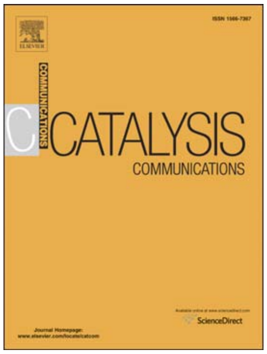


A facile strategy for preparation of phosphorus modified HZSM-5 shape-selective catalysts and its performances in disproportionation of toluene

Na Liu, Xingxing Zhu, Songjie Hua, Dengfeng Guo, Hongyun Yue, Bing Xue, Yongxin Li

PII: S1566-7367(16)30027-9
DOI: doi: 10.1016/j.catcom.2016.01.027
Reference: CATCOM 4572

To appear in: *Catalysis Communications*

Received date: 13 November 2015
Revised date: 19 January 2016
Accepted date: 25 January 2016

Please cite this article as: Na Liu, Xingxing Zhu, Songjie Hua, Dengfeng Guo, Hongyun Yue, Bing Xue, Yongxin Li, A facile strategy for preparation of phosphorus modified HZSM-5 shape-selective catalysts and its performances in disproportionation of toluene, *Catalysis Communications* (2016), doi: 10.1016/j.catcom.2016.01.027

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

Na Liu[a, b], Xingxing Zhu[b], Songjie Hua[b], Dengfeng Guo[b], Hongyun Yue[c], Bing Xue[b *], Yongxin Li[b *]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, China

[b] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China

[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China

*Corresponding author. Tel: (+86) 519 86330135; Fax: (+86) 519 86330135;

E-mail: xuebing_cn@163.com (Bing Xue), liyxluck@163.com (Yongxin Li)

Abstract: The phosphorous modified HZSM-5 catalysts were prepared by using phosphoric acid as the precursor with 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.

Key words: Toluene disproportionation; shape-selective catalysis; phosphorous; HZSM-5

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 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 Cu Kα (λ=1.54 Å) 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 (TENSOR 27) with the KBr pellet technique. FT-IR spectra with pyridine adsorption were carried out using a Bruker FT-IR spectrometer (TENSOR 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 fix 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 a 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 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 are of type I, showing characteristics of micro-porous zeolite type materials [25]. This indicated that the main structure of HZSM-5 was retained after modification with phosphoric acid. The textural parameters of the P/HZSM-5 catalysts were summarized in Table 3. As shown in Table 3, the BET surface area and the micropore volume of P/HZSM-5(E) catalysts decreased gradually with increasing the amount of phosphorous. It was worth noting that a high BET surface area (273 m^2/g) was maintained even for 5.0% P/HZSM-5(E) catalyst. As shown in Table 3, the BET surface area and the micropore volume of P/HZSM-5(H) catalysts decreased obviously with increasing the amount of phosphorous. As for 5.0% P/HZSM-5(H) catalyst, only a BET surface area of 177 m^2/g and a micropore volume of 0.087 cm^3/g were observed, which were much lower than that of 5.0% P/HZSM-5(E) catalyst.

The FT-IR spectra of the HZSM-5 and 5.0% P/HZSM-5 catalysts were shown in Fig. 2. The asymmetric stretching, symmetric stretching and bending vibrations of Si–O–Si were observed at 1100, 800 and 450 cm^{-1}, respectively. The absorptions at 1230 and 550 cm^{-1} corresponded to the presence of five-membered ring chains and different ring structures, respectively. These features were basically identical for the HZSM-5 zeolite [26]. This indicated that the structure of HZSM-5 zeolite was preserved after phosphoric acid modification. Compared with the FT-IR spectrum of HZSM-5, obvious absorptions at about 1300-1400 cm^{-1} were presented on the spectra of the 5.0% P/HZSM-5 catalysts, which was ascribed to the P–O stretching. As reported previously, the hydroxyl bands observed at 3668 cm^{-1} were assigned to P-OH groups. This confirmed the successful loading of phosphorous over the surface of HZSM-5 zeolite [27].

