

SUPPORTING INFORMATION FOR:

Iron chloride supported on pyridine-modified mesoporous silica: an efficient and reusable catalyst for the allylic oxidation of olefins with molecular oxygen

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1. Materials and instruments:

Porous silica (Tond AX₁, SiO₂ ≥ 95%, Surface area ≥ 190 m²·g⁻¹) was from Shanxi Tond Chemical Company. It was activated at 200 °C in muffle for 10 h before use. β-IP (β-IP ≥ 98%, α-IP ≤ 1.5%) was provided by Zhejiang NHU Company. The α-pinene, cyclohexene, 1-methyl-cyclohexene, and 1-phenyl-cyclohexene were from Acros organics. Other reagents and solvents were pure analytical grade materials purchased from commercial sources and were used without further purification unless otherwise indicated.

The metal content of the heterogeneous catalyst was obtained by HITACHI-180-80 atomic absorption spectrophotometer. The pore size and surface area analysis via N₂ adsorption evaluation were performed on an AUTOSORB-1-C apparatus. FT-IR spectra was recorded on a Bruker APEX-III spectrometer using KBr

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pellets in the 400-4000 cm^{-1} region. The purity of raw materials and products was analyzed using a Shang Feng GC-112A gas chromatography fitted with a SE-30 column (50 m, 0.025 μm diameters) and a flame ionization detector. The structure of products and by-products were further identified using a HP6890 GC/MS spectrometer by comparing retention times and fragmentation patterns with authentic samples.

2. Reuse procedure of pyridine in the synthesis of pyridine-modified silica.

When the activated silica was filtrated off, another 0.3 ml of pyridine was added into the mixture (Elemental analysis confirmed that about 0.3 ml of pyridine was consumed in the first recycle). Then, 2.0 g fresh silica was added in the mixture and was activated with the same procedure. In the experiment, the mixture was reused for 10 cycles. Elemental analysis measured the N content (%) and atomic absorption spectroscopy (AAS) measured the Fe content ($\text{mmol}\cdot\text{g}^{-1}$) for each cycle (See **Table S1**).

Table S1 The N and Fe content of the supported Fe(III)/SiO₂ catalysts ^a.

Cycle	1	2	3	4	5
N content (%)	2.38	2.29	2.33	2.35	2.34
Fe content ($\text{mmol}\cdot\text{g}^{-1}$)	4.94	4.71	4.80	4.75	4.90
Cycle	6	7	8	9	10
(N)%	2.31	2.37	2.27	2.40	2.33
N content (%)	4.79	4.99	4.82	5.03	4.86

^a the mixture of pyridine and ethanol was reused for 10 cycles.

3. Characterization of the Fe(III)/SiO₂ catalysts

1) BET analysis:

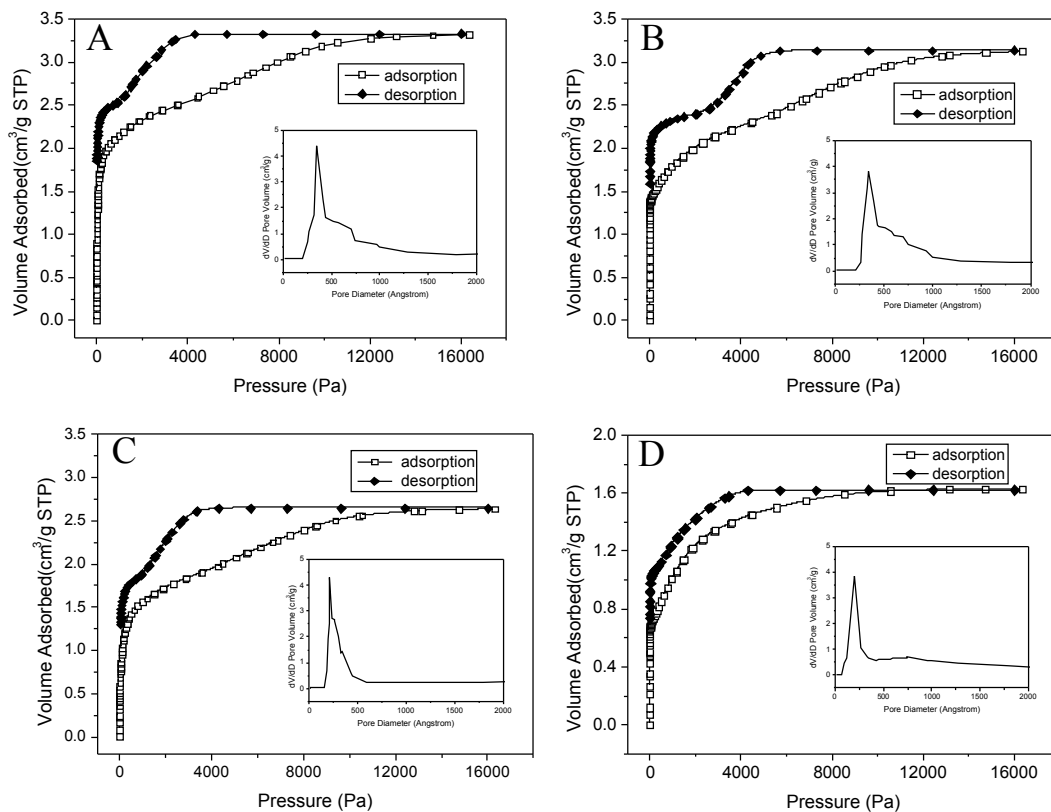


Fig. S1. N₂ adsorption-desorption isotherms and pore size distribution profiles of the porous and the immobilized catalysts: (A) porous silica; (B) porous silica immobilized iron chloride without pyridine; (C) porous silica immobilized iron chloride with pyridine; (D) the catalyst was recycled for four times.

