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A Facile Strategy to Prepare Shaped ZSM-5 Catalyst with Enhanced para-Xylene Selectivity and Stability for Toluene Methylation

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Abstract: This work describes the catalytic performances of attapulgite/ZSM-5 extrudate in comparison to conventional alumina-bound ZSM-5 extrudate in toluene methylation. The novel attapulgite/ZSM-5 extrudate is prepared by using natural clay attapulgite as binder which introduces mobile alkaline species and macropores to the extrudate. In contrast to alumina-bound extrudate, this novel extrudate shows significantly higher para-selectivity and stability. By using characterization techniques, including in-situ XRD, SEM, NH_3 temperature programmed desorption (TPD), thermogravimetric analysis and n-hexane/cyclohexane physical adsorption, the catalytic performance improvement of attapulgite/ZSM-5 extrudate is correlated with the neutralization of Brønsted acid sites by mobile alkaline species during calcination and reaction process. Moreover, a higher para-selectivity was obtained over attapulgite-bound modified ZSM-5 extrudate. The strategy of extruding ZSM-5 catalysts with attapulgite as binder is facile and universal. Such method paves a new way for preparation of shaped toluene methylation catalyst with enhanced para-selectivity and stability.

Keywords: toluene methylation; zeolite extrudates; para-xylene selectivity; attapulgite; binder; stability

1. Introduction

para-Xylene, a critical raw material for polyester manufacture, is the most lucrative petrochemical commodity in three xylene isomers [1-4]. The high profit of para-xylene production has created incentives for researchers to work on various aspects of the technologies. Among the routes for on-purpose production of para-xylene, toluene alkylation with methanol to para-xylene is promising to become an important process in the chemical industry, because toluene is produced beyond market demand [4,5] and methanol is expected to be extensively obtained from converting coal and natural gas [4,6,7].

Medium-pore zeolite ZSM-5 is attractive to be used as para-selective alkylation catalyst owing to its pore size comparable to para-xylene dimension [1,8]. However, mixed xylenes with composition close to thermodynamic equilibrium distribution (ortho:meta:para xylene ratio of ~22:53:25 [9]) are produced over unmodified ZSM-5 zeolites, especially nano-sized ZSM-5 zeolites [10]. para-Xylene is separated from other xylene isomers through a very expensive and energy-intensive process of distillation, adsorption and cryogenic crystallization [11,12]. Thus, improving para-selectivity in xylene product, as an effective way to reduce the cost, is the first priority for catalyst design. Commonly used techniques include impregnation of with salts like boron, phosphorous or magnesium compounds [13-15], silanization by deposition of teraethyl orthosilicate [10,13], tuning the crystal size [3] and pre-coking [5].

Most zeolites, such as ZSM-5, are obtained and used as research catalysts in powder form. To implement zeolites in large-scale reactors, shaping process of zeolites (i.e. dispersing zeolites in a binder and shaping to the desired shape) is required to avoid high pressure drop in catalyst beds [16]. However, the preparation of zeolite catalysts from powder to industrially relevant shapes and the influence of shaping on the resulting catalysts are largely neglected in academic investigations. Until recently, the need for a better understanding of shaping process is highlighted in the vibrant area of zeolite catalysis [16-18]. The zeolite-binder interactions result in multiple effects on catalyst activity, stability and product selectivity, with the type of binder playing a pivotal role [17,19-21].

Attapulgite, a fibrous like morphology clay, belongs to hydrated magnesium aluminum silicate minerals. There are significant reserves of attapulgite in China, America and Spain [22,23]. In recent years, attapulgite has received many attention from the academic world due to its structural morphology, surface properties, low-cost and eco-friendly nature [23,24]. Attapulgite is mainly used as sorbent in the removal of metal ions [24,25], catalyst support for various reactions [26], polymer additive for mechanical improvement [27] and synthesis additive for new materials [22,28]. The abundant hydroxyl groups on attapulgite's surface makes it a good binder as well [29]. These hydroxyl groups are dehydrated and cross-linked between adjacent binder particles after calcination, thereby increasing mechanical strength of the shaped catalyst [19].

In this study, a facile strategy for one-step preparation of shaped toluene methylation catalyst with enhanced para-selectivity and stability is developed by extruding ZSM-5 with attapulgite as binder. The major objective of this work is to evaluate the performance of ZSM-5/attapulgite extrudate in toluene methyaltion reaction. As expected, compared with conventional binder boehmite, attapulgite promotes the longevity and the para-xylene selectivity of ZSM-5 zeolite catalyst without a significant deterioration of catalytic activity. The physicochemical properties of the extrudates were obtained and linked to their catalytic behavior based on comprehensive characterization. The strategy's universality was also tested by extruding with modified ZSM-5.