The NH_3-TPD profiles of HZSM-5 and 5.0% P/HZSM-5 catalysts are presented in Fig. 3. As for HZSM-5 zeolite, the strong peak at about 520 K can be associated with the desorption of physisorbed ammonia and/or ammonia adsorbed on weak acid sites, and the strong peak at about 730 K may be attributed to the desorption of ammonia adsorbed on strong acid sites [28]. It can be observed that 5.0% P/HZSM-5(E) also exhibited typical double-peak characteristic. However, the intensities of the two peaks were obviously lower compared with HZSM-5 zeolite. Particularly, only one peak at about 510 K was observed on the NH_3-TPD curve of 5.0% P/HZSM-5(H) catalyst. This indicated that the strong acid sites over 5.0% P/HZSM-5(H) had disappeared.

FT-IR spectra with pyridine adsorption of HZSM-5 and P/HZSM-5 catalysts were illustrated in Fig.4. Pyridine adsorbed on HZSM-5 and the P/HZSM-5 catalysts resulted in the appearance of bands characteristic of pyridine adsorbed on Brønsted acid sites around 1545 cm^{-1}, on Lewis acid sites at 1450 cm^{-1} [29]. It was found that the intensities of the peaks belonging to Brønsted acid sites and Lewis acid sites both decreased progressively with increasing the amount of phosphorous. As shown in Fig. 2, the absorptions at about 3668 cm^{-1} on the spectra of the 5.0% P/HZSM-5 catalysts were ascribed to the P–OH group. However, as for the P/HZSM-5 catalysts, the bands characteristic of pyridine adsorbed on Brønsted acid sites decreased significantly. This indicated that the P-OH did not contribute to the Brønsted acid sites of the samples. Furthermore, the amount of Brønsted acid sites over P/HZSM-5(E) catalysts is higher than that over P/HZSM-5(H) catalysts with the same phosphorous loadings. This is consistent with the results of NH_3-TPD characterization.

The acidic properties of P/HZSM-5 catalysts were also elucidate by the cracking of 1,3,5-triisopropylbenzene (1,3,5-TIPB) and cumene (IPB) (Table 4). Compared with HZSM-5 zeolite, the conversion of 1,3,5-TIPB and conversion of IPB all decreased over all the P/HZSM-5 catalysts, which corresponded to the decrease in the amount of acid sites after modification of phosphoric acid. Compared with the 5.0% P/HZSM-5(H) catalyst, the lower conversion of 1,3,5-TIPB and the higher conversion of IPB were observed over 5.0% P/HZSM-5(E) catalyst. This indicated that most of the acid sites on the external surface of HZSM-5 were covered and most of the acid sites in the pores of HZSM-5 were retained after modification by phosphoric acid with the addition of ethanol. Compared with HZSM-5 sample, the much low conversion of

1,3,5-TIPB over 5.0% P/HZSM-5(E) catalyst indicated that about 90% acid sites on the external surface of HZSM-5 had been covered.

Based on the evidence presented above, it was speculated that the addition of ethanol during the impregnation process had a decisive impact on the shape-selective catalytic performances of the phosphorous modified HZSM-5 catalysts. As reported previously, catalytic synthesis of *p*-xylene by toluene disproportionation has been mostly considered as a typical acid-catalyzed process and *p*-xylene is obtained as the primary product over the Brønsted acid sites of the catalyst [30]. Subsequently, isomerization of *p*-xylene occurred easily over the surface Brønsted acid sites of zeolite because the *meta*-isomer has been reported to be thermodynamically more stable than the other isomers [2]. In order to improve the *para*-selectivity, it is necessary to cover the acid sites on the external surface of zeolite. Although an excellent *para*-selectivity was achieved over P/HZSM-5(H) catalysts, but the catalytic activity was poor. The results of XRD and N_2 adsorption/desorption suggested that the pore structure of HZSM-5 zeolite had been blocked after phosphoric acid modification. Therefore, the amount of the acid sites, especially for the strong acid sites, decreased severely. However, as for P/HZSM-5(E) catalysts, a relatively high catalytic activity along with an outstanding *para*-selectivity was obtained. This indicated that the cover of the external acidic sites and the reservation of the acidic sites in the HZSM-5 zeolite channels were accomplished simultaneously. With the addition of ethanol during the impregnation process, the molecular of phosphoric acid can react with ethanol to form phosphate, such as ethyl phosphate (6.9×4.6 Å), diethyl phosphate (9.5×5.6Å) and triethyl phosphate (8.9×8.4 Å) (Scheme 1). These phosphates were mainly restricted on the external surface of HZSM-5 zeolite because of the large molecular sizes (As shown in Fig. S2). The high micropore volume (Table 3) and the high amount of Brønsted acid sites (Fig.4) of P/HZSM-5(E) catalysts could be used to confirm the explanation mentioned above. Therefore, an excellent shape-selective catalytic performance was achieved in toluene disproportionation over P/HZSM-5(E) catalysts.

