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Article

Highly hydrothermally stable FePO₄-SBA-15 synthesized using a novel one-pot hydrothermal method

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ABSTRACT

The hydrothermal stability of FePO₄-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 N₂-physisorption methods. It was found that the hydrothermal stabilities of OP samples remained high and showed little difference over the FePO₄-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 FePO₄-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 FePO₄ 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.

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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 stabi-

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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 $\equiv\text{Si-O-Si}\equiv$ 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 $\text{Cr}^{6+}/\text{Cr}^{5+}$ ions can create more negative charges on the pore wall surfaces, which could repel attacks by water molecules and OH^- groups on the $\equiv\text{Si-O-Si}\equiv$ 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 $\text{HBr}/\text{H}_2\text{O}$ 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 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (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 : $n\text{Fe}$: 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 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 $\text{Cu K}\alpha$ (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

loading on the hydrothermal stability of the OP samples. Two methods were used to evaluate the OP sample hydrothermal stability: treatment with boiling water at 100 °C for 7 d or with pure steam at 800 °C for 24 h. Small-angle XRD and N₂ physisorption were used to examine the structural properties of the OP samples before and after hydrothermal treatments.

Fig. 1(a) shows the small-angle XRD patterns of 50P, 50P-b100, and 50P-s800. It can be seen that all these samples had similar XRD patterns, with only one clear diffraction peak at 0.9°–1.1°, which can be attributed to the (100) facets of SBA-15; the peaks corresponding to the (110) and (200) facets were less prominent. Furthermore, a comparison of the fresh and treated 50P samples shows that the relative intensity of the (100) peak changed slightly after treatment with boiling water at 100 °C or pure steam at 800 °C. It is therefore concluded that 50P retained an ordered hexagonal mesostructure after the hydrothermal treatments. However, after treatment with pure steam at 800 °C, the (100) diffraction peak of 50P shifted to a larger 2θ value, suggesting that the sample mesopores shrank during treatment with pure steam at 800 °C. Similarly, as shown in Fig. 1(b), the XRD patterns of fresh and treated 40OP indicated that these samples still had hexagonal mesostructures after the different hydrothermal treatments; however, the sample mesopores shrank during treatment with pure steam at 800 °C for 24 h. The results for the 40OP samples are similar to those for 50P, which implies that the SBA-15 silicates modified with FePO₄ have excellent hydrothermal stabilities over a wide FePO₄-doping range.

The XRD results were confirmed using N₂ physisorption. Fig. 2(a) and (b) shows the N₂ adsorption-desorption isotherms and corresponding pore size distributions of 50P, 50P-b100,

Fig. 1. Small-angle XRD patterns of 50P samples (a) and 40OP samples (b) before and after hydrothermal treatment.

and 50P-s800, respectively. To eliminate interference from the tensile strength effect of the adsorbed phase [28], the pore size distribution of 50P was derived from the adsorption branch of

Fig. 2. N₂ adsorption-desorption isotherms and corresponding pore size distributions for 50P samples (a, b) and 40OP samples (c, d) before and after hydrothermal treatment.

the isotherm using the BJH method. The isotherm curves of 5OP, 5OP-b100, and 5OP-s800 were all type IV curves with H1 hysteresis loops, which are typical features of ordered hexagonal mesostructures. The pore size distributions of these samples were all narrow and centered at 7.8, 9.5, and 6.5 nm for 5OP, 5OP-b100, and 5OP-s800, respectively. It should be noted that the pore diameter of the 5OP sample decreased after treatment with pure steam at 800 °C, indicating mesopore shrinkage during the high-temperature hydrothermal treatment; this is consistent with the XRD results. Similarly, the N_2 adsorption-desorption isotherms and corresponding pore size distributions of fresh and treated 40OP (Fig. 2(c) and (d)) show that the ordered mesostructures of 40OP were well preserved after the different hydrothermal treatments, and mesopore shrinkage occurred during steam treatment at 800 °C.