2. Results and Discussion

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2.1 Preparation and Characteristics of ZSM-5 Extrudates

Two zeolite extrudates (the novel extrudate Z5-atp and the conventional extrudate Z5-bo) were obtained following a standard industrial protocol (Figure 1) using HZSM-5 zeolite and attapulgite or boehmite binders respectively (zeolite:binder dry mass ratio 50:50). Herein, the compositional difference between two binders is noteworthy. Boehmite (AlOOH), a traditional binder, becomes Al_2O_3 after calcination in air [18]. As a natural clay, attapulgite is composed of 66.4 SiO_2/15.7 MgO/10.2 Al_2O_3/5.3 Fe_2O_3/1.5 CaO/0.9 K_2O, revealed by X-ray fluorescence spectroscopy analysis.

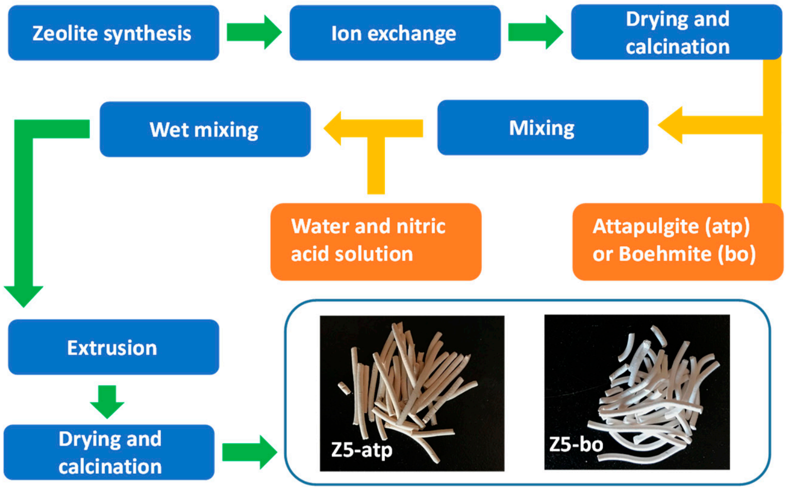

Figure 1. Steps in the preparation of zeolite extrudates with attapulgite and boehmite and the key sample photos accordingly.

XRD patterns of zeolite HZSM-5 and the attapulgite binder are shown in Figure 2. Before calcination, attapulgite exhibits a typical crystalline structure. The peaks at 8.4°, 13.8°, 19.8°, 27.3° and 35.4° are the characteristic diffraction peaks of attapulgite (JCPDS: 21-0958). After calcination, the crystalline structure of attapulgite binder was destroyed. The peaks at 20.3° and 26.6° is characteristic of quartz (JCPDS: 46-1045). The in-situ XRD patterns of the dried Z5-atp and Z5-bo were collected during a step-wise temperature-programmed process (Figure 3). Evidenced by the five characteristic diffraction peaks of MFI topology at 7.8°, 8.8°, 23°, 23.9° and 24.4° (JCPDS: 44-0003) discovered in every patterns in Figure 3, it is clearly that the ZSM-5 structure was not damaged by extrusion or calcination process. As the temperature raised, binders were gradually decomposed. Z5-atp and Z5-bo became mixture of ZSM-5 zeolite and amorphous oxides after calcination at 540 °C.

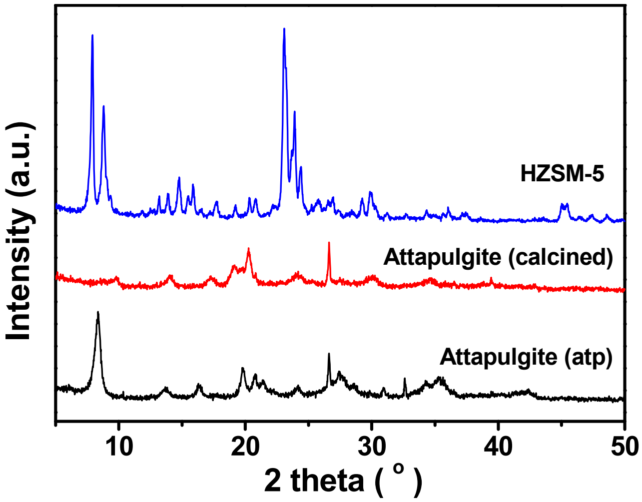

Figure 2. XRD patterns of HZSM-5 powder, the attapulgite binder before and after calcination.

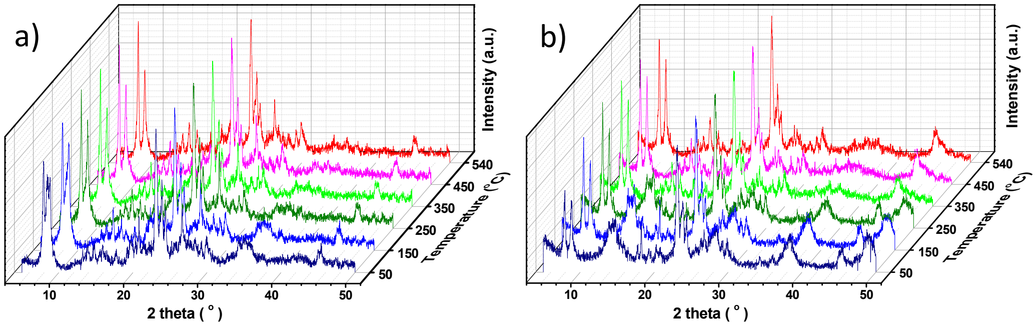

Figure 3. In-situ XRD patterns of Z5-atp (a) and Z5-bo (bo).