The catalytic performances of P/ZSM-5(E) samples at similar toluene conversion levels by changing the weight hourly space velocity expressed in terms of gram of feed per gram catalyst per hour (WHSV) are shown in Table 5. As for HZSM-5 zeolite, conversion of toluene decreased obviously with increasing the WHSV, while the selectivity for *p*-xylene was slightly affected. As for the 2.5% P/ZSM-5(E) samples, the increase in selectivity for *p*-xylene were also negligible compared with the decrease in conversion of toluene with increasing the WHSV. It is obvious that the improvement in selectivity for *p*-xylene over P/ZSM-5(E) samples should be ascribed to the modification of phosphorus.

Fig.5 shows the effects of time-on-stream in the synthesis of *p*-xylene by disproportionation of toluene over 5.0% P/HZSM-5(E) catalyst. Obviously, the toluene conversion was maintained above 15% for about 20 h, and then decreased gradually with time-on-stream. The deactivation can be attributed to coke deposition on the Brønsted-acid sites of the catalyst. The selectivity for *p*-xylene was maintained during 28 h on stream.

4. Conclusions

In conclusion, we have developed a very facile and economical strategy for preparation of phosphorous modified HZSM-5 zeolite shape-selective catalysts by addition of ethanol during the impregnation process. This novel strategy accomplished the coverage of the external acid sites and protection of the inner acid sites on zeolite simultaneously. An excellent *para*-selectivity along with a high catalytic activity was achieved in the synthesis of *p*-xylene by disproportionation of toluene.

Acknowledgements:

The authors thank the finacial support from the National Natural Science Foundation of China (21076027), the Natural Science Foundation of Jiangsu College (12KJB530002), and Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology (BM2012110).

References

[1] V.V. Dung, M. Manabu, N. Norikazu, E. Yasuyuki, U. Korekazu, J. Catal., 243 (2006) 389-394.

[2] S. Al-Khattaf, S.A. Ali, A.M. Aitani, N. Zilkova, D. Kubicka, J. Cejka, Cat. Rev.-Sci. Eng., 56(2014)333–402.

[3] L.B. Young, S.A. Butter, W.W. Kaeding, J. Catal., 76 (1982)418-432.

[4] J.Cejka, N.Zilkova, B.Wichterlova, Zeolites, 17(1996)265-271.

[5] J.Cejka, B. Wichterlova, Cat. Rev.-Sci. Eng., 44(2002)375-421.

[6] Z.R. Zhu, Q.L. Chen, Z.K. Xie, W.M. Yang, D.J. Kong, C. Li, J. Mol. Catal. A: Chem. 248(2006)152-158.

[7] S.R. Zheng, A. Jentys, J.A. Lercher, J. Catal. 219(2003)310-319.

[8] F. Bauer, W.H. Chen, Q. Zhao, A. Freyer, S.B. Liu, Micropor. Mesopor. Mater. 47 (2001) 67-77.

[9] J.H. Kim, A. Ishida, M. Okajima, M. Niwa, J. Catal. 161 (1996) 387-392.

[10] R.W. Weber, K.P. Möller, M. Unger, C.T. O'Connor, Micropor. Mesopor. Mater. 23 (1998) 179-187.

[11] A.B. Halgeri, J. Das, Catal. Today. 73 (2002) 65-73.

[12] S. Zheng, H. Tanaka, A. Jentys, J.A. Lercher, J. Phys. Chem. B. 108 (2004) 1337-1343.

[13] F. Bauer, W.H. Chen,E. Bilz, A. Freyer, V. Sauerland, S.B. Liu, J. Catal. 251 (2007) 258-270.

[14] B. Xue, Y.X. Li, L.J. Deng, Catal. Commun. 10(2009)1609-1614.

[15] B. Xue, H. Li, J. Xu, P. Liu, Y. Zhang, Y. Li, Catal Commun .29(2012)153-157.

[16] L. Fu, B. Xue, J. Xu, W. Zhang, Y. Li, Speciality Petrochemicals (China) 29(2012) 48-53.

[17] Y. Zhang, B. Xue, J Xu, P. Liu, Y. Li, Petrochemical technology (China), 41(2012)277-282.

