Supporting Information for

Iron-functionalized Al-SBA-15 for benzene hydroxylation

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Experimental Details

Synthesis of materials

A typical synthesis procedure for Fe-Al-SBA-15 materials is as follows: 2 g of P123 surfactant (Aldrich) was dissolved in 70 mL of HCl solution at pH value of 1.5 (solution A). TMOS (Aldrich, 3.2 mL), an appropriate amount of iron nitrate (Fe/Si molar ratio = 0.03 for Fe-Al-SBA-15 (A) and 0.01 for Fe-Al-SBA-15 (B)) and aluminum isopropoxide (Al/Si molar ratio is 0.10) were mixed with 5 mL of deionized water to obtain solution B. Solution B was stirred at room temperature for about 10 min to a clear solution and then it was added drop wise to solution A. The mixture of solution A and B was stirred vigorously for 20 h at 313 K. The resulting mixture was transferred into an autoclave and aged for 24 h at 373 K. The resultant solid was filtered, washed, and dried at 333 K for 15 h. Finally, the mesoporous Fe-Al-SBA-15 materials were obtained after been calcined at 773 K for 10 h.

The preparation procedure of Fe-SBA-15 materials is similar that of Fe-Al-SBA-15: 2 g of P123 was dissolved in 70 mL of HCl solution at pH value of 1.5 (solution A). TMOS (3.2 mL) and a certain amount of iron nitrate (Fe/Si molar ratio = 0.01 for Fe-SBA-15 (A) and 0.10 for Fe-SBA-15 (B)) were mixed with 5 mL of deionized water to get solution B. All the following steps are the same with the preparation of Fe-Al-SBA-15.

The preparation procedure of Al-SBA- 15 materials is described as follows: 2 g of P123 were dissolved in 70 mL of HCl solution with different pH value to get solution A. Then, 3.2 mL of TMOS and a certain amount of aluminum isopropoxide (Al/Si molar ratio of 0.10) were added to 5 mL of HCl aqueous solution at pH 1.5 to get solution B. All the following steps are the same with the preparation of Fe-Al-SBA-15.

A Fe/ZSM-5 zeolite was prepared by hydrothermal synthesis in an autoclave. To this end, 102.4 g tetraethylorthosilicate (TEOS) (Acros; 98%) was added to 150 g organic template tetrapropylammonium hydroxide (TPAOH) (Fluka; 20% in water) and vigorously stirred overnight. Appropriate amounts of solutions containing iron nitrate (Fe(NO3)3·9H2O, 98%; Merck) and aluminum nitrate (Al(NO3)3·9H2O, 99%;Janssen) of different concentration(s) were added with vigorous stirring. The autoclave was kept at 443 K for 5 days. After filtration,

washing, and drying at 383 K overnight, white zeolite powder was obtained. The successful synthesis of zeolite with the MFI topology was confirmed by X-ray diffraction. Subsequently, the organic template was carefully removed by the following calcination procedure: (i) zeolite was treated in 100 ml min^{-1} N_2 during heating to 823 K at a ramp rate of 1 $Kmin^{-1}$ and kept at this temperature for 8 h. (ii) The material was further treated in 100 ml min^{-1} 20 vol.% O_2 in N_2 at 823 K for another 4 h.

Steam activation of the catalysts was carried out by heating the catalysts in a flow of 20 vol.% O_2 in N_2 to 973 K at a rate of 1 $K.min^{-1}$, followed by exposure to a mixture of 10 vol.% H_2O and 18 vol.% O_2 in N_2 for 3 h.

Characterization

Diffuse reflectance UV-Vis spectra in the range of 200-800 nm were taken on a JASCO V-550 UV-Vis spectrophotometer equipped with a diffuse reflectance attachment, using $BaSO_4$ as reference. Raman spectra were collected at room temperature with a Jobin-Yvon T64000 triple-stage spectrograph with a spectral resolution of 2 cm^{-1}. The laser line at 325 nm of a He-Cd laser was used as an exciting source with an output of 25 mW. The power of the laser at the sample was about 3.0 mW. The 244 nm line from a Coherent Innova 300 Fred laser was used as an excitation source in the deep UV region. The power of the 244 nm line at the sample was below 1.0 mW.

