

Direct synthesis of Zn-ZSM-5 with novel morphology

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Abstract

Zinc-containing ZSM-5 zeolite with novel morphology was firstly synthesized in a one-step route using $[\text{Zn}(\text{NH}_3)_4]^{2+}$ aqueous solution as zinc resource and *n*-butylamine as template. The materials were characterized by XRD, SEM, diffuse reflectance UV–vis spectra, FTIR for pyridine adsorption. The results showed that the formation of this novel structure might be related to the introduction of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ aqueous solution and the zinc existent state in zeolite.

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1. Introduction

Over the last few decades, transition metal ions modified zeolites have gained a great deal of attention since the first successful synthesis and application of TS-1 zeolite [1]. The incorporation of transition metals endows zeolite many special catalytic properties besides the zeolite's own properties (acidity and shape-selectivity). Among them, metal-modified ZSM-5 (M=Cu, Zn, Co, Fe, Cr, V etc) were most intensively investigated. These materials exhibited excellent catalytic activities in the reactions of deNO_x [2,3], light alkanes' aromatization to BTX [4], phenol oxidation [5], water gas shift reaction [6], cracking of FCC naphtha [7] etc. Most of the preparation of metal-containing ZSM-5 was an indirect way of ion-exchanging (in solution or solid state) or impregnation. The direct synthesis method of incorporating metal ions into the ZSM-5 zeolite during the synthesis of zeolite, is simplified and more importantly, rather superior for obtaining better dispersion and stability of metal species in zeolite; but up to now, there are only a few research works reported on this aspect [8–10]. In this paper, we report a novel one-step synthesized Zn-ZSM-5 structure by introducing $[\text{Zn}(\text{NH}_3)_4]^{2+}$ aqueous solution into the ZSM-5 gel precursors. To the best of our knowledge, this novel structure and synthesis method has never been reported before.

2. Experimental

The synthesis gel mixtures of molar composition ($\text{SiO}_2:0.01\text{-Al}_2\text{O}_3:0.09\text{Na}_2\text{O}:0.20n\text{-butylamine}:(0\text{-}0.02)\text{ZnO}:41.5\text{H}_2\text{O}$)

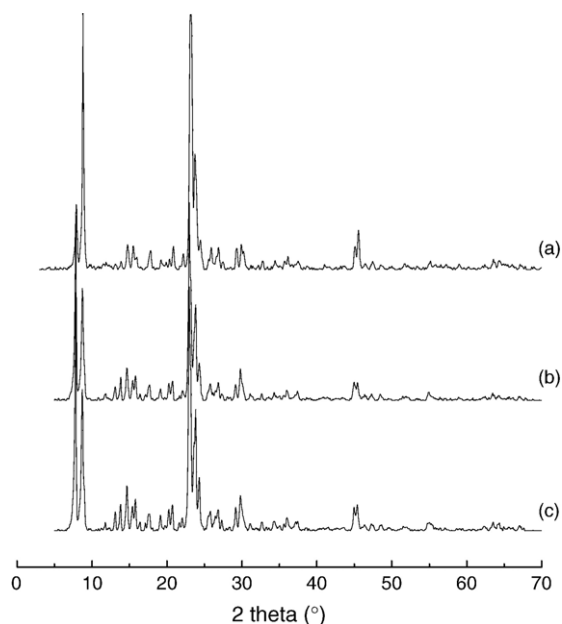


Fig. 1. The XRD patterns of Zn-ZSM-5 (a) ZSM-5 (Zn 0 wt.%); (b) Zn-ZSM-5 (Zn 1.25 wt.%); (c) Zn-ZSM-5 (Zn 1.83 wt.%).