[18] J. Zhang, B. Xue, J. Xu, P. Liu, Y. Li, J Mol Catal (China), 25(2011) 514-519.

[19] B. Xue, J. Su, Q. Huang, J. Xue, Y.X. Li, Catal Commun .45(2014)49-53.

[20] B. Xue, G. Zhang, N. Liu, J. Xu, Q.M. Shen, Y.X. Li, J. Mol. Chem. A: Chem. 395(2014)384-391.

[21] B. Xue, S. Wu, X. Song, N. Liu, J. Su, Y.X. Li, Acta Petrolei Sinica (Petroleum Processing Section), 31(2015)1056-1062.

[22] M. Ghiaci, A. Abbaspur, M. Arshadi, B. Aghabarari, Appl. Catal. A: Gen., 316 (2007) 32-46.

[23] W.W. Kaeding, C. Chu, L.B. Young, B. Weinstein, S.B. Butter, J. Catal., 67 (1981) 159-174.

[24] S.B. Kulkarni, V.P. Shiralkar, A.N. Kotasthanc, R.B. Borade, P. Ratnasamy, Zeolites, 2(1982)313-318.

[25] L. Gora, B. Sulikowski, E.M. Serwicka, Appl. Catal. A: Gen. 325 (2007) 316-321.

[26] J.C. Jansen, F.J. van der Gaag, H. van Bekkum, Zeolites, 4 (1984) 369–372.

[27] G. Dworezkow, G. Rumplmayer, H. Mayer, J.A. Lercher, Stud. Surf. Sci. Catal. 21 (1985) 163-172.

[28] F. Lonyi, J. Valyon, Microp. Mesop. Mater. 47 (2001) 293–301.

[29] V.V. Ordomsky, I.I. Ivanova, E.E. Knyazeva, V.V. Yuschenko, V.I. Zaikovskii, J.Catal. 295(2012)207-216.

[30] B. Mitra, J.P. Chakraborty, D. Kunzru, AIChE J. 57(2011)3480-3495.

Figure captions

Fig. 1 N_2 adsorption/desorption isotherms of HZSM-5 and P/HZSM-5 samples

Fig. 2 FT-IR spectra of HZSM-5 and P/HZSM-5 samples

Fig. 3 NH_3-TPD profiles of HZSM-5 and P/HZSM-5 samples

Fig. 4 FT-IR spectra with pyridine adsorption of HZSM-5 and P/HZSM-5 samples

Fig. 5 Effect of time-on-stream on the synthesis of p-xylene by disproportionation of toluene over 5.0% P/HZSM-5(E) catalyst (temperature=673 K; WHSV=0.8 h^{-1})

Scheme 1 Reaction of phosphoric acid with ethanol and the deposition of phosphorus on HZSM-5 zeolite

Fig. 1

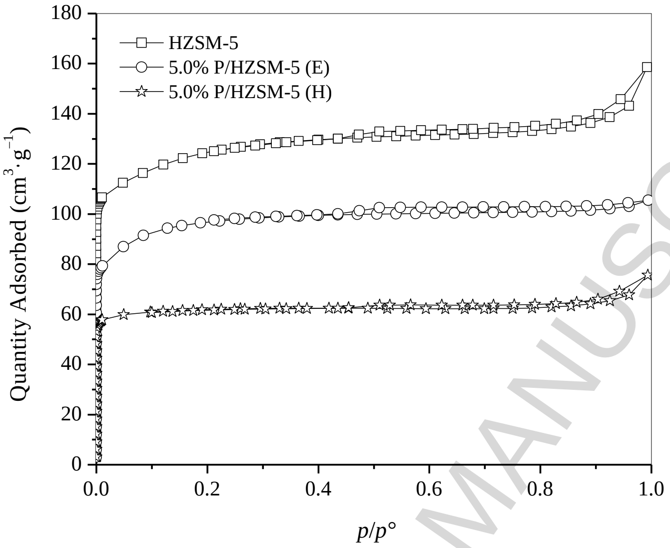

HZSM-5
5.0% P/HZSM-5 (E)
5.0% P/HZSM-5 (H)
Quantity Adsorbed (cm^3·g^{-1})
0
20
40
60
80
100
120
140
160
180
0.0
0.2
0.4
0.6
0.8
1.0
$p/p°$