Table 1 lists the structural parameters of the samples before and after hydrothermal treatments. It was found that the changes in the structural parameters of the two OP samples with different $FePO_4$ loadings (5 and 40 wt%) after hydrothermal treatment were very similar. After treatment in boiling water at 100 °C, the total pore volumes of the OP samples decreased slightly, and their micropore volumes decreased greatly. However, after treatment with steam at 800 °C, the total pore volumes of the OP samples decreased considerably, and their micropores nearly disappeared. The BET surface areas of the OP samples decreased significantly, and their reduced surface areas were very similar after the two hydrothermal treatments. The BET surface areas of the two fresh OP samples were reduced by 40.2%–44.9% after treatment with boiling water at 100 °C, and by 73.2%–79.4% after treatment with pure steam at 800 °C. The serious decreases in the surface areas are caused by extensive destruction of micropores and collapse of mesopores, as shown in Table 1.

The above results show that OP samples with $FePO_4$ loadings of 5 and 40 wt% had very similar behavior during the dif-

ferent hydrothermal treatments, i.e., the $FePO_4$ loading does not have a great impact on the hydrothermal stabilities of the samples synthesized using the one-pot hydrothermal method; these results are totally different from those previously reported for mesoporous-silica-supported metal oxides [20,21,24]. Li et al. [20] reported that Al-SBA-15 samples with low Al contents were more stable than those with high Al contents under steam at 800 °C. However, Selvaraj et al. [21,24] found that Cr-SBA-15 or Ga-SBA-15 with high amounts of Cr or Ga had better hydrothermal stabilities under steam at 800 °C than samples with lower Cr or Ga contents. They suggested that formation of a protective metal layer or stable Si–O–metal species might result in good hydrothermal stabilities of these mesoporous-silica-supported metal oxides. In our previous report [25], for an OP sample with a $FePO_4$ loading of 10 wt%, diffuse reflectance ultraviolet-visible (UV-vis) spectroscopy showed that large amounts of $FePO_4$ species were present in bulk $FePO_4$, and a small amount of $FePO_4$ species were present in the SBA-15 framework; $FePO_4$ granules with micron diameters were also observed in scanning electron microscopy images, and the elemental components were confirmed using energy-dispersive X-ray spectroscopy. In this study, to understand why the hydrothermal stabilities of OP samples with different $FePO_4$ loadings were the same, the presence of $FePO_4$ in the OP samples was examined using wide-angle XRD. Fig. 3 shows that the OP samples with different $FePO_4$ loadings had similar XRD patterns, with distinct peaks ascribable to $FePO_4$ crystals, even for a low $FePO_4$ loading of 5 wt%. We deduced that the protective $FePO_4$ layer on the surfaces of both OP samples might protect silica against attack by water molecules during hydrothermal treatments, leading to their very similar stabilities in boiling water at 100 °C or pure steam at 800 °C.

In addition to the mesostructures, the presence of Fe in the OP samples after hydrothermal treatment was also significant. The wide-angle XRD patterns of the samples after hydrothermal treatment are shown in Fig. 3. The Fe in 40OP-b100 was in the forms $FePO_4$ and $FePO_4 \cdot 2H_2O$. For 40OP-s800, most diffraction peaks were ascribed to $FePO_4$ crystals, but the residual peaks were unidentified. After treatment at 600 °C, these uni-

Table 1

Physical properties of the $FePO_4$ -SBA-15 samples before and after hydrothermal treatments.

