



Short communication

Direct synthesis, characterization and catalytic performance of Al-Fe-SBA-15 materials in selective catalytic reduction of NO with NH₃



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ARTICLE INFO

Article history:

Received 29 July 2015

Received in revised form 15 October 2015

Accepted 17 October 2015

Available online 19 October 2015

Keywords:

Al-Fe-SBA-15

Mesoporous

NH₃-SCR

Brønsted acid

ABSTRACT

A series of Al-Fe-SBA-15 catalysts were synthesized by microwave methods with various iron and aluminum contents. The samples were characterized by XRD, SEM, TEM, BET, NH₃-TPD, FT-IR. Results indicated that all the samples that exhibited well-ordered hexagonal arrays of mesopores, disk-like and petal-like morphologies were observed for different catalysts. NH₃-TPD indicated that the introduction of Al results in the generation of Brønsted acid originated from Al-OH. Brønsted acid played important roles in the selective catalytic reduction of NO by NH₃. NO_x conversion over Al-Fe-SBA-15 samples increased rapidly as temperature increased and achieved 95% at about 360 °C.

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1. Introduction

Nitrogen oxides (NO, NO₂ and N₂O) in the exhaust gases from combustion of fossil fuels remain a major source for air pollution. Selective catalytic reduction (SCR) of NO_x with ammonia is current efficient technology for reducing nitrogen oxides emissions from power plants [1–3]. Many transition metal (Fe, Cu, Co, etc.) doped zeolites (ZSM-5, MOR, BEA, FER) have been reported to be active for NH₃-SCR [4,5]. Among all of these zeolites, newly achieved mesoporous SBA-15 receives rapid attention due to its narrow and controllable pore size, high surface area and thermal stability [6,7]. However, pure silica framework of SBA-15 is chemically inert for SCR reaction due to lack of acid sites, therefore, the incorporation of transition metals is an efficient way to improve the activity of SBA-15 [8,9].

It is well known that Fe, Al doped catalysts showed excellent properties for NH₃-SCR. Some reports demonstrated that monomeric and bridged iron species could contribute to NH₃-SCR for iron-zeolites [10–12]. Oppositely, Joyner and Stockenhuber [13] suggested that it was clustered iron species that played a fatal role in NH₃-SCR, but the function of iron species is still controversial and needs a further research. However, the existence of aluminum also had an obvious effect on Fe in zeolite. Ying Li et al. [14] proposed that the simultaneous incorporation of Fe and Al could lead to an increase of Fe content in the final mesoporous silica material compared to the aluminum-free case.

Generally, a great number of methods, such as incipient wetness impregnation, direct synthesis, and ion exchange metal-organic chemical vapor deposition [15–22] have been used for the synthesis of transition

metal incorporation SBA-15. A new microwave synthesis method has attracted great attention because of the distinct superior (homogeneous thermal, dispersed system and high efficiency) to conventional hydrothermal synthesis. In this work, Fe-Al-SBA-15 catalysts with various iron and aluminum contents were prepared by microwave method and characterized by variety of techniques.

2. Experimental

2.1. Sample synthesis

Al-Fe-SBA-15 samples with different iron-silica ratio (Fe: Si = 0.04, 0.07, 0.10) and alumina-silica ratio (Al: Si = 0.04, 0.07, 0.10) were synthesized using Pluronic P123 as structure-directing agent, and tetraethyl orthosilicate (TEOS) as the silicate source under acidic conditions. A typical synthesis procedure was as follows: 4 g P123 was dissolved into 140 mL HCl solution at pH value of 1.5 (solution A). 6.53 g TEOS and stoichiometric of iron nitrate and aluminum isopropoxide (Fe: Si = 0.04, 0.07, 0.10, Al: Si = 0.04, 0.07) were mixed with 10 mL deionized water to obtain solution B. Solution B was stirred at room temperature for about 20 min to get a clear solution, then it was added dropwise to solution A and further maintained under microwave condition of 40 °C for 4 h. The gel solutions were transferred into a Teflon bottle and heated at 100 °C for 24 h. After cooling to room temperature, Al-Fe-SBA-15 was recovered by filtering and drying at room temperature in air. Then, all samples were calcined at 550 °C to remove the copolymer template. The catalysts prepared in this way were denoted as Al(x)-Fe(y)-SBA-15, where x and y represented the alumina-silica ratio and iron-silica ratio respectively.

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2.2. Characterizations

Samples were compactly flattened on a glass slides for XRD characterization, X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Advance diffractometer using Cu K α radiation. The scanning electron microscope (SEM) images were obtained with an LEO-1530VP scanning electron microscope. Transmission electron micrographs (TEM) were acquired with a Philips CM30UT electron microscope. Before NH₃-TPD characterization, about 0.3 g 40–60 mesh catalyst was loaded in U-tube. Temperature-programmed desorption (TPD) was carried out on automated chemisorption analyzer (Quantachrome Instruments), TPD was performed by ramping the temperature at 10 K/min to 700 °C in He (50 mL/min), desorption of NH₃ was detected by a thermal conductivity detector (TCD). Before FT-IR characterization, appropriate catalyst was grind mixed with potassium bromide together in a mortar, then pressed by tableting machine, and the FT-IR spectra were obtained using a diffuse reflectance accessory connected to a FT-IR spectrometer (Thermo Nicolet IS10).

