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Synthesis of mesoporous iron-incorporated silica-pillared clay and catalytic performance for phenol hydroxylation

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ABSTRACT

Fe-incorporated silica-pillared clays (Fe-SPCs) with ordered interlayer mesoporous structure have been synthesized through a new two-step procedure including the modification of the silica nano-pillars with potassium ferricyanide ($K_3Fe(CN)_6$) and successive calcination. X-ray diffraction, nitrogen adsorption–desorption, Fourier transform infrared spectra, X-ray fluorescence analyses, diffuse reflectance UV–vis spectra and X-ray absorption near-edge structure spectra were used to characterize the structures and the synthesizing mechanism of Fe-SPCs. Results show that all iron species were tetrahedrally coordinated with the interlayer silica nano-pillars, and the cationic surfactant molecule plays an important role in the intercalation of tetraethoxysilane and the introduction of iron into the intragallery silica framework. Moreover, the structural parameters of Fe-SPC can be adjusted by controlling the concentration of $K_3Fe(CN)_6$, as the concentration of $K_3Fe(CN)_6$ increases from 1 M to 2 M, the gallery height of Fe-SPC increases from 2.51 to 2.66 nm, while the Brunauer–Emmett–Teller (BET) surface area, pore volume and Barrett–Joyner–Halenda (BJH) pore size decrease from 856 to 794 m^2/g, 0.75 to 0.69 cm^3/g, and 2.2 to 2.0 nm, respectively. The Fe-SPCs show good catalytic activity in phenol hydroxylation using H_2O_2 as oxidant (phenol:H_2O_2 = 1:1, water), specifically, the phenol conversion is 46.2%, and the selectivity of dihydroxybenzenes is 70.6% at 343 K.

1. Introduction

Pillared interlayered clays (PILCs), a family of new porous materials, have attracted great attention, because these materials contain micropores that are larger than those of conventional zeolites, and thus exhibit new properties according to the nature of the pillars [1–3]. The most often used PILC is silica-pillared clay (SPC) owing to its hydrophobicity and good thermal stability [4,5]. However, SPC with single silica pillar lacks diverse functions. Incorporation of foreign atoms and organic functional groups into SPC frameworks has been found to be an effective strategy to widen its functional applications [6]. Recently, several metal-ion-doped SPCs, such as Ti-SPC [7], Al-SPC [8], and Ni/Co-SPC [9], have been synthesized.

It is well known that Fe-containing materials are good catalysts in oxidation–reduction reactions, such as phenol hydroxylation [10], Friedel–Crafts reaction [11], Fenton oxidation [12,13] and ethylbenzene dehydrogenation [14], etc. In order to get high resistance to leach in application, iron was often incorporated into various MCM frameworks; moreover, the tetrahedrally coordinated iron also affords excellent catalytic performance [15–18]. However, the existed synthesis methods of iron incorporated MCMs are complex (requiring a great deal of tetraethoxysilane and taking a long time), and the synthesized iron incorporated MCMs generally have poor hydrothermal stability, limiting their recycling use [19]. In contrast, SPC with an MCM-like porous silica structure between clay layers [20] shows a good thermal stability. More importantly, the main raw material is montmorillonite clay, which is environmentally friendly, naturally abundant and economic. In 2012 we gave the first report on incorporating iron into the silica pillars [21]. Unfortunately, there are still some Fe species formed out of the frameworks, and these Fe species tend to agglomerate during calcination, and thus hamper the active sites. Therefore, developing an alternative strategy to synthesize Fe-SPC without extra framework Fe atoms is a necessary and interesting topic.

This article presents a facile method to incorporate Fe into the intra-gallery tetrahedral silica framework by modifying the silica nano-pillar with potassium ferricyanide prior to calcination. The phase of iron oxides and mesoporous structure were investigated in detail. Their catalytic performance in hydroxylation of phenol, which is supposed to be sensitive to the framework iron species [22,23], was also evaluated.

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2. Experimental

2.1. Materials

The natural montmorillonite clay (MMT), of which an anhydrous structural (layer) formula of $[Si_{7.86}Al_{0.14}][Al_{2.84}Fe_{0.30}Mg_{0.86}]O_{20}(OH)_4$, was obtained from Inner Mongolia Autonomy (Tianhong Mining Company, China). Dodecyl dimethyl benzyl ammonium chloride (C_{12}DMBACl) (A.R.) was purchased from Tianjin Surfactants Company, China. Tetraethoxysilane (TEOS) (A.R.) and ammonia (25%) were got from Beijing Chemical Reagents Company, China. Potassium ferricyanide ($K_3Fe(CN)_6$) was purchased from Shanghai Chemical Reagent Company, China.

2.2. Synthesis of uncalcined SPC

MMT used was pre-treated using 1 N H_2SO_4 at 300 K for converting Na^+-MMT into H^+-MMT, followed by washing with water for three times and drying in an oven at 90 °C. During this acid treatment process, the iron contained in the layers of MMT was also removed completely. And then the obtained H^+-MMT (1.00 g) was added into 30 mL water to form a clay suspension.

C_{12}DMBACl was dissolved in ethanol to get a C_{12}DMBACl solution, to which TEOS was added and stirred for 0.5 h to form a clear solution. The solution was then slowly dropped into the clay suspension (the molar ratio of clay, surfactant, TEOS, ethanol and water was 1:2:30:1.2:250). After stirred for 0.5 h, the mixture was filtered to remove extra aqueous TEOS, and the product was the TEOS-intercalated clay.

