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The state of iron sites in the calcined $FeAlPO_4$-5 and its tuning to the property of microporous $AlPO_4$-5 molecular sieve

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ABSTRACT

The dispersion and coordination is critical to the nature of metal phases. This article describes an approach of single Fe sites preparing under microporous environment via calcination of the Fe incorporated $FeAlPO_4$-5 as well as the tuning to the property of $AlPO_4$-5 molecular sieve. The UV, Raman, EPR spectroscopies and H_2-TPR characterization revealed through the extraction of framework Fe inside the micropore by calcination, extra-framework Fe sites were generated, the dispersion of which was higher than Fe sites of impregnated $Fe_2O_3/AlPO_4$-5, and it indicated that part of Fe sites of $FeAlPO_4$-5 can be with coordination vacancy. It is notable that the presence of single Fe sites was directly observed by Cs-corrected STEM micrograph. NH_3-TPD and toluene-TPD results both exhibited an enhanced acidity and π bond adsorption ability of $FeAlPO_4$-5 toward $AlPO_4$-5 and the impregnated sample $Fe_2O_3/AlPO_4$-5. Finally, the $FeAlPO_4$-5 turned out to perform higher thiophene desulfurization rate against $AlPO_4$-5 and impregnated sample, which can be related to the improvement in the adsorption ability and reactivity for the single Fe sites inside the microporous environment.

1. Introduction

The reactivity of the metal site is deeply affected by its dispersion and coordination [1]. Bulk metal phase with poor dispersion which commonly prepared by impregnation or precipitation methods often suffers from unfavorable activity due to the excessively overlap of active sites and unreasonable coordination state. The main reason for this problem is that the small metal particles tend to re-agglomerate during the uncontrollable drying of solvent or the inhomogeneous mixing process of precipitator and precursor [2–4], under the action of surface energy.

Contrast to the bulk metal phase, highly dispersed metal particles or even nanoparticles possess different character of molecular orbital and much larger surface of exposure which can save the consumption amount of metals as well [5,6]. The achievement on controlling the distribution of metal particles provides a game-changing opportunity, for the distribution advancement of the metal particles can evoke greater improvement of reactivity [7,8]. Series of attempts have managed to improve the dispersion of the metal particles including ion exchange method [9], chemical grafting [10], hydrothermal treatment [11,12] and improved impregnation method such as using precursor [13] and promoter [14] etc., the improved methods demonstrated to be promising approaches to prepare high performance supported catalysts.

In addition to the approaches mentioned above, the introduction of metals or metal oxides into porous materials (mostly mesoporous materials) seems to be of attraction enough to us for it combines both stable active sites and suitable spaces for the reaction to be carried. The metal and its oxide particles confined inside the micro/mesopores or CNTs have exhibited unique natures which can hardly be observed under bulk phase or metal clusters on the surface [15,16].

In our previous works on the applications of $AlPO_4$-5 molecular sieve, $AlPO_4$-5 turned out to perform good aromatics removal activity due to the PO_4 structure [17]. However, the acidity, adsorption capacity and reactivity of $AlPO_4$-5 is still restricted by its neutral

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framework which leads to the inadequate of active sites [18], and the traditional way to overcome this disadvantage is to introduce doping metals to $AlPO_4$-5 [19–22]. Considering the oxides of Fe are also Lewis acids, the property of $AlPO_4$-5 molecular sieves would be tuned after the introduction of Fe, which may also be beneficial to the adsorption and removal of sulfur compound such as thiophene.

Described in some previous works, the relatively large 12 member ring tunnels of $AlPO_4$-5 brings possibilities to synthesis within nanoscales under the confinement of its microporous environment [23,24]. Cheng et al. have reported the characterization results of $FeAlPO_4$-5 as catalyst in selective catalytic reduction (SCR) of N_2O with CH_4, and concluded that the isolated Fe(III) and oligonuclear $Fe(III)_xO_y$ in $FeAlPO_4$-5 was prior to impregnated Fe_2O_3 as active sites in SCR reactions [25]. However, to the best of our knowledge, there is no report on the state of Fe derived from the calcination of $FeAlPO_4$-5, and the property varieties of the calcined $FeAlPO_4$-5 compared to $AlPO_4$-5 is also worth to study.

In this work, iron incorporated $FeAlPO_4$-5 was prepared, and we found that part of the incorporated Fe can form the single Fe sites inside micropore after calcination, meanwhile the vast amount of framework Fe were still well preserved. The forming of single Fe sites was directly observed by Cs-corrected STEM in addition to EPR, H_2-TPR. And the improved adsorption property of $FeAlPO_4$-5 was compared with $AlPO_4$-5 and $AlPO_4$-5 impregnated by the same amount of Fe_2O_3 through toluene-TPD and the reaction of thiopnene HDS.

2. Experimental

2.1. Preparation of materials

The $FeAlPO_4$-5 molecular sieve was prepared through hydrothermal synthesis. Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) was used as iron source and added by dropwise into the system after dissolved. A gel with the molar composition $1.0Al_2O_3{:}0.1Fe{:}1.06P_2O_5{:}1.47Et_3N{:}45H_2O$ was hydrothermal crystalized in a teflon-lined autoclave at 463 K for 16 h. After crystallization, the product was filtrated, washed and dried at 353 K for 6 h and kept in an as-synthesized form. The template-free sample was obtained by calcination of the as-synthesized sample at 823 K for 4 h.

