available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

One-step post-synthesis treatment for preparing hydrothermally stable hierarchically porous ZSM-5

Jian Ding, Teng Xue, Haihong Wu *, Mingyuan He

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:

Received 31 August 2016

Accepted 30 September 2016

Published 5 January 2017

Keywords:

Desilication

Phosphorus stabilization

One-step modification

Hydrothermal stability

Hydrocarbon cracking

ABSTRACT

Hierarchically porous ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 \approx 120$) containing phosphorus was prepared by a one-step post-synthesis treatment involving controlled desilication and phosphorous modification. The hierarchically porous ZSM-5 featured high thermal and hydrothermal stability. The obtained ZSM-5 zeolites were systematically characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, N_2 adsorption-desorption, NH_3 temperature-programmed desorption, and ^{27}Al and ^{31}P magic-angle spinning nuclear magnetic resonance spectroscopy. The prepared ZSM-5 displayed enhanced activity and prolonged lifetime toward hydrocarbon cracking. The high activity was attributed to improved coke tolerance owing to the presence of the highly stable mesoporous network of ZSM-5 and acid sites introduced upon phosphorus modification. Additionally a mechanism of the stabilization of the zeolites by phosphorus was proposed and discussed.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
Published by Elsevier B.V. All rights reserved.

1. Introduction

ZSM-5, a typical zeolite with the topological structure of MFI, plays an important role in catalysis [1]. Owing to its high catalytic activity and unique shape-selectivity, it has been widely studied and used in many industrial processes such as alkylation, disproportionation, isomerization, and cracking [2–5]. However, the relatively small pore size ($< 2 \text{ nm}$) of conventional ZSM-5 zeolites causes mass-transfer issues, thereby limiting the broad applications of ZSM-5 [6–9]. To overcome this drawback, hierarchically porous ZSM-5, possessing at least two levels of porosity (typically micropores and mesopores), has been extensively investigated. The combined microporosity and mesoporosity can alleviate diffusion limitation issues, thereby improving accessibility to acidic sites of large mole-

cules. These advantages can lead to reduced catalyst deactivation and enhanced activity during specific catalysis processes [6–9]. Various strategies for preparing hierarchically porous ZSM-5 have been described in the literature over the past few decades [10–14]. Among them, desilication is a promising approach owing to its low cost, high efficiency [15,16], and convenient operation [17,18].

Additionally, the stability of the mesoporous network plays an important role in the activity and lifetime of a catalyst in practical applications. When the catalyst is exposed to a thermal and/or hydrothermal environment, dealumination typically occurs, leading to collapse of the mesoporous structure and depletion of acidic sites. Thus, it is necessary to stabilize the zeolite structure and acid sites in hierarchically porous zeolites. Phosphorus modification has been proven to be an

* Corresponding author. Tel/Fax: +86-21-62238510; E-mail: hhwu@chem.ecnu.edu.cn

This work was supported by the National Natural Science Foundation of China (21403070, 21573073), National Key Technology Research and Development Program (2012BAE05B02), and Shanghai Leading Academic Discipline Project (B409).

DOI: 10.1016/S1872-2067(16)62549-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 1, January 2017

efficient method for structure stabilization [19–21]. The framework aluminum pairs can be stabilized by extra-framework cationic species formed by protonation of orthophosphoric acid [22]. As a result, dealumination is inhibited and lattice aluminum is less susceptible to leaving the zeolite framework upon interaction between the framework aluminum and phosphorus [23,24]. These modifications and resulting stabilization are typically conducted on the microporous zeolites. However, mesopores formed by silicon extraction are always disordered and less stable than the microporous structure [25]. Thus, it is important to stabilize the mesoporous network in hierarchically structured zeolites. Although stabilization by phosphorus is demonstrated to be a promising technique to enhance the hydrothermal stability of zeolites, reduction in acid strength occurs inevitably [26–28]. Upon interaction with the zeolitic framework, phosphorus species can substitute the protons on the oxygen of the bridging hydroxyl groups in the zeolitic framework to form P–OH by replacing Al–OH [29]; such a mechanism maintains the level of acidity of the resulting framework. Accordingly, achieving a balance between stabilization and weakening of acid sites upon phosphorus modification is important to design highly efficient catalysts.

In our previous work [30], hierarchically porous high-silica ZSM-5 with high hydrothermal stability was prepared by desilication and subsequent inorganic phosphorus modification. The obtained hierarchically porous ZSM-5 displayed excellent performance in various acid-catalyzed reactions. However, the synthesis procedure was complex and tedious as it involves multiple steps. Therefore, synthesizing hierarchically porous ZSM-5 with high hydrothermal stability using a more direct and convenient approach is of great interest. Moreover, the stabilization modification was limited to the following phosphorus species: H_3PO_4 , sodium phosphates, and ammonium phosphates. These phosphorus species would non-selectively distribute in the zeolite channels [31–33]. To more effectively use the phosphorus species, understanding the insertion of phosphorus into the zeolitic framework is important.

Herein, organic quaternary phosphonium hydroxide (TEPOH) was chosen as a novel phosphorus source to enhance the accessibility and interaction with aluminum in the zeolite framework and to avoid leaching of phosphorus from the zeolite channels. Hierarchically porous ZSM-5 zeolites containing phosphorus were prepared using a newly developed method. Subsequently, the catalytic performance of the prepared hierarchically porous ZSM-5 toward dealkylation of 1,3,5-triisopropylbenzene (TIPB) and cracking of 1-octene was examined.

2. Experimental

2.1. Chemicals

The properties of chemicals used in this work are as follows: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (AR, SCRC), H_2SO_4 (98%, SCRC), water glass (SiO_2 , 27.1 wt%), TEABr (99%, Sigma-Aldrich), TPAOH (1 mol/L in water, Sigma-Aldrich), NaOH (AR, SCRC), TEPBr (99%, Alfa Aesar), Ag_2O (AR, SCRC), TEAOH (25 wt% in water, SCRC),

and $(\text{NH}_4)_2\text{HPO}_4$ (AR, SCRC).