Low-temperature nitrous oxide decomposition was carried out by heating an appropriate amount of catalyst in He to 1173 K followed by a step change from He to N_2O/He at 523 K. The amount of evolved N_2 was quantified by an online mass spectrometer.

Reactivity measurements

Reaction data were collected using a plug flow reactor operating at atmospheric pressure extensively described elsewhere (Ref. 12). For the oxidation of benzene to phenol by nitrous oxide, typically an amount of 0.1 g catalyst (sieve fraction 125 μm – 425 μm) was mixed with SiC. Benzene was fed to the reaction mixture by a liquid mass flow controller (Bronkhorst). The final feed mixture contained 1 vol.% benzene and 4 vol.% nitrous oxide in helium at a total flow rate of 100 $ml.min^{-1}$. The gas hourly space velocity was 30000 h^{-1}. All valves and most tubing of the reaction system was placed in an oven system and heated to 453 K to avoid condensation of

heavy product molecules. The gas-phase composition was determined by a combination of online gas chromatography (Hewlett-Packard GC-5890 equipped with an HP-5 column, FID) and a mass spectrometer system (Balzers TPG-215). The reaction products included phenol, water, carbon monoxide and carbon dioxide. We calculated the nitrous oxide and benzene conversions, the nitrous oxide selectivity (the fraction of oxygen atoms from nitrous oxide incorporated in phenol), the benzene selectivity (the fraction of benzene converted to phenol) and the rate of phenol formation. The carbon and nitrogen mass balances closed at 98% after prolonged reaction times.

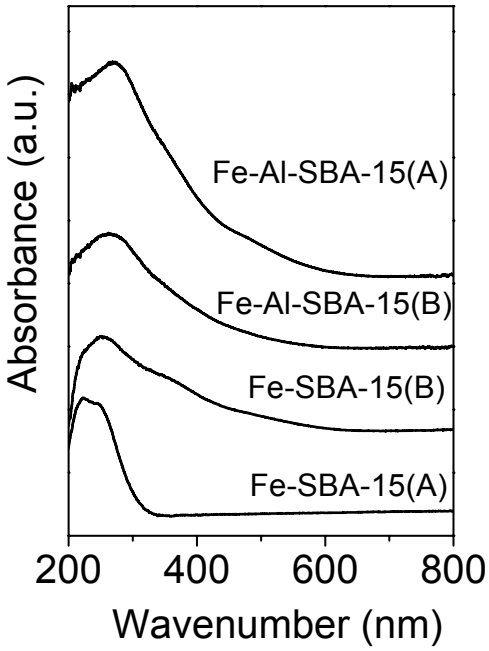

Figure S1. UV-Vis spectra for Fe-SBA-15(A and B) and Fe-Al-SBA-15 (A and B).

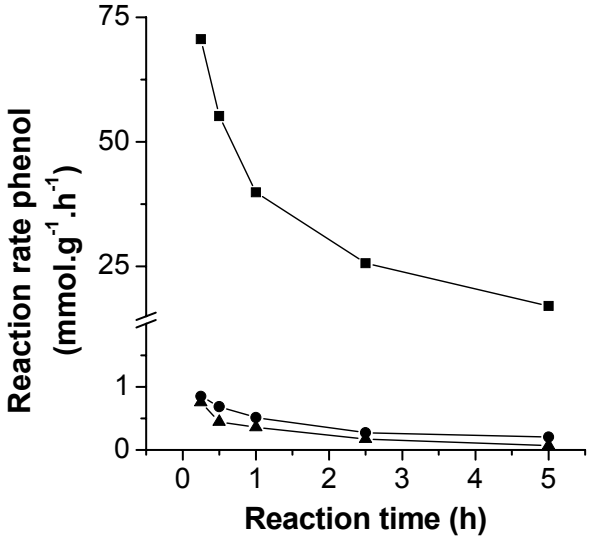

Figure S2. Reaction rate of phenol as a function of reaction time for calcined (▲) and steamed (●) Fe-Al-SBA-15(A) and steamed Fe/ZSM-5 (■).