The dehydrated $FeAlPO_4$-5 (denoted as D-$FeAlPO_4$-5) was obtained by treating template-free $FeAlPO_4$-5 at 623 K under vacuum for 8 h. The rehydrated $FeAlPO_4$-5 (denoted as DS-$FeAlPO_4$-5) was obtained by soaking D-$AlPO_4$-5 with 0.1 wt% NaOH solution for 8 h, and dried at 393 K for 4 h.

The $AlPO_4$-5 sample was prepared with the proportion and condition the same as $FeAlPO_4$-5, only without addition of Fe sources. The removal of the template was processed under the same condition with $FeAlPO_4$-5.

The iron impregnated sample was prepared by impregnating the template-free $AlPO_4$-5 sample with iron nitrate solution by incipient-wetness impregnation method. The composition of Fe was determined by the XRF result of $FeAlPO_4$-5. After the impregnation, the sample was calcined under 753 K for 4 h so that the supported Fe_2O_3 can be prepared by the decomposition of nitrate. And the impregnated sample was denoted as $Fe_2O_3/AlPO_4$-5.

In the evaluation experiment, the materials were prepared by smashing and sieving the tabletted template-free sample powders, and the particles between 40 and 60 meshes were used.

2.2. Characterizations

The crystal phases of the samples were examined by X-ray powder diffraction (XRD) results obtained through a Panalytical X'pert PRO X-ray diffractometer using the Cu Kα radiation at 40 kV and 40 mA with scanning rate of 2 K/min. The morphologies of the crystals were observed with a FEI Quanta 200F scanning electron microscope. The X-ray photoelectron spectrum (XPS) results were acquired through a Thermo Fisher K-Alpha photoelectron spectrometer using Al Kα radiation. For those experiments, Fe 2p, Al 2p, P 2p, and O 2p bands were recorded. The X-ray florescence (XRF) result was obtained to determine the element composition of the bulk phase of the molecular sieve. The experiment was carried out on a Panalytical AxiosMax X-ray fluorescence spectrometer. The porosity data of the samples were determined by measuring N_2 isotherm at 77 K with a Micromeritics ASAP 2020 automated system. The pore size distribution (PSD) was determined by the desorption branch of the data of N_2 adsorption–desorption. The total surface area was calculated according to the BET isothermal equation. The microporous volume, mesoporous volume, and external surface area were evaluated by the *t*-plot method. UV–Vis diffusion reflection spectroscopy (DRS) of the molecular sieves were recorded on a Hitachi U-4100 spectrophotometer using corresponding support as reference. EPR results of the samples were obtained through a JOEL JES-FA200 X-band electron paramagnetic resonance spectroscopy under 113 K. The amount of the sample was 0.01 g. The dispersion state of Fe species were observed on a JOEL JEM-2100 transmitting electron microscope (TEM), and a probe corrected JOEL JEM-ARM200F scanning transmitting electron microscope (STEM) operated at 200 kV and equipped with a cold field emission gun. NH_3-TPD results were obtained by a Micromeritics ASAP 2920 instrument and 0.2 g of samples were used. Before NH_3 desorption procedure, the samples were pretreated under N_2 on 873 K for 1 h. The H_2-TPR were performed on a Finetec Finesorb-3010 instrument equipped with a TCD and the results were recorded on line at a heating rate of 10 K/min. The samples used for H_2-TPR were: template-free $FeAlPO_4$-5 and $AlPO_4$-5 samples obtained by calcination of the as-synthesized samples at 823 K for 4 h, $Fe_2O_3/AlPO_4$-5 sample impregnated by iron nitrate and calcined under 753 K for 4 h. Before reduction procedure, the samples were pretreated under N_2 on 723 K for 1 h. Same sample were used for toluene-TPD, also performed on a Finetec Finesorb-3010 instrument, and the heating rate was 10 K/min, and the results were recorded on line. Before desorption, the samples were degassed through vacuum treatment at 623 K for 4 h, and after that the samples were transferred to a vessel filled with toluene vapor at 353 K and kept in the vessel for 4 h as toluene adsorption.

2.3. Hydrodesulphurization evaluation of the materials

The hydrodesulphurization (HDS) performances of the molecular sieves were carried out in a continuous flow fixed-bed reactor under evaluation condition as follows: a model feed of thiophene dissolved in decane with sulfur content of 1000 μg/g, a catalyst load of 1.0 g, a reaction temperature of 593 K, a reaction pressure of 3.0 MPa, a feed flow rate of 3.6 mL/h, and a H_2/oil of 500. Before regular evaluation, the catalysts were pre-sulfieded with a sulfiding feed as 10 vol% CS_2 in decane at 593 K and 3.0 MPa for 3 h. After the system reached the steady state, the products were collected periodically and the sulfur content was measured by ultraviolet florescence method on a RPP-2000SN spectroscopy. The desulphurization rate was defined as follows:

$$R_{HDS} = (C_0 - C)/C_0$$

where C_0 is the sulfur content of the feed, and C is the sulfur content of the product.