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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Mesoporous Zirconium Phosphonate Hybrid Bentonite as a Novel Efficient Catalyst for the Removal of Trace Olefins from Aromatics[1]

Mei Wu[a,b,*], Haifeng Han[d], Lingli Ni[a], Songlan Zhang[a], Shuang Li[a], Yuqi Wang[a], Jinlong Jiang[a,], Yichang Pan[c], and Jing Chen[a]**

[a] *Faculty of Chemical Engineering, Huaiyin Institute of Technology, Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province, 223003 Huai'an, China*
[b] *Huai'an Research Center of Chemical and Advanced Materials, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Huai'an, 223005 Jiangsu, China*
[c] *State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing University of Technology, 210009 Nanjing, China*
[d] *Jiangsu Hanbon Sci. & Tech, Co., Ltd., Huai'an City, Jiangsu Province, China*
*e-mail: *meiwu@hyit.edu.cn; **jljiang@hyit.edu.cn*

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Abstract—A novel mesoporous zirconium phosphonate hybrid bentonite (MZrPHB) catalyst was prepared for the removal of trace olefins from refining aromatic oil. Pyridine-FTIR, NH_3–TPD, XRD, and N_2 adsorption-desorption analysis were applied to characterize acidic properties and textural properties of catalysts. And its olefins removal performance of MZrPHB catalyst was evaluated in comparison with commercial clay catalyst. It is found that the MZrPHB catalyst possesses an abundance of weak Lewis acid centers, large surface area, and regular mesopore, and thus, exhibits a longer treat life and higher olefins conversion compared to commercial clay catalyst. MZrPHB prepared in this report can be considered as a promising and superior alternative material to commercial clays for the purification of aromatics.

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INTRODUCTION

As an important basic raw material in pharmaceutical intermediates and petrochemical processes, aromatic hydrocarbon is of rush demands in recent years. Naphtha reforming is the principal method to prepare aromatic hydrocarbon. However, aromatic product obtained from this process contains unavoidable trace olefins, and whose content will increase continually with the reforming meanness level enhancing. These undesirable olefins with high activity are harmful to the following separation and applications processes of aromatic products. And thus studies on olefins removal have attracted more and more interest these years [1, 2].

Commercial active clay, with economic applicability, was the most widely used catalyst to remove trace olefins from reforming aromatics. Unfortunately, it tends to suffer from limited lifetime and pollution due to its insufficient surface area and undesirable acid properties. In addition, aromatic molecule is 0.7 nm in diameter, greater than the pore size of conventional clay (0.5 nm). Aromatic molecules were restricted to access into the pore and cannot participate in the alkylation reaction during clay treat, which result in low olefins purification efficiency, and even deactivation [3].

The performance of clay treatment on aromatic purifying mainly depends on surface adsorption and acid catalytic alkylation reaction [4]. Hence the acidic properties in combination with textural properties including surface area and pore size of catalysts play an important role in

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[1] The text was submitted by the authors in English.

determining their catalytic performance. Regulating the acidity and the textural properties of the clay surface can increase its ability to remove olefin without increasing the cost of catalyst dramatically.

Novel acid-catalyzed alkylation catalysts using as alternatives such as ionic liquids [5], organic-inorganic hybrid silica [6], modified zeolites [7], and solid superacid catalysts [8] have been studied. Among them, sulfated zirconia (ZrO_2/SO_4^{2-}) solid superacid catalyst is a considerable material [9, 10], whose initial activity is very high. However, such a strong acidic catalyst is known to deactivate rapidly due to deposition of carbonaceous species on the catalyst surface. Besides, high cost makes above mentioned catalysts difficult to be alternative catalysts applied widely.

Mesoporous zirconium phosphonate (MZrP) hybrid materials have attracted much interest very recently because of their high surface area, large pore volume, uniform mesoporosity, abundant acidity and high stability [11]. Further, since the mesopores in the MZrP allow the reactants to access additional active acid sites in the pores, which results in improved rates of acid catalysis [12]. They have been employed into a significant number of acid-catalyzed reactions, such as Friedel–Crafts reaction [13], esterification [14], hydration, and hydrolysis [15]. However, not many studies are reported so far on the MZrP or its hybrid material for aromatic purifying.

