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Catalysis Today 74 (2002) 137–143

CATALYSIS TODAY

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Study on physico-chemical properties and catalytic activity of BSiZrAPO-5 catalysts in linear alkylbenzene synthesis

Peiyong Lian[a], Wenyi Gao[a], Fushan Yan[a], Weiqiao Liu[a], Gong Li[a],
Haoping Wang[a,*], Guida Sun[b,1]

[a] *Fushun Petroleum Institute, Fushun 113001, China*
[b] *Beijing Institute of Petrochemical Technology, Beijing 102600, China*

Abstract

Boro-silico-zirconio-aluminophosphate molecular sieves (BSiZrAPO-5) with the structure similar to $AlPO_4$-5 were synthesized using the hydrothermal synthesis method. Substitutions of Al and P atoms in the $AlPO_4$-5 framework with Si, B and Zr atoms were demonstrated by the variation in unit cell volume, chemical analysis, IR spectrum and ^{27}Al, ^{31}P MAS NMR data. The IR spectrum of adsorption of pyridine and temperature programmed desorption of NH_3 indicate that BSiZrAPO-5 contains more Brønsted and Lewis acid sites than $AlPO_4$-5. BSiZrAPO-5 possesses a significant catalytic activity, a high selectivity of 2-phenylalkane (2-LAB) and 3-phenylalkane (3-LAB) and a long life period in the alkylation of benzene with linear olefins. BSiZrAPO-5 may replace HF as an environmentally benign catalyst in linear alkylbenzene production.

Keywords: Aluminophosphate molecular sieve; Alkylation; Linear alkylbenzene; Environmentally benign catalyst; Olefin

1. Introduction

The synthesis of a large number of new microporous molecular sieves based on the aluminophosphate framework ($AlPO_4$-*n*) was first reported 19 years ago by researchers at the Union Carbide [1,2]. Later, Lok et al. [3] reported the synthesis of silicon substituted aluminophosphate molecular sieves denoted as SAPO-*n*. The metal substituted crystalline microporous aluminophosphates (MeAPO-*n*) in which the substituent metal is one of the divalent metals of Mg, Fe, Co, etc. was reported by Flanigen et al. [4].

The crystal structure of $AlPO_4$-5 has been well established [5]. It has a novel three-dimensional microporous crystal framework structure with hexagonal symmetry (cell constants $a = b = 1.373\,\text{nm}$, $c = 0.848\,\text{nm}$ and $\gamma = 120^\circ$; unit cell composition $12AlPO_4 \cdot nH_2O$) and contains $AlO_2{}^+$ and $PO_2{}^-$ structural units as lattice constituents and one-dimensional channels (pore diameter $= 0.8\,\text{nm}$) parallel to the *c*-axis. $AlPO_4$-5 has a neutral framework with no extra framework cations and a weak acidity. The substitution of metals in $AlPO_4$-*n* may cause negative charges on the framework of MeAPO-*n*, which exhibits ion-exchange and/or catalytic properties similar to the prior known aluminosilicate and SAPO-*n* molecular sieve compositions, and have stronger Brønsted and Lewis acid.

Zirconia is an important material as catalyst and catalyst support [6,7]. The presence of Zr in the catalyst enhances the life of the catalyst in reactions like skeletal isomerization of linear butanes [8] and isomerization of toluidines [9]. Because of the

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[*] Corresponding author.
[1] Co-corresponding author.

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PII: S0920-5861(01)00539-9

Table 1
Properties of BSiZrAPO-5

Sample	Surface area (m^2/g)	Amount of Al_2O_3 (%)	Amount of P_2O_5 (%)	Amount of SiO_2 (%)	Amount of B_2O_3 (%)	Amount of ZrO_2 (%)	Amount of acid (mmol/g)
1	171	48.59	40.27	1.40	0.73	0.32	0.63
2	162	47.28	40.30	1.31	0.89	0.33	0.69
3	150	47.16	40.32	1.04	1.59	0.35	0.64

difficulty in preparation as highly dispersed state with high surface area, it has limited industrial applications. Dongare et al. [10] have studied the synthesis and physico-chemical properties of Zr incorporated $AlPO_4$-5 molecular sieves (ZrAPO-5), which show increased activity and stability in *m*-xylene isomerization reaction.

