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Article

Highly hydrothermally stable $FePO_4$–SBA-15 synthesized using a novel one-pot hydrothermal method

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ABSTRACT

The hydrothermal stability of $FePO_4$–SBA-15 synthesized using a novel one-pot hydrothermal method (OP) was systematically investigated using two methods: treatment with pure steam at 800 °C or with boiling water at 100 °C. The structural changes in the samples were monitored using small angle X-ray diffraction and N_2-physisorption methods. It was found that the hydrothermal stabilities of OP samples remained high and showed little difference over the $FePO_4$-doping range 5–40 wt%. These results differ from previous reports that the loading of heterogeneous metal atoms significantly influences the hydrothermal stability of the host ordered mesoporous material. For comparison, the hydrothermal stabilities of $FePO_4$–SBA-15 synthesized using an impregnation method (IMP) and commercially obtained SBA-15 were also studied. The order of the sample hydrothermal stabilities was OP > IMP >> SBA-15. The formed $FePO_4$ protective layers helped to prevent mesostructure degradation during hydrothermal treatment, therefore modified samples showed superior hydrothermal stabilities compared with pure SBA-15. The superior performance of OP samples over IMP samples is mainly attributed to the formation of stable Si–O–Fe bonds and more micropores in OP samples.

1. Introduction

Since the discovery of the M41S silicate family in 1992 [1,2], highly ordered mesoporous silicates have attracted great interest because of their properties such as high surface areas, large pore volumes, and tunable pore sizes. Much research has focused on the use of ordered mesoporous silicate materials as catalysts and catalyst supports [3–5].

Catalyst reactivity and stability are the most important factors in catalysis, therefore the hydrothermal stabilities of materials, especially in 100% steam at 600–800 °C, are crucial factors in industrial applications such as steam reforming and catalytic cracking [4,6,7]. Much research has been performed on improving the hydrothermal stabilities of mesoporous silicates. It has been reported that mesoporous silicates with thicker walls, more micropores, and silica walls with higher degrees of polymerization are more stable under hydrothermal conditions [8–14]. Some effective approaches have been developed to improve the hydrothermal stabilities of mesoporous materials, such as high-temperature treatments [8,15], carbon-propping thermal treatments [8], and addition of inorganic salts [16–19]. These approaches increase the polymerization degree of the silica framework or protect mesoporous channels against collapse, thereby improving the hydrothermal stabili-

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ties of mesoporous silicates. It has also been demonstrated that the introduction of a metal into mesoporous silica greatly improves its hydrothermal stability, and the metal loading significantly affects the hydrothermal stability, especially in treatments in pure steam at 800 °C [20–24]. Li et al. [20] reported that Al–SBA-15 samples, prepared using a post-synthesis method, with lower Al contents were more stable under steam at 800 °C than samples with higher Al contents. With increasing Al content, more micropores on the pore walls are buried by the Al layer, and micropores are important in improving the hydrothermal stability of mesoporous silicate. At high Al contents, the Al species easily form agglomerates during steam treatment, therefore the protective Al layer is destroyed and many ≡Si–O–Si≡ bonds are exposed to the steam. However, Selvaraj et al. [24] found that Cr–SBA-15 samples with higher amounts of Cr showed better hydrothermal stabilities than those with low Cr amounts. They suggested that Cr–SBA-15 with higher amounts of Cr had more Si–O–Cr bonds, which are relatively stable to further attack by water molecules, and more tetrahedral Cr^{6+}/Cr^{5+} ions can create more negative charges on the pore wall surfaces, which could repel attacks by water molecules and OH^- groups on the ≡Si–O–Si≡ bonds of the framework. They also found that Ga–SBA-15 behaves like Cr–SBA-15 in hydrothermal treatment [21]. There is still a debate on the effect of metal atoms on the hydrothermal stability of a mesoporous material.