Sample	D^a (nm)	V_t^b (cm^3/g)	V_m^c (cm^3/g)	S_{BET}^d (m^2/g)	Reduced area ^e (%)
5OP	7.8	0.93	0.169	898	—
5OP-b100	9.5	0.96	0.022	537	40.2
5OP-s800	6.5	0.35	0	185	79.4
40OP	6.6	0.85	0.087	615	—
40OP-b100	7.9	0.84	0.013	339	44.9
40OP-s800	5.0	0.33	0	165	73.2
SBA-15	6.6	1.06	0	532	—
SBA-15-s700	—	0.41	0	181	66.0
SBA-15-s800	—	0.18	0	17	96.8
5IMP	3.9	0.92	0.007	506	—
5IMP-s800	—	0.39	0	56	88.9
40IMP	6.6	0.38	0	184	—
40IMP-s700	3.3	0.22	0	87	52.7
40IMP-s800	2.8	0.20	0	65	64.7

^a The pore diameters were calculated by the desorption or adsorption branches of the isotherms.

^b Total pore volume. ^c Micropore volume. ^d BET specific surface area.

^e The reduced surface area was calculated according to the formula: $(S_{BET}(\text{pre-steamed}) - S_{BET}(\text{post-steamed}))/S_{BET}(\text{pre-steamed})$.

Fig. 3. Wide-angle XRD patterns of samples.

identified diffraction peaks remained, excluding the possibility of $\text{FePO}_4 \cdot n\text{H}_2\text{O}$. The FePO_4 phase of 40OP was stable during hydrothermal treatment.

3.2. Differences among hydrothermal stabilities of OP, IMP, and SBA-15 samples

To further understand the hydrothermal stabilities of OP samples, we compared the hydrothermal stabilities of OP samples, IMP samples, and commercially available SBA-15. Fig. 4(a) shows the small-angle XRD patterns of SBA-15 before and after hydrothermal treatments. It can be seen that SBA-15 had three strong diffraction peaks at 1.0° , 1.6° , and 1.9° indexed to (100), (110), and (200) facets with $P6mm$ symmetry, respectively,

suggesting a highly ordered mesostructure. After treatment with steam at 600°C , the intensity of the (100) facet diffraction peak decreased, whereas those of the (110) and (200) facet peaks became almost invisible; this suggests that the mesostructure became disordered but was still hexagonal. However, when the steam treatment temperature was increased to 700 or 800°C , no diffraction peak was detected, indicating that the SBA-15 mesostructure was completely destroyed by steam treatment at 700 or 800°C for 24 h. These results were confirmed using N_2 physisorption. Fig. 5(a) and 5(b) show the N_2 adsorption-desorption isotherms and pore size distributions of SBA-15 before and after hydrothermal treatment, respectively. The isotherm of fresh SBA-15 was type IV with an H1 hysteresis loop; these are typical features of or-

Fig. 4. Small-angle XRD patterns of SBA-15 (a), 5IMP (b), and 40IMP (c) samples before and after hydrothermal treatment.

Fig. 5. N_2 adsorption-desorption isotherms and corresponding pore size distributions of SBA-15 (a, b), 5IMP (c, d), and 40IMP (e, f) samples before and after hydrothermal treatment.

dered hexagonal mesostructures. These structures were completely destroyed after treatment in pure steam at 700 or 800 °C, leading to large decreases in the total pore volumes and specific surface areas, as shown in Table 1. However, as discussed in Section 3.1, the OP samples can withstand steam treatment even at 800 °C for 24 h. The OP samples are therefore more hydrothermally stable than SBA-15, suggesting that loading FePO₄ on SBA-15 using the one-pot hydrothermal method significantly enhanced the hydrothermal stability of SBA-15. These results are in agreement with reports that metal addition, using a one-pot hydrothermal method, improves the hydrothermal stabilities of mesoporous silicate materials [20,29,30].

