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ARTICLE

UV Raman Spectroscopic Studies on the Synthesis Mechanism of FeAlPO$_4$-5

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Abstract: FeAlPO$_4$-5 samples with various iron contents were investigated by UV resonance Raman spectroscopy and UV-Vis spectroscopy. The Raman spectra of FeAlPO$_4$-5 show four feature bands related to the framework iron at 630, 1060, 1140, and 1210 cm^{-1} when excited by 266 nm laser. It is found that only part of ferric ions could enter into the framework, while the others exist in the extra-framework in the form of six-coordinated state. This kind of iron gives characteristic Raman band at 285 cm^{-1}. Combined with UV resonance Raman spectroscopy, UV-Vis spectroscopy, and X-ray diffraction, the crystallization process of FeAlPO$_4$-5 (Al/Fe = 760) was studied. It is found that, in the early stages of the crystallization, the iron species exist in the form of six-coordinated state while attached to the end of the 1-dimensional AlPO$_4$ chain. The Fe–O bonds in the six-coordinated state hamper the crystallization of AlPO$_4$. The crystallization of the FeAlPO$_4$-5 began when the reaction between the 1-dimensional AlPO$_4$ chains occurred. At the same time, the six-coordinated ferric ions converted to the tetrahedral iron.

Key words: iron; AlPO$_4$-5 zeolite; UV Raman spectroscopy; resonance Raman effect; synthesis mechanism

The discovery of AlPO$_4$-*n* is regarded as a milestone in the development of molecular sieves [1]. The incorporation of heteroatoms into aluminophosphates has played an important role in enhancing their applications in the fields of adsorption, separation, formation of host-guest advanced materials, and catalysis. Fe-containing molecular sieves have attracted widespread interest because of their unique catalytic properties in a number of reactions, especially in redox catalysis. Fe-ZSM-5 zeolite is especially interesting because of its excellent catalytic performance in environmental catalysis and in selective oxidation etc [2]. Understanding the active sites on Fe-ZSM-5 is important in this field. Generally, the coordinatively unsaturated iron species present in the non-framework positions within the pores of the zeolite are thought to be the active sites [2–8]. However, framework iron is considered to be the active center in the FeAlPO$_4$-*n* catalyst. Ren et al. [9] reported that iron phosphate can serve as a catalyst for benzene hydroxylation with high selectivity exceeding 85% and the Fe(III) ions are tetrahedrally coordinated in the catalyst. The iron atoms are always tetrahedrally coordinated in the framework of the AlPO$_4$-5 structure and they are very good catalysts for several oxidation reactions with molecular oxygen as an oxidant [10,11]. Shiju et al. [12] found that tetrahedral iron atoms in the framework are the active centers during benzene hydroxylation. Wei et al. [13] reported that only when the Fe(III) in the framework is reduced to Fe(II) the catalyst can become active for N$_2$O decomposition. Thus, information about the framework iron atoms is very important for reactions where FeAlPO$_4$-*n* is the catalyst. However, information on the incorporation of transition metal ions into molecular sieves is difficult to obtain because the amount of metals incorporated into zeolite frameworks is usually very low [14]. UV Raman spectroscopy has been shown to be a powerful tool for the characterization of molecular sieves because of decreased fluorescence and increased sensitivity [15,16]. In addition, because of the resonance Raman effect information about

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heteroatoms in the framework of molecular sieves can be selectively obtained [17–24].

In this work, UV resonance Raman spectroscopy and UV-Vis absorption spectroscopy were used to investigate $FeAlPO_4$-5 with different iron contents. The evolution of the iron species during the crystallization of $FeAlPO_4$-5 was also studied. The results demonstrate that the iron species transform from a six-coordinated state to a tetrahedral state during hydrothermal crystallization. Some of the iron species cannot enter the framework and they exist in the six-coordinated state when the iron content is relatively high. This work sheds light on the general mechanism of transition metal substituted molecular sieves synthesis.