Here, we reported for the first time the synthesis of mesoporous zirconium phosphonate hybrid bentonite material (MZrPHB), which prepared by introducing mesoporous materials MZrP into conventional clay. Compared to a widely used commercial active clay and raw bentonite, the prepared MZrPHB possesses structured mesoporous framework, high surface area (about 245.5 $m^2 g^{-1}$), as well as increased weak L acid sites. It is verified MZrPHB is more efficient in removing trace olefins from aromatic oil.

EXPERIMENTAL

Materials. The aromatic hydrocarbons were obtained from the bottom of the naphtha reforming column at the Sinopec Yangzi Refining and Chemical Company. The bromine index (BI) was 1020 mg Br/100 g. The components are shown in Table 1. The bentonite used in catalyst was purchased from XuYi, China. The commercial active clay catalyst was taken from Nan Jing, China.

Table 1. Aromatic hydrocarbon components

Components	Content, wt %
Nonaromatics	13.91
Benzene	8.95
Toluene	21.84
Ethylbenzene	3.51
p-Xylene	5.18
m-Xylene	11.38
o-Xylene	6.61
C_9 and C_9 + aromatics	28.62

Catalysts preparation. A 200 mL bentonite expansion solution (bentonite : H_2O = 1 : 100) was prepared at room temperature for 12 h. Hexadecyltrimethylammonium bromide (CTAB) (2.5 g) was added, leading to a CTAB modified bentonite sample (CTAB–bentonite).

A colorless transparent $Zr(SO_4)_2$ solution obtained through the reaction of H_2SO_4 and $Zr(OH)_4$ was added into above CTAB–bentonite samples dropwise under efficient stirring for 2 h, followed by heating to 120°C for two days in a closed polypropylene beaker. And then the precipitate was filtered and dried at 100°C. The dried precipitate was mixed into phosphoric acid solution (0.42 mol) with stirring for 2 h, and then filtered and dried. Finally, MZrPHB product was obtained by calcining at 500°C for 5 h.

Catalytic tests in laboratory. As shown in Fig. 1, catalytic activity tests were performed in a fixed-bed tubular microreactor that was equipped with flow controllers and a heating system. Two milliliters of the synthesized catalyst was placed between two quartz sands (40–60 mesh) and inserted into the reactor. The reaction was carried out at a pressure of 1 MPa and a weight hourly space velocity (WHSV) of 30 h^{-1}. The reaction temperature was maintained at 453 K. Inlet and effluent liquids to and from the reactor was analyzed using the LC-2 bromine index detector.

The quality of aromatic products was quantified by the BI, which is defined as the number of milligrams of bromine that would react with trace olefins present in

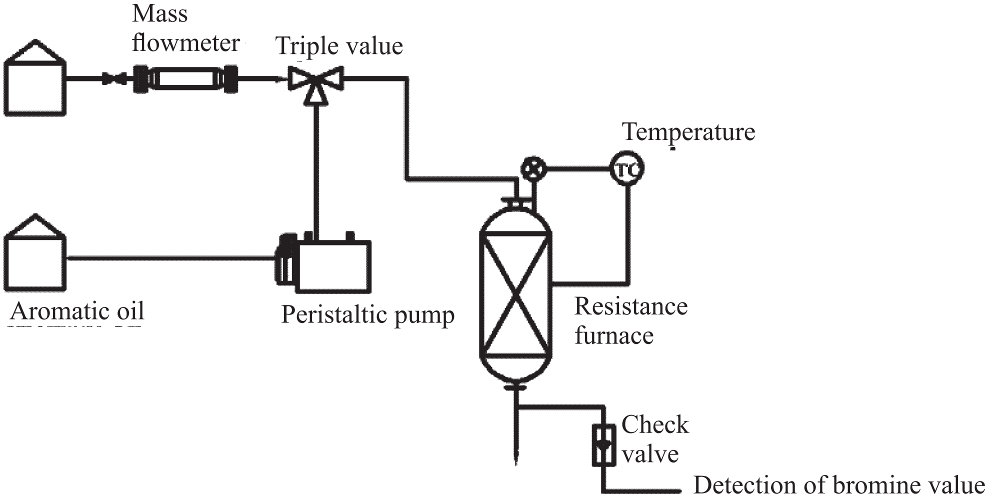

Fig. 1. Flow scheme of the catalytic performance test process.