IMP samples with high and low FePO₄ loadings (5 and 40 wt%) were used to investigate the hydrothermal stability of commercially available SBA-15-supported FePO₄. Fig. 4(b) shows the small-angle XRD patterns of 5IMP samples before and after hydrothermal treatment. The pattern of 5IMP displayed a strong diffraction peak at 0.9°, indexed to (100) facet with *P6mm* symmetry, suggesting an ordered mesostructure. After treatment with steam at 700 °C, a weakened diffraction peak was detected, suggesting that the mesostructure was preserved to some extent. However, no diffraction peak was detected for 5IMP-s800, suggesting that the mesostructure was completely destroyed after hydrothermal treatment in pure steam at 800 °C. These results were confirmed using N₂ physisorption. Fig. 5(c) and (d) shows the N₂ adsorption-desorption isotherms and pore size distributions of 5IMP samples before and after hydrothermal treatments, respectively. To eliminate interference by the tensile strength effect of the adsorbed phase [28], the pore size distribution of 5IMP was derived from the adsorption branch of the isotherm using the BJH method. It was found that the isotherm of 5IMP was type IV with an H1 hysteresis loop and narrow pore size distribution, which are typical features of ordered hexagonal mesostructures. As in the case of pure SBA-15, the mesostructures of the impregnated samples were completely destroyed after treatment with pure steam at 800 °C, resulting in large decreases in the total pore volumes and specific surface areas, as shown in Table 1. These observations were consistent with the XRD results.

The small-angle XRD patterns of 40IMP before and after hydrothermal treatments, shown in Fig. 4(c), indicate that fresh 40IMP displayed only a weak diffraction peak at 1.0°. This might be because of the large FePO₄ loading partly blocking the SBA-15 pores. Fig. 5(e) and (f) shows the N₂ adsorption-desorption isotherms and pore size distributions of 40IMP samples before and after hydrothermal treatments, respectively. The isotherm of 40IMP was type IV with an H1 hysteresis loop, which are typical features of ordered hexagonal mesostructures. The samples obtained by treatment with pure steam at 600 and 700 °C, i.e., 40IMP-s600 and 40IMP-s700, also had type IV isotherms with H1 hysteresis loops, indicating that the hexagonal mesostructures were well preserved. The pore size distributions of 40IMP, 40IMP-s600, and 40IMP-s700 were all narrow. However, the 40IMP-s800 isotherm showed a hysteresis loop with a flat slope, different from those of the other

three 40IMP samples, indicating that the ordered mesostructure of 40IMP was destroyed after steam treatment at 800 °C. Based on the above analysis, we can conclude that the hydrothermal stabilities of the samples follow the order OP > IMP >> SBA-15.

3.3 Interpretation of protective role of FePO₄

Si–O–Si bonds can be attracted by water and hydrolyzed to Si–OH in boiling water, as shown in Eq. (1):

Si–OH can be dehydroxylated again to Si–O–Si by thermal treatment, and this process is dominant under high-temperature steam [8,29]. Here, it is reasonable to suppose that the good hydrothermal stabilities of the OP and IMP samples can be ascribed to the protective layer formed by deposition of FePO₄ species on the SBA-15 surface. The protective layer of FePO₄ can repel attack by water molecules on Si–O–Si bonds; it can also cover Si–OH bonds and prevent their condensation with each other, thereby protecting the surface framework of SBA-15 from further disintegration. As reported previously [20,29], a similar protective layer has been used to explain the improvements in the hydrothermal stabilities of Al–MCM-41 and Al–SBA-15. Although the amount of Al species in MCM-41 is not high enough to form Al-rich surface species to cover all the MCM-41 surfaces, it has been suggested that the surface Al species protect not only the adjacent Si atoms but also those distant from the Al species [29,31]. The same mechanism can be used to explain the superior hydrothermal stabilities of OP and IMP materials compared with that of SBA-15.