Fig. 2

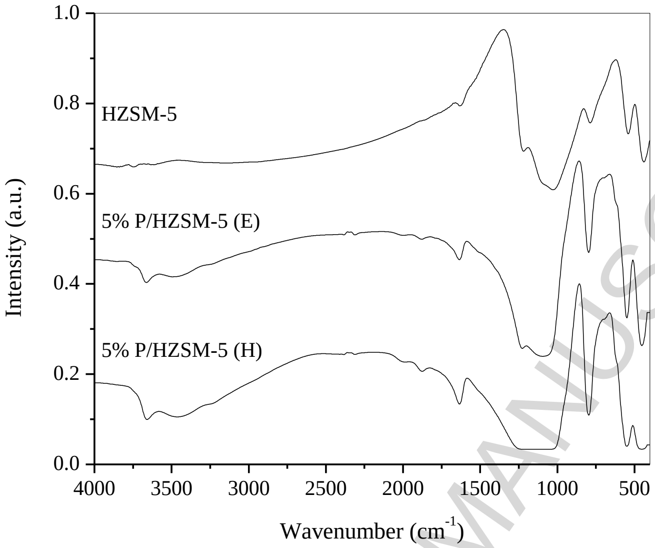

1.0
0.8
0.6
0.4
0.2
0.0
Intensity (a.u.)
HZSM-5
5% P/HZSM-5 (E)
5% P/HZSM-5 (H)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

Fig. 3

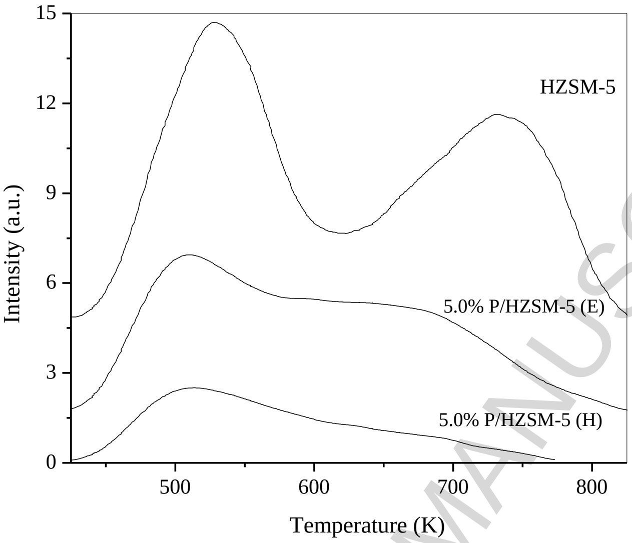

15
12
9
6
3
0
Intensity (a.u.)
500
600
700
800
Temperature (K)
HZSM-5
5.0% P/HZSM-5 (E)
5.0% P/HZSM-5 (H)

Fig. 4

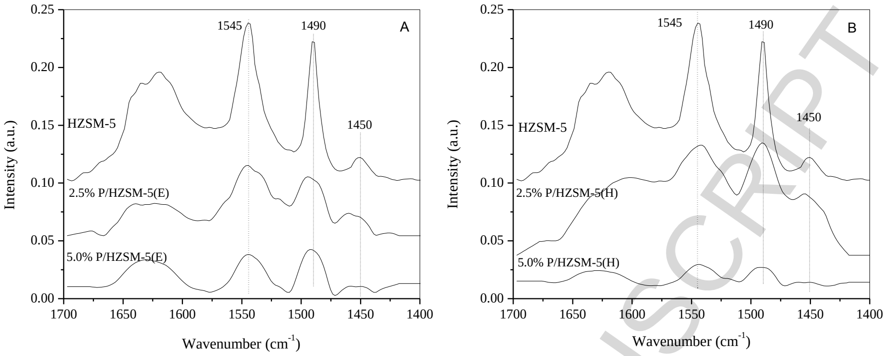
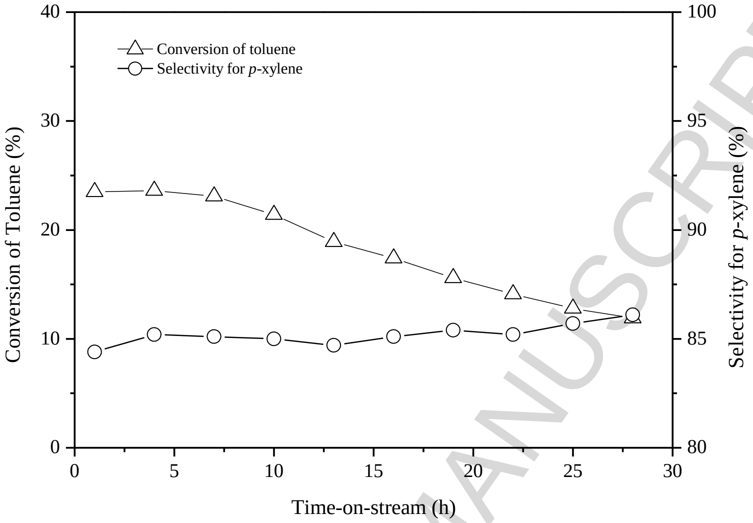