The interlamellar hydrolysis of above TEOS-intercalated clay was conducted in an ammonia solution (pH = 10). The reaction was conducted by dispersing the TEOS-intercalated clay (1.00 g) in an ammonia solution (50 mL) with stirring for 2 h at room temperature. The product was purified by filtration, and dried in an oven at 90 °C. The prepared sample was denoted as uncalcined SPC.

2.3. Synthesis of Fe-SPC

1.0 g uncalcined SPCs were dispersed into 50 mL of 1 M $K_3Fe(CN)_6$ aqueous solution under stirring at room temperature for 6 h. Then, the obtained product was filtered, washed with deionized water, dried (the sample before calcined was named as uncalcined Fe-SPC), and finally calcined at 550 °C for 6 h in a flow of air with a heating rate of 2 °C/min. The obtained sample was denoted as Fe-SPC-1. The Fe-SPC-2 was synthesized using 2 M $K_3Fe(CN)_6$ aqueous solution under the same condition.

2.4. Synthesis of comparable sample

In order to compare the catalytic properties of Fe-SPCs prepared in the present work with that reported before (coded as Fe-SPC-c) [21], Fe-SPC-c with a lamellar structure was synthesized. Besides the presence of tetrahedral coordination of iron ions in silica framework, some extra-framework iron species were also formed in the Fe-SPC-c. The structural parameters of Fe-SPC-c are; the gallery height is 2.36 nm; the BET surface area, pore volume, and pore size are 615 m^2/g, 0.67 cm^3/g, and 1.8 nm, respectively; the content of Fe_2O_3 is 6.37%.

2.5. Catalytic performance testing for the phenol hydroxylation

The hydroxylation of phenol was carried out at 343 K in a three-necked flask (50 mL) equipped with a reflux condenser and a temperature controllable water bath. In a standard reaction, 0.47 g of phenol and 0.03 g of Fe-SPC sample were added into 15 mL of deionized water. H_2O_2 (the mole ratio of phenol to H_2O_2 was 1:1) was added into the flask and allowed to react for 3 h with stirring [24]. The liquid products were separated and analyzed by gas chromatography (GC). Phenol, catechol (CAT), hydroquinone (HQ) and benzoquinone (BQ) in products were also identified using gas chromatography–mass spectrometry (GC–MS).

The conversion of the phenol, and the selectivity of dihydroxybenzenes (CAT and HQ) were defined as follows:

$$\textit{The conversion of phenol (Xphenol)}: X_{\text{phenol}} = \frac{c^0_{\text{phenol}} - c_{\text{phenol}}}{c^0_{\text{phenol}}} \times 100\%$$

$$\textit{The selectivity of CAT (SCAT)}: S_{\text{CAT}} = \frac{c_{\text{CAT}} \times M_{\text{Phenol}}/M_{\text{CAT}}}{c^0_{\text{phenol}} - c_{\text{phenol}}} \times 100$$

$$\textit{The selectivity of HQ (SHQ)}: S_{\text{HQ}} = \frac{c_{\text{HQ}} \times \left(M_{\text{phenol}}/M_{\text{HQ}}\right)}{c^0_{\text{phenol}} - c_{\text{phenol}}} \times 100\%$$

$$\textit{The selectivity of dihydroxybenzenes}\,(S_{\text{diphenol}}): S_{\text{diphenol}} = S_{\text{CAT}} + S_{\text{HQ}}$$

where c^0 and c are the initial and final concentrations of relative substance, respectively. M is the relative molecular mass.

The used catalysts were obtained by filtration and then dried in an oven at 90 °C for 4 h. And then the dried powder catalysts were calcined at 300 °C for 3 h in a flow of air with a heating rate of 2 °C/min. The reclaimed catalysts were used for recycle catalytic performance.

2.6. Characterization

X-ray diffraction (XRD) was performed on a Rigaku D/Max 2500 VBZ+/PC diffractometer (Rigaku Company, Japan) using Cu Kα radiation (40 kV, 50 mA) in the range between 0.5 and 10°, and Cu Kα radiation (40 kV, 200 mA) in the range between 3 and 90°.

X-ray fluorescence analysis (XRF) was performed on a Magix-601 X-ray fluorescence spectrometer (Philips, Japan). The quantitative results were used to analyze elements and calculate the heteroatom content of each sample.

The N_2 adsorption–desorption isotherms were obtained using a Micromeritics ASAP 2000 instrument (Micromeritics Company, USA). The samples were degassed at 115 °C for 12 h before the measurements. The specific surface area (S_{BET}) was estimated by the Brunauer–Emmett–Teller (BET) equation, while the radius distribution of pores and the mesopore analysis were obtained from the adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method.

Fourier transform infrared (FTIR) spectra from 4000 to 400 cm^{-1} were recorded on a Vector 22 spectrometer (Bruker Company, Germany) using a KBr disk.

The diffuse reflectance UV–vis (DR UV–vis) spectra over the range of 200–800 nm were recorded using a UV2401PC UV/Vis recording spectrophotometer (Shimadzu Company, Japan) equipped with a diffuse reflectance attachment using $BaSO_4$ as the background standard.

X-ray absorption near-edge structure (XANES) spectroscopy analysis of the Fe K-edge was performed at the U7C beam line in the National Synchrotron Radiation Laboratory (NSRL) of China.

GC was performed on a HP5890 instrument (Hewlett-Packard Company, USA) equipped with a SPB-50 coated capillary column and an FID detector was used.

GC–MS system consisted of an HP 5890 Series II gas chromatograph with a Hewlett-Packard 5972 mass spectrometer (Hewlett-Packard company, USA) fitted with HP-5MS column (30 m × 0.25 mm).

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