100 g of an aromatic sample. Therefore, the value of the BI was an indication of the relative amount of olefins. In this study, the olefins conversion (Y) was obtained by the following Eq. (1):

$$Y = (BI_0 - BI)/BI_0 \times 100\%, \quad (1)$$

where BI_0 stands for the bromine index of the inlet aromatic feedstock, and BI stands for the bromine index of the effluent aromatic hydrocarbons after the reaction.

Characterization of catalyst. Surface acidity of catalysts was determined by Fourier transform infrared spectroscopy with pyridine as probe molecule (Pyridine–FTIR) and temperature programmed desorption using NH_3 as a probe molecule (NH_3–TPD).

FTIR spectra were collected using a PE Frontier FTIR spectrometer (4000–400 cm^{-1}). The finely ground self-supported sample wafer (16.5–16.9 mg) loaded into the in-situ cell was pretreated to eliminate the moisture at 623 K for 2 h under vacuum condition (under 0.1 Pa), followed by pyridine adsorption for 30 min after cooling down to 293 K. Finally, the wafers were thermally desorbed at 473 K for 2 h.

NH_3–TPD detection was carried out in the conventional flow system equipment (ChemBET 2920) with the thermal conductivity detector (TCD). After being pretreated at 400°C under He flow (30 mL min^{-1}), the catalyst (100 mg) was cooled to 100°C under He flows, and then adsorbed to saturation by NH_3 at 100°C for 15 min physically adsorbed NH_3 on catalyst was removed by flushing the sample with He gas at the adsorption temperature. The heating rate was 10°C min^{-1}.

The X-ray diffraction (XRD) was performed using a D8-Discover diffractometer (Bruker) using CuK_α radiation from 1.0° to 40.0°. The low angle XRD was to characterize the long range order of all samples.

N_2 adsorption and desorption data were measured with the Micromeritics TriStar II 3020 at 77 K. Samples were out gassed for 3 h at 300°C in N_2 atmosphere before the measurements. The total surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The total pore volume was calculated from the desorption branch of the isotherm at $P/P_0 = 0.99$, assuming complete pore saturation. The *t*-plot method was adopted to evaluate the mesopore volume.

RESULT AND DISCUSSION

Textural properties play important roles in the performance of olefin removal catalysts. Lager surface area means more reaction active sites exposure, and can remove more olefin from aromatics through adsorption. As shown in Table 2, N_2 adsorption and desorption was applied to investigate textural properties of commercial clay catalyst. The BET surface area, pore volume and pore diameter are 177.3 $m^2 g^{-1}$, 0.34 $cm^3 g^{-1}$ and 7.7 nm, respectively. The obvious drawback of the commercial sample is the low surface area. Once it reaches adsorption equilibrium, it will be deactivated soon. Textural properties of the synthesized MZrPHB catalyst and raw

Table 2. Textural properties of olefins removing catalysts

Catalysis	Surface area, $m^2\,g^{-1}$	Pore volume, $cm^3\,g^{-1}$	Pore diameter, nm
Commercial catalyst	177.3	0.34	7.7
Bentonite	202.7	0.21	4.9
MZrPHB catalyst	245.5	0.24	5.8

bentonite clay were also evaluated and listed in Table 2. Mesoporous zirconium phosphonate hybridization led to an increase in average pore diameter from 4.9 to 5.8 nm, and a corresponding increase in pore volume from 0.21 to 0.24 $cm^3\,g^{-1}$. It was worth noting that the BET surface area of the raw bentonite clay had a favorable enhancement from 202.7 to 245.5 $m^2\,g^{-1}$, which was 67 $m^2\,g^{-1}$ higher than that of commercial clay. This increase in surface area will offer the synthesized MZrPHB catalyst better performance on olefin removal.

