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Lanthanum–phosphorous modified HZSM-5 catalysts in dehydration of ethanol to ethylene: A comparative analysis

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ABSTRACT

The catalytic dehydration of ethanol into ethylene was studied over HZSM-5, phosphorous modified HZSM-5 and lanthanum–phosphorous modified HZSM-5 in the low temperature range from 473 K to 573 K. The experimental results demonstrated the lanthanum–phosphorous modified HZSM-5 offered the outstanding catalytic performance and the enhanced anti-coking ability markedly, especially for 0.5%La-2%PHZSM-5. Characterizations revealed that the improved catalytic performance and the excellent anti-coking ability of lanthanum–phosphorous modified HZSM-5 could be attributed to the harmonious acid sites and pore structure by the modification with lanthanum and phosphorous.

1. Introduction

To alleviate the dependence on the nonrenewable fossil resource, the path for biomass is chosen alternatively [1]. Ethylene as light olefin is an important chemical intermediate in the petrochemical industry, which obtained mainly from the petrochemical route based on stream cracking of petroleum liquids and natural gas feedstock. In view of finite petroleum resources, the increasing researchers have been paying attention to the dehydration of bio-based ethanol to ethylene [2–9]. Among the numerous reported dehydration catalysts, HZSM-5 zeolite is promising in the aspect of industrial application, while which is limited to unsatisfactory catalytic performance and low anti-coking ability. Recently, Zhang et al. [8] and Ramesh et al. [9] both reported the higher ethylene selectivity and anti-coking ability could be obtained by the modification with phosphorous, which could be attributed to the presence of weak acid sites with relative weak strength and the elimination of strong acid sites which were responsible for higher hydrocarbon and coking formation after phosphorous modification. Nevertheless, high reaction temperature (>573 K) was necessary for the increased ethanol conversion, ethylene selectivity and the enhanced anti-coking ability [8,9]. In view of technologic energy-saving, the development of a low-temperature catalyst with high catalytic performance and stability is very essential. Mao et al. [10] and Ouyang et al. [7] reported that the catalytic activity of HZSM-5 could be improved by modification with rare earth lanthanum at low temperature, while the low weigh hourly space velocity (WHSV) was necessary.

However, there has been no report on lanthanum–phosphorous modified HZSM-5 for dehydration of ethanol to ethylene so far. In continuation of our interest in using zeolites as green and efficient catalysts in the chemical transformation of biobased chemicals [11,12], we report herein that the addition of lanthanum could improve the catalytic performance and anti-coking ability of phosphorous modified HZSM-5 greatly at low temperature. Relevant characterizations of XRD, BET, NH_3-TPD and TG/DTG/DTA were carried out to reveal the modification mechanism of phosphorous and lanthanum.

2. Experimental

2.1. Catalysts preparation

The commercial HZSM-5 zeolite with SiO_2/Al_2O_3 radio 50 was supplied by Shanghai Fuxu zeolite Ltd., Shanghai, China. The phosphorus modified HZSM-5 (2%PHZSM-5) and lanthanum modified HZSM-5 (0.5%LaHZSM-5) were prepared by impregnation method with taking the appropriate amounts of H_3PO_4 and $La(NO_3)_3 \cdot 6H_2O$ solution, respectively, calculated to yield the desired percentage of phosphorus or lanthanum element. The volume of solution used was the same as the volume of zeolites. The mixture was continuously stirred at room temperature for 2 h and evaporated at

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353 K, followed by drying at 393 K overnight, and then calcined at 823 K for 6 h. The resulting 2%PHZSM-5 was modified with lanthanum by the similar procedure with the content of 0.25 wt%, 0.5 wt% and 1 wt%, respectively. Thus the obtained lanthanum–phosphorous modified HZSM-5 (La-2%PHZSM-5) were compressed into tablets, crushed and then sieved to 20–30 mesh for catalytic testing and characterization. The samples prepared as above were designated as 0.25%La-2%PHZSM-5, 0.5%La-2%PHZSM-5, 1%La-2%PHZSM-5, respectively.

2.2. Characterization

The phase structure of the catalysts was characterized by X-ray diffraction (Thermo ARL X'TRA X-Ray Diffractometer) with Cu Kα radiation operated at 45 kV and 35 mA. The 2-theta value was scanned in the range of 5–50°. The acidity of catalysts was estimated by temperature programmed desorption of ammonia measurements (NH_3-TPD), which was performed by the BEL-CAT-B-82 instrument connected to a thermal conductivity detector. On the basis of nitrogen adsorption isotherms obtained at 77 K with a Micromeritics ASAP 2020 apparatus, the micropore width was obtained from the Horvath–Kawazoe method, and the specific surface area and micropore volume were calculated by Brunauer–Emmet–Teller (BET) method and *t*-plot method, respectively. Thermogravimetric-difference thermal analysis (TG/DTG/DTA) technique of samples after reaction was carried out to monitor the amount of coke deposition in the catalytic process, recorded by the NETZSCH STA 409 PC equipment.