1 Experimental

1.1 Sample preparation

The aluminum and phosphorus sources were pseudoboehmite (55% Al_2O_3) and H_3PO_4, respectively. Triethylamine (TEA, 99.5%) was used as a structure-directing agent. An appropriate amount of H_3PO_4 was stirred with H_2O at room temperature for 30 min followed by the addition of pseudoboehmite. The mixture was stirred for 120 min and TEA was added to the mixture in a dropwise manner. Finally, the $FeCl_3$ solution was added to the above-mentioned gel and stirred for 120 min. Crystallization was completed in stainless steel autoclaves for 2160 min at 413 K. The solid products were collected by filtration, washed with distilled water, and dried at 353 K.

For the study on the evolution of iron species during hydrothermal crystallization, samples were taken from the autoclaves at different time intervals, collected by filtration, washed with distilled water, and dried at 353 K.

1.2 Sample characterization

XRD patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu K_α radiation (40 kV and 50 mA). UV Raman spectra were recorded on a home-assembled UV Raman spectrograph using a Jobin-Yvon T64000 triplestage spectrograph with a spectral resolution of 2 cm^{-1}. The laser line at 325 nm of an He-Cd laser was used as an exciting source with an output of 50 mW. The power of the laser at the samples was about 1.0 mW. The laser at 266 nm comes from the double-frequency of a DPSS 532 Model 200 532 nm laser.

2 Results and discussion

2.1 Powder XRD patterns and UV-Vis spectra of $FeAlPO_4$-5 with different Al/Fe ratios

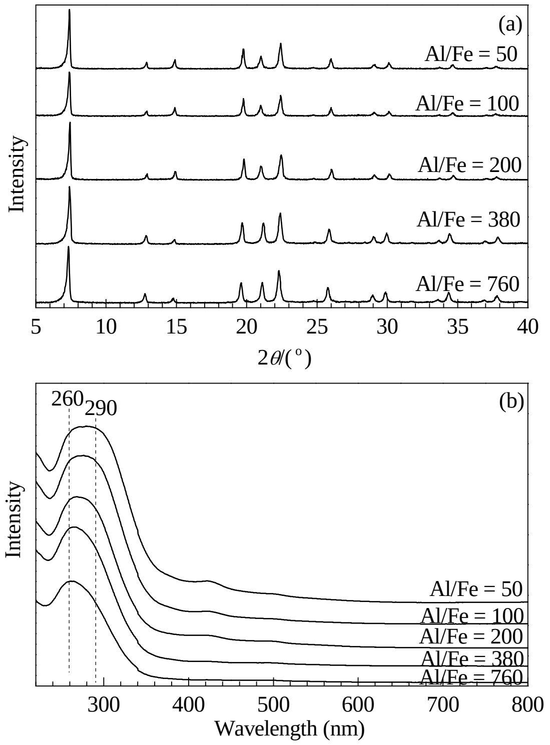

Fig. 1. XRD patterns (a) and UV-Vis spectra (b) of $FeAlPO_4$-5 with different Al/Fe ratios.

Figure 1(a) shows the XRD patterns of $FeAlPO_4$-5 with different Al/Fe ratios, which all exhibit characteristic XRD patterns of AFI topology. Figure 1(b) shows UV-Vis spectra of $FeAlPO_4$-5 with different Al/Fe ratios, which are dominated by one band around 260 nm as a result of oxygen-to-metal (Fe^{3+}) charge transfer (CT). This band is characteristic of Fe^{3+} at the isolated tetrahedral framework sites. With an increase in the iron content, one shoulder band at 290 nm appears and it comes from the isolated octahedral Fe^{3+} complex. This result shows that the amount of Fe^{3+} that can enter the framework is limited.

2.2 Raman spectra of $FeAlPO_4$-5 with different Al/Fe ratios

Figure 2(a) shows the Raman spectra of $FeAlPO_4$-5 with different Al/Fe ratios upon excitation at 266 nm, which is within the range of the charge-transfer bands at 260 nm. Apart from the characteristic bands of the AFI structure at 260, 400, 500, 1140, and 1240 cm^{-1} [25] the UV Raman spectra of $FeAlPO_4$-5 with various iron content exhibit new bands at 630, 1060, and 1210 cm^{-1}. In our previous work [19,26,27], the transitions responsible for these Raman bands were determined by DFT calculations. The bands at 630 and 1060 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of $Fe(OP)_4$, respectively. The band at 1210 cm^{-1} was attributed to the symmetric stretching vibrations of FeO_4 because of the asymmetric stretching of the P−O−Al connected