Figure 2 shows powder XRD patterns of the obtained MZrPHB catalyst, raw bentonite and commercial catalyst from 1° to 40°. Within the scope of the low-angle, only MZrPHB catalyst exhibits a diffraction peak at 2.5°. This is characteristic of mesostructured materials with long-range order in the pore arrangement [16]. It is indicated that the synthesized MZrPHB has regular and well-defined mesopore channel systems, which will facilitate the transfer of aromatic during olefin removal reaction. In the scope of wide-angle, both raw bentonite and commercial clay catalyst presented characteristic peaks at 5.6°, which correspond to *d*(001) basal spacing of bentonite layered structure (JCPDS file no. 03-0019) [17]. Other peaks existed at 19.8°, 20.9°, 26.55° are ascribed to some excess silica (JCPDS file no. 84-0384) in bentonite. MZrPHB catalyst reserves the typical characteristic peak of bentonite in the scope of wide-angle. However, an apparent band shift from 5.6° to 6.5° was found. It indicated that interlayer spacing of bentonite was decreased by mesoporous zirconium phosphonate hybridization.

The pyridine–IR spectrum of commercial catalyst and MZrPHB catalyst are exhibited in Fig. 3. Both of two samples displayed many bands in the wave-number range of 1400–1700 cm^{-1}, which were attributed to the interaction of pyridine with Lewis (L) and Brønsted (B) acid sites on the catalyst surfaces. The spectra present bands of adsorption at 1450, 1490, and 1610 cm^{-1} are assigned to the contribution of pyridine adsorbed on Lewis acid sites. Another band could be seen at around 1540 cm^{-1} is typical of pyridine adsorbed at the Brønsted acid sites [18]. According to Fig. 3, both of the synthesized MZrPHB catalyst and the commercial clay catalyst contain L and B acid sites. While the amount of the total L and B acid sites are quite different according to the area of adsorption peaks, which reflects the information of acid content. It indicated that the content of L acid site on MZrPHB catalyst is more abundant than that on commercial catalyst.

The pyridine adsorption, which is measured after desorption at 473 K, is the total acid sites [3]. The quantitative acid information from the Pyridine-IR spectral data was obtained in Table 3, it reveals that the total amount of the L acid on the synthesized MZrPHB catalyst is 0.0186 mmol g^{-1}, higher than that on commercial clay catalyst (0.00932 mmol g^{-1}). This is in accordance with above Pyridine-IR spectrum and can be concluded that the increase in activity of the catalyst is contributed to the increase in the amount of the L acid.

NH_3–TPD was used to examine the distribution of surface acidity for the MZrPHB catalyst and the commercial clay catalyst. Desorption peaks placed at about 180–350°C are ascribed to weak surface acid sites. Characteristic peaks around 400–700°C are due to

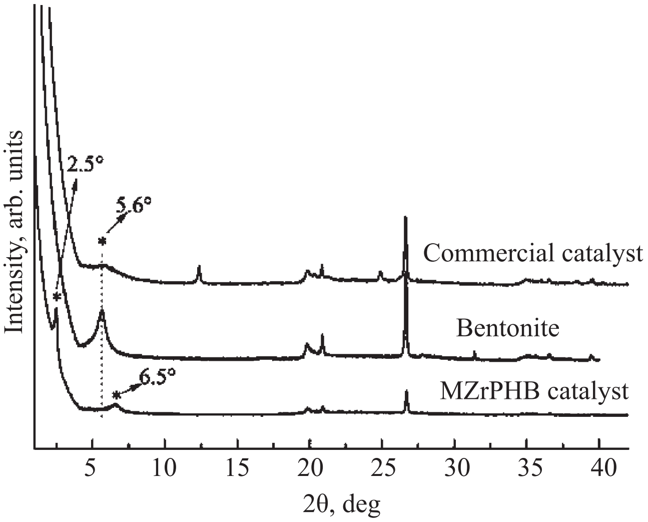

Fig. 2. XRD patterns of olefin removing catalysts.

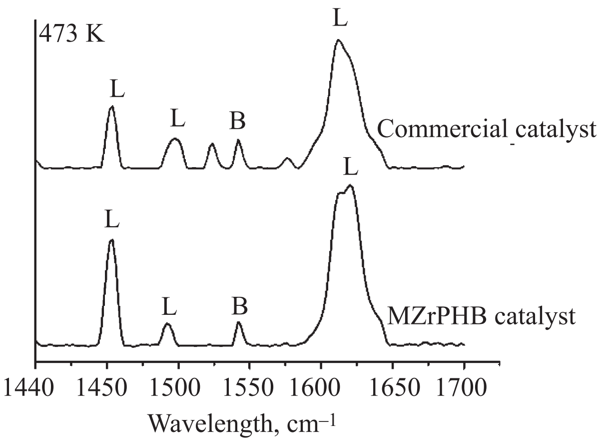

Fig. 3. Pyridine-IR patterns of olefin removing catalysts.

