The state of iron sites in the calcined FeAlPO₄-5 and its tuning to the property of microporous AlPO₄-5 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 FeAlPO₄-5 as well as the tuning to the property of AlPO₄-5 molecular sieve. The UV, Raman, EPR spectroscopies and H₂-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 Fe₂O₃/AlPO₄-5, and it indicated that part of Fe sites of FeAlPO₄-5 can be with coordination vacancy. It is notable that the presence of single Fe sites was directly observed by Cs-corrected STEM micrograph. NH₃-TPD and toluene-TPD results both exhibited an enhanced acidity and π bond adsorption ability of FeAlPO₄-5 toward AlPO₄-5 and the impregnated sample

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$\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$. Finally, the $\text{FeAlPO}_4\text{-5}$ turned out to perform higher thiophene desulfurization rate against $\text{AlPO}_4\text{-5}$ 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.

Key words: $\text{AlPO}_4\text{-5}$; Fe incorporation; calcination; dispersion; iron state; Cs-corrected STEM

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 $\text{AlPO}_4\text{-5}$ molecular sieve, $\text{AlPO}_4\text{-5}$ turned out to perform good aromatics removal activity due to the PO_4 structure [17]. However, the acidity, adsorption capacity and reactivity of $\text{AlPO}_4\text{-5}$ is still restricted by its neutral framework which leads to the inadequate of active sites [18], and the traditional way to overcome this disadvantage is to introduce doping metals to $\text{AlPO}_4\text{-5}$ [19-22]. Considering the oxides of Fe are also Lewis acids, the property of $\text{AlPO}_4\text{-5}$ 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 $\text{AlPO}_4\text{-5}$ brings possibilities to synthesis within nanoscales under the confinement of its microporous environment [23-24]. Cheng et al have reported the characterization results of $\text{FeAlPO}_4\text{-5}$ as catalyst in selective catalytic reduction (SCR) of N_2O with CH_4 , and concluded that the isolated Fe(III) and oligonuclear $\text{Fe(III)}_x\text{O}_y$ in $\text{FeAlPO}_4\text{-5}$ 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 $\text{FeAlPO}_4\text{-5}$, and the property varieties of the calcined $\text{FeAlPO}_4\text{-5}$ compared to $\text{AlPO}_4\text{-5}$ is also worth to study.

In this work, iron incorporated $\text{FeAlPO}_4\text{-5}$ 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 were directly observed by Cs-corrected STEM in addition to EPR, H₂-TPR. And the improved adsorption property of FeAlPO₄-5 was compared with AlPO₄-5 and AlPO₄-5 impregnated by the same amount of Fe₂O₃ through toluene-TPD and the reaction of thiophene HDS.

2. Experimental

2.1 Preparation of materials:

The FeAlPO₄-5 molecular sieve was prepared through hydrothermal synthesis. Iron nitrate (Fe(NO₃)₃·9H₂O) was used as iron source and added by dropwise into the system after dissolved. A gel with the molar composition 1.0Al₂O₃:0.1Fe:1.06P₂O₅:1.47Et₃N:45H₂O was hydrothermal crystalized in a teflon-lined autoclave at 463K for 16h. After crystallization, the product was filtrated, washed and dried at 353K for 6h and kept in an as-synthesized form. The template-free sample was obtained by calcination of the as-synthesized sample at 823K for 4h.

The dehydrated FeAlPO₄-5 (denoted as D-FeAlPO₄-5) was obtained by treating template-free FeAlPO₄-5 at 623K under vacuum for 8h. The rehydrated FeAlPO₄-5 (denoted as DS-FeAlPO₄-5) was obtained by soaking D-AlPO₄-5 with 0.1wt% NaOH solution for 8h, and dried at 393K for 4h.

The AlPO₄-5 sample was prepared with the proportion and condition the same as FeAlPO₄-5, only without addition of Fe sources. The removal of the template was

processed under the same condition with FeAlPO₄-5.