The SEM images show the size and morphology of HZSM-5, the attapulgite binder and the calcined Z5-atp extrudate. As shown in Figure 4, HZSM-5 is aggregates of cuboids which crystal size is about 100 nm. Attapulgite adopts a rod-like morphology with diameters of 40-60 nm and lengths of 200 nm to 2 μm. The morphology of calcined Z5-atp extrudate is a ZSM-5/attapulgite complex, in which the rod-like attapulgite binder particles wrap around HZSM-5 aggregates. It shows the intimate contact between the HZSM-5 particles and the highly dispersed attapulgite binder. Interestingly, though the crystalline structure of attapulgite was destroyed after calcination, its morphology remained.

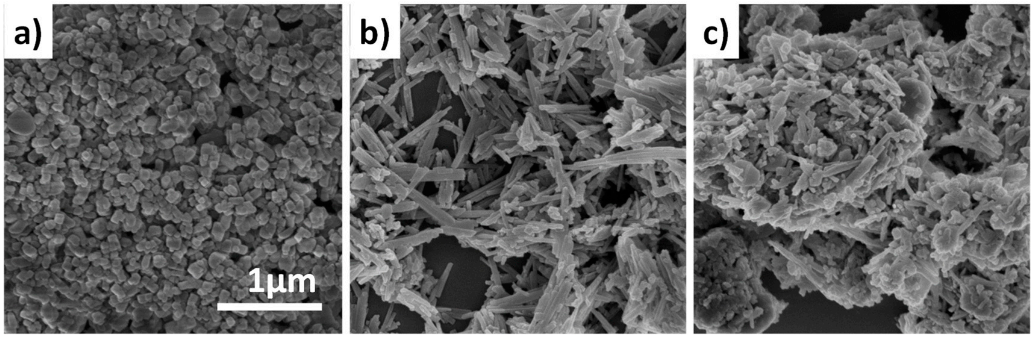

Figure 4. SEM images of HZSM-5 (a), attapulgite (b) and calcined ZSM-5 extrudate Z5-atp (c). The scale bar represents 1 μm and applies to all images.

The N_2 physical adsorption at -196 °C of zeolite extrudates (Z5-atp and Z5-bo) and their powder constituents are presented in Figure 5. The N_2 adsorption isotherm of HZSM-5 powders exhibits type I(b) behavior, according to IUPAC classification [30]. The major uptake at low relative pressure is associated with micropore filling. The uptake after 0.8 relative pressure is referred to the intracrystalline mesopores and macropores caused by small crystal aggregation, which is observed in SEM. The N_2 adsorption/desorption isotherms of bohemite-derived Al_2O_3 binder powder belong to type IV(a) accompanied by a type H2(a) hysteresis loop. Such isotherms indicated that bohemite-derived Al_2O_3 binder is a purely mesoporous material containing mesopores with diameters less than

5 nm. The N_2 adsorption isotherm of the attapulgite-derived binder powder features type II characteristics with a gradual increase and large uptakes at high relative pressure, indicating the presence of macropores in the material. Consistent with the proportional contribution of the component phase, Z5-atp and Z5-bo extrudates exhibit the mixed isotherm of the pure binders and HZSM-5. Isotherm with shape that are intermediate between type I(b) and type II is observed on Z5-atp. Likewise, isotherm of Z5-bo features type I/IV characteristics. In both isotherms, the reduction in the low relative pressure uptakes of Z5-atp and Z5-bo are resulted from the incorporation of binders. Additionally, significant uptakes are observed at high relative pressures with respect to the filling of the mesopores and macropores created by binders. The values of BET surface area, total pore volume are listed in Table 1. The BET surface areas of extrudates are in a good agreement with the calculated surface areas based on the proportional contributions of the zeolite and binder phases, implying that micropores is accessible and not blocked due to interaction of zeolite with binders.

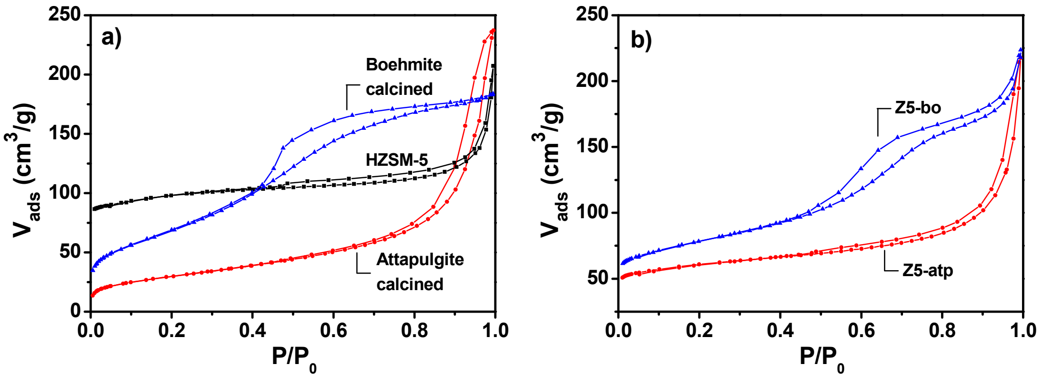

Figure 5. Nitrogen adsorption/desorption isotherms of powders (a) and extrudates (b).

