



Short communication

A facile strategy for preparation of phosphorus modified HZSM-5 shape-selective catalysts and its performances in disproportionation of toluene



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ABSTRACT

The phosphorous modified HZSM-5 catalysts were prepared by using phosphoric acid as the precursor with the addition of ethanol during the impregnation process and their shape-selective performances in the synthesis of *p*-xylene by disproportionation of toluene were investigated. An excellent *para*-selectivity along with a relatively high catalytic activity was achieved over the phosphorous modified HZSM-5 catalysts. The addition of ethanol during the impregnation process promotes the transition of phosphoric acid to phosphate, which accomplished the cover of the external acid sites and the reserve of the acid sites in the pores of HZSM-5 zeolite after phosphorous modification.

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1. Introduction

p-Xylene, one of the most important aromatic compounds, is widely used as a raw material for the manufacture of polyesters [1]. ZSM-5 zeolite is the most suitable catalyst for the synthesis of *p*-xylene because of its 10-membered ring channel well fitted to the molecular dimensions of *p*-xylene [2]. However, in most cases, the concentrations of the xylene isomers produced over parent ZSM-5 zeolite were close to the thermodynamic equilibrium ratios (23.5% *p*-xylene, 52.1% *m*-xylene and 24.4% *o*-xylene) [3]. This can be ascribed to the acidic sites on the external surface of ZSM-5 zeolite, which cause some side reactions and diminish the *para*-selectivity [4,5]. To obtain high *para*-selectivity, it is necessary to cover the acid sites on the external surface of zeolites. A number of modification techniques have been reported, such as impregnation of metallic or non-metallic compounds [6,7], pre-coking [8], chemical vapor deposition of silica [9] and chemical liquid deposition of silica [10]. Although chemical vapor deposition of silica or chemical liquid deposition of silica with simple silica alkoxides, such as tetra-ethyl-orthosilicate (TEOS), is the usual method for improving *para*-selectivity of zeolite [11,12]. However, to obtain the desired *para*-selectivity, a long and complicated process is necessary. Pre-coking is often difficult to control, and needs to be repeated after the recovered zeolite catalysts are regenerated by calcinations [13]. By comparison, modification of zeolites by

coating with metallic or non-metallic compounds is a convenient approach.

Metal or non-metal oxides could be used to cover the external surface acid sites of zeolite and achieved an excellent *para*-selectivity, but this would also block the acid sites in the channels and then decrease the catalytic activity [14]. To prevent the acidic sites located in the channels of zeolite from being covered by the metal or non-metal oxide during the impregnation process, we have developed a novel method for preparing MgO modified zeolite shape-selective catalysts using a complexation-impregnation method [15–19]. Furthermore, some borate and phosphate were also used as the precursor of non-metal oxides for preparing shape-selective catalysts [20,21]. All these catalysts exhibited exceptional performances in shape-selective catalysis, but the complicated process or the high cost hampered their practical application in industries. Therefore, it is imperative to search a more facile and economical strategy for the preparation of shape-selective catalysts.

Phosphoric acid is the most common precursor for the preparation of phosphorus modified zeolite shape-selective catalysts [22,23]. However, the activity of the catalysts always decreased significantly with increasing the amount of phosphorus. Recently, we found the addition of ethanol during the preparation of phosphorous modified ZSM-5 shape-selective catalysts by using phosphoric acid as the precursor could affect the dispersion of phosphoric acid on the surface of ZSM-5 zeolite, and then influence the structure and acidity of the zeolite. The experimental results evidenced that the catalytic activity and the shape-selectivity were unambiguously influenced by the addition of ethanol during the

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preparation of phosphorous modified ZSM-5 shape-selective catalysts. In this paper, the role of ethanol in the preparation of phosphorous modified ZSM-5 shape-selective catalysts by using phosphoric acid as the precursor was investigated and a facile method for the preparation of phosphorous modified zeolite shape-selective catalysts was suggested.

2. Experimental

2.1. Catalyst preparation

ZSM-5 zeolite (Si/Al = 50) was synthesized by hydrothermal crystallization according to an established procedure [24]. The NH_4^+ form of the as synthesized ZSM-5 zeolites was obtained by ion-exchange with aqueous NH_4NO_3 solution, and then calcined at 823 K for 3 h. The phosphorus modified HZSM-5 catalysts was prepared as follows. The phosphoric acid (85% wt.) was dissolved in anhydrous ethanol. HZSM-5 was impregnated with an ethanol solution containing phosphoric acid. The mixture was stirred for 1 h and allowed to stand overnight. Afterwards, the mixture was evaporated in a constant temperature bath at 353 K for 6 h and then dried in an oven at 383 K for 6 h. Then, the resulting materials were calcined at 823 K for 5 h in an air stream. The obtained catalyst was denoted as x% P/HZSM-5(E), where the x represented the mass percentage of phosphorus based on the zeolite. In contrast, phosphorus modified HZSM-5 catalysts were also prepared by using phosphoric acid aqueous solution as the precursor without the addition of ethanol, and the samples were denoted as x% P/ZSM-5(H).