The iron impregnated sample was prepared by impregnating the template-free AlPO₄-5 sample with iron nitrate solution by incipient-wetness impregnation method. The composition of Fe was determined by the XRF result of FeAlPO₄-5. After the impregnation, the sample was calcined under 753K for 4h so that the supported Fe₂O₃ can be prepared by the decomposition of nitrate. And the impregnated sample was denoted as Fe₂O₃/AlPO₄-5.

In the evaluation experiment, the materials were prepared by smashing and sieving the tabletted template-free sample powders, and the particles between 40-60 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 K α radiation at 40kV and 40mA with scanning rate of 2K/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 K α radiation. For those experiments, Fe 2p, Al 2p, P 2p, and O 2p bands were recorded. The X-ray fluorescence (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 N₂ isotherm at 77K with a Micromeritics ASAP 2020

automated system. The pore size distribution (PSD) was determined by the desorption branch of the data of N₂ 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 113K. The amount of the sample was 0.01g. 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 200kV and equipped with a cold field emission gun. NH₃-TPD results were obtained by a Micromeritics ASAP 2920 instrument and 0.2g of samples were used. Before NH₃ desorption procedure, the samples were pretreated under N₂ on 873K for 1h. The H₂-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 10K/min. The samples used for H₂-TPR were: template-free FeAlPO₄-5 and AlPO₄-5 samples obtained by calcination of the as-synthesized samples at 823K for 4h, Fe₂O₃/AlPO₄-5 sample impregnated by iron nitrate and calcined under 753K for 4h. Before reduction procedure, the samples were pretreated under N₂ on 723K for 1h. Same sample were used for toluene-TPD, also performed on a Finetec Finesorb-3010 instrument, and the heating rate was 10K/min, and the results were recorded on line. Before desorption,

the samples were degassed through vacuum treatment at 623K for 4h, and after that the samples were transferred to a vessel filled with toluene vapor at 353K and kept in the vessel for 4h 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 μ g/g, a catalyst load of 1.0g, a reaction temperature of 593K, a reaction pressure of 3.0MPa, a feed flow rate of 3.6mL/h, and a H₂/oil of 500. Before regular evaluation, the catalysts were pre-sulfided with a sulfiding feed as 10% vol CS₂ in decane at 593K and 3.0MPa for 3 hours. 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 C₀ is the sulfur content of the feed, and C is the sulfur content of the product.

3. Results& discussion

The XRD patterns for calcined FeAlPO₄-5, AlPO₄-5 and Fe₂O₃/AlPO₄-5 samples are shown in figure 1. XRD patterns indicated that all three samples possess pure AFI framework. The peak position and intensity of FeAlPO₄-5 are similar to AlPO₄-5. The

change in the relative intensity of diffraction peaks after the Fe impregnation indicating that the impregnation may bring some damage to the framework. No agglomeration of Fe oxides phases are presented in the XRD patterns.

The SEM images of the $\text{FeAlPO}_4\text{-5}$, $\text{AlPO}_4\text{-5}$ and $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ samples are shown in figure 2. Both the particles of $\text{FeAlPO}_4\text{-5}$ and $\text{AlPO}_4\text{-5}$ samples are presented in aggregation of small crystals. Despite they have slight difference in the level of aggregation, the size and shape of their crystals are of no great difference. After impregnation, the crystal of $\text{AlPO}_4\text{-5}$ was destroyed seriously for well-defined particle can hardly be seen in SEM image of $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample in figure 2c.

The bulk and surface compositions of the samples (calculated by XRF and XPS respectively) are shown in table 1a. For the bulk composition, the impregnated $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample has the same trend with the $\text{AlPO}_4\text{-5}$ sample that their Al% is higher than P% suggesting the Fe impregnation won't change the total Al/P ratio for that was fixed when the molecular sieve formed. On the other hand, $\text{FeAlPO}_4\text{-5}$ has lower Al% than P%, because of the framework Al substitution by Fe. Although the bulk Fe% for the $\text{FeAlPO}_4\text{-5}$ and $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ are very close, they have exhibited an obvious difference in surface Fe%, which may imply a distribution disparity for Fe species, and the environment of Fe species was further studied and discussed later in this work.