2.2. Synthesis of parent ZSM-5 (Z5)

Parent ZSM-5 (denoted as Z5) was synthesized according to a literature procedure [30]. Briefly, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was used as the aluminum source and dissolved in sulfuric acid solution (0.65 mol/L). Then, the solution was mixed with water glass, tetraethylammonium bromide (TEABr), and seeding gel to obtain a mixture with a molar composition of $230\text{SiO}_2:1\text{Al}_2\text{O}_3:11.5\text{Na}_2\text{O}:11.5\text{TEABr}:6900\text{H}_2\text{O}$. The seeding gel, containing 0.5 wt% SiO_2 , was prepared with a molar composition of $\text{SiO}_2:0.35\text{tetraethylammonium hydroxide (TEAOH)}:19.6\text{H}_2\text{O}$ at 80 °C for 3 d. The mixture was hydrothermally treated at 175 °C for 3 d to induce crystallization. Then, the as-prepared powder was recovered by filtration, washed with deionized water several times until the pH of the liquor was neutral, and dried at 100 °C overnight. The resulting zeolite Z5 was obtained after calcination at 550 °C in atmospheric pressure and ion-exchanged to obtain the H-form of the zeolite.

2.3. One-step post-synthesis treatment of Z5 for preparing Z5-AT@TEP⁺-a

To prepare the hierarchically porous ZSM-5 containing phosphorus, Z5 was subjected to a one-step treatment at 70 °C in an aqueous alkaline solution containing 0.2 mol/L of OH^- -based solution. Typically, 1 g of Z5 was uniformly dispersed into a pre-heated alkaline solution containing NaOH, TEPOH (prepared by TEPBr and Ag_2O), and TEAOH with a concentration molar ratio of $(\text{TEP}^+ + \text{TEA}^+)/\text{OH}^-$ of 0.2 [34]. The amount of TEP^+ was pre-calculated based on the expected P_2O_5 loading of 1.5 wt% on the zeolite. After stirring for 30 min, the mixture was quickly cooled to room temperature and washed until the pH of the supernatant was neutral. After drying overnight at 100 °C, the hierarchically porous ZSM-5 containing phosphorus was obtained and denoted as Z5-AT@TEP⁺-a, where AT@TEP⁺ refers to the concurrent alkaline treatment (AT) and phosphorus (TEP⁺) modification applied.

2.4. Preparation of reference samples Z5-AT, Z5-AT@PO₄³⁻-a, and Z5-AT-PO₄³⁻-a

For comparison, three reference samples, i.e., Z5-AT (obtained upon alkaline treatment only, i.e., without phosphorus modification), Z5-AT@PO₄³⁻-a (obtained upon alkaline treatment in an inorganic phosphorus-containing solution with concurrent inorganic $(\text{NH}_4)_2\text{HPO}_4$ modification), and Z5-AT-PO₄³⁻-a (obtained upon alkaline treatment, followed by inorganic $(\text{NH}_4)_2\text{HPO}_4$ impregnation), were prepared as follows.

Alkali treatment of Z5 was performed in an aqueous solution of 0.2 mol/L OH^- -based solution at 70 °C. Typically, 1 g of Z5 was uniformly dispersed into a pre-heated alkaline solution containing both NaOH and TEAOH at a TEAOH-to- OH^- concentration molar ratio of 0.2. After stirring for 30 min, the mixture was cooled rapidly in an ice-water bath. After thorough washing, drying overnight at 100 °C, calcination at 550 °C for 6 h in

atmospheric pressure, and ion-exchange, Z5-AT in H-form was obtained [30].

Z5-AT@PO₄³⁻-a was prepared by desilication in a pre-heated alkaline solution of 0.2 mol/L OH⁻-based solution, which contained NaOH, TEAOH ([TEAOH]/[NaOH] = 0.25) and a known amount of (NH₄)₂HPO₄ (based on the expected P₂O₅ loading of 1.5 wt% on the zeolite). After 30 min of stirring, the mixture was quickly cooled to room temperature and washed until the pH of the supernatant was neutral. Z5-AT@PO₄³⁻-a was obtained after drying at 120 °C for 8 h.

Z5-AT-PO₄³⁻-a was prepared by subsequent phosphorus impregnation of Z5-AT. Z5-AT was added to a (NH₄)₂HPO₄ solution (the mass percentage of zeolite was 1.5% calculated by P₂O₅). The mixture was stirred at room temperature for 4 h and subsequently heated at 80 °C under stirring until the mixture turned to a paste. The paste was dried at 120 °C for 8 h to remove residual moisture [30].

2.5. Hydrothermal activation and steam-aging

Activation of the phosphorus element in the prepared zeolites was performed on an FCC catalyst steam-aging equipment (Beijing Wekindu Technology Co. Ltd.). Specifically, Z5-AT@TEP⁺-a, Z5-AT@PO₄³⁻-a, and Z5-AT-PO₄³⁻-a were activated at 550 °C for 3 h in 100% steam (4.4 g H₂O/min). Following calcination and ion-exchange, the phosphorus-containing samples were obtained in H-form and labeled as Z5-AT@TEP⁺, Z5-AT@PO₄³⁻, and Z5-AT-PO₄³⁻, respectively. The H-type zeolites were also steam-aged at 800 °C for 17 h in 100% steam (4.4 g H₂O/min), and the aged products were denoted with the suffix “-HT”.