In this work, we present a novel class of MeAPO-5 molecular sieves, which are crystalline microporous boro-silico-zirconio-aluminophosphate molecular sieves (BSiZrAPO-5) in which the substituent metals are Zr, Si and B. Replacing HF catalyst, the BSiZrAPO-5 catalysts show a significant catalytic activity and a high selectivity for the linear alkylbenzene synthesis.

2. Experimental

The BSiZrAPO-5 molecular sieves were synthesized hydrothermally according to Ref. [11]. A solution was prepared by combining 85% orthophosphoric acid (H_3PO_4) with deionized water and $ZrO(NO_3)_2$ or $ZrOCl_2$, and then mixed with a hydrated aluminum oxide (pseudo-boehmite), 4.5% H_3BO_3 solution and 4.5% silica sol, and to the resulting mixture triethylamine was added. The mixture was placed in a sealed stainless steel pressure vessel lined with an inert Teflon material and crystallized in an oven at autogeneous pressure at 438 K for 44 h. After the vessel was cooled, the solids were recovered by filtration, washed with deionized water three times and dried at 373 K overnight. The product was calcined in an oven at 873 K for 3 h in order to remove the organic template. The calcined sample denoted as BSiZrAPO-5 was stored at room temperature.

A part of the sample was treated by 3% HCl solution at 353 K for 40 min with agitation, and then filtrated. The filter cake was washed with deionized water up to pH = 7, then filtered and dried at 120 °C, and then heated at 873 K for 1.5 h. The obtained product was named as sample 1.

The samples treated repeatedly with HCl solution for two and three times were named as sample 2 and sample 3, respectively. Some properties of sample 1, 2 and 3 are listed in Table 1.

The powder XRD measurement was carried out using D/max-rb X-generator with the Ni-filtered Cu Kα radiation.

IR spectra of chemisorbed pyridine and temperature programmed desorption of NH_3 (NH_3-TPD) were used to determine the acidic sites at different temperature. Framework vibration of BSiZrAPO-5 was detected by IR spectra using Nicolet 5DX FT-IR spectrometer.

The magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of the samples were obtained using Bruker DRX400 NMR spectrometer. The ^{31}P chemical shifts were referred to 85% orthophosphoric acid aqueous solution and the ^{27}Al chemical shifts to external $Al(H_2O)^{3+}$ derived from an $Al(NO_3)_3$ aqueous solution.

The catalytic activity of BSiZrAPO-5 in the alkylation of benzene with linear C_{10}–C_{13} olefins was determined in a small fixed bed reactor (diameter: 10 mm) connected to the gas chromatograph under the following conditions: catalyst, 3 ml; reaction temperature, 518 K; reaction pressure, 4.8 MPa; WHSV, $1\,h^{-1}$ and molar ratio of benzene to olefins 8:1.

A mixture of linear C_{10}–C_{13} olefins directly from an industrial process was used as reactants which contained alkenes 10.7%, alkanes 82.5% and isomerous alkanes 6.8%. The products were analyzed by Br-index method to measure conversion of the olefins. The selectivity of products of linear alkylbenzenes was measured by gas chromatograph.

Chemical compositions of BSiZrAPO-5 were analyzed by the chemical analysis method.

Table 2
XRD data for $AlPO_4$-5 and BSiZrAPO-5

$AlPO_4$-5		BSiZrAPO-5	
d (Å)	I/I_0 (%)	*d* (Å)	I/I_0 (%)
11.8	100	11.9	100
6.82	15	6.85	27
5.93	9	5.94	11
4.50	34	4.50	39
4.24	44	4.21	61
3.96	65	3.96	85
3.57	3	3.59	12
3.43	24	3.44	26
3.07	13	3.07	22
2.97	17	2.97	21
2.66	4	2.66	12
2.60	11	2.59	16
2.42	3	2.37	13

