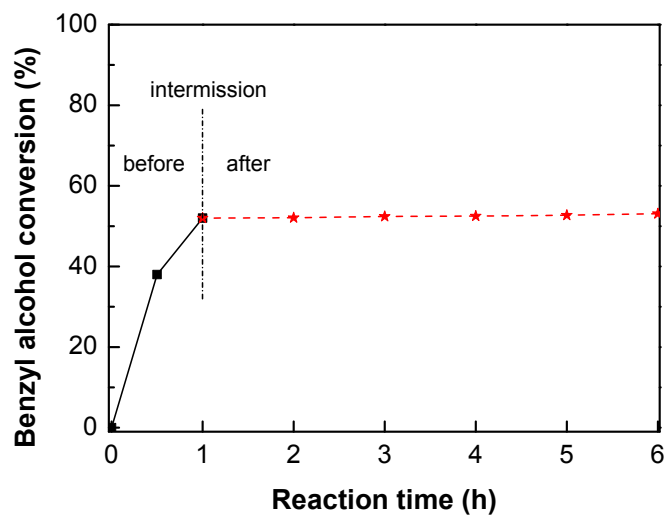


Fig. S3 Leaching experiment of 5wt% FeO_x/MC-1 by continuing the reaction after filtration of the catalysts. Dashed lines indicate the benzyl alcohol conversion after removing the catalysts. Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.3 g), solvent (toluene 10 mL), 80 °C, air (1 bar).

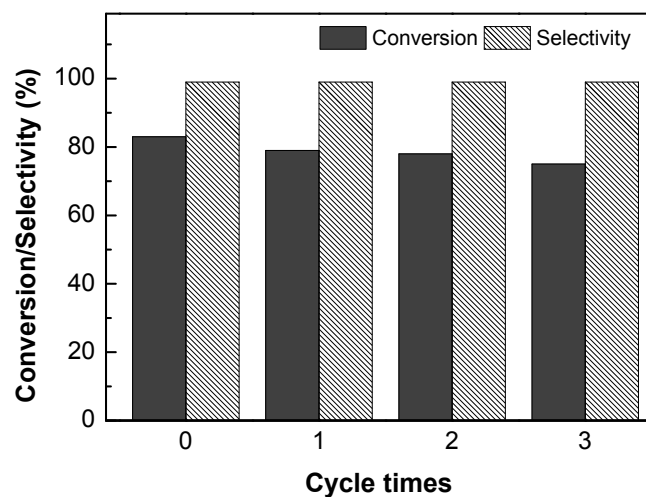


Fig. S4 Reusability of 5wt% FeO_x/MC-1 for air oxidation of benzyl alcohol.

Reaction conditions: benzyl alcohol (1 mmol), catalyst (0.3 g), solvent (toluene 10 mL), 80 °C, 6 h, air (1 bar). The reaction time for the latter two cycles is 8 h and 10 h.

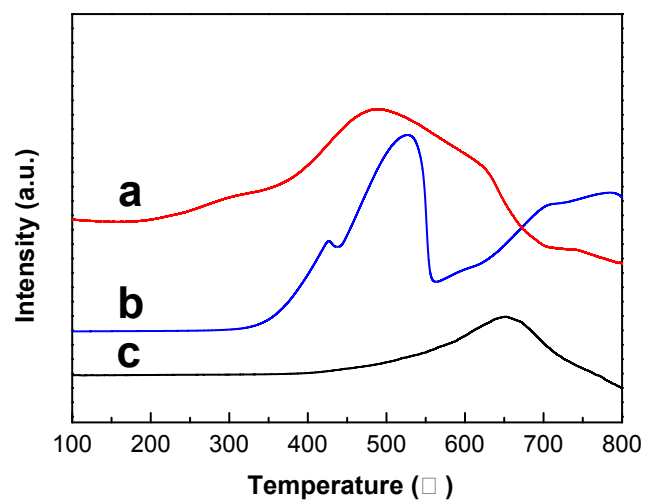


Fig. S5 H₂-TPR of profiles of (a) 5wt%FeO_x/MC-1; (b) bulk iron oxide and (c) 5wt%FeO_x/CMK-3.

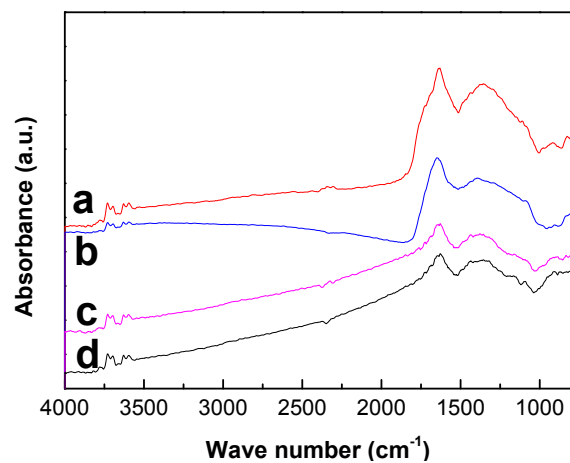


Fig. S6 DRIFT spectra of various carbon supports: (a) MC-1; (b) MC-Na; (c) MC-T and (d) MC-R.

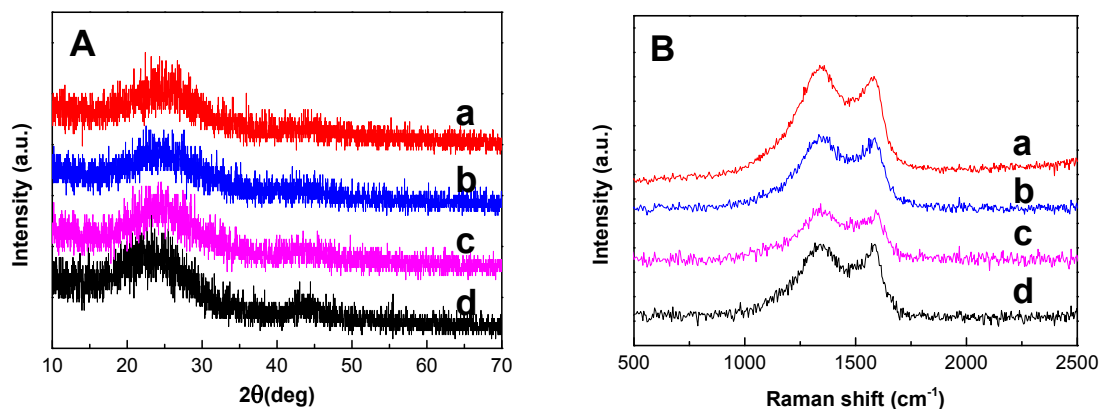


Fig. S7 XRD patterns (A) and Raman spectra (B) of iron oxide catalysts with fresh and treated MC as supports: (a) FeO_x/MC-1; (b) FeO_x/MC-Na; (c) FeO_x/MC-T and (d) FeO_x/MC-R.

Table S4: Texture properties of iron oxide catalysts with fresh and treated MC as supports.

Sample	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size ^a (nm)
5wt%FeO _x /MC-1	1392	1.67	6.5
5wt%FeO _x /MC-Na	1135	1.43	5.0
5wt%FeO _x /MC-T	1238	1.41	4.5
5wt%FeO _x /MC-R	1135	1.16	4.0

^a Average pore diameters calculated from desorption branches using the BJH model.