2.6. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV powder diffractometer using Cu K_α radiation (λ = 0.154184 nm) over a 2θ range of 5°–50°; the accelerating voltage and applied current were 35 kV and 25 mA, respectively. The relative crystallinity of the products was determined from the peak area within a 2θ range of 22.5°–25° using a commercial ZSM-5 sample, as a reference, supplied by Nankai University Catalyst Co., Ltd. Scanning electron microscopy (SEM) was performed on a HITACHI S-4800 scanning electron microscope, operating at an accelerating voltage of 3 kV. High-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) images were collected on a JEM-2010, operating at 200 kV. The SiO₂/Al₂O₃ ratio and P content in the products were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. N₂ adsorption-desorption isotherms were recorded on a Quantachrome Autosorb-3B instrument at –196 °C. The mesopore size distribution was determined from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. ²⁷Al solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a VARIAN VNMRS-400WB spectrometer. ³¹P NMR measurements

were performed with a 4.0-mm MAS probe on a Bruker Avance III spectrometer. NH₃ temperature-programmed desorption (NH₃-TPD) was conducted on a Tianjin XQ TP5080 automatic adsorption apparatus fitted with a thermal conductivity detector. For the measurements, 100 mg of the H-type samples was pretreated at 550 °C for 2 h under helium flow, and NH₃ adsorption was conducted at 100 °C. After removing the physically adsorbed NH₃, the samples were heated to 550 °C at a rate of 10 °C/min.

2.7. Catalytic tests

The cracking of 1-octene was performed at atmospheric pressure in a microreactor fitted with a quartz tube with an inner diameter of 8 mm. Before the reaction, 50 mg of 20–60 mesh mixture pellets of zeolite and silica gel (Qingdao), prepared by mass-equal grinding, was packed in a fixed-bed reactor and heated at 650 °C for 1 h in a stream of N₂. Then, 1-octene was fed with N₂ at a constant temperature of 650 °C. The weight hourly space velocity of 1-octene was 121 h⁻¹. The products were analyzed by two on-line gas chromatograph instruments, GC-9890A (Shanghai Linghua, HP-5 capillary column, 60 m × 0.32 mm × 0.25 μm) and GC-14B (Shimadzu, DM-plot alumina capillary column, 50 m × 0.25 mm × 10 μm), both equipped with a flame ionization detector. Thermogravimetric (TG) analysis of the spent catalysts was performed on NETZSCH/STA 449 F3; the measurements were conducted in flowing air at a heating rate of 10 °C/min.

The dealkylation of TIPB was evaluated in a microreactor fitted with a quartz tube of an inner diameter of 6 mm. Prior to the catalytic reaction, 50 mg of 20–60 mesh zeolite ZSM-5 pellets prepared without a binder was pre-treated at 380 °C for 60 min in a stream of N₂. Then, while maintaining a constant temperature of 380 °C, 0.5 μL of substrate was injected into the catalyst bed with N₂ fed from the top of the reactor. The flow of the carrier gas was 80 mL/min. The TIPB cracking products were analyzed by an on-line gas chromatograph instrument (GC-9800A, Shanghai Kechuang; FFAP capillary column, 30 m × 0.25 mm × 0.25 μm), equipped with a flame ionization detector.

3. Results and discussion

3.1. Zeolitic properties

XRD analysis was performed to investigate possible structural changes in ZSM-5 that occurred upon alkaline treatment and phosphorus modification. The alkaline-treated samples and the organic and inorganic phosphorus-modified samples displayed diffraction patterns similar to that of the untreated zeolite (Z5) (Fig. 1). The intensity of the peaks of all post-synthesis-treated samples decreased slightly. This decrease could be attributed to the removal of Si from the framework [17]. Though the different post-synthesis treatments led to different degrees of structural collapse, the long-range ordering of the microporous network of all the samples were maintained. Furthermore, the relative crystallinity of all samples was higher than 80%. This result indicates

Fig. 1. XRD patterns of the different ZSM-5 samples prepared using different treatments.

that the framework silicon was removed in a controlled fashion with the aid of TEA⁺ cations [35].

Fig. 2 presents the N₂ adsorption-desorption isotherms and pore size distributions of the different ZSM-5 samples prepared in the present study. Parent Z5 displayed a typical Type I isotherm, which is characteristic of a microporous system. In contrast, Z5-AT and Z5-AT@TEP⁺ exhibited Type IV isotherms, characterized by a high N₂ uptake at high p/p_0 values. This fea-

ture indicated that mesoporosity was efficiently introduced in the zeolite framework during desilication. Table 1 presents the physicochemical properties of all the samples prepared. The external surface area (S_{ext}) and mesopore volume (V_{meso}) of Z5-AT increased considerably from 35 m²/g and 0.07 cm³/g (Z5) to 159 m²/g and 0.37 cm³/g, respectively. When compared with the S_{ext} and V_{meso} of Z5-AT, those of Z5-AT@TEP⁺ increased to 166 m²/g and 0.37 cm³/g, respectively. Z5-AT@PO₄³⁻ and Z5-AT-PO₄³⁻ displayed similar isotherms and textural properties.

Additionally, Z5-AT, Z5-AT@PO₄³⁻, and Z5-AT-PO₄³⁻ featured comparable pore size distribution profiles. This result indicates that the free inorganic phosphate or organic quaternary phosphonium species in solution had minimal influence on desilication. However, the physicochemical properties of Z5-AT following steam-aging changed considerably, indicating an obvious collapse in the framework, as listed in Table 1. Specifically, S_{ext} of Z5-AT-HT decreased to 74 m²/g (from 159 m²/g for Z5-AT); however, the Type IV isotherm features were preserved. In contrast, the phosphorus-modified hierarchically porous ZSM-5 could maintained their textural properties even under severe steam-aging. The level of preservation of the S_{ext} value (calculated by the ratio of S_{ext} before steam-aging to S_{ext} after steam-aging, presented in parentheses below) decreased in the order of Z5-AT@TEP⁺-HT (86%) > Z5-AT-PO₄³⁻-HT (79%) > Z5-AT@PO₄³⁻-HT (51%) > Z5-AT-HT (46%), relative to the S_{ext} before steam-aging. The phosphorus-containing zeolite sample, Z5-AT@TEP⁺-HT, displayed a lower degree in re-

Fig. 2. N₂ adsorption-desorption isotherms (a) and pore size (b) of Z5 (1), Z5-AT (2), Z5-AT@PO₄³⁻ (3), Z5-AT-PO₄³⁻ (4), and Z5-AT@TEP⁺ (5). The closed markers represent the as-prepared samples and the opened markers represent the steam-aged samples.