3. Results and discussion

Table 2 gives the X-ray powder diffraction data of BSiZrAPO-5. For the purpose of comparison, the XRD pattern of $AlPO_4$-5 [12] is also listed. It can be seen that BSiZrAPO-5 has AFI ($AlPO_4$-5) topology. Its X-ray powder diffraction pattern is essentially similar to that of $AlPO_4$-5, but great differences in the relative intensities of some diffraction peaks are observed. The intensities of the (0 0 2) and (2 1 1) reflections for BSiZrAPO-5 are higher than those for $AlPO_4$-5. This effect indicates the occurrence of preferred orientation of the crystals. The isomorphous substitution of one framework atom for another atom of different size can be judged by studying the unit cell parameters. The average Al–O and P–O bond are 1.75 and 1.54 Å, Si–O and B–O bond are 1.61 and 1.47 Å. Substitution of Al or P should show a change in the unit cell dimensions. The unit cell parameters were obtained from the (4 0 0) and (2 2 0) reflections (*a*) and the (0 0 2) and (2 1 1) reflections (*c*). In all the cases, the peak at $2\theta = 28.4^\circ$ of silicium ($h\,k\,l = 1\,1\,1$) was taken as reference. The results are listed in Table 3. The data in Table 3 indicate that all of the unit cell parameters of BSiZrAPO-5 are basically similar to those of $AlPO_4$-5 (from Ref. [13]).

Table 3
Unit cell parameters of $AlPO_4$-5 and BSiZrAPO-5[a]

Sample	$a = b$ (Å)	c (Å)	V (Å^3)	Composition
$AlPO_4$-5	13.64	8.43	1358.8	$Al_{12}P_{12}$
BSiZrAPO-5	13.71	8.47	1378.7	$Al_{11.5}P_{10.8}$

[a] The parameters of $AlPO_4$-5 from Ref. [13].

According to the chemical analytic results, we can determine by calculation that there are 13.96 aluminum atoms, 8.46 phosphorus atoms and 1.58 atoms of Si, B and Zr in unit cell of the sample 1 if all of the atoms are located in the framework. It is obvious that this will break the rule in the zeolite sieve framework, which is that AlO_4 cannot directly connect with AlO_4. This implies that quite a few Al atoms locate out of the framework. In order to confirm this result, solid-state MAS NMR has been used to investigate the chemical characteristics and coordination of P and Al in the samples. Fig. 1 illustrates ^{27}Al MAS NMR spectra of samples 1 and 2. The spectra show a strong peak with a 38 ppm chemical shift. This shift is consistent with tetrahedral Al in Al(4P) environment. Al(*n*P) denotes Al atom linked via oxygen bridging atoms to *n*P atoms, where $n = 1, 2, 3, 4$. The data are in agreement with those reported in previous studies on $AlPO_4$-5 [14]. The samples show additional resonances near 8 and −12 ppm. Fyfe et al. [15] considered that the 8 ppm chemical shift can be assigned to fivefold coordinated Al arising from the coordination of two water molecules into a tetrahedrally coordinated Al site in the framework. This Al site is produced due to incomplete hydration and may be an intermediate between tetrahedrally and octahedrally

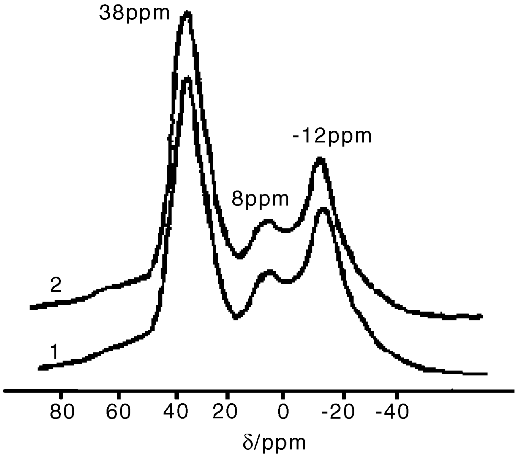

Fig. 1. ^{27}Al MAS NMR spectra of BSiZrAPO-5: (1) sample 1; (2) sample 2.

coordinated Al. A −16 ppm chemical shift is assigned to octahedrally coordinated Al arising from the coordination of two water molecules into a tetrahedrally coordinated Al site in the framework [15]. However, from the integration of the peak areas in Fig. 1, it can be seen that about 37% of Al sites in sample 1 and sample 2 are in 8 and −12 ppm. $AlPO_4$-5 has a high water adsorption capacity (up to 28% of its dry weight) and it was found that up to 40% of the Al sites in hydrated $AlPO_4$-5 could be octahedrally coordinated [14]. But the present samples had adsorbed merely a small amount of water during the MAS NMR measurements. Therefore, we consider that the peaks near 8 and −12 ppm are probably assigned to non-framework Al sites. According to the amount of Al in the framework, it can be deduced that the composition of unit cell is 11.5 Al atoms, 10.8 P atoms for sample 1 and 11.4 Al atoms, 10.9 P atoms for sample 2. This is a logical result. The BSiZrAPO-5 framework was formed by the replacement of Al and P atoms in $AlPO_4$-5 framework with Si, Zr and B atoms. The variation of cell volume is observed (see Table 3), which could be taken as evidence for the replacement of P and Al atoms with Si, Zr and B atoms.