Possible influences of extrusion on the acidity and acidic strength were investigated by using temperature-programmed desorption of ammonia (NH_3-TPD). The area under the profile was integrated and calculated to determine the amount of total acid sites of the catalysts (presented in

Table 1). The peak desorption temperature reflects the acidic strength. As shown in Figure 6, the HZSM-5 catalyst exhibits three acid sites, i.e., weak (a low temperature peak at around 220 °C), medium (a medium temperature peak at around 300 °C) and strong (a high temperature peak at around 450 °C) acid sites. The amount of total acid sites of the zeolite extrudates Z5-atp and Z5-bo are much less than HZSM-5, showing the diluting effect of binders [31]. Compared with Z5-Bo, Z5-atp exhibited a lower total acidity and weaker acid strength. Since no evidence of pore blocking was detected in N_2 physical adsorption, there may be a solid-state ion exchange of some of the mobile species in attapulgite (e.g., MgO) [29,32].

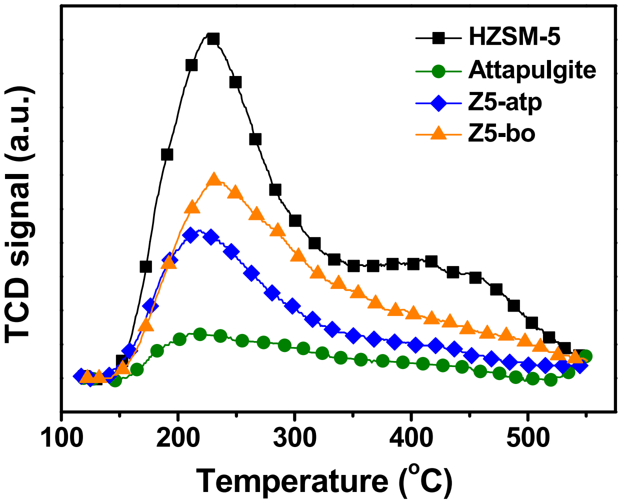

Figure 6. NH3-TPD profiles of zeolite extrudates and their constituents.

Table 1. Characterization and performance data of the pure powder and extruded zeolite catalysts

Catalyst	S_{BET}[a] (m^2/g)	V_{total}[b] (cm^3/g)	C_{acid}[c] (μmol/g)	C_T[d] (%)	S_{PX}[d] (%)	Activity loss[e] (%)
HZSM-5	376	0.21	385	16.4	30.0	--
Attapulgite	107	0.23	--	0.2	58.2	--
Boehmite	255	0.28	--	0.2	54.5	--
Z5-atp	227	0.21	153	16.1	55.9	17.5
Z5-bo	283	0.28	235	15.9	43.5	50.1

[a] BET surface area calculated from the adsorption branch; [b] Pore volume estimated from the single-point amount adsorbed at $P/P_0 = 0.95$; [c] Concentration of total acid sites per gram of zeolite derived

from the NH_3-TPD; [d] Toluene conversion and para-selectivity are the average of samples collected from 4-6 h on stream; [e] Activity loss: [(toluene conversion $_{initial}$- toluene conversion $_{100\ h}$)/ toluene conversion $_{initial}$] ×100%.

2.2 Catalytic Performance in Toluene Methylation Process

The prepared zeolite extrudates were utilized to catalyze the toluene methylation reaction. The performance of the zeolite extrudates as well as their powder constituents were listed in Table 1. To achieve an equivalent weight hourly space velocity of 15 $g_{toluene + methanol}\ g_{zeolite}^{-1}\ h^{-1}$, the mass of the zeolite extrudates was doubled compared with pure HZSM-5 catalyst. The results demonstrate that the binders (attapulgite and boehmite) did not exhibit catalytic activity for toluene methylation. The HZSM-5 catalyst gave a toluene conversion of 16.4%, but its para-selectivity was near-equilibrium. Comparatively, the zeolite extrudate exhibited much higher para-selectivity (i.e., 55.9% for Z5-atp and 43.5% for Z5-bo) with a small decrease on toluene conversion compared with HZSM-5. Figure 7 depicts the plot of toluene conversion and para-selectivity as a function of time on stream (TOS) over the two zeolite extrudates. It is shown that toluene conversion decreased with TOS and para-selectivity increased with TOS on both Z5-atp and Z5-bo. For fresh zeolite extrudates, the initial toluene conversions were both 16.1% for Z5-atp and Z5-bo. The initial para-selectivities were 53.7% for Z5-atp and 42.2% for Z5-bo. After 100 h on stream, the para-selectivity reached 68.3% for Z5-atp and 55.2% for Z5-bo. Meanwhile, the toluene conversion decreased to 13.3% for Z5-atp and 8.0% for Z5-bo. The novel zeolite extrudate Z5-atp exhibited higher para-selectivity and more excellent stability than the conventional zeolite extrudate Z5-bo.