Table 1

Physicochemical properties of the different zeolite samples prepared using different treatments.

Sample	SiO ₂ /Al ₂ O ₃	P content ^a (%)	R.C. ^b (%)	<i>A</i> _{BET} ^c (m ² /g)	<i>A</i> _{ext} ^d (m ² /g)	<i>V</i> _{micro} ^d (cm ³ /g)	<i>V</i> _{meso} (cm ³ /g)	NH ₃ capacity (mmol NH ₃ /g)
Z5	145	— ^e	100	378	35	0.14	0.07	0.254
Z5-HT	152	—	93	362	45	0.13	0.11	0.031
Z5-AT	105	—	92	464	159	0.12	0.37	0.277
Z5-AT-HT	111	—	81	326	74	0.10	0.24	0.044
Z5-AT@PO ₄ ³⁻	95	—	90	470	173	0.12	0.38	0.291
Z5-AT@PO ₄ ³⁻ -HT	102	—	79	339	88	0.10	0.30	0.054
Z5-AT-PO ₄ ³⁻	109	1.40	93	437	189	0.12	0.31	0.192
Z5-AT-PO ₄ ³⁻ -HT	113	1.34	95	448	150	0.11	0.39	0.068
Z5-AT@TEP ⁺	115	1.44	91	430	153	0.12	0.35	0.215
Z5-AT@TEP ⁺ -HT	110	1.46	89	396	131	0.11	0.37	0.107

^a Calculated based on the expected P₂O₅ loading in the zeolite. ^b Calculated within a 2θ range of 23°–25°.^c Calculated by the Brunauer-Emmett-Teller (BET) method. ^d Calculated by the *t*-plot method. ^e Undetected.

duction in *S*_{ext} than the phosphorus-free zeolite Z5-AT-HT. Similarly, the level of retention of *V*_{meso} decreased in following order: Z5-AT-PO₄³⁻-HT (126%) > Z5-AT@TEP⁺-HT (106%) > Z5-AT@PO₄³⁻-HT (79%) > Z5-AT-HT (65%). This trend demonstrates that the phosphorus-modified samples possess higher hydrothermal stability than the phosphorus-free sample. The textural properties of Z5-AT@TEP⁺-HT, especially the mesoporosity, were better preserved than those of Z5-AT-PO₄³⁻-HT. Thus, higher hydrothermal stability of the mesoporous network was achieved in Z5-AT@TEP⁺-HT than in Z5-AT-PO₄³⁻-HT. Furthermore, the degree of complexity of the one-step post-synthesis treatment employed is lower when compared with that of previous report [11]. Notably, similar textural properties of both Z5-AT@PO₄³⁻-HT and Z5-AT-HT were obtained following steam-aging. As observed in Table 1, no phosphorus species was detected in Z5-AT@PO₄³⁻. This result indicates that almost no inorganic phosphorus species remains after desilication and related subsequent treatments. Thus, the stabilizing effect provided by phosphorus modification was minimal in Z5-AT@PO₄³⁻-HT.

SEM images of the samples subjected to different treatment are presented in Fig. 3. The parent Z5 consisted of uniform crystals of ~2 μm, possessing a typical coffin-like morphology (Fig. 3(a)). No obvious changes in the morphology were ob-

served after the various post-synthesis treatments, indicating that desilication occurred in a controlled fashion in the presence of organic cations [34]. Fig. 3(f) shows a HAADF-STEM image of Z5; the bright area highlights a crystalline particle, featuring microporosity only. The presence of extensive intracrystalline mesoporosity formed in Z5-AT@TEP⁺ zeolite could readily be distinguished by the dark spots against the original bright area, outlining the crystalline particle, in Fig. 3(g). The presence of the newly created mesopores in Z5-AT@TEP⁺ observed by HAADF-STEM was consistent with the N₂ adsorption-desorption results. The results of the mesopore size and *V*_{meso} (developed upon treatment in a mixed solution of NaOH, TEAOH, and TEPOH) of Z5-AT@TEP⁺ were considerably different from those of Z5 (Fig. 2 and Table 1).

NH₃-TPD measurements were conducted to determine the strength and amount of acid sites on the zeolite samples. As observed from Table 1 and Fig. 4, the NH₃ capacity on Z5-AT and Z5-AT@PO₄³⁻ was slightly larger than that of the parent Z5 because of the lower SiO₂/Al₂O₃ ratio after desilication [36]. The NH₃-TPD profile of Z5-AT@TEP⁺ indicated that the introduction of phosphorus species into the zeolite, especially those adsorbed on strong acid sites, reduced the NH₃ capacity. This result confirmed the acid-weakening effect of phosphorus on the zeolite [24]. A similar phenomenon was observed for

Fig. 3. SEM images of Z5 (a), Z5-AT (b), Z5-AT@PO₄³⁻ (c), Z5-AT-PO₄³⁻ (d), and Z5-AT@TEP⁺ (e); HAADF-STEM images of Z5 (f) and Z5-AT@TEP⁺ (g).

Fig. 4. NH_3 -TPD profiles of the ZSM-5 zeolites prepared using different treatments. The solid lines refer to the as-prepared samples and the dotted lines refer to the steam-aged samples.