Fig. 2 presents ^{31}P MAS NMR spectra for BSiZrAPO-5. It can be seen that BSiZrAPO-5 shows a single broad asymmetric resonance centered at −27 ppm similar to $AlPO_4$-5 [15]. The ^{27}Al and ^{31}P MAS NMR spectra indicate that BSiZrAPO-5 has a similar structure to $AlPO_4$-5 and the substitution of Al and P with Si, B and Zr does not obviously affect the ^{27}Al and ^{31}P NMR spectra.

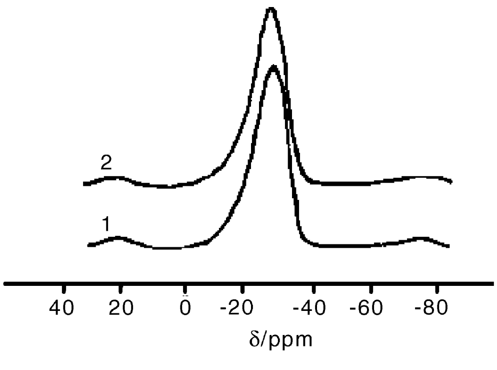

Fig. 2. ^{31}P MAS NMR spectra of BSiZrAPO-5: (1) sample 1; (2) sample 2.

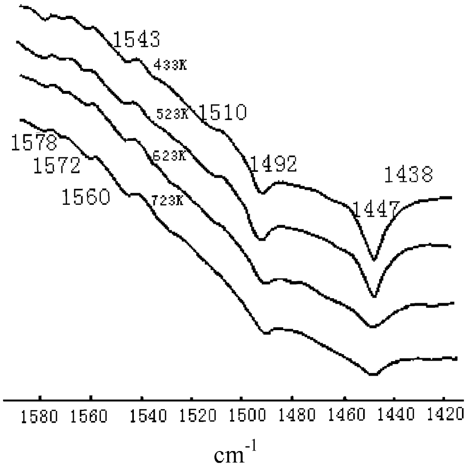

Fig. 3. IR spectra of pyridine adsorbed on sample 2 obtained at different temperatures.

The IR spectra of pyridine chemisorbed BSiZrAPO-5 at 433, 523, 623 and 723 K (see Fig. 3) show significant absorbance at 1447 and 1543 cm^{-1}, which are close to the usual values for Lewis and Brønsted acid sites. They should be assigned to those species. The small band near 1438 cm^{-1} corresponds to weakly acidic sites, since it disappears after evacuation between 433 and 523 K. The bands of 1560, 1572 and 1578 cm^{-1} correspond to strong protonic acidic sites, since they do not disappear in the range of experiment temperatures. From Figs. 3 and 4, it can be found that all Brønsted acidic sites in the sample are strong acidic sites. Their amounts do not vary with temperature, but the Lewis acid sites decrease with the increase in temperature.

The IR spectrum of BSiZrAPO-5 (see Fig. 5) shows that the surface hydroxyl group peaks at 3678 and

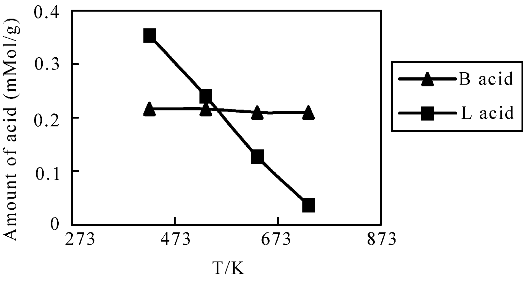

Fig. 4. Effect of temperature for B acid and L acid of BSiZrAPO-5.

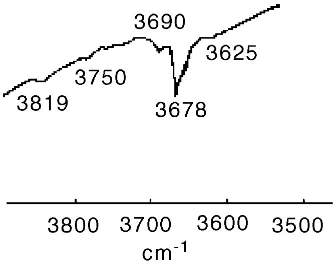

Fig. 5. IR spectra of BSiZrAPO-5 at 433 K.