0.25
0.20
0.15
0.10
0.05
0.00
Intensity (a.u.)
1545
1490
1450
A
HZSM-5
2.5% P/HZSM-5(E)
5.0% P/HZSM-5(E)
1700
1650
1600
1550
1500
1450
1400
Wavenumber (cm-1)
B
2.5% P/HZSM-5(H)
5.0% P/HZSM-5(H)

Fig.5


Conversion of toluene
Selectivity for *p*-xylene
Conversion of Toluene (%)
Selectivity for *p*-xylene (%)
Time-on-stream (h)
0
10
20
30
40
80
85
90
95
100
0
5
10
15
20
25
30

Scheme 1

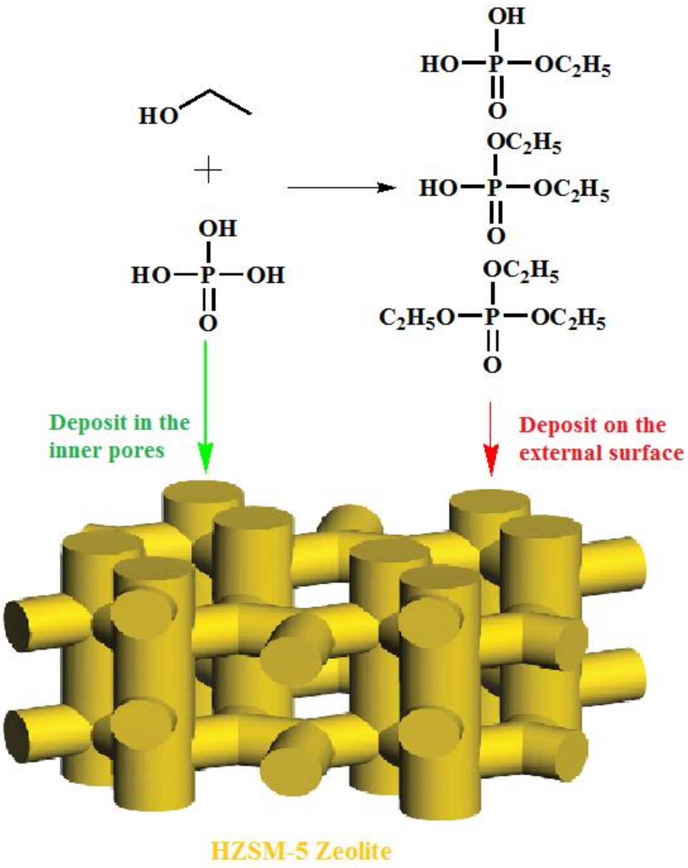

HO
+
OH
HO—P—OH
O
OH
HO—P—OC₂H₅
O
OC₂H₅
HO—P—OC₂H₅
O
OC₂H₅
C₂H₅O—P—OC₂H₅
O
Deposit in the inner pores
Deposit on the external surface
HZSM-5 Zeolite

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(%)					
para-xylene	23.4	27.5	47.6	62.0	84.1
meta-xylene	51.9	48.1	32.4	23.1	9.4
ortho-xylene	24.7	24.4	20.0	14.9	6.5
Para-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

Table 2 Catalytic performances of P/ZSM-5(H) samples[a]

Catalysts	P/HZSM-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(%)				
para-xylene	23.7	30.6	50.9	89.8
meta-xylene	50.4	37.4	19.2	5.5
ortho-xylene	25.9	32.0	29.9	4.7
Para-xylene yield(%)	4.5	4.0	3.7	2.6