Z5-AT-PO_4^{3-} , as consistent with the results in the literature [30]. The total adsorption capacity of NH_3 for all samples decreased significantly after steam-aging at 800 °C for 17 h. This phenomenon was attributed to the occurrence of dealumina-

tion and related reduction in acid site density on these samples. The level of retention of acid site density of the steamed samples decreased in the order of $\text{Z5-AT@TEP}^+\text{-HT}$ (50%) > $\text{Z5-AT-PO}_4^{3-}\text{-HT}$ (35%) > $\text{Z5-AT@PO}_4^{3-}\text{-HT}$ (18%) > Z5-AT-HT (16%) > Z5-HT (12%). The acid site density in the phosphorus-containing samples, especially $\text{Z5-AT@TEP}^+\text{-HT}$, after steam-aging was better preserved than in the phosphorus-free samples [22]. It could be concluded that the acid sites were stabilized because dealumination of the zeolitic framework was inhibited by phosphorus modification [24]. The higher level of preservation of acid site density in $\text{Z5-AT@TEP}^+\text{-HT}$ when compared with that of $\text{Z5-AT-PO}_4^{3-}\text{-HT}$ suggests the efficacy of this simple post-synthesis treatment.

The ^{27}Al and ^{31}P MAS NMR analysis results presented in Fig. 5 provide information on the coordination state of aluminum and phosphorus in the samples prepared using different treatments. In the ^{27}Al MAS NMR spectra of ZSM-5, several peaks, corresponding to different species, were observed at the following positions: ~55 ppm (tetrahedral aluminum in the zeolite framework), ~0 ppm (typical octahedral aluminum in extra-framework positions), ~36 ppm (intermediate aluminum species, tetrahedral aluminum in a distorted environment probably in the zeolite framework or $(\text{SiO})_x\text{Al}(\text{OP})_{4-x}$ sites formed by substitution of some silicon with phosphorus atoms at high temperatures), ~10 ppm (octahedral aluminum in a distorted environment attached to phosphate) and ~-10 ppm (octahedral aluminum attached to phosphorous) [20,31,37–41]. Only one intense and sharp signal at 57 ppm was observed in the spectrum of Z5-AT , indicating that all the

Fig. 5. ^{27}Al (a) and ^{31}P (b) MAS NMR spectra of the ZSM-5 samples prepared using different treatments.

aluminum atoms were tetrahedrally coordinated. Z5-AT-HT contains approximately half extra-framework aluminum (resonance signal observed at 0 ppm) owing to the occurrence of dealumination during steam-aging. Similar spectra were obtained for Z5-AT@PO₄³⁻ before and after steam-aging. In the phosphorus-containing samples, most aluminum maintained their tetrahedral coordination in a phosphorus-interacted environment (resonances at 52 ppm). In the spectra of Z5-AT-PO₄³⁻ and Z5-AT@TEP⁺, minor signals were observed at -10 ppm, indicating the interaction between newly formed octahedral coordinated aluminum and phosphate during hydrothermal activation. After severe steam-aging, an intense signal at 36 ppm was observed in the spectrum of Z5-AT@TEP⁺-HT. In contrast, the spectrum of Z5-AT-PO₄³⁻-HT displayed a weak signal at 30–58 ppm and an intense peak at 10 ppm. These results reveal that more framework aluminum have been preserved and stabilized during organic phosphorus modification than during inorganic phosphorus modification. This phenomenon can be ascribed to the fact that TEP⁺ can appropriately ion-exchange with Na⁺ ions, which are mainly located near the aluminum atoms to balance the framework charge. Thus, the propensity of interaction between phosphorus and framework aluminum is enhanced.

³¹P MAS NMR spectroscopy was used to further investigate the state of phosphorus in the phosphorus-containing samples. As shown in Fig. 5(b), both the spectra of Z5-AT@PO₄³⁻ and Z5-AT@PO₄³⁻-HT did not feature any signals, attributed to the loss of phosphorus species during preparation of the zeolites. The spectra of the phosphorus-containing samples subjected to hydrothermal activation displayed broad peaks from -7 to -50 ppm and centered at -14 ppm. The signals could be ascribed to either phosphorus in pyrophosphoric acid or terminal groups of polyphosphates not attached to Al (-6 to -8 ppm), middle and terminal groups of polyphosphates either attached or not attached to Al (-12 to -30 ppm), and middle groups of highly condensed polyphosphates attached to Al (-32 to -40 ppm) [22,31,42–44]. Upon subsequent aging, the coordination of phosphorus changed further. For instance, the spectrum of Z5-AT-PO₄³⁻-HT displayed a narrow and sharp signal centered

at -31 ppm, which is related to amorphous aluminum phosphate [45]. In contrast, the spectrum of Z5-AT@TEP⁺-HT displayed a broad and intense resonance from 0 to -17 ppm. This result indicates that the phosphorus species is in a lower state of condensation than that in Z5-AT-PO₄³⁻-HT. Condensation is closely related to the dispersion of phosphorus species on zeolites. The lower degree of phosphorus condensation indicates the presence of enhanced interaction between phosphorus and aluminum on Z5-AT@TEP⁺-HT rather than the occurrence of self-condensation.

Scheme 1 shows a possible stabilization mechanism for hydrothermal activation according to the information gathered on the coordination of Al and P species from the ²⁷Al/³¹P MAS NMR spectra in Fig. 5 and a previously reported mechanism [30]. During activation, the phosphorus species in TEP⁺ transform to (poly)phosphates [46]. Most of the framework aluminum retain their tetrahedral coordination state (52 ppm), whereas a few tetrahedral aluminum in Z5-AT@TEP⁺ are removed from the framework as octahedral aluminum (0 ppm in the ²⁷Al NMR spectrum of Z5-AT@TEP⁺), and the octahedral aluminum interact with phosphorus (-10 ppm). Consequently, in this process, two possible phosphorus–aluminum structures form as presented in Scheme 1 (structures 1 and 2). These structures include both the framework aluminum and extra-framework aluminum attached to the phosphorus. In the subsequent steam-aging process, most of the framework aluminum attach to the phosphorus in a newly distorted environment (36 ppm in the ²⁷Al NMR spectrum of Z5-AT@TEP⁺-HT). Additionally, a few extra-framework aluminum attach to the phosphorus. Based on this information, we propose that the stabilized structures (structures 3 and 4; broad signal detected ranging from -7 to -50 ppm in the ³¹P NMR spectrum of Z5-AT@TEP⁺-HT) are derived upon changes in the structures 1 and 2 during steam-aging.