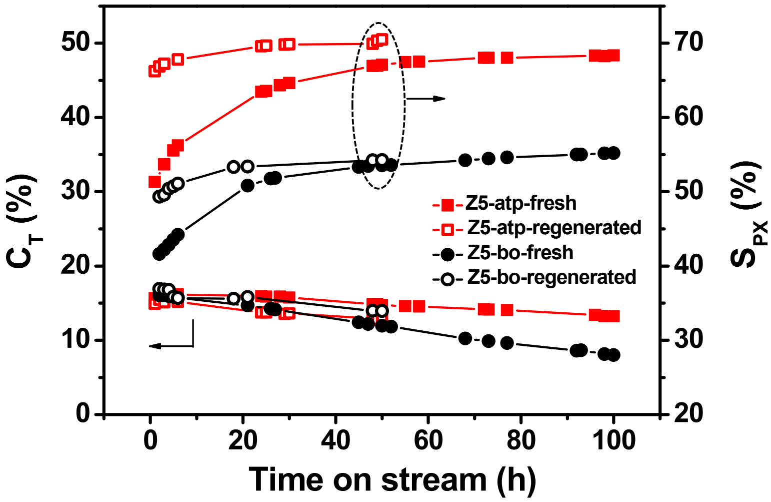

Figure 7. Toluene conversion and para-selectivity as a function of time on stream over Z5-atp (square) and Z5-bo (circle). Solid for fresh catalysts and open for regenerated catalysts.

After continuously 100 h on stream, spent catalysts were unloaded and their coke contents were investigated using thermogravimetric analysis (TGA). TGA curves of these spent catalysts are shown in Figure 8. Both spent samples displayed a two-stage weight loss. The first weight loss was in the range of 25 to 300 ^{o}C, which was attributed to desorption of organics and water adsorbed on catalyst surface [15,33]. The second weight loss was in the range of 300 to 800 ^{o}C, which was ascribed to the decomposition of coke species deposited on catalyst surface [15,33]. Quantification of the coke content on spent Z5-atp was much less than Z5-bo illustrated that attapulgite inhibited the rate of coke formation during toluene methylation.

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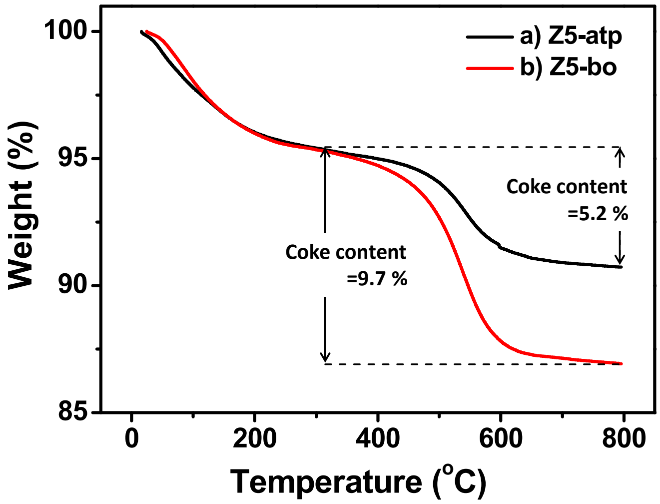

Figure 8. TGA curves of Z5-atp (black) and Z5-bo (red) after toluene methylation reaction. Coke content was calculated by ([mass of 300 ºC] – [mass of 800 ºC])/[mass of 800 ºC] × 100%.

The commonly recognized mechanism for selective production of para-xylene in the toluene methylation reaction is the deactivation of external acidic surface sites along with the controlled reduction in the catalyst pore openings. For the data shown in Figure 7 and the characteristic results in section 2.1, extrusion with attapulgite provides a promising strategy to obtain a shaped catalyst with higher para-selectivity and prolonged catalyst lifetime. As has been shown by other authors before, Brønsted acid sites in zeolite extrudates could be partially neutralized due to the solid state ion-exchange with mobile alkaline species in binders, such as sodium in montmorillonite [32] or magnesium in attapulgite [29]. Revealed in SEM image, the attapulgite binder wrapped around the HZSM-5 zeolite particles, showing an intimate zeolite-binder interaction. Thus, it is reasonable to assume that the partial neutralization resulting from the zeolite-binder interaction started at the external surface of HZSM-5 zeolite. The enhanced para-selectivity over Z5-atp could be attributed to the partial neutralization of external acid sites. At high temperature, it is reported that mass transfer within shaped zeolite catalysts is dominated by diffusion in the macropores [17,34]. In this regard, transport rates of molecules in Z5-atp were more enhanced than Z5-bo due to more macropores introduced via attapulgite. The prolonged lifetime of Z5-atp could be ascribed to the less extra-framework aluminum introduced in extrusion. Prior studies have reported that extra-framework aluminum species catalyze the formation of coke (and methane) in methanol to olefins (MTO) conversion [17,29]. Moreover, aluminum in alumina-bound extrudates can migrate to the zeolite surface, forming additional Brønsted acid sites [21,31]. These extra Brønsted acid sites facilitate coking, resulting a higher coke formation rate.