Although the OP and IMP samples both have protective FePO₄ layers, there are differences between these samples. First, the OP samples have much larger numbers of micropores than the IMP samples, as shown in Table 1. According to the report by Zhang et al. [8], the large number of micropores should contribute to the higher structural stability on treatment with steam. Secondly, the locations of FePO₄ in the OP and IMP materials are different as shown using diffuse reflectance UV-vis spectroscopy in our previous work [25]. It was found that bulk FePO₄ and structural iron were both formed in the OP material, whereas only isolated FePO₄ species were formed on the outer surface of SBA-15 for IMP material. The Si–O–metal bonds formed in the OP materials are more stable than the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds [24,32]; this might be another reason for the superior hydrothermal stabilities of OP materials compared with IMP materials. Lastly, in addition to these differences between the properties of these SBA-15-supported FePO₄ samples, the phases of the FePO₄ species are different. In contrast to the FePO₄ crystals formed in OP with FePO₄ loadings of 5 and 40 wt%, highly dispersed FePO₄ was formed in 40IMP, with only a very broad diffraction peak related to amorphous silica as confirmed in Fig. 3; this is consistent with a previous report [33]. We therefore speculate that these differences contribute to the superior hydrothermal stabilities of OP over IMP samples. However, whether there are any differences between the protective layers formed by FePO₄ crystals and highly dispersed FePO₄ remains to be resolved in further studies.

4. Conclusions

OP samples with low and high FePO_4 contents synthesized using a novel one-pot hydrothermal method showed the same hydrothermal stabilities in boiling water at 100 °C or pure steam at 800 °C. This is different from reports in the literature that the loading on SBA-15-supported metal oxides has an important effect on the hydrothermal stability in pure steam at 800 °C. A comparison of the hydrothermal stabilities of OP, IMP, and pure SBA-15 samples showed that their hydrothermal stability order was $\text{OP} > \text{IMP} \gg \text{SBA-15}$. The protective FePO_4 layer on the surfaces of mesoporous silicates might protect silica against attack by water molecules, therefore the protective FePO_4 layer on OP and IMP might contribute to the better hydrothermal stabilities. The superior hydrothermal stabilities of OP samples over IMP samples might be related to the much larger proportion of micropores, the crystal phase of FePO_4 , and the presence of Fe in the SBA-15 framework, which is evident from the formation of Si–O–Fe bonds.

References

- [1] Kresge C T, Leonowicz M E, Roth W J, Vartuli J C, Beck J S. *Nature*, 1992, 359: 710
- [2] Beck J S, Vartuli J C, Roth W J, Leonowicz M E, Kresge C T, Schmitt K D, Chu C T W, Olson D H, Sheppard E W, Mccullen S B, Higgins J B, Schlenker J L. *J Am Chem Soc*, 1992, 114: 10834
- [3] Taguchi A, Schüth F. *Microporous Mesoporous Mater*, 2005, 77: 1
- [4] Corma A. *Chem Rev*, 1997, 97: 2373
- [5] Perego C, Millini R. *Chem Soc Rev*, 2013, 42: 3956
- [6] Da J W, Song C M, Qian L, Su J M, Xu X Z. *J Porous Mater*, 2008, 15: 189
- [7] Eswaramoorthi I, Dalai A K. *Int J Hydrogen Energy*, 2009, 34: 2580
- [8] Zhang F Q, Yan Y, Yang H F, Meng Y, Yu C Z, Tu B, Zhao D Y. *J Phys Chem B*, 2005, 109: 8723
- [9] Mokaya R. *Chem Commun*, 2001: 633
- [10] Liu H, Wang M Y, Hu H J, Liang Y G, Wang Y, Cao W R, Wang X H. *J Solid State Chem*, 2011, 184: 509
- [11] Li Q, Wu Z X, Feng D, Tu B, Zhao D Y. *J Phys Chem C*, 2010, 114: 5012
- [12] Shindo T, Nakazawa Y, Ozawa S. *J Porous Mater*, 2009, 16: 481
- [13] Mody H M, Kannan S, Bajaj H C, Manu V, Jasra R V. *J Porous Mater*, 2008, 15: 571
- [14] Liu Z Y, Zhu Z B, Wang R Y, Zhu X D. *Chin J Catal* (刘子玉, 朱子彬, 王仁远, 朱学栋. 催化学报), 2008, 29: 928
- [15] Sangchoom W, Mokaya R. *J Mater Chem*, 2012, 22: 18872
- [16] Ryoo R, Jun S. *J Phys Chem B*, 1997, 101: 317
- [17] Jun S, Kim J M, Ryoo R, Ahn Y S, Han M H. *Microporous Mesoporous Mater*, 2000, 41: 119
- [18] Kim J M, Jun S, Ryoo R. *J Phys Chem B*, 1999, 103: 6200
- [19] Song M J, Zou C L, Niu G X, Zhao D Y. *Chin J Catal* (宋明娟, 邹成龙, 牛国兴, 赵东元. 催化学报), 2012, 33: 140
- [20] Li Q, Wu Z X, Tu B, Park S S, Ha C S, Zhao D Y. *Microporous Mesoporous Mater*, 2010, 135: 95
- [21] Selvaraj M, Kawi S, Park D W, Ha C S. *Microporous Mesoporous Mater*, 2009, 117: 586
- [22] Selvaraj M, Kawi S, Park D W, Ha C S. *J Phys Chem C*, 2009, 113: 7743
- [23] Mokaya R. *J Phys Chem B*, 2000, 104: 8279
- [24] Selvaraj M, Kawi S. *Chem Mater*, 2007, 19: 509
- [25] Wang R Q, Lin R H, Ding Y J, Liu J, Wang J H, Zhang T. *Appl Catal A*, 2013, 453: 235
- [26] Lin R H, Ding Y J, Gong L F, Dong W D, Chen W M, Lu Y. *Catal Today*, 2011, 164: 34
- [27] Selvaraj M, Park D W, Ha C S. *Microporous Mesoporous Mater*, 2011, 138: 94
- [28] Groen J C, Perez-Ramirez J. *Appl Catal A*, 2004, 268: 121
- [29] Shen S C, Kawi S. *J Phys Chem B*, 1999, 103: 8870
- [30] Shao Y F, Wang L Z, Zhang J L, Anpo M. *Microporous Mesoporous Mater*, 2008, 109: 271