The textural data for each sample are shown in table 1b. The surface area and pore volume of $\text{FeAlPO}_4\text{-5}$ are similar to $\text{AlPO}_4\text{-5}$, demonstrating that it has acceptable pore structure though the incorporation of Fe atoms may generate

framework breakage. The $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ has poor surface area and little pore volume, which can be attributed to the structure destruction of Fe impregnation and the blockage of pores by the surface resided Fe oxides.

The environment of Fe species was studied by UV-Vis DRS and the results of DRS characterization are shown in figure 3. According to the study of Fe incorporated ZSM-5 by Villa et al. [26], the peak around 247nm can be attributed to the both tetrahedral and octahedral Fe complexes, which implies the existence of framework Fe; and the peak at 280nm corresponds to the adsorption of octahedral complexes in extra-framework positions, and the distribution state for the Fe species correspond to 280nm can be isolated or clustered [27]. $\text{FeAlPO}_4\text{-5}$ has a distinct wide shoulder peak around 220~280nm which implies the existence of the mixture of framework and extra-framework Fe species. As for $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample, the absorbance peak has shifted to higher wavelength, and the peak at about 280nm demonstrates only extra-framework Fe in $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample. The $\text{AlPO}_4\text{-5}$ sample has a weak and flatter peak over 300nm, and the intensity of the signal can nearly be neglected compared to iron containing samples.

Figure 4 shows the Raman spectra of the calcined $\text{FeAlPO}_4\text{-5}$, $\text{AlPO}_4\text{-5}$ and $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ samples at a wavelength of 244nm which is within the range of the charge-transfer bands at 260 nm. The $\text{AlPO}_4\text{-5}$ sample has its characteristic peak at 260 400, 500, 1140, 1240 cm^{-1} as a typical AFI structure [28-29]. The intensity of the peak around 260 cm^{-1} is very small, but in the $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample, the presence of the peak at 260 cm^{-1} is instead more obvious and recognizable. New bands for the UV

Raman spectra of $\text{FeAlPO}_4\text{-5}$ appear at 630, 1060, and 1210cm^{-1} , which can be corresponded to the symmetric, asymmetric stretching vibrations of Fe(OP)_4 and symmetric stretching vibrations of FeO_4 , respectively [30-31]. For $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample, it has similar peaks to $\text{AlPO}_4\text{-5}$, and due to the relatively large loading amount of Fe oxides, the signal to noise ratio is higher than other two samples. This fact combined with the observations drawn above suggests that the AFI structure was destroyed severely after impregnation, the reason for the damage is the low pH of Fe^{3+} containing solution during impregnation process. Peaks at 630 and 1060cm^{-1} in $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ can be attributed to small amount of $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$ generated during the calcination process [32].

The coordination state and the location of the Fe species were studied by EPR and the results are shown in figure 5. The pure $\text{AlPO}_4\text{-5}$ has a silent signal indicating that there is no metal ions incorporated. All the Fe containing samples show signals at $g=4.3$ and $g=2.0$. According to the studies of Goldfarb and Liu [33-34], the signals at $g=2.0$ and $g=4.3$ are not suggested to be used as the sole evidence of confirmed framework incorporation. The high spin Fe^{3+} signal at $g=2.0$ is regarded only the necessary condition to framework Fe incorporation in Fe substituted samples, which may also contributed by extra-framework. The signal at $g=4.3$ is often related to the Fe species connected with terminal oxigens in defect sites, and can be produced by extra-framework Fe too. The tiny signal at $g=8.2$ is referred to the isolated mononuclear Fe, for the impregnated sample, it is plausible to explain the signal at $g=8.2$ by the generating of $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$ phase. The template-free $\text{FeAlPO}_4\text{-5}$