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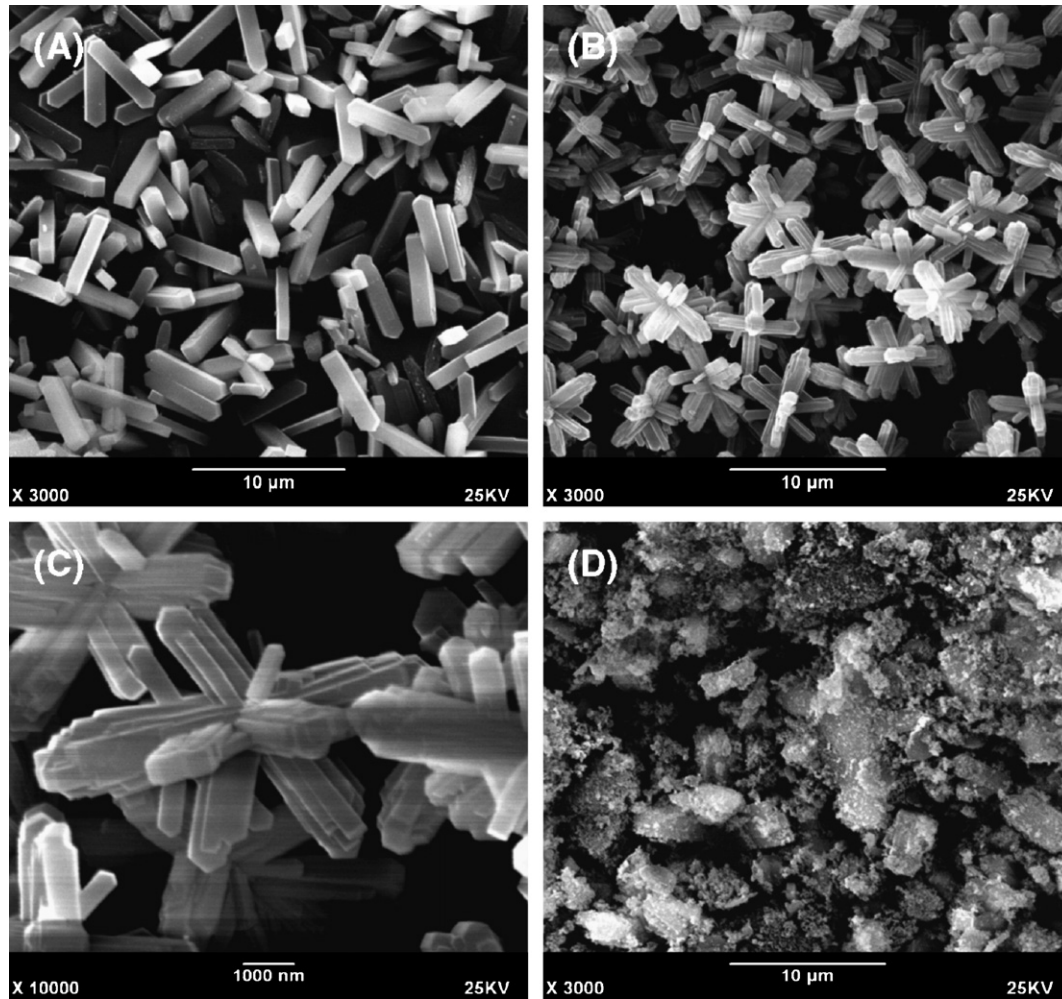


Fig. 2. The morphology of Zn-ZSM-5 (A) ZSM-5 (Zn 0 wt.%); (B, C) Zn-ZSM-5 (Zn 1.25 wt.%); (D) Zn-ZSM-5 ($\text{Zn}(\text{NO}_3)_2$ as zinc resource, Zn 2.53 wt.%).

were prepared as follows. A proper amount of fumed silica was dissolved in deionized water, then, sodium hydroxide was added under stirring at room temperature. After that, aluminium sul-

phate and *n*-butylamine were added to the gel separately with vigorous stirring. After 30 min of aging, the 0.1 M $[\text{Zn}(\text{NH}_3)_4]^{2+}$ aqueous solution, prepared by the reaction of ammonia with Zn

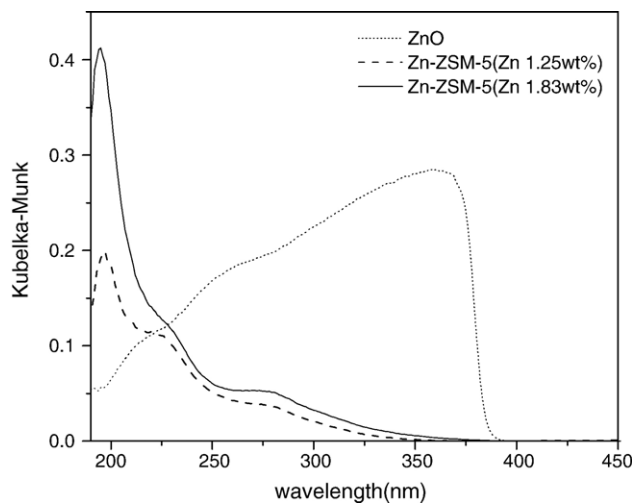


Fig. 3. Diffuse reflectance UV-vis spectra of Zn-ZSM-5.

