



Improved performance of hierarchical Fe-ZSM-5 in the direct oxidation of benzene to phenol by N₂O



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ABSTRACT

Hierarchical Fe-ZSM-5 zeolites were directly synthesized from a zeolitic synthesis system in the presence of a silane coupling agent 3-glycidoxypropyltrimethoxysilane (GPTMS). The structure and morphology of the hierarchical Fe-ZSM-5 synthesized with different amount of GPTMS were characterized by XRD, SEM, TEM, and N₂ adsorption-desorption techniques. UV–vis and NH₃-TPD were used to investigate the state of iron species and acidity, respectively. The steaming activated hierarchical Fe-ZSM-5 were used as catalysts in the direct oxidation of benzene to phenol (BTOP) with N₂O as oxidant, showing an improved performance in terms of both activity and stability compared to Fe-ZSM-5 synthesized in the absence of GPTMS. A comparison study on the *n*-butane uptakes in Fe-ZSM-5 zeolites indicated the internal mass-transfer limitations of the hierarchical Fe-ZSM-5 zeolites were significantly improved.

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1. Introduction

Phenol, as an important industrial intermediate, finds its wide applications in the production of many chemicals such as bisphenol A, phenolic resins, caprolactam, alkyl phenols, adipic acid, and so on [1]. Currently, the dominant production route is the partial oxidation of cumene via the Hock rearrangement with acetone being co-produced [2]. As a result, the economy of the above process is governed by the demand for both phenol and the co-produced acetone.

An attractive alternative to produce phenol is a so-called direct oxidation of benzene to phenol (BTOP) with nitrous oxide (N₂O) as the oxidizing agent via the reaction: C₆H₆ + N₂O → C₆H₅OH + N₂ [3,4]. A most selective catalyst is Fe-ZSM-5 zeolite, over which the selectivity for phenol is nearly 100% [4–8]. However, as well known, Fe-ZSM-5 zeolite is a typical microporous material, in which strong mass transfer limitations are encountered. The slow diffusivity of benzene and phenol is inclined to the formation of coke in the zeolite, resulting in severe deactivation due to the

micropore blockage [9–14]. Reduction of the reaction temperatures could ease the coke formation [15], which can be achieved by improving of the activity of Fe-ZSM-5 through steaming activation [16,17]. However, the improvement is restricted to the limitations of Fe species content in zeolite. The efficient way to retard the deactivation is to enhance the mass transport in zeolite by introducing multiple pore systems to zeolites [18–23]. Previous work has shown that the hierarchically structured micro-/mesoporous Fe-ZSM-5 zeolite can be obtained via desilication of Fe-ZSM-5 crystals in alkaline medium. Improved performance of the meso-Fe-ZSM-5 zeolites in the BTOP reaction in terms of both activity and stability was observed due to the significant enhancement of the internal mass-transfer limitations [24]. However, the extra-framework Fe³⁺ species, i.e. the active sites in the BTOP reaction, might be meanwhile washed away during the alkaline treatment [24,25]. Additionally, the efficiency of the alkaline treatment is restricted to the range of the Si/Al ratio of zeolite [18].

Direct synthesis of hierarchical Fe-ZSM-5 zeolite catalysts have been reported by adding an amphiphilic organosilane [3-(trimethoxysilyl)propyl]octadecyldimethyl ammoniumchloride (TPOAC) to a Fe-ZSM-5 synthesis gel, showing a much lower deactivation rate compared to conventional Fe-ZSM-5 [26–28]. Recently, by

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using simple silane coupling agents of 3-aminopropyl-triethoxysilane (APTES) and 3-glycidioxypropyltrimethoxysilane (GPTMS) as mesoporegens, we developed a facile method to synthesize hierarchical ZSM-5 zeolites. The silane coupling agent drives the formation of microspheres consisting of ZSM-5 crystallites and improves the mesoporosity of ZSM-5 samples [29,30].

In this contribution, we extended the silane coupling agent aided method to the synthesis of hierarchical Fe-ZSM-5 and investigated the catalytic performance in the BTOP reaction. The enhanced mass transport in the hierarchical Fe-ZSM-5 zeolite accounts for the improvements in the BTOP reaction, confirmed by *n*-butane uptake experiments.

2. Experimental

2.1. Materials

Tetrapropylammoniumbromide (TPABr, 98%) was purchased from Aladdin Industrial Inc. Water glass (26.5wt% SiO₂ and 10.6wt% Na₂O) and 3-glycidioxypropyltrimethoxysilane(GPTMS, 98%) were purchased from Sigma–Aldrich Co., Ltd. Aluminum sulfate [Al₂(SO₄)₃·18H₂O, A.R.], ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O, AR], and benzene (C₆H₆, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis

The synthesis was according to ref. [30] except the addition of Fe(NO₃)₃. In brief, TPABr was dissolved into deionized water followed by dropwise addition of water glass and GPTMS. After vigorous stirring for 3 h, 5.0 mol/l H₂SO₄ was added dropwise to form a hydrogel, then 0.2 mol/l Fe(NO₃)₃ solution was added. Finally, Al₂(SO₄)₃ solution was added to make the final composition in molar ratio of 0.07 Na₂O: 1 SiO₂: 0.02 Al₂O₃: 25 H₂O: 0.2 TPABr: *x* GPTMS: 0.005 Fe. After stirring for another 3 h, the mixture was transferred into a Teflon-lined autoclave and heated at 383 K for 2 d and then 453 K for 4 d. Then the product was filtered, washed with deionized water, and dried at 383 K overnight. The final white powder was referred to as FZ-G_{*x*}, where *x* is the amount of GPTMS in the synthesis gel composition. All the as-synthesized samples were calcined at 823 K for 5 h to remove the organic species. The template free samples were ion exchanged with a 0.2 M NH₄NO₃ solution (liquid-to-solid ratio = 30:1 ml/g) for three times at 343 K. The ion-exchanged samples were calcined at 823 K for 5 h in order to get the H-form Fe-ZSM-5 zeolites. Afterwards, the H-form zeolites were activated in the flow of a mixture of nitrogen (30 ml/min) and steam (a partial pressure of 300 mbar) at atmospheric pressure and 823 K for 5 h in order to obtain the final Fe-ZSM-5 catalysts.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'PertPW 3040/60 diffractometer using CuK α radiation ($\lambda = 0.154$ nm) with generator voltage of 40 kV and current of 40 mA. The scanning step and dwelling time were set to 0.0167° and 20 s, respectively. Scanning electron microscopy (SEM) images were obtained using a HITACHIS-4800 microscope equipped with a field emission gun. The acceleration voltage was set to 5 kV. The samples were stuck on the observation holder by conductive tape and sprayed with gold vapor under high vacuum for about 20 s. Transmission electron microscopy (TEM) observations were carried out on a JEOL JEM-1200 working at 300 kV. The sample was diluted in ethanol to give a 1:5 volume ratio and sonicated for 10 min to prepare ethanol slurry, which was then dropped onto a Cu grid covered with a thin film of carbon. Nitrogen adsorption isotherms

were measured at 77 K using a Micromeritics ASAP 2020 analyzer. Prior to the measurements, the samples were degassed at 573 K for 8 h. The BET specific surface area were calculated using the relative pressure ranging from 0.1 to 0.3. The *t*-plot analysis based on de Boer thickness method was used to evaluate the micropore volume and external surface area. The total pore volume were calculated by the adsorption amount at the relative pressure of 0.98. Ultra-violet–visible spectroscopy (UV–vis) was recorded on a Thermo Nicolet Evolution 500 spectrometer against BaSO₄ under ambient conditions. Temperature-programmed desorption of NH₃ (NH₃-TPD) was carried out on a Micromeritics AutoChem II chemisorption analyzer with a TCD detector. Typically, about 50 mg of Fe-ZSM-5 sample was loaded in a quartz reactor and pretreated at 673 K in a He flow at 40 ml/min for 2 h. Then the reactor was heated to 773 K at a ramp of 10 K/min.

2.4. *n*-Butane uptakes

The uptakes of *n*-butane in Fe-ZSM-5 zeolites were measured using a NETZSCH STA 449C thermogravimetric analyzer (TGA) with an accuracy of 0.1 μ g. The amount of the zeolite crystals loaded in the sample cell was *ca.* 15 mg. Prior to the uptake experiments, the zeolite crystals were treated at 573 K in a He flow of 30 ml/min for 3 h to remove any impurities adsorbed. After the temperature was lowered and kept stable at 373 K, the He flow was shifted to a gas mixture (C₄H₁₀/He = 1/9) and then the data were collected for 1 h.

2.5. BTOP reaction

The direct oxidation of benzene to phenol (BTOP) was performed in a fixed-bed catalytic apparatus at 593 K and 101 kPa. Details of the reaction have been described elsewhere [24]. Prior to the reaction, the catalyst was pretreated in flowing He at 773 K for 1 h. Afterwards, the temperature was cooled down to 593 K and a feed stream of C₆H₆-N₂O-He (60 ml/min) with molar ratio of 1:1:28 was introduced through the catalyst bed with a total weight hourly space velocity (WHSV) of 18,000 ml g_{catal}⁻¹ h⁻¹. The concentrations of the outlet stream were periodically determined by an on-line GC (Agilent 6820) equipped with an FID detector and an OV-101 capillary column ($\Phi = 0.025$ mm, L = 50 m). The line connected the outlet and the GC was heated to 393 K to ensure the full gasification of flows before entering the GC.

3. Results and discussion

XRD patterns indicate the samples of FZ-G_{*x*} synthesized with different dosages of GPTMS (ranging from 0 to 0.15) show a typical MFI structure (Fig. 1). Additionally, no diffraction peak attributed to α -Fe₂O₃ (reflections at $2\theta = 33.2^\circ$ and 35.7°) or any other iron oxides are observed [31], indicating that Fe-ZSM-5 have been successfully synthesized. Intensity of the characteristic MFI structural diffraction peaks at 7.0–9.5° and 22.0–25.0° decreases and meanwhile the shape becomes broader as increasing the GPTMS dosage. According to the Scherrer equation, the peak at $2\theta = 7.9^\circ$ was used to calculate the crystallite sizes [perpendicular to plane (011)], which are 43.9, 42.1, 30.7, and 27.9 nm for FZ-G₀, FZ-G_{0.05}, FZ-G_{0.10}, and FZ-G_{0.15}, respectively. The silane coupling agent of GPTMS plays a retarding role in the crystallization, leading to the decline of the crystallinity and size of ZSM-5 [30].

From the SEM images (Fig. 2), one can see the changes of morphology with increasing the dosage of GPTMS. The sample of FZ-G₀ displays morphology of aggregations consisting of needle-like crystals (Fig. 2A). When GPTMS was used, the morphology of the synthesized Fe-ZSM-5 changes to spherical shape with diameter of about 1.2 μ m (Fig. 2B). A further increase of the amount of

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