sample has signals at $g=2.3$ and $g=3.3$. Goldfarb ascribed the signal at $g=2.3$ to the rehydration of small interstitial Fe oxide groups [33]. However Lin ascribed these two signals to tricoordinated Fe which is coordinated vacant due the removal of binding template [35]. Upon dehydration, this site exhibits some rather asymmetric electric field and shows stronger signal at $g=3.3$. After rehydration, the adsorbate sensitive Fe in the defect site would be coordinated with H_2O then enhances the local symmetry and shows a stronger signal at $g=2.3$. Despite the controversy, their opinions have been met with that the signal at $g=2.3$ presents after the incoming molecules such as H_2O are contacted [33, 35-36]. As thus the EPR pattern of D- $AlPO_4-5$ obtained by treating $FeAlPO_4-5$ at 623K under vacuum for 8h and rehydrated DS- $AlPO_4-5$ obtained by soaking D- $AlPO_4-5$ with 0.1% NaOH by weight were ex situ recorded. As shown in the pattern of D- $AlPO_4-5$, the signal at $g=3.3$ strengthened as the signal at $g=2.3$ weakened implies the vacancy between Fe and adsorbate molecules, after rehydration, the signal at $g=3.3$ disappeared totally and $g=2.3$ was still presented as the dominant signal for adsorbate sensitive site.

The difference between the Fe species were determined by H_2 -TPR approach. The H_2 -TPR results of each sample are shown in figure 6. No distinct reduction peak can be seen for pure $AlPO_4-5$, while the $FeAlPO_4-5$ sample has three identifiable reduction peaks at 775, 860K, 982K, and $Fe_2O_3/AlPO_4-5$ has mainly one reduction peak at 703K. The peak below 800K can be classified to the extra-framework Fe species [36], the peak at 703K of $Fe_2O_3/AlPO_4-5$ implies that the bulk Fe can easily be reduced; the reduction peak at 775K of $FeAlPO_4-5$ indicates that the

extra-framework Fe is located inside 12 member ring tunnel, for its reduction should be posterior to the H₂ diffusion into micropores, which increases the difficulty of reduction manifested a much higher reduction temperature. The peak at 860K and the peak at 982K are related to the pseudo tetrahedral Fe species in the defect sites and the framework tetrahedral Fe sites, respectively, and the reason for their presence at high temperature (860K and 982K) can be ascribed to the shielding effect of the zeolitic framework, which protects the Fe from hydrogen attack [36]. Cheng's work also reported the H₂-TPR profile of FeAlPO₄-5, unfortunately they did not show the peak above 873K [25]. By comparing the reduction peak area of framework and extra-framework Fe of FeAlPO₄-5 sample, it is not difficult to find that the framework Fe still appears as the majority part of the total iron in the FeAlPO₄-5 sample, this behavior is different from Fe containing Y zeolites [37] and deemed to be the advantage of forming single Fe site.

The TEM micrographs of template-free FeAlPO₄-5 (figure 7a) does not show any identifiable iron-related phase suggesting that all the Fe species is presented in a highly dispersed state after calcination. The Fe₂O₃/AlPO₄-5 has distinct Fe particles (figure 7b) the diameter of which varies from 3-8nm. Because the Fe particles of Fe₂O₃/AlPO₄-5 are larger than the pores of AlPO₄-5 (0.73nm), these particles can only be surface located. In order to investigate the real distribution state of Fe species of calcined FeAlPO₄-5, Cs-corrected STEM was used, and the micrograph in figure 7c shows that the Fe species are single sites which are small enough to be located in the pores. The Fe particle in figure 7d (bright field) observed by Cs-corrected STEM also

confirmed the result obtained by TEM.