2) SEM analysis:

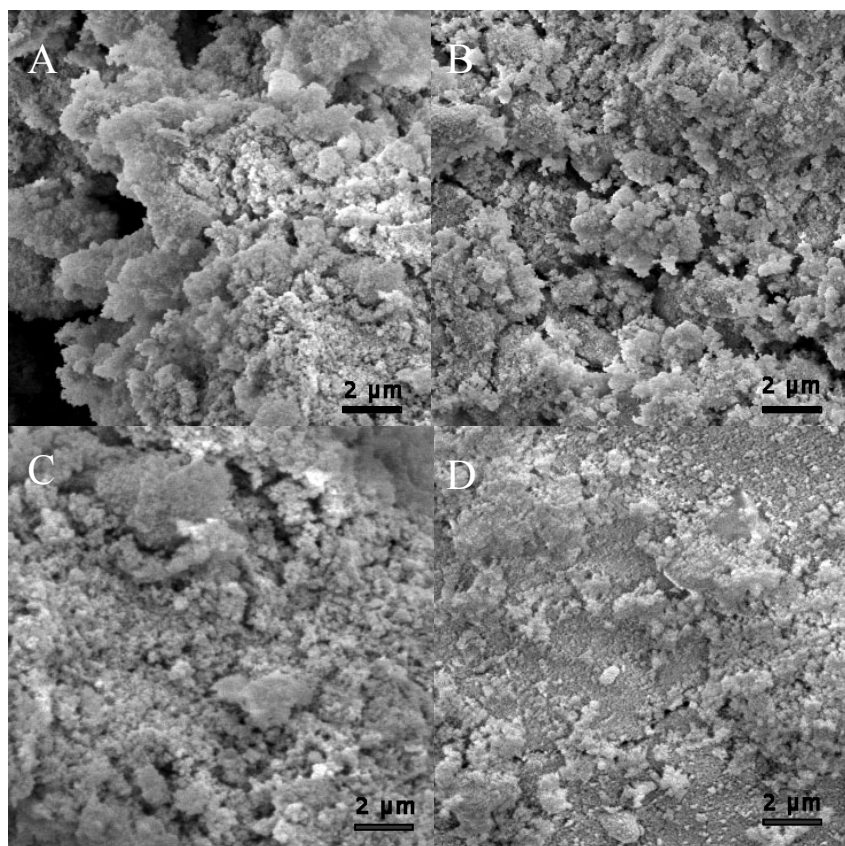


Fig. S2. SEM image analysis of the porous and the immobilized catalysts: (A) porous silica; (B) porous silica immobilized iron chloride without pyridine; (C) porous silica immobilized iron chloride with pyridine; (D) the catalyst was recycled for four times.

3) FT-IR spectroscopy:

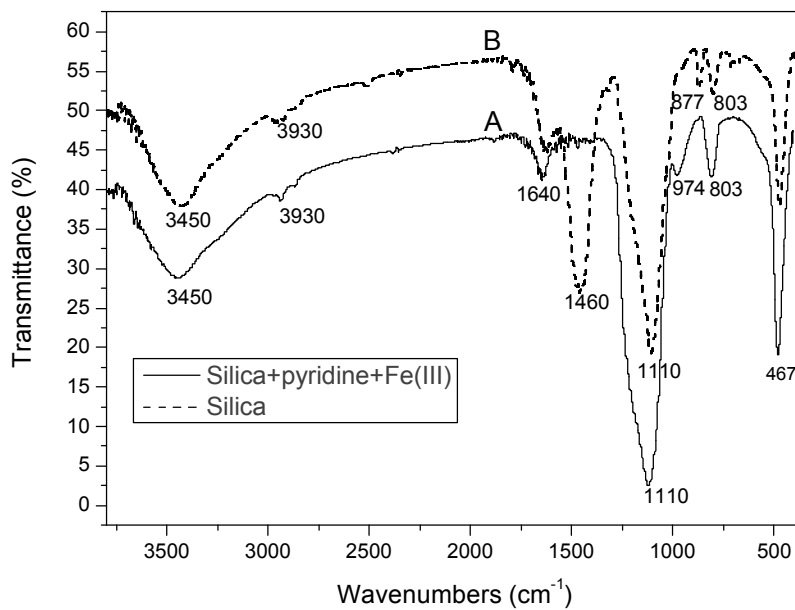


Fig. S3. FT-IR spectra of: (A) porous silica; (B) iron chloride immobilized on the pyridine-modified porous silica.