2.3. Activity test

The SCR reaction was evaluated in a fixed-bed reactor. 0.5 mL sample was put in a reaction tube and placed for 2 h in simulated flue gas. The gas mixture contained 1000 ppm NO, 1000 ppm NH₃, 5% O₂, with N₂ used as balance gas. Catalyst activity was recorded by measuring the inlet and outlet gas using a flue gas analyzer (Kane International Limited) at temperatures between 150 and 480 °C. The conversion was calculated according to the following equation:

$$\text{NO}_x \text{ conversion} = \frac{([\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}})}{[\text{NO}_x]_{\text{in}}} \times 100\%$$

3. Results and discussion

3.1. Structure and morphology

Fig. 1A shows the small angle XRD patterns of Fe-SBA-15. For all samples in Fig. 1A, three well-resolved peaks (100), (110) and (200) which are characteristic of mesoporous material can clearly be observed [23]. Table 1 reveals that as the Fe content increase, diffraction angle obviously moves to lower angle, implying the dilation of the structure. Considering Fe–O bond length (0.197 nm) longer than Si–O bond length (0.161 nm), it can be inferred that Fe species may be incorporated into the framework of SBA-15. At a higher angle of XRD patterns (Fig. S1 in Supplementary material), no characteristic peaks of crystalline Fe₂O₃ have been observed, which suggests that Fe species might be in the framework or highly dispersed on the surface of SBA-15.

Table 1
Description of different catalysts.

Samples	100			110		200
	2 θ /°	d ₁₀₀ /nm	a ₀ /nm	2 θ /°	2 θ /°	
Fe(0.04)-SBA-15	0.8672	10.14	11.71	1.4839	1.7100	
Fe(0.07)-SBA-15	0.8467	10.43	12.04	1.4633	1.6483	
Fe(0.10)-SBA-15	0.8467	10.43	12.04	1.4222	1.6483	
Al(0.04)-Fe(0.03)-SBA-15	1.0933	8.08	9.33	1.6278	1.8539	
Al(0.07)-Fe(0.03)-SBA-15	1.0111	8.74	10.09	1.5455	1.7305	

a₀: unit cell parameter (a₀ = 2 × d₁₀₀/3^{1/2}).

Fig. 1B shows the XRD patterns of Al-Fe-SBA-15. Diffraction peaks can be observed, confirming the integrity of mesoporous structure after introduction of Al. When Al/Si increased from 0.04 to 0.07 (Fig. 1B a–b), peak shift could be found from 1.09° to 1.01°, considering Al–O bond (0.175 nm) larger than Si–O bond (0.161 nm), demonstrating that Al has been mainly incorporated into the framework of SBA-15, leading to the increase of interplanar spacing from 8.08 nm to 8.74 nm (see Table 1). Small angle X-ray diffraction peak is not observed when Al content increased to 0.10, inferring that too much aluminum could influence the mesoporous structure of SBA-15.

The SEM micrographs of Al-Fe-SBA-15 are shown in Fig. 2. Fe(0.04)-SBA-15 samples (A and B) exhibit a typical disk-like morphology with a diameter about 1.5 μ m. However, as can be seen (C and D), the morphology of Al(0.07)-Fe(0.03)-SBA-15 samples is completely different, the samples are constituted by “petal-like” particles with length of about 30 μ m, and these particles are constituted by a large number of small slices with thickness of about 200 nm.

The structural order of the samples can be directly observed by TEM. Fig. 3A–C shows the TEM images of Fe-SBA-15. Fe-SBA-15 exhibits disk-like morphology and well-ordered hexagonal arrays of mesopores (Fig. 3A and B), Fe_xO_y clusters or Fe₂O₃ particles (see UV–vis analysis in Supplementary material) on surface of Fe(0.07)-SBA-15 sample (Fig. 3C) are more than Fe(0.04)-SBA-15 (Fig. 3B), indicating that Fe mainly existed in the form of isolated framework Fe³⁺ ions when Fe/Si was 0.04, Fe_xO_y clusters and Fe₂O₃ particles generated when Fe content increased to 0.07. Integrity of mesoporous structure can still be maintained after introduction of Al (Fig. 3D and E), gradually clear mesoporous structure and dilated pore diameter with Al content increasing to 0.07 suggested that most aluminum species have been introduced into the framework of SBA-15 because Al³⁺ was larger than Si⁴⁺.

Fig. S3 shows the N₂ adsorption–desorption isotherms and pore size distributions of catalysts. The rapid increase in adsorption capacity at relative lower pressure (P/P₀ < 0.1) was assigned to N₂ monolayer adsorption on the micropores of siliceous walls of sample, and this

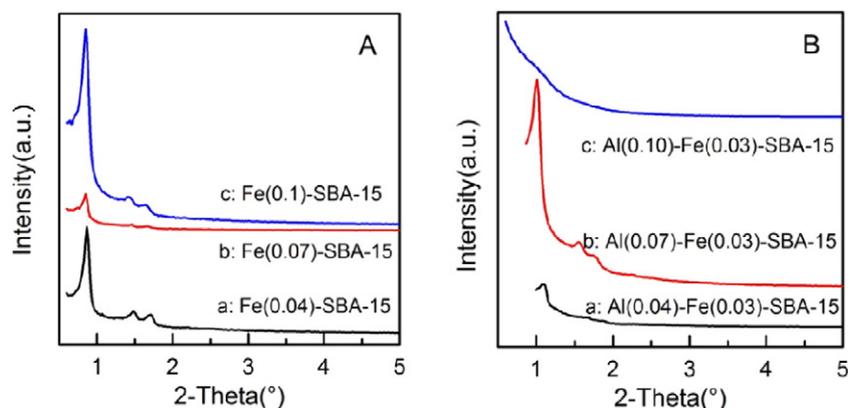


Fig. 1. Small angle X-ray diffraction patterns of catalysts.

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