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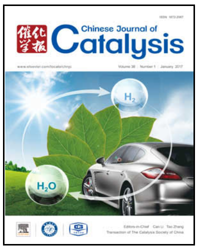

Article

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

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Hierarchically porous ZSM-5 ($SiO_2/Al_2O_3 \approx 120$) 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.

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 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 molecules. 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

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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: $Al_2(SO_4)_3·18H_2O$ (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 $(NH_4)_2HPO_4$ (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, $Al_2(SO_4)_3·18H_2O$ 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 $230SiO_2$:$1Al_2O_3$:$11.5Na_2O$:11.5TEABr:$6900H_2O$. The seeding get, containing 0.5 wt% SiO_2, was prepared with a molar composition of SiO_2:0.35 tetraethylammonium hydroxide (TPAOH):$19.6H_2O$ 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 (TEP^+ + TEA^+)/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@PO_4^{3-}-a, and Z5-AT-PO_4^{3-}-a

For comparison, three reference samples, i.e., Z5-AT (obtained upon alkaline treatment only, i.e., without phosphorus modification), Z5-AT@PO_4^{3-}-a (obtained upon alkaline treatment in an inorganic phosphorus-containing solution with concurrent inorganic $(NH_4)_2HPO_4$ modification), and Z5-AT-PO_4^{3-}-a (obtained upon alkaline treatment, followed by inorganic $(NH_4)_2HPO_4$ 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