2.3 In-situ Ion Exchange Modification Effect of Attapulgite

As shown in Figure 7, para-selectivity increased slowly and toluene conversion decreased slowly over both zeolite extrudates during reaction. Such performance could be owing to the coke species deposited on catalyst surface which blocked some external acid sites and channel openings [5]. It is noteworthy that the initial para-selectivity gap between Z5-atp and Z5-bo was 11.5%, while this gap expanded to 13.1% after 100 h on stream. Interestingly, the coke content on Z5-bo was higher than Z5-atp. It means that the para-selectivity gap should went smaller after 100 h on stream if coking is the only cause for para-selectivity increment. Thus, there were other causes for the enhanced para-selectivity during reaction.

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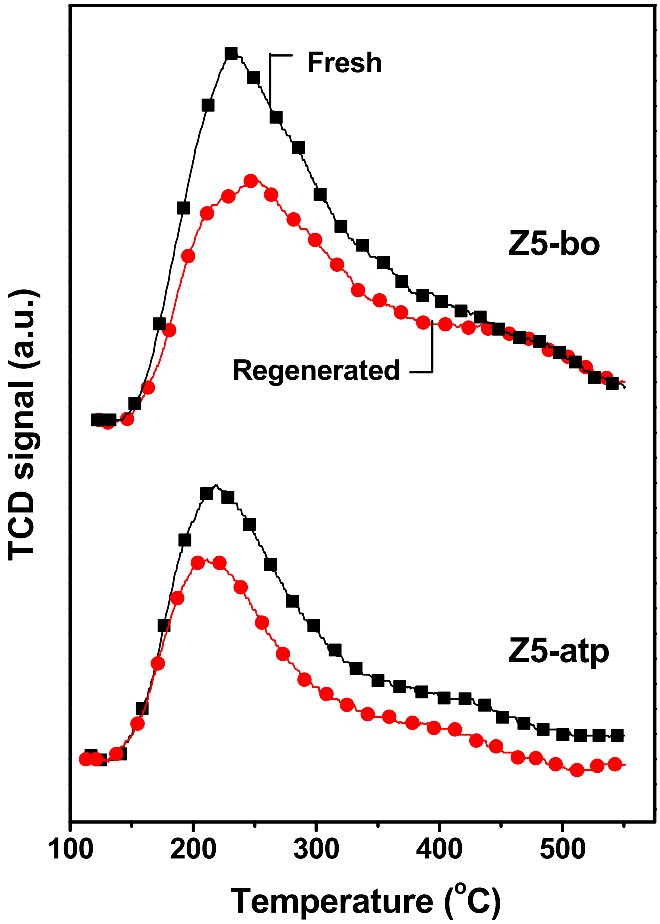

Figure 9. NH3-TPD profiles of fresh (black) and regenerated (red) zeolite extrudates.

As mentioned in section 2.2, earlier studies have found that a solid-state ion exchange between protons of the zeolites and mobile alkaline species of the binder happens during the calcination process subsequent to the extrusion [32]. Breen et al. have also shown that boron modified ZSM-5 can be produced in-situ by either placing a physical mixture of boric acid and ZSM-5 in the reactor at the reaction temperature or placing a boric acid layer directly upstream of ZSM-5 bed [14]. Therefore, it is reasonable to assume that Mg species or other alkali oxides presented in attapulgite can also neutralize the Brønsted acid sites of zeolite throughout the reaction. In toluene methylation reaction conditions, stream are co-fed with reactants. The flushing steam in reactor would be a help for soluble ions migration.

To prove this hypothesis, the reusability of the two zeolite extrudates were tested. Spent Z5-atp and Z5-bo were regenerated at 540 ^{o}C in air for 4 h. The performance of regenerated catalysts are shown in Figure 7. Toluene conversions of regenerated catalysts were equivalent to the fresh analogue. In the second cycle, the initial para-selectivity for Z5-bo was 49.3%, lower than the 55.2% para-selectivity after the first cycle. However, the initial para-selectivity for Z5-atp after regeneration was 66.2%, similar to its para-selectivity before regeneration. Moreover, the para-selectivity of regenerated Z5-atp continuously increased with TOS and reached 70.5% after 50 h, higher than the 68.3% para-selectivity after its first cycle, signaling an in-situ modification effect of attapulgite. To support the assumption, acidity changes of fresh and regenerated zeolite extrudates were characterized by NH_3-TPD. As shown in Figure 9, the amount of total acid sites of Z5-bo and Z5-atp both decreased after regeneration. The decreased acidity of Z5-bo was mainly weak and medium acid sites, whereas all three kinds of acid sites decreased after Z5-atp regeneration. Compared with fresh analogue, the strength of strong acid sites in Z5-atp decreased after regeneration as well. These changes in acidity is consistent with the para-selectivity variation observed in catalyst reusability test and the assumed in-situ modification effect of attapulgite.

