



Fe/ZSM-5 zeolites for organic-pollutant removal in the gas phase: Effect of the iron source and loading



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ABSTRACT

In the present work, Fe/ZSM-5 zeolites were prepared by hydrothermal synthesis using two different iron sources as iron precursors: ammonium iron citrate (AIC) and iron chloride. The obtained catalysts were characterized using XRD, BET, SEM, FTIR, ICP and TPD-NH₃. The Fe/ZSM-5 that was synthesized with AIC showed a high BET surface area, eminent dispersion, greater Fe content, better crystallinity and low acidity than that synthesized with iron chloride. The prepared catalysts were tested for the adsorptive degradation of toluene and ethyl benzene in the gas phase. The consequence of different Fe sources of Fe/ZSM-5 on the catalytic removal of organic pollutants was observed in terms of toluene and ethylbenzene reduction. The catalytic tests were conducted in a tedler bag in the batch operation mode at atmospheric pressure and room temperature. The effect of the mass ratio of the Fe/Al component on ZSM-5 was also studied by varying the molar ratios of Fe in the starting mixture gel during hydrothermal synthesis. The results in this manuscript show that the nature of the iron source and pollutant and Fe/Al ratio strongly affect the adsorptive catalytic removal capacity of the materials, which affects the formation of ultimate mineralized product CO₂. The optimal molar ratio of Fe₂O₃ in the starting gel was found to be 2 mol, which makes it a promising catalyst.

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1. Introduction

Volatile organic carbons (VOCs) are the main cause of air pollution, of which toluene and ethylbenzene are considered to be representatives. In many countries, environmental regulations have been established to strictly regulate the emissions of VOC [1]. Adsorptive catalytic porous materials are important because of their functions as adsorbents and catalysts for air-cleaning and decontamination processes. When catalysts such as TiO₂, Fe₂O₃ and an adsorbing material are combined, their properties also combine in the porous material, which creates a well-known synergistic effect that enhances the reaction rate. This effect occurs because of the interface between the adsorbent phase and catalyst phase, which coexist in the material [2]. The proper selection of adsorbents increases the thorough dispersion of the catalyst, surface area, pore volume and low acidity, which are prime

parameters for pollutant removal. For this purpose, ZSM-5 zeolite with hetero atoms was proven to facilitate both catalysis and adsorption [3–6]. A number of science workers studied the transition metal ZSM-5 considering their role as catalysts [7,8–10]. Overall, the reactivity of the Fe/ZSM-5 catalyst is based on the amount of Fe species and its dispersion in the MFI (Namely, (M) for Mobil (FI) for Five). So MFI (Mobil Five Structure has five membered rings) structure of ZSM-5.

Our previous studies have presented that Fe/ZSM-5 zeolites have improved adsorptive catalytic ability for the removal of phenol from water and good recyclability. Considering these results, a rational presumption is that the use of a ZSM-5 adsorbent, which has a high surface area and good pore volume, can enhance the reaction rate of Fe/ZSM-5 material to destroy volatile organic carbon (VOCs) in the gas phase [11]. In addition, ZSM-5 zeolite is an important crystalline mineral of aluminosilicates with high-temperature stability and excellent adsorption. It has well-defined pores, and the channel system enables its shape-selective properties.

In addition, few available studies in the literature address the air-cleaning applications of Fe/ZSM-5 at room temperature and

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pressure [12–15]. The application of catalytic oxidation to mitigate gaseous contaminants may be restricted because of high humidity, notably a low reactant concentration, and the formation of undesired products [15]. Therefore, coupling can be used in one step by using Fe/ZSM-5 zeolite adsorbents, which can enhance the catalytic oxidation and subsequent adsorption. Concurrently, catalytic regeneration of the material may also occur [2,16–19].

Different researchers have studied the catalytic removal of organic molecules, toluene and benzene in the water and gas phases. To the best of our knowledge, the optimization of ZSM-5/Fe₂O₃ in terms of the molar composition in the starting gel and its effect on the adsorptive catalytic properties to remove typical indoor air contaminants, such as toluene and ethylbenzene, in the gas phase in the presence of indoor humidity have not been mentioned.

In this study, the catalytic adsorptive performance of different ZSM-5/Fe₂O₃ zeolites for the removal of toluene and ethylbenzene from the air is assessed. The optimization of Fe₂O₃ in the starting gel in terms of AIC and iron chloride was correlated to the catalytic and physicochemical properties of ZSM-5 zeolites.

2. Experimental

2.1. Adsorptive catalyst preparation

The zeolite material was synthesized as follows. Silica sol. (SiO₂ 40%), sodium hydroxide (NaOH), sodium aluminate (NaAlO₂), H₂O and tetrapropylammonium hydroxide (TPAOH) were used to prepared ZSM-5 as reported in the literature with little modification [20,21]. In our study, ZSM-5 was formed by dissolving 0.7481 g of NaAlO₂ and 1.5968 g of NaOH in 65 mL of H₂O in one plastic boat.