2.3. Activity measurements

Ethanol dehydration experimental setup was carried out in a homemade fixed bed reactor at atmospheric pressure, with WHSV of 2.0 h^{-1}, in the temperature range of 473–573 K. A 0.5 g catalyst was placed in a quartz tube reactor (8 mm i.d). The feed was 50 wt% ethanol solution, introduced by an infusion pump into reactor. After each increment, the catalyst was activated for 30 min and then the system was allowed to stabilize for 90 min on stream under nitrogen (15 mL min^{-1}) before measuring. Then the gas and liquid reaction products were condensed and analyzed off-line using an Aglient 6890 gas chromatograph, equipped with thermal conductivity detector using an AT. Pora-Q capillary column and flame ionization detector using a FFAP capillary column, respectively.

3. Results and discussion

3.1. Texture properties

The XRD patterns for parent and modified HZSM-5 catalysts (Fig. 1) confirmed that the MFI structure of the HZSM-5 maintained well for all the modified catalysts and none of the lanthanum and phosphorous related species was observed in the XRD patterns. It is suggested that modification by phosphorous and lanthanum has no effect on the basic phase structure of the HZSM-5 zeolite. The XRD profiles also showed that the 2%PHZSM-5 sample exhibited lower crystallinity compared to the parent HZSM-5 indicated by a decrease in the intensity of diffraction peaks, as was attributed to partial dealumination of HZSM-5 [8,9,13]. While the diffraction peaks intensity of La-2%PHZSM-5 zeolites were enhanced compared to 2%PHZSM-5, which showed the lanthanum modification could effect the crystallinity phase of the catalyst.

The surface area (S_{BET}) and micropore volume of 2%PHZSM-5 (Table 1) both decreased as the incorporation of phosphorous, which is likely due to the reduction of pore dimensions or partial pore blockage of the HZSM-5 by the phosphorous species introduced during the treatment process [14,15]. The S_{BET} and micropore volume of La-2%PHZSM-5 were slightly higher than these of the 2%PHZSM-5, while the S_{BET} and micropore volume of the 0.5%LaHZSM-5 were higher than those of HZSM-5, which may be the result of the mutually interaction with phosphorous species which might be eluted from 2%PHZSM-5 zeolite during the process of the second impregnation upon the addition of lanthanum.

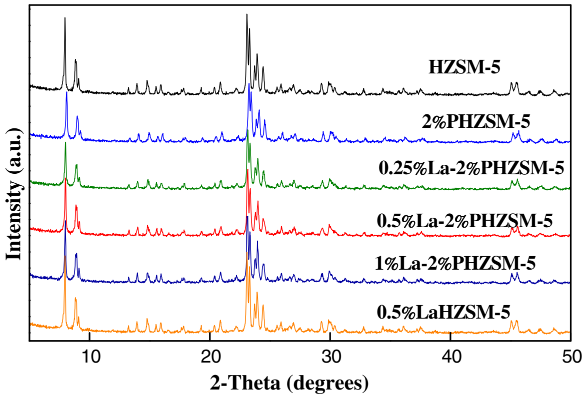

Fig. 1. XRD patterns (Cu Kα) of parent and modified HZSM-5 catalyst powders.

Table 1
Texture characteristics of parent and modified HZSM-5 zeolite.

Catalysts	S_{BET} (m^2 g^{-1})	V_{micro} (cm^3 g^{-1})	Pore width (nm)
HZSM-5	253	0.14	0.5615
2%PHZSM-5	187	0.13	0.5476
0.25%La-2%PHZSM-5	192	0.14	0.5489
0.5%La-2%PHZSM-5	194	0.14	0.5496
1%La-2%PHZSM-5	211	0.15	0.5665
0.5%LaHZSM-5	297	0.17	0.5623

The NH_3-TPD profiles of parent and modified HZSM-5 catalysts were illustrated in Fig. 2. Two peaks were presented for HZSM-5 catalysts at 420 K and 600 K, clearly suggesting two types of acidic sites. Generally, the peak at lower temperature was attributed to weak acid sites and that at the higher temperature could be associated with strong acid sites. As the literature [8,9] reported the strong acidic sites of HZSM-5 were eliminated significantly and the total acid amount was reduced markedly upon the modifica-

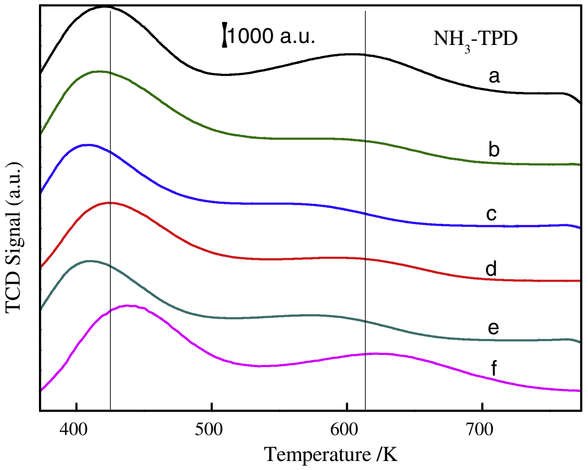

Fig. 2. NH_3-TPD profiles of parent and modified HZSM-5 catalysts. (a) HZSM-5, (b) 2%PHZSM-5, (c) 0.25%La-2%PHZSM-5, (d) 0.5%La-2%PHZSM-5 and (e) 1%La-2%PHZSM-5, (f) 0.5%LaHZSM-5.