The tuning to the property of different state of Fe species was determined through NH_3 -TPD and toluene-TPD respectively. The NH_3 -TPD results for each sample are shown in figure 8. The increase in both the strength and amount of the acidity in $\text{FeAlPO}_4\text{-5}$ sample compared with pure $\text{AlPO}_4\text{-5}$ and $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample is observed. The acidity changes in the Fe incorporated sample is attributed to the Lewis acidity property possessed by Fe and framework doping of iron, and the better dispersion of Fe results in more exposure of acid sites. The toluene-TPD results in figure 9 further illustrates that Fe incorporated sample has more suitable π bond adsorption for $\text{FeAlPO}_4\text{-5}$ has both highly separated Fe sites and well reserved micropore. The coverage of pores and the destroying to the structure may be the reason of the sharp decrease in acidity and toluene adsorption in $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ sample.

For the HDS reaction, thiophene was selected considering that the size of its molecule can adapt the pores of AFI structure. The evaluation results of the three samples are 57.0% ($\text{FeAlPO}_4\text{-5}$), 47.8% ($\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$) and 40.3% ($\text{AlPO}_4\text{-5}$). $\text{FeAlPO}_4\text{-5}$ has the highest sulfur removal, and the HDS rate of $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ is higher than pure $\text{AlPO}_4\text{-5}$ by about 10%.

By comparing the hydrodesulphurization result of $\text{FeAlPO}_4\text{-5}$ and $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$, an interesting relationship can be concluded: despite the $\text{FeAlPO}_4\text{-5}$ has a higher Fe reduction temperature and lower extra-framework Fe amount proved by H_2 -TPR, the desulfurization rate of it is higher than $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ by about 10%,

the extra-framework Fe of which is dominant. Although the exact active phase of iron containing $\text{AlPO}_4\text{-5}$ in thiophene HDS is yet to discover. The enhanced hydrodesulphurization result of $\text{FeAlPO}_4\text{-5}$ may be explained that the single Fe sites have better adsorption capacity to thiophene, which has also π electron property, and the reserved 12 member ring tunnel in $\text{FeAlPO}_4\text{-5}$ at the same time accommodates the adsorption and C-S breaking, while $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ has only stacking of bulk Fe oxides phase and most of the tunnels were block off after impregnation thus no suitable room for the reaction is supplied. At last, $\text{AlPO}_4\text{-5}$ sample has no active center for thiophene hydrogenation, although it has well reserved tunnels. The result it performed is mainly attributed to the reaction carried on the surface of the steel tube of fixed-bed reactor which can also provide a few Fe sites for thiophene reaction.

4. Conclusions

In the calcined $\text{FeAlPO}_4\text{-5}$ sample, Fe species was reserved majorly framework substituted, meanwhile extra-framework Fe resulted by calcination existed inside the micropore, by observations of UV-Vis DRS and the EPR spectroscopy. EPR results further discovered part of the Fe species can be interacted with incoming molecules such as H_2O due to coordination vacancy. $\text{H}_2\text{-TPR}$ results implied that the dispersion of inner pore extra-framework Fe in $\text{FeAlPO}_4\text{-5}$ was higher than in $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$, and this conclusion was supported by the observation of TEM micrographs. Cs-corrected STEM micrograph directly proved the existence of Fe in calcined $\text{FeAlPO}_4\text{-5}$ was single sites while the impregnated sample had larger particles. As

shown in NH_3 -TPD result, $\text{FeAlPO}_4\text{-5}$ had an increased amount and strength of the acidity, which can be attributed to the Lewis acidity of extra-framework single Fe sites and framework doping of iron. Apart from acidity, an enhanced adsorption ability for toluene-TPD results could also be obtained by $\text{FeAlPO}_4\text{-5}$. The improvement of acidity and adsorption ability under reserved microporous environment was believed to be correlated to the higher sulfur removal performance of $\text{FeAlPO}_4\text{-5}$ in thiophene HDS reactions. And the confirming of true active Fe phase needs further study.