3819 cm^{-1} are assigned to P–OH and Al–OH, respectively. However, peaks of 3750, 3690 and 3625 cm^{-1} may be related to Zr, Si and B incorporated into the framework [10]. After adsorption of pyridine, all of the bands disappeared, which indicates that all of the OH groups are acidic. Effect of acid treatment on the acidity of BSiZrAPO-5 is given in Fig. 6. Fig. 6 shows that with the increase in the number of times of acid treatment for BSiZrAPO-5, the acid capacities of L acid and B acid increase remarkably. The IR spectrum of framework vibration of the sample is given in Fig. 7. The peaks of 1113 and 630 cm^{-1} which are different from those of $AlPO_4$-5 indicate the possibility of replacement of P or Al in $AlPO_4$-5 with B, Zr and Si. It is noteworthy that the IR spectrum of BSiZrAPO-5 is basically similar to that of ZrAPO-5 [10], which indicates that Zr was isomorphously substituted in the $AlPO_4$-5 structure.

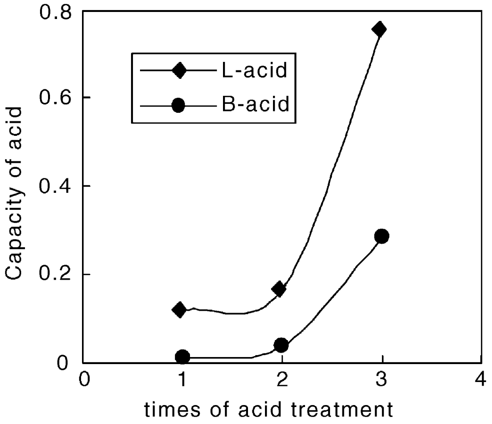

Fig. 6. Effect of acid treatment on B acid and L acid of BSiZrAPO-5.

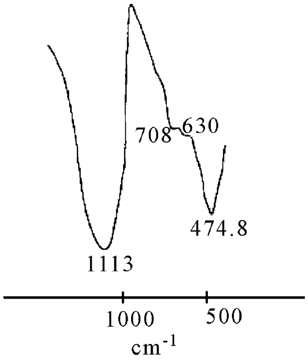

Fig. 7. The IR spectrum of framework vibration of BSiZrAPO-5.

Temperature programmed desorption of ammonia has been proposed as a measure of total acidity and acidic strength distribution in solids. Fig. 8 shows the profiles of NH_3-TPD of BSiZrAPO-5. From Fig. 8, it can be seen that the NH_3-TPD patterns of BSiZrAPO-5 give two desorption peaks at about 523 K and at about 800 K and the $AlPO_4$-5 has merely a desorption peak at about 470 K, which indicates that the acidity of BSiZrAPO-5 is higher than that of $AlPO_4$-5. The 523 and 800 K peaks can be assigned to acid sites with medium acidic strength and strong acidic strength respectively, and related to Zr, Si, B atoms incorporated into the framework. Fig. 8 also shows that the intensity of the second peak for BSiZrAPO-5 increases via acid treatment. The sample 2 treated with HCI solution for two times

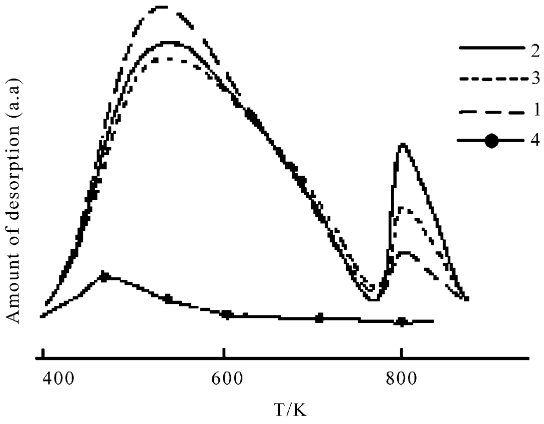

Fig. 8. The profiles of NH_3-TPD of BSiZrAPO-5 and $AlPO_4$-5: (1) sample 1; (2) sample 2; (3) sample 3; (4) $AlPO_4$-5.