3.2. Catalytic activity

The catalytic activity of all steam-aged samples was evaluated toward cracking of 1-octene. The evolution of the catalytic

Scheme 1. Proposed mechanism of the interaction between Al and P during hydrothermal activation and steam-aging processes.

activity of the five steam-aged samples as a function of time on stream is shown in Fig. 6(a). High initial conversions (> 95%) were obtained over all the steam-aged samples. However, the 1-octene conversion over Z5-HT rapidly decreased within 3–15 h of reaction from ~100% to ~75%. In contrast, the rate of conversion over Z5-AT-HT reduced at a slower pace; the reduced conversion rate was attributed to enhanced coke toler-

Fig. 6. Conversion profiles (a) and coke content (b) during 1-octene cracking and conversion and selectivity profiles of TIPB cracking over the steam-aged zeolites (c).

ance. Z5-AT@PO₄³⁻-HT displayed a trend similar to that of Z5-AT-HT; the lack of catalytic performance over that sample was attributed to the absence of effective phosphorus modification. The conversion of 1-octene remained mostly steady (i.e., ~98%) within 10 h of reaction over Z5-AT@TEP⁺-HT. A similar trend was observed for Z5-AT-PO₄³⁻-HT, which displayed a conversion of ~97%. When the reaction period was extended further to 20 h, a slight decrease in conversion occurred over Z5-AT-PO₄³⁻-HT (87%) and Z5-AT@TEP⁺-HT (91%). Based on these results, it can be deduced that the presence of hierarchical porosity and stable acid sites in the zeolite catalyst can realize sustainably high conversions of reduced spatial-constrained molecules in an acid-catalyzed reaction.

Coke formation within micropores causes more significant deactivation than that on the external surface owing to pore channel blockage and active site coverage [13]. To further investigate the catalytic performance of the prepared catalyst samples, the coke content on the used samples was analyzed by TG (Fig. 6(b)). The highest coke content was detected on the used Z5-AT@TEP⁺-HT. This result indicated that the relatively higher mesoporosity and acid density of Z5-AT@TEP⁺-HT led to higher coke tolerance and longer catalyst lifetime when compared with Z5-HT and Z5-AT-HT [47,48].

The catalytic performance of TIPB cracking is illustrated in Fig. 6(c). TIPB cracking conversion over the differently treated ZSM-5 samples decreased in the order of Z5-AT@TEP⁺-HT > Z5-AT-PO₄³⁻-HT > Z5-AT-HT > Z5-AT@PO₄³⁻-HT > Z5-HT. This trend demonstrated that diffusion of TIPB was accelerated by mesopore introduction. Furthermore, higher product selectivity of terminal cracking products benzene (BZ) was observed over Z5-AT@TEP⁺-HT, indicating that the stabilized acid sites favored the typical acid-catalyzed reactions [49]. Furthermore, the catalytic testing results reveal that hierarchical ZSM-5 containing phosphorus performs better than the parent ZSM-5 and hierarchically porous phosphorus-free ZSM-5. Additionally, comparison of the zeolites stabilized by phosphorus reveals that the zeolite prepared via a one-step method shows superior catalytic performance than phosphorus-modified zeolites prepared by conventional methods.

4. Conclusions

A convenient, one-step post-synthesis treatment to introduce mesopores and phosphorus moieties in high-silica ZSM-5 was successfully developed by controlled desilication under the protection of TEA⁺. Phosphorus was integrated near framework aluminum in the form of quaternary phosphonium. The characterization studies showed that porosity optimization and structure stabilization were efficiently realized by the one-step method. Consequently, Z5-AT@TEP⁺ displayed superior catalytic performance than traditionally post-synthesis-treated hierarchically porous ZSM-5 modified with phosphorus. Higher conversions in TIPB dealkylation and remarkably prolonged catalytic performance of Z5-AT@TEP⁺-HT in 1-octene cracking were realized. Such excellent performance was ascribed to both the optimized porosity and the reduced propensity of structure collapse and acid sites poisoning.