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Tables:

Tab.1 Elemental composition and textural structure of the template-free $\text{AlPO}_4\text{-5}$, $\text{FeAlPO}_4\text{-5}$ and $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$

Sample	a. Elemental compositions (atomic, %)						b. Textural structures				
	Bulk			Surface			S_{BET} m ² /g	S_{EXT} m ² /g	V_{total} cm ³ /g	V_{micro} cm ³ /g	V_{meso} cm ³ /g
	Fe	Al	P	Fe	Al	P					
$\text{AlPO}_4\text{-5}$	0	51.7	48.3	0	47.8	52.2	291.8	46.9	0.24	0.12	0.12
$\text{FeAlPO}_4\text{-5}$	3.7	48.0	48.3	2.5	44.5	53.0	250.6	50.4	0.20	0.10	0.10
$\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$	3.2	49.2	47.6	3.7	46.4	49.9	67.11	10.1	0.05	0.03	0.02

Figure Captions:

Fig.1. X-ray diffraction patterns of the calcined $\text{AlPO}_4\text{-5}$ (a), $\text{FeAlPO}_4\text{-5}$ (b), and impregnated sample $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c)

Fig.2. SEM images of the crystal of as-made samples: $\text{AlPO}_4\text{-5}$ (a), $\text{FeAlPO}_4\text{-5}$ (b), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c)

Fig.3. UV-Vis spectra of the template samples: $\text{AlPO}_4\text{-5}$ (a), $\text{FeAlPO}_4\text{-5}$ (b), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c)

Fig.4. Raman spectra of the template samples: $\text{AlPO}_4\text{-5}$ (a), $\text{FeAlPO}_4\text{-5}$ (b), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c)

Fig.5. EPR results at 113K of template-free $\text{AlPO}_4\text{-5}$ (a), template-free $\text{FeAlPO}_4\text{-5}$ (b), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c), as-synthesized $\text{FeAlPO}_4\text{-5}$ (d), D- $\text{FeAlPO}_4\text{-5}$ (e), DS- $\text{FeAlPO}_4\text{-5}$ (f). For dehydration, the D- $\text{AlPO}_4\text{-5}$ was obtained by treating template-free $\text{FeAlPO}_4\text{-5}$ at 623K under vacuum for 8h. And the rehydrated sample DS- $\text{AlPO}_4\text{-5}$ was obtained by soaking D- $\text{AlPO}_4\text{-5}$ with 0.1% by weight of NaOH solution.

Fig.6. H_2 -TPR results of the calcined samples: $\text{AlPO}_4\text{-5}$ (a), $\text{FeAlPO}_4\text{-5}$ (b), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c)

Fig.7. TEM micrograph calcined $\text{FeAlPO}_4\text{-5}$ (a), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (b), and Cs-corrected STEM micrograph of calcined $\text{FeAlPO}_4\text{-5}$ (c), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (d)

Fig.8. NH_3 -TPD results of the calcined samples: $\text{AlPO}_4\text{-5}$ (a), $\text{FeAlPO}_4\text{-5}$ (b), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c)

Fig.9. Toluene-TPD results of the calcined samples: $\text{AlPO}_4\text{-5}$ (a), $\text{FeAlPO}_4\text{-5}$ (b), $\text{Fe}_2\text{O}_3/\text{AlPO}_4\text{-5}$ (c)

Figure

Figure

HV	HFW	mag	□	det	WD	10 μ m	
30.00 kV	25.6 μ m	10 000 x		ETD	10.5 mm	CUP	

Figure

HV	HFW	mag	□	det	WD	10 μ m	
30.00 kV	25.6 μ m	10 000 x		ETD	11.0 mm	CUP	

Figure

HV	HFW	mag	□	det	WD	10 µm	
20.00 kV	25.6 µm	10 000 x		ETD	10.5 mm	CUP	

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