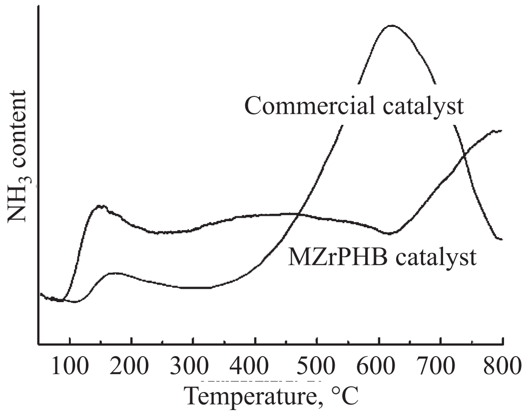

Fig. 4. NH_3-TPD patterns of olefin removing catalysts.

strong acid sites. According to the profiles (Fig. 4), most of the acid sites in MZrPHB catalyst were distributed in weak acidic zone. In comparison with the commercial clay catalyst, MZrPHB has more abundant of weak acid sites , while it has far less strong acid sites. These results are in consistent with above pyridine-IR results. It is well known that strong acid sites accelerate olefins polymerize [19], and become the main reason for clay catalyst deactivation. The study of acidic properties of commercial clay modified with metal halides reveals that the L acid, especially the weak L acid plays an important role in the reaction of aromatic purifying [20]. As a result, the abundant weak L acid sites may explain why the MZrPHB catalyst activity is much better than that of the commercial clay catalyst.

Table 3. The surface acid content of olefin removing catalysts

Catalysis	Comercial catalyst	MZrPHB catalyst
B_T, mmol g^{-1}	0.00386	0.00318
L_T, mmol g^{-1}	0.00932	0.01860

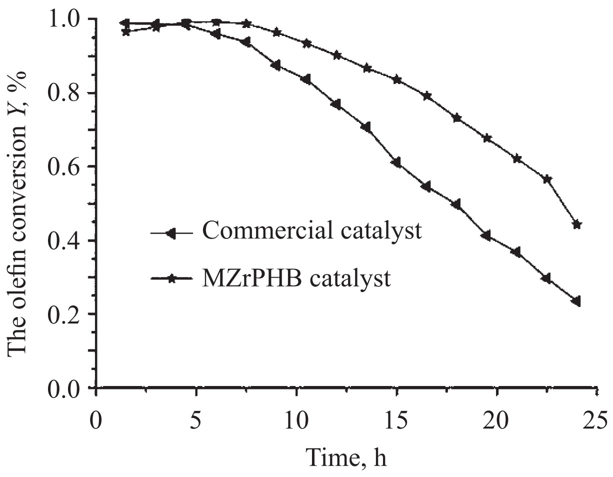

Fig. 5. Catalytic performances of different catalysts for olefin removal reaction.

Catalytic performances of the MZrPHB catalyst and the commercial clay for olefins removal reaction were evaluated with optimal reaction conditions. In Fig. 5 it is demonstrated that the MZrPHB catalyst shows great superiority over the commercial clay. The initial conversion of olefins catalyzed by commercial clay was considerable, but it rapidly inactivate after treating for 5 h. The rapid deactivation rate substantially limited its service life. As a comparison, olefins were catalytically converted almost completely with of MZrPHB over a long usage time and the conversion of olefins remained as appreciable as 90% even after 15 h later. According to above characteristic data, larger surface area, organized mesopore, and more abundance weak L acid site make MZrPHB a superior catalyst in the reaction of aromatic purifying. It is indicated that MZrPHB can be considered as a promising and superior alternative material to commercial clays for aromatics purification.

CONCLUSIONS

A novel mesoporous zirconium phosphonate hybrid bentonite (MZrPHB) catalyst was prepared for removal of trace olefins from refining aromatic oil. It is revealed that the obtained MZrPHB catalyst possesses abundance of weak Lewis acid centers, large surface area, and regular mesopore. Compared to commercial clay catalyst, MZrPHB exhibited longer treat life and higher olefins conversion. And these superior performances are attributed to its acidic properties in combination fine with textural properties.

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