Graphical Abstract

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

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FePO_4 -SBA-15 samples prepared using a new one-pot method showed excellent hydrothermal stabilities in either pure steam at 800 °C or boiling water at 100 °C, regardless of the FePO_4 loading (5 or 40 wt%).

- [31] Sano T, Nakajima Y, Wang Z B, Kawakami Y, Soga K, Iwasaki A. *Microporous Mater*, 1997, 12: 71
- [32] Wang K X, Lin Y J, Morris M A, Holmes J D. *J Mater Chem*, 2006, 16: 4051
- [33] Wang Y, Wang X X, Su Z, Guo Q, Tang Q H, Zhang Q H, Wan H L. *Catal Today*, 2004, 93-95: 155

水热合成一锅法制备 FePO_4 -SBA-15及其水热稳定性

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摘要: 通过两种水热处理方式,即800℃水汽条件和100℃沸水处理,考察了一锅法制备的 FePO_4 -SBA-15(OP)的水热稳定性. 水热处理前后样品的结构变化通过小角X射线衍射和 N_2 物理吸附表征. 研究发现,经水热条件下原位生成 FePO_4 修饰后的OP样品具有良好的水热稳定性,并且 FePO_4 的担载量(5%和40%)对OP样品的水热稳定性几乎没有影响. 这与文献报道的金属担载量会影响介孔材料水热稳定性的结果不同. 此外,还对比研究了浸渍法制备的 FePO_4 /SBA-15(IMP)和商品SBA-15的水热稳定性. 结果表明,各样品水热稳定性由强到弱的顺序是OP>IMP>>SBA-15. OP和IMP样品水热稳定性优于纯硅分子筛SBA-15的原因可能是 FePO_4 保护层能抑制介孔材料在水热环境下的结构塌陷. OP样品水热稳定性较IMP样品好的原因可能主要是由于OP样品中存在稳定的Si-O-Fe键和较多的微孔.

关键词: 磷酸铁; SBA-15; 介孔材料; 水热稳定性; 水蒸气; 金属担载量

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