Table 4
Catalytic activity, selectivity and longevity for BSiZrAPO-5

Catalyst	Conversion of alkenes (%)	Selectivity of LAB (%)	Life period (h)	Selectivity of 2- and 3-LAB (%)
Sample 1	99.0	>98	>480	95.0
Sample 2	99.5	>98	>480	95.4
Sample 3	99.1	>98	>480	95.2

possesses the most medium strong acid sites in the three samples.

The catalytic activity in the alkylation of benzene with linear olefins and its variation with the temperature are presented in Table 4 and Fig. 9.

Linear alkylbenzenes (LABs) are used in detergent production. Currently, linear alkylbenzenes are produced by alkylation of benzene with linear C_{10}–C_{13} olefins in the presence of HF catalyst following the UOP process. It is of great interest in relation to environment, industrial hazard and corrosion problems to replace HF catalyst by non-corrosive solid acid catalysts. To find out environmentally benign catalysts is always an important aim for researchers in many countries. However, until now the aim does not come true. Many solid acids possess catalytic activity in the alkylation of benzene with linear olefins, but these catalysts are easily deactivated because of coke formation in the surface of the catalyst. From Table 4, it can be seen that BSiZrAPO-5 molecular sieve treated with HCl solution for two times (sample 2) shows a significant catalytic activity (conversion of linear olefins 99.5%) and a high selectivity for linear alkylbenzenes (>98%) in the alkylation of benzene with linear olefins. Especially, the catalysts exhibit a very high selectivity for 2-phenylalkane (2-LAB) (>60%) and 3-phenylalkane (3-LAB) (>30%) and the alkylation activity did not decrease in the period of the reaction experiment. The catalytic activity and selectivity of the samples varies with reaction temperature. Higher reaction temperature will cause coke formation and catalyst deactivation. Although the surface area of BSiZrAPO-5 decreases with the increase of acid treatment times (see Tables 1 and 4), its catalytic activity does not decrease. The medium strong acid sites are 39.3% of all its acid sites for sample 1, 53.6% for sample 2 and 51.2% for sample 3. The sample 3 also shows higher catalytic activity. Therefore, it was assumed that the medium strong acid sites mainly are the active centers with higher stability.

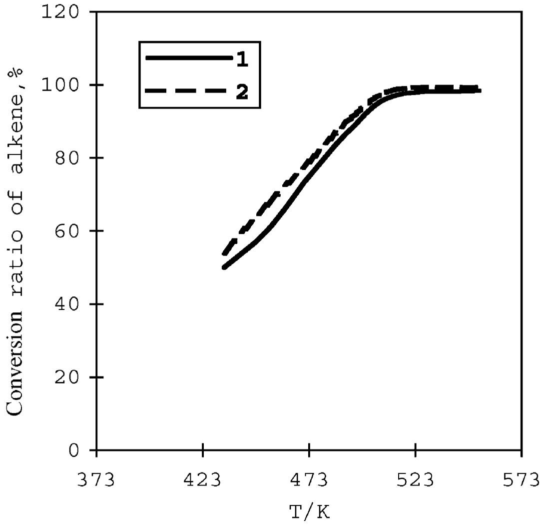

Fig. 9. Effect of temperature on conversion of alkenes for BSiZrAPO-5: (1) sample 1; (2) sample 2.

4. Conclusion

A novel class of crystalline microporous boro-silico-zirconio-aluminophosphate molecular sieves (BSiZrAPO-5) has been synthesized using the hydrothermal synthesis method. Physico-chemical characterization by XRD, MAS NMR, FT-IR and TPD of NH_3 indicates that Zr, B, and Si were incorporated into the $AlPO_4$-5 structure. BSiZrAPO-5 has a similar crystal framework structure to $AlPO_4$-5 molecular sieve and contains Brønsted and Lewis acid sites. Its Brønsted and Lewis acidity is higher than that of $AlPO_4$-5. Therefore, BSiZrAPO-5 shows a significant catalytic activity, a high selectivity of 2-LAB and 3-LAB and high stability in the alkylation of benzene with linear olefins. BSiZrAPO-5 may replace HF as an environmentally benign catalyst in linear alkylbenzene production.

Acknowledgements

The authors are grateful to Prof. Min Enze of Research Institute of Petroleum Processing for his long term guidance and contribution in this work. The project is supported by National Science Foundation of China (NSFC) and China Petrochemical Corporation (SINOPEC).

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