In our previous work [25], $FePO_4$–SBA-15 (OP) synthesized using a novel one-pot hydrothermal method showed good catalytic activity and excellent stability during oxybromination of methane for 1000 h; this reaction requires severe reaction conditions, i.e., a high temperature of about 600 °C and corrosive HBr/H_2O as the feedstock. These results suggest that the OP sample is very stable and resistant to severe conditions for a long time. A deeper understanding and exploration of the reasons for the hydrothermal stabilities of OP samples will help in the development of hydrothermally stable catalysts and other materials. In this study, we investigated the hydrothermal stabilities of OP samples with low and high $FePO_4$ loadings, namely 5 and 40 wt%, by treating them with boiling water at 100 °C or pure steam at 800 °C. In addition, we compared the hydrothermal stabilities of OP samples with $FePO_4$–SBA-15 (IMP) samples prepared using an impregnation method and commercially available SBA-15. X-ray diffraction (XRD) and N_2 physisorption were used to determine the changes in the structural properties caused by the hydrothermal treatments.

2. Experimental

2.1. Synthesis

$FePO_4$–SBA-15 was prepared using a previously reported one-pot hydrothermal method [25]; the synthetic procedure was as follows. A certain amount of $Fe(NO_3)_3·9H_2O$ and tetraethyl orthosilicate (TEOS, 8.2 mL) were hydrolyzed in deionized water (10 mL) for 30 min to obtain solution A. A nonionic triblock copolymer surfactant ($EO_{20}PO_{70}EO_{20}$ (P123), 4 g) was dissolved in 85 wt% H_3PO_4 and deionized water and stirred at 35 °C for 2 h to obtain solution B. Solution A was added dropwise to solution B with stirring, and then subsequently stirred vigorously for 20 h at 35 °C. The mixture was then aged in an autoclave for 24 h at 90 °C. The resultant solid was filtered, washed with deionized water, and dried at 60 °C for 12 h in air. Calcination involved two steps: heating at 250 °C for 3 h, and then at 600 °C for 4 h. The molar composition of the initial solution was 1.0 TEOS : 0.017 P123 : nFe : 1.5 H_3PO_4 : 208 H_2O (n = 0.02091 and 0.26490). The obtained $FePO_4$–SBA-15 samples with $FePO_4$ loadings of 5 wt% and 40 wt% were denoted by 5OP and 40OP, respectively.

For comparison, $FePO_4$–SBA-15 was also prepared using a previously reported incipient wetness impregnation method with $Fe(NO_3)_3·9H_2O$ and H_3PO_4 as precursors [26]. SBA-15 was purchased from the Changchun Jilin University High Tech. Co., Ltd. The obtained samples with $FePO_4$ loadings of 5 wt% and 40 wt% were denoted by 5IMP and 40 IMP, respectively.

2.2. Hydrothermal stability evaluation

The hydrothermal stability was investigated by treating the OP samples in a closed bottle at 100 °C for 7 d under static conditions. The obtained solid products were denoted by 5OP-b100 and 40OP-b100.

The high-temperature hydrothermal stability was investigated by exposing the OP, IMP, and SBA-15 samples to pure steam (100% water vapor) at 600, 700, and 800 °C at autogenous pressure for 24 h. The obtained samples were denoted by xOP-sT, xIMP-sT, and SBA-15-sT, respectively, where x (%) is the $FePO_4$ loading (x = 5 or 40), and T is the hydrothermal treatment temperature (T = 600, 700, or 800 °C).

2.3. Characterization

The structural properties of the samples were determined by N_2 physisorption using a physical adsorption instrument (Quantachrome, USA). Before the measurements, the samples were outgassed at 300 °C in a vacuum for 3 h. The specific surface areas were calculated using the BET method. The total pore volumes were estimated from the amounts adsorbed at a relative pressure of 0.99. The micropore volumes were determined using V–t plots. The pore size distributions were derived from the desorption branches of the isotherms using the BJH method, except in the cases of 5OP and 5IMP, which were derived from the adsorption branches of the isotherms using the BJH method. Powder XRD patterns were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer using Cu K_α (40 kV, 40 mA) radiation.

3. Results and discussion

3.1. Effect of $FePO_4$ loading on hydrothermal stabilities of OP samples

The metal loading has an important effect on the hydrothermal stabilities of ordered mesoporous materials supported metal samples [20–23,27]. We investigated the effect of $FePO_4$