References

- [1] W. W. Kaeding, L. B. Young, C. C. Chu, *J. Catal.*, **1984**, 89, 267–273.
- [2] C. Feng, K. Khulbe, T. Matsuura, R. Farnood, A. Ismail, *J. Membr. Sci. Res.*, **2015**, 1, 49–72.
- [3] B. M. Weckhuysen, J. Yu, *Chem. Soc. Rev.*, **2015**, 44, 7022–7024.
- [4] D. Kubička, O. Kikhtyanin, *Catal. Today*, **2015**, 243, 10–22.
- [5] W. W. Kaeding, C. Chu, L. B. Young, S. A. Butter, *J. Catal.*, **1981**, 69, 392–398.
- [6] A. Corma, *Chem. Rev.*, **1997**, 97, 2373–2420.
- [7] J. Pérez-Ramírez, F. Kapteijn, J. C. Groen, A. Doménech, G. Mul, J. A. Moulijn, *J. Catal.*, **2003**, 214, 33–45.
- [8] M. Hartmann, *Angew. Chem. Int. Ed.*, **2004**, 43, 5880–5882.
- [9] T. Tago, H. Konno, Y. Nakasaka, T. Masuda, *Catal. Surv. Asia*, **2012**, 16, 148–163.
- [10] J. Pérez-Ramírez, C. H. Christensen, K. Egeblad, C. H. Christensen, J. C. Groen, *Chem. Soc. Rev.*, **2008**, 37, 2530–2542.
- [11] J. Ding, J. B. Hu, T. Xue, Y. M. Wang, H. H. Wu, P. Wu, M. Y. He, *RSC Adv.*, **2016**, 6, 38671–38679.
- [12] H. Mochizuki, T. Yokoi, H. Imai, S. Namba, J. N. Kondo, T. Tatsumi, *Appl. Catal. A*, **2012**, 449, 188–197.
- [13] M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, *Nature*, **2009**, 461, 246–249.
- [14] B. K. Singh, D. D. Xu, L. Han, J. Ding, Y. M. Wang, S. Che, *Chem. Mater.*, **2014**, 26, 7183–7188.
- [15] F. L. Bleken, K. Barbera, F. Bonino, U. Olsbye, K. P. Lillerud, S. Bordiga, P. Beato, T. V. W. Janssens, S. Svelle, *J. Catal.*, **2013**, 307, 62–73.
- [16] J. Li, X. Y. Li, G. Q. Zhou, W. Wang, C. W. Wang, S. Komarneni, Y. J. Wang, *Appl. Catal. A*, **2014**, 470, 115–122.
- [17] J. C. Groen, J. A. Moulijn, J. Pérez-Ramírez, *J. Mater. Chem. A*, **2006**, 16, 2121–2131.
- [18] S. Mitchell, M. Milina, R. Verel, M. Hernández-Rodríguez, A. B. Pinar, L. B. McCusker, J. Pérez-Ramírez, *Chem. Eur. J.*, **2015**, 21, 14156–14164.
- [19] H. E. Van Der Bij, F. Meirer, S. Kalirai, J. Wang, B. M. Weckhuysen, *Chem. Eur. J.*, **2014**, 20, 16922–16932.
- [20] M. Derewinski, P. Sarv, X. Sun, S. Müller, A. C. van Veen, J. A. Lercher, *J. Phys. Chem. B*, **2014**, 118, 6122–6131.
- [21] Q. Fu, C. P. Kelkar, G. Smith, B. Yilmaz, US Patent 8940652, **2015**.
- [22] T. Blasco, A. Corma, J. Martínez-Triguero, *J. Catal.*, **2006**, 237, 267–277.
- [23] T. F. Degnan, G. K. Chitnis, P. H. Schipper, *Microporous Mesoporous Mater.*, **2000**, 35, 245–252.
- [24] N. H. Xue, X. K. Chen, L. Nie, X. F. Guo, W. P. Ding, Y. Chen, M. Gu, Z. K. Xie, *J. Catal.*, **2007**, 248, 20–28.
- [25] R. Chal, C. Gérardin, M. Bulut, S. Van Donk, *ChemCatChem*, **2011**, 3, 67–81.
- [26] K. Y. Lee, H. K. Lee, S. K. Ihm, *Top. Catal.*, **2010**, 53, 247–253.
- [27] H. G. Jang, H. K. Min, S. B. Hong, G. Seo, *J. Catal.*, **2013**, 299, 240–248.
- [28] J. J. Huangfu, D. S. Mao, X. L. Zhai, Q. S. Guo, *Appl. Catal. A*, **2016**, 520, 99–104.
- [29] J. A. Lercher, G. Rumpelmayr, *Appl. Catal.*, **1986**, 25, 215–222.
- [30] J. Ding, M. Wang, L. M. Peng, N. H. Xue, Y. M. Wang, M. Y. He, *Appl. Catal. A*, **2015**, 503, 147–155.
- [31] G. Caeiro, P. Magnoux, J. M. Lopes, F. R. Ribeiro, S. M. C. Menezes, A. F. Costa, H. S. Cerqueira, *Appl. Catal. A*, **2006**, 314, 160–171.
- [32] D. Minoux, C. Adam, N. Nesterenko, S. Van Donk, J. P. Dath, W. Vermeiren, US Patent 9249066, **2016**.
- [33] D. H. Choo, H. C. Kim, S. J. Kim, J. M. Kim, T. J. Kim, S. Choi, S. H. Oh, Y. S. Kim, D. S. Park, Y. K. Park, C. W. Lee, H. Y. Kim, W. C. Choi, N. Y. Kang, B. S. Song, US Patent 9056308, **2015**.
- [34] K. Sadowska, K. Góra-Marek, M. Drozdek, P. Kuśtrowski, J. Datka, J. Martínez Triguero, F. Rey, *Microporous Mesoporous Mater.*, **2013**, 168, 195–205.
- [35] J. C. Groen, L. A. A. Peffer, J. A. Moulijn, J. Pérez-Ramírez, *Chem. Eur. J.*, **2005**, 11, 4983–4994.
- [36] J. C. Groen, J. C. Jansen, J. A. Moulijn, J. Pérez-Ramírez, *J. Phys. Chem. B*, **2004**, 108, 13062–13065.
- [37] Z. M. Yan, D. Ma, J. Q. Zhuang, X. C. Liu, X. M. Liu, X. W. Han, X. H. Bao, F. X. Chang, L. M. Xu, Z. Liu, *J. Mol. Catal. A*, **2003**, 194, 153–167.
- [38] Y. Y. Shu, D. Ma, X. C. Liu, X. W. Han, Y. D. Xu, X. H. Bao, *J. Phys.*

Graphical Abstract

Chin. J. Catal., 2017, 38: 48–57 doi: 10.1016/S1872-2067(16)62549-4

One-step post-synthesis treatment for preparing hydrothermally stable hierarchically porous ZSM-5

Jian Ding, Teng Xue, Haihong Wu*, Mingyuan He
East China Normal University

Hierarchically porous ZSM-5 with high hydrothermal stability was obtained by a one-step post-synthesis treatment involving simultaneous controlled desilication and phosphorous modification. The prepared catalyst displayed prolonged catalytic activity and stability toward hydrocarbon cracking.