It is well known that in addition to the reduction of acidity, the zeolite modification with oxide can reduce the effective dimensions of the catalyst pore openings [10]. The restricted pore openings increase diffusional resistance and, consequently, the para-selectivity in toluene methylation is improved. The extent of pore openings reduction of regenerated zeolite extrudates was evaluated by using n-Hexane and cyclohexane adsorption. n-Hexane can enter a ten-member ring channels of zeolite readily while the diffusion of cyclohexane in a ten-member ring channel is limited [35].

Therefore, the adsorption ratio of n-hxane to cyclohexane over samples shows the reduction extent of the pore openings [10,35]. The higher ratio means the larger reduction extent. Figure 10 shows the adsorption curves of n-hexane and cyclohexane over the fresh and regenerated zeolite extrudates. The four samples exhibited a similar adsorption rates, yet the saturation adsorption amounts of n-hexane or cyclohexane for four samples were different. Calculated from the saturation adsorption amounts, the adsorption ratio for Z5-bo increased from 1.8 to 1.9 after regeneration, whereas the adsorption ratio for Z5-atp decreased from 1.9 to 1.7 after regeneration. It means that the initial para-selectivity increment for regenerated Z5-bo was not only due to the reduced acidity but partially due to the more restricted pore opening which might be caused by the aluminium species migration in alumina-bound ZSM-5 extrudates [21,31]. In the Z5-atp case, the extent of pore opening reduction decreased after regeneration, which indicated that the continuously decreased acidity of Z5-atp was the main reason for para-selectivity increment.

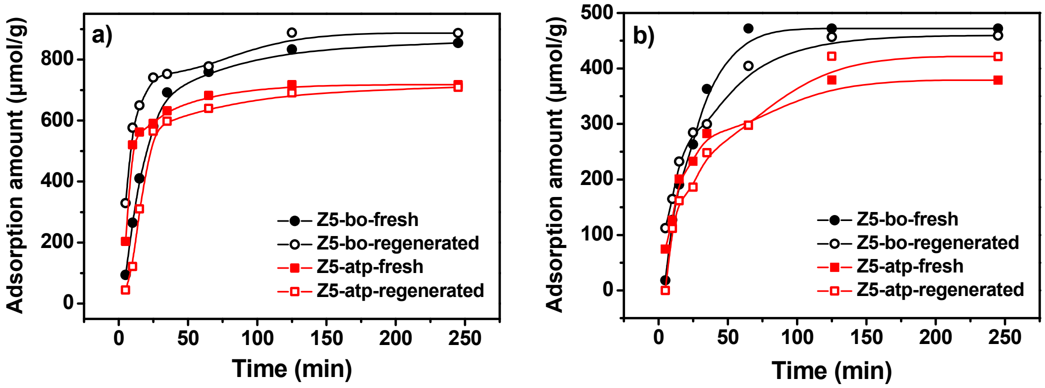

Figure 10. n-Hexane (a) and cyclohexane (b) adsorption of fresh and generated zeolite extrudates.

2.4 Catalytic Performance of Attapulgite-Bound Modified ZSM-5 Extrudates

In previous sections, it has been shown that extrusion with attapulgite is a facile strategy to obtain shaped catalyst with good para-selectivity. We expected that this strategy could be applied to other powder catalysts. To test its universality, a modified ZSM-5 catalyst (M-ZSM-5) was extruded with attapulgite as binder. Figure 11 shows the catalytic performance in toluene alkylation with methanol over M-ZSM-5 and the corresponding extrudate catalysts (MZ5-atp). As shown in the plot, para-selectivity increased from 69.8% to 90.1% after extrusion. Such result shows that alkaline oxide species in attapulgite can not only modify HZSM-5 but also a modified ZSM-5 catalyst. Though the para-selectivity of M-ZSM-5 extrudate increased at the expanse of toluene conversion, the yield of para-xylene increased significantly after extrusion with attapulgite.

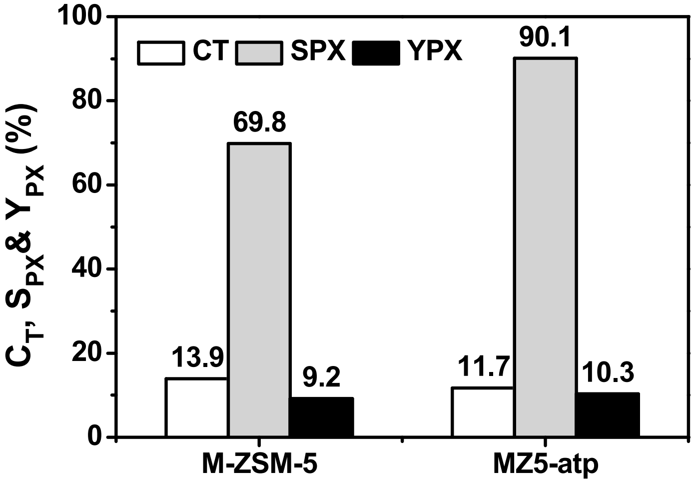

Figure 11. Toluene conversion, para-selectivity and yield of para-xylene over modified ZSM-5 (M-ZSM-5) and its extrudate with attapulgite (MZ5-atp).