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were conducted using a Rigaku D/max2500PC diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation. N_2 adsorption/desorption analyses were obtained at 77 K using a physical adsorption instrument (Micromeritics ASAP 2020, USA). The phosphorus contents of the P/HZSM-5(E) samples were obtained using a Panalytical Magix PW2403 spectrometer (XRF). Sample acidity was measured by NH_3 temperature-programmed desorption (NH_3 -TPD) using a Quantachrome CHEMBET-3000 instrument. FT-IR spectra of the samples were recorded using a Bruker FT-IR spectrometer (SENSOR 27) with the KBr pellet technique. FT-IR spectra with pyridine adsorption were carried out using a Bruker FT-IR spectrometer (SENSOR 27) together with a high temperature vacuum chamber. Cracking of 1,3,5-triisopropylbenzene (1,3,5-TIPB) and cumene (IPB) was carried out using a fixed bed reactor at 723 K under N_2 flow with a WHSV (weight hourly space velocity) of 1 h^{-1} .

2.3. Disproportionation of toluene

Disproportionation of toluene was carried out in a fixed bed continuous down-flow reactor. About 3 g of the catalyst (as pellets of 20–40 mesh) was packed in the middle of the reactor and calcined in a dry nitrogen flow for about 1 h at 673 K before reaction. Toluene was introduced at the top of the reactor by means of an infusion pump. The products were collected in an ice-cooled condenser attached to the end of the reactor and analyzed by gas chromatography (GC-2010, SHIMADZU) using a FFAP capillary column and flame ionization detector.

3. Results and discussion

3.1. Catalytic performances of P/HZSM-5 catalysts

The catalytic performances of P/HZSM-5(E) and P/ZSM-5(H) catalysts in the synthesis of *p*-xylene by disproportionation of toluene were presented in Tables 1 and 2, respectively. As shown in Table 1, HZSM-5

Table 1
Catalytic performances of HZSM-5 and P/HZSM-5(E) samples^a.

Catalysts	HZSM-5	P/HZSM-5(E)			
		1.0%	2.5%	3.7%	5.0%
P(wt.%) ^b	–	0.94	2.37	3.61	4.86
Conversion of toluene(%)	56.3	52.8	45.9	36.2	22.6
Xylene selectivity(%)	36.7	39.1	41.5	44.0	47.3
Xylene isomers(%)					
<i>para</i> -xylene	23.4	27.5	47.6	62.0	84.1
<i>meta</i> -xylene	51.9	48.1	32.4	23.1	9.4
<i>ortho</i> -xylene	24.7	24.4	20.0	14.9	6.5
<i>Para</i> -xylene yield(%)	4.8	5.7	9.1	9.9	9.0

^a Conditions: temperature = 673 K, WHSV = 0.8 h^{-1} ;

^b Obtained by XRF.

exhibited the highest conversion of toluene among the investigated catalysts. However, the selectivity for *p*-xylene (23.4%) was close to the equilibrium composition of xylene isomers. After modification by phosphoric acid with the addition of ethanol, the conversion of toluene over P/HZSM-5(E) catalysts decreased gradually from 56.3% to 22.6% with increasing the amount of phosphorus to 5.0%. Notably, a relatively high conversion of toluene was retained even for 5.0% P/HZSM-5(E) catalyst. Meanwhile, the selectivity for *p*-xylene over P/HZSM-5(E) catalysts increased obviously with increasing the amount of phosphorus. The highest selectivity for *p*-xylene, about 84.1%, was observed over 5.0% P/HZSM-5(E) catalyst. The catalytic performances of P/HZSM-5(H) catalysts in disproportionation of toluene differed from those of P/HZSM-5(E) catalysts. Although the selectivity for *p*-xylene over P/HZSM-5(H) catalysts was also significantly improved with increasing the amount of phosphorus, the catalytic activities decreased severely, as shown in Table 2. As for 5.0% P/HZSM-5 catalysts, the conversion of toluene over P/HZSM-5(E) catalyst was markedly higher than those over P/HZSM-5(H). In particular, only a 6.8% conversion of toluene was acquired over 5.0% P/HZSM-5(H) catalyst.

3.2. Catalysts characterizations

Fig. S1 shows the XRD patterns of HZSM-5 and P/HZSM-5 catalysts with different phosphorous loadings. As shown in Fig. S1(A), compared with HZSM-5, no obvious changes in the position and intensity of peaks belonging to HZSM-5 zeolite were detected in the XRD patterns of the P/HZSM-5(E) catalysts. This indicated that the structure of HZSM-5 zeolite was retained without any significant changes after modification with phosphoric acid with the addition of ethanol. No peaks due to phosphorous compound were observed even for 5.0% P/HZSM-5(E) catalyst. Similarly, no peaks corresponding to phosphorous compound were detected even for 5.0% P/HZSM-5(H) catalyst. Careful examination of Fig. S1(B) revealed that the intensities of peaks belonging to HZSM-5 zeolite in the XRD patterns of P/HZSM-5(H) samples decreased obviously with increasing in the phosphorous loadings.

The isotherms for HZSM-5 and 5.0% P/HZSM-5 catalysts were displayed in Fig. 1. It can be seen that all the isotherms of the samples

Table 2
Catalytic performances of P/ZSM-5(H) samples^a.

Catalysts	P/ZSM-5(H)			
	1.0%	2.5%	3.7%	5.0%
Conversion of toluene(%)	50.9	32.5	17.2	6.8
Xylene selectivity(%)	37.6	40.4	42.6	43.1
Xylene isomers(%)				
<i>para</i> -xylene	23.7	30.6	50.9	89.8
<i>meta</i> -xylene	50.4	37.4	19.2	5.5
<i>ortho</i> -xylene	25.9	32.0	29.9	4.7
<i>Para</i> -xylene yield(%)	4.5	4.0	3.7	2.6

^a Conditions: temperature = 673 K; WHSV = 0.8 h^{-1} .

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