The measured volume of silica sol was placed in a beaker, and the measured volume of TPAOH was added drop-wise with the previously mixed solution into the silica sol with stirring. The molar composition of the mixture gel was: 1 Al₂O₃: 50.4 SiO₂: 6.2 Na₂O: 1.5 TPAOH: 1248 H₂O. The mixture solution was aged at 50 °C temperature and 200 rpm stirring in an incubator for 3 days. Then, the mixture was shifted to a Teflon-lined steel autoclave for a hydrothermal reaction at 180 °C under autogenous pressure for three days. Subsequently, the material was collected, filtered and washed until the filtrate pH reached 8.0. The solid material was dried at 100 °C for 5 h in an air-circulated oven. Then, this dried material was calcined at 550 °C for 6 h in an air-flowing furnace and thoroughly characterized. The general synthesis procedure was similar to that in reference [21]. The sample was named Z1.

Fe/ZSM-5 was prepared using two methods. First, in a typical in situ synthesis process, all of the steps were similar to the described synthesis of ZSM-5; the only difference was the calculated

amounts of AIC (Ammonium iron citrate is a chelate compound, which is soluble even at high pH 8–10) and FeCl₃·6H₂O 4, each of which was separately dissolved in 20 mL of H₂O and subsequently mixed with silica sol and other solutions with continuous stirring. The samples formed with 1–3 molar ratios of iron sources AIC and FeCl₃ were named Z2, Z3, and Z4 and Z5, Z6, and Z7, respectively, as shown in Table 1.

2.2. Characterization

The crystalline and MFI (Mobil Five) structure of ZSM-5 materials were studied with a Rigaku D/Max-2500 X-ray diffractometer. The instrument was equipped with Cu K α and a Ni filter. A scanning speed of 3°/min was applied to gather the diffraction patterns in the 2 θ angle range of 5–50°. FTIR analysis was performed with a Perkin Elmer Fourier transform infrared (FTIR) spectrometer with KBR pellets to indicate the presence of double ring characteristics and iron in the ZSM-5 zeolites. The spectra were recorded with a single-beam spectrometer with 60 added scans at a 2 cm⁻¹ resolution. A Perkin Elmer (Optima 7300 DV) inductively coupled plasma optical emission spectrometer (ICP-OES) was applied to measure the total Fe content in the materials. The total surface area (BET) was obtained using the Brunauer-Emmett-Teller method after the N₂ adsorption and desorption isotherm was measured using a Micromeritics TriStar II 3020 at 77 K. The ZSM-5 zeolite surface morphology was analysed using a scanning electron microscope (SEM) (Hitachi S-4800, Japan). EDX mapping was also performed for the prepared samples using a TEM (transmission electron microscope). A temperature programmed desorption of ammonia (NH₃-TPD) analysis was performed in the temperature range of 30–600 °C for the prepared materials to determine the acidity strengths. The ammonia molecules desorbed from the zeolites were quantified using a mass spectrometer, which was connected to the microreactor outlet with a heated line. A linear heating rate of 10 °C/min in a flow of pure helium (100 mL/min) was maintained for the desorption.

2.3. VOC removal tests

The removal performance was conducted in the batch mode in a transparent tedlar bag with size of 1–10 L. First, 1 mg of Fe/ZSM-5/7 mL of VOC was used as an adsorbent throughout the entire experiments. Gas cylinders (Air, liquid Australia) with fixed 50 ppm concentrations of toluene/N₂ and ethylbenzene/N₂ were used as the VOC feed. The catalytic material was pre-heated at 105 °C for 24 h in an air-circulated oven to remove any moisture. Then, the VOC mixture and catalyst were sequentially introduced into the reactor. The VOC removal process proceeded, reduced the VOC

Table 1
Physicochemical properties of the reference and prepared materials.

Detail	Added metals (wt. %)		ICP (wt.%)			BET (m ² /g)	Pore Volume (cm ³ /g)	micro (cm ³ /g)	Meso (cm ³ /g)	Pore Size (nm)	Acidity (mmol/g)	Adsorption (%)	
	Si/Al	Fe/Al	Si/Al	Fe/Al	Si/Fe							T	E
Z1 ZSM-5 Ref.	36.00	–	35.24	0.03	1174	400	0.1348	0.114	0.020	1.98	2.21	65	77
Z2 ZSM-5(AIC)	36.00	2.60	50.27	2.13	23.60	340	0.1426	0.104	0.039	2.10	2.50	91	95
Z3 ZSM-5(AIC)	36.00	5.20	72.38	2.30	31.46	250	0.1434	0.095	0.048	2.29	2.11	75	71
Z4 ZSM-5(AIC)	36.00	7.50	63.71	2.84	22.43	212	0.1613	0.082	0.079	3.04	1.86	32	53
Z5 ZSM-5 (FeCl ₃)	36.00	2.60	39.34	1.49	26.40	190	0.061	0.030	0.031	3.00	3.50	58	83
Z6 ZSM-5 (FeCl ₃)	36.00	5.20	8.24	3.71	2.22	166	0.3430	0.059	0.248	7.34	1.40	46	51
Z7 ZSM-5 (FeCl ₃)	36.00	7.50	6.14	4.74	1.30	93	0.0704	0.030	0.040	23.3	1.01	17	22

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