3. Experimental

3.1 Catalyst Preparation

Na-ZSM-5 zeolite (SiO_2/Al_2O_3 = 26) was synthesized according to the procedures reported previously [36]. Na-ZSM-5 was converted to the protonic form ZSM-5 by ion-exchange four times at 80 °C for 2 h with a 1 M NH_4NO_3 solution (solid/liquid ratio, 10 g/50 mL). The solid was separated from the slurry by centrifugation and washed with deionized water each time. The material was then dried at 120 ^{o}C for 12 h, and calcined at 540 ^{o}C for 4 h. The obtained protonic form ZSM-5 catalyst was coded as HZSM-5. The binders investigated in this study included attapulgite (coded atp) and boehmite (coded bo). HZSM-5 and binder (50:50 dry mass ratio, accounting for the weight loss upon calcination to 540 ^{o}C) were blended thoroughly and then a predetermined amount of 0.5 M HNO_3 solution and water were added into the solid mixture to form pastes for extrusion. The resulting extrudates were dried at 120 ^{o}C for 12 h, and calcined in air at 540 ^{o}C for 4 h. The obtained catalysts using attapulgite and boehmite as binders were coded as Z5-atp and Z5-bo. For further investigation, HZSM-5 was modified with 6 wt% SiO_2, 5 wt% P_2O_5 and 3 wt% MgO according to procedures described in our previous investigations [10], coded M-ZSM-5. The extrudate obtained from above-mentioned procedure using M-ZSM-5 and attapulgite was coded MZ5-atp.

3.2 Catalyst Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab(9) diffractometer, using a nickel-filtered Cu Kα X-ray source at a scanning rate of 8 ^{o}/min between 5 ^{o} and 50 ^{o}. In-Situ X-ray diffraction (IXD) was also carried out on the same equipment using an in-situ reactor XRK-900. The temperature of the reactor was raised from 50 ^{o}C to 540 ^{o}C under synthetic air at flow rate of 50 ml/min. During this process, the IXD patterns were collected every 100 ^{o}C. SEM images were taken using a field-emission scanning electron microscopy (NOVA NanoSEM 450) at an accelerating voltage of 10.0 kV. N_2 adsorption/desorption isotherms at -196 ^{o}C were recorded in a Quantachrome Quantasorb-SI gas adsorption analyzer after evacuation of the samples at 300 ^{o}C for 10 h. Temperature programmed desorption of ammonia (NH_3-TPD) was performed on an automated chemisorption analyzer (Quantachrome ChemBET Pulsar TPR/TPD) from 120 to 650 ^{o}C at a temperature ramp rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a SDT Q600 thermal gravimetric analyzer (TA Instruments) in the temperature range of 25-800 °C under air atmosphere at a ramping rate of 10 °C/min. Isothermal adsorption of n-Hexane and cyclohexane were measured on a home-made apparatus by a flow gravimetric method at 25 °C. The sample was dehydrated before measurement at 350 °C under nitrogen atmosphere for 1 h.

3.3 Catalytic studies

The gas phase alkylation of toluene (T) with methanol (M) was studied in a fixed-bed reactor with a stainless steel tube under atmospheric pressure. Hydrogen and steam were used as carrier gas with molar ratios of $H_2/(T+M)=2$ and $H_2O/(T+M)=2$. In each test, 0.5g of the catalyst was employed and heated at 500 °C for 1 h under a hydrogen flow prior to reaction. The reaction was carried out at 460 °C. The mixture of toluene and methanol (molar ratio 4:1) was introduced via an HPLC pump with a WHSV (weight hourly space velocity of toluene and methanol) of 15 h^{-1}. The reactor effluent was collected in a cold trap and analyzed by Agilent GC6890 gas chromatography (GC) equipped with an INNOWAX capillary column (60 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID).

The toluene conversion (C_T) and the selectivity of para-xylene or para-selectivity (S_{PX}) were defined in the following equations:

$$C_T\ (\%) = \left(1 - \frac{\text{toluene in product}}{\text{toluene in reactant}}\right) \times 100\% \qquad (1)$$

$$S_{PX}\ (\%) = \frac{\textit{para}\text{-xylene}}{\textit{para}\text{-xylene}+\textit{meta}\text{-xylene}+\textit{ortho}\text{-xylene}} \times 100\% \qquad (2)$$

4. Conclusions

The use of the novel attapulgite-bound extrudates of ZSM-5 provides several advantages in toluene methylation reactions:

1) Alkali oxides species presented in attapulgite neutralize the Brønsted acid sites of zeolite during calcination process and throughout the reaction. The decreased acidity caused by the neutralization is correlated with the enhanced para-selectivity and stability in toluene methylation.
2) The macropores induced via attapulgite enhanced mass transfer within shaped zeolite catalysts. As a consequence, there is no significant deterioration of toluene conversion compared with HZSM-5 powder catalysts.
3) Extruding ZSM-5 catalysts with attapulgite as binder is a facile and universal strategy to optimize the acidity and acid sites distribution in shaped catalysts. Other than attapulgite/HZSM-5 extrudate, a higher para-selectivity was obtained over attapulgite-bound modified ZSM-5 extrudate.

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