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

Table 3 Textural parameters of HZSM-5 and P/HZSM-5(E) samples

Samples	A_{BET}/m^2 g^{-1}	A_M/m^2 g^{-1}	V_T/cm^3 g^{-1}	V_M/cm^3 g^{-1}
HZSM-5	374	267	0.245	0.141
1.0% P/HZSM-5(E)	336	265	0.194	0.136
2.5% P/HZSM-5(E)	311	246	0.186	0.129
3.7% P/HZSM-5(E)	282	225	0.172	0.122
5.0% P/HZSM-5(E)	273	218	0.166	0.114
2.5% P/HZSM-5(H)	248	216	0.149	0.103
5.0% P/HZSM-5(H)	177	148	0.103	0.087

A_{BET} – BET surface area; A_M – Micropore area; V_T – Total pore volume; V_M - Micropore volume;

Table 4 Cracking of 1,3,5-TIPB and IPB over 5.0% P/HZSM-5 catalysts[a]

Catalysts	Conversion of 1,3,5-TIPB(%)	Conversion of IPB(%)
HZSM-5	23.8	22.4
5.0% P/HZSM-5(E)	2.7	16.9
5.0% P/HZSM-5(H)	5.2	9.7

[a] Conditions: temperature=723 K; WHSV=1.0 h^{-1}

Table 5 Catalytic performances of P/ZSM-5(E) samples at similar toluene conversion levels[a]

Catalysts	HZSM-5	P/HZSM-5(E)	
		2.5%	5.0%
WHSV(h^{-1})	4.2	2.9	0.8
Conversion of toluene(%)	23.4	24.7	22.6
Xylene selectivity(%)	37.5	43.2	47.3
Xylene isomers(%)			
para-xylene	23.6	49.1	84.1
meta-xylene	49.4	29.7	9.4
ortho-xylene	27.0	21.2	6.5

[a] Conditions: temperature=673 K

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

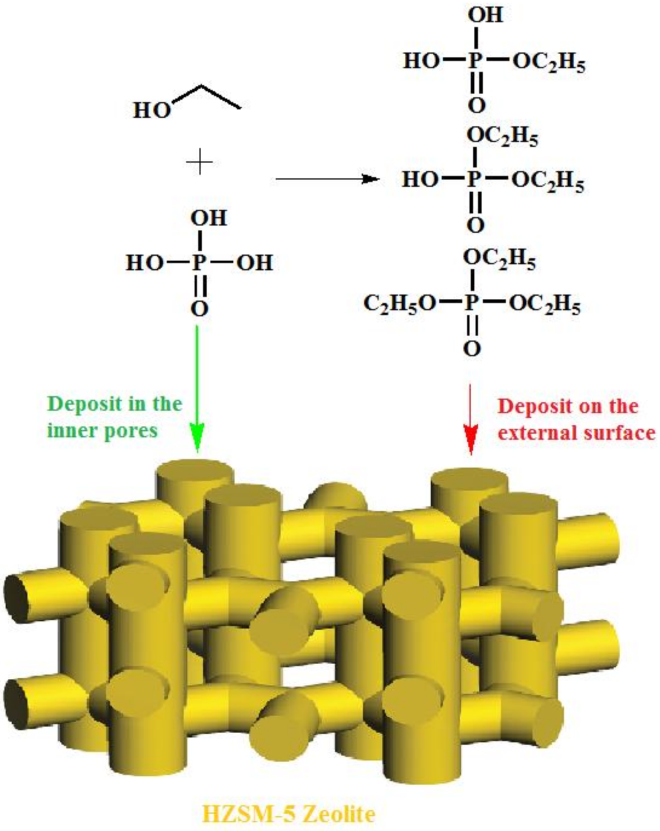
Na Liu[a, b], Xingxing Zhu[b], Songjie Hua[b], Dengfeng Guo[b], Hongyun Yue[c], Bing Xue[b *], Yongxin Li[b *]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, China

[b] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China

[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China

Graphical abstract



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

Na Liu[a, b], Xingxing Zhu[b], Songjie Hua[b], Dengfeng Guo[b], Hongyun Yue[c], Bing Xue[b *], Yongxin Li[b *]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, China

[b] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China

[c] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China

Highlights

- Phosphorus modified HZSM-5 prepared by impregnation with addition of ethanol.
- Excellent performance was obtained in disproportionation of toluene.
- The addition of ethanol promotes the transition of phosphoric acid to phosphate.