- Chem. B*, **2000**, 104, 8245–8249.
- [39] C. A. Fyfe, *Solid State NMR for Chemists*, CFC Press, Guelph, Ont., **1983**.
- [40] R. F. Nogueira, M. I. B. Tavares, R. A. San Gil, A. G. Ferreira, *Mater. Sci. Appl.*, **2011**, 2, 453.
- [41] Z. Li, J. Martínez-Triguero, J. Yu, A. Corma, *J. Catal.*, **2015**, 329, 379–388.
- [42] J. Caro, M. Bülow, M. Derewinski, J. Haber, M. Hunger, J. Kärger, H. Pfeifer, W. Storek, B. Zibrowius, *J. Catal.*, **1990**, 124, 367–375.
- [43] N. H. Xue, R. Olindo, J. A. Lercher, *J. Phys. Chem. C*, **2010**, 114, 15763–15770.
- [44] K. Damodaran, J. W. Wiench, S. M. Cabral de Menezes, Y. M. Lam, J. Trébosc, J. P. Amoureux, M. Pruski, *Microporous Mesoporous Mater.*, **2006**, 95, 296–305.
- [45] P. M. Bautista, J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas, A. A. Romero, *Appl. Catal. A*, **1993**, 96, 175–199.
- [46] T. Sonoda, T. Maruo, Y. Yamasaki, N. Tsunooji, Y. Takamitsu, M. Sadakane, T. Sano, *J. Mater. Chem. A*, **2015**, 3, 857–865.
- [47] Y. Nakasaka, J. i. Nishimura, T. Tago, T. Masuda, *Chem. Eng. J.*, **2015**, 278, 159–165.
- [48] R. Javai, K. Urata, S. Furukawa, T. Komatsu, *Appl. Catal. A*, **2015**, 491, 100–105.
- [49] S. Al-Khattaf, J. A. Atias, K. Jarosch, H. de Lasa, *Chem. Eng. Sci.*, **2002**, 57, 4909–4920.

一步处理法制备高水热稳定多级孔 ZSM-5 分子筛

丁 键, 薛 腾, 吴海虹*, 何鸣元

华东师范大学化学与分子工程学院上海市绿色化学与化工过程绿色化重点实验室, 上海 200062

摘要: ZSM-5 具有较高的催化活性和独特的择形选择性, 因而被广泛用于精细化工和石油炼制等工业过程。但其较小的孔道尺寸导致其在反应中尤其在催化过程中的传质受到影响, 从而严重影响催化剂寿命。为了解决反应过程中分子筛中底物及产物的扩散限制问题, 近年来关于介孔复合多级孔道分子筛的研究在分子筛合成领域引起了广泛兴趣, 并取得一定进展。但直接合成法存在成本及复杂性问题, 因此在量产的分子筛上进行后改性引入介孔表现出明显优势。在这一大类处理过程中, 碱处理造介孔因成本低以及可操作性较高而备受青睐。但由于脱硅所形成的介孔往往无序, 稳定性较差, 因此提高其水热稳定性具有重要意义。

文献已有较多报道通过磷元素修饰抑制分子筛在水热环境中脱铝, 从而提高分子筛骨架稳定性。但传统的磷元素修饰一般采用后续浸渍法, 过程繁琐。本课题组开发了一步法后处理制备高水热稳定多级孔 ZSM-5 分子筛, 将脱硅过程与磷引入过程相结合, 以四乙基氢氧化磷(TEPOH)为磷源, 直接处理微孔分子筛得到含磷的多级孔分子筛。相比于传统的分子筛磷修饰过程, 该磷物种在处理中优先交换分子筛骨架上铝原子附近用来平衡电荷的钠离子, 从而增加了磷物种与铝物种相互作用的可能性, 提高了稳化骨架的效果。基于此, 本文利用氮吸附-脱附、元素分析、X 射线粉末衍射(XRD)、扫描电镜(SEM)、透射电镜(TEM)、氨程序升温脱附(NH₃-TPD)以及 ²⁷Al 和 ³¹P 固体核磁(NMR)等一系列表征技术, 证明该一步后处理法对分子筛催化性能的作用。

SEM 和 XRD 结果表明, 分子筛在进行各种处理前后, 相对结晶度和分子筛形貌变化不大, 说明大部分微孔得到保留。TEM 测试表明, 经过该一步后处理法得到的分子筛实现了介孔的引入, 介孔孔径在 10–20 nm。元素分析结果表明, 几乎所有的磷源物质在该过程中被引入到分子筛上, 实现了介孔和磷物种的同时引入。NH₃-TPD 测试表明, 含磷分子筛在老化前后较无磷分子筛具有更高的酸性位密度保留度, 说明磷元素对分子筛上的酸性位起到了稳化作用。孔结构特性数据不仅说明了脱硅过程中成功引入介孔, 而且含磷分子筛老化前后的介孔特性数据保留度明显高于无磷样品, 实现了磷元素对介孔结构的稳化作用。²⁷Al 和 ³¹P NMR 结果从理论上证明了该样品上磷元素对抑制骨架脱铝的稳化效应, 证实了分子筛在处理后的水热稳定性的提高。

基于前期的研究工作, 本文完善了磷元素对分子筛稳化作用的机理过程。TEPBr 在水热活化过程中转变成磷酸盐, 并修饰分子筛的骨架铝以及部分难以避免的非骨架铝。该过程中形成的磷铝物种在后续的水热老化过程中进一步修饰分子筛骨架铝, 使骨架铝得到稳化。而在脱硅过程中存在的“反插铝”过程往往使大部分骨架铝位于介孔孔道中, 磷元素与铝元素的相互作用同时也对介孔进行了稳化。通过正辛烯和 1,3,5-三异丙苯的裂化测试发现, 处理后的分子筛由于其优化后的孔道性能和酸性性质, 大大提高了底物分子的转化率以及其自身的容碳能力, 从而延长了催化寿命。

关键词: 脱硅; 磷修饰; 一步处理法; 水热稳定性; 烃类裂解

收稿日期: 2016-08-31. 接受日期: 2016-09-30. 出版日期: 2017-01-05.

*通讯联系人. 电话/传真: (021)62238510; 电子邮箱: hhwu@chem.ecnu.edu.cn

基金来源: 国家自然科学基金(21403070, 21573073); 国家科技支撑计划(2012BAE05B02); 上海市教委重点学科建设项目(B409).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).