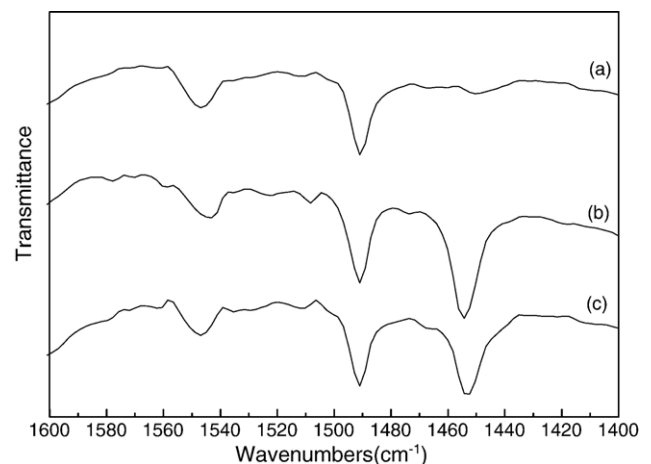


Fig. 4. IR spectra of pyridine adsorption at 423 K over Zn-ZSM-5 samples. Zn-ZSM-5 with Zn content: (a) 0 wt.%; (b) 1.25 wt.%; (d) 1.83 wt.%.

(NO₃)₂ solution, was introduced to the mixture. The gel was stirred for 60 min and then, transferred into Teflon-lined steel autoclave. Crystallization was achieved at 448 K under auto-genous pressure for five days. The product was then cooled and separated from the mother liquor by centrifugation. At last, zeolite was obtained after drying and calcinations at 823 K to remove the templates. The samples were characterized by X-ray diffraction patterns (XRD) recorded on a Rigaku D/Max RB diffractometer (Cu K α radiation, 40 kV, 40 mA, scanning range: 5–70 $^\circ$), scanning electron microscopy (SEM, KYKY1000B, at an accelerating voltage of 25 kV), diffuse reflectance UV–vis spectra (JASCO V-550 UV–Vis spectrometer, the spectra were recorded in the 190–500 nm wavelength range, with a scan rate of 100 nm/min), and infrared spectra for pyridine adsorption (EQUINOX 55 FTIR spectrometer, pretreated in vacuum at 773 K for 1 h and recorded at room temperature after pyridine adsorption).

3. Results and discussion

Fig. 1 shows the XRD patterns of the series Zn-ZSM-5. All the samples show the typical characteristic pattern of MFI structure and no peaks corresponding to ZnO ($2\theta=31.6^\circ, 34.2^\circ, 36.1^\circ, 56.6^\circ$) can be obviously observed, even over the sample with zinc content up to 1.83 wt.%, indicating that the zinc species were highly dispersed in the zeolites.

The morphology of the Zn-ZSM-5 samples is shown in Fig. 2. It can be seen that the sample of ZSM-5 without zinc exhibits a typical MFI structure (Fig. 2A). ‘Boat-like’ hexagonal-shaped crystal rods are quite uniform with crystal size of 6–8 μm in length. But after zinc was introduced into ZSM-5 initial gel in the form of $[\text{Zn}(\text{NH}_3)_4]^{2+}$, the final product morphology changed greatly. Snowflake-like crystal clusters with high crystallinity can be seen in Fig. 2B. The crystals seen in Fig. 2A seem to aggregate round a center point and stretch crosswise to the round. A clearer image (Fig. 2C) shows that in each direction, there is not just one crystal, but numerous crystals grown in parallel. Moreover, we found that with the increase of zinc content in a proper range, more hexagonal-shaped crystals aggregated round the same core, forming a larger cluster, indicating that the scale of this novel crystal cluster depends on zinc amount. As a comparison, we prepared a sample using Zn(NO₃)₂ solution as a zinc resource (other synthesis conditions unchanged). The sample morphology is shown in Fig. 2D. It is clear that the sample crystallinity is very poor and no snowflake-shaped crystal clusters can be observed. This result may be ascribed to the unfavourable effect caused by the formation of zinc hydroxide to the synthesis of ZSM-5. We also synthesized Cu(Co,Pd)-ZSM-5 using the method above with $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Pd}(\text{NH}_3)_4]^{2+}$ aqueous solution as the metal resource separately, but these materials all exhibit similar morphology as that shown in Fig. 2a. The results above strongly suggest that the formation of this novel crystal structure was directly related with the properties of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ species. If there was no *n*-butylamine, we proved that the self-existence of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ could not form any ZSM-5 crystals. Therefore, the $[\text{Zn}(\text{NH}_3)_4]^{2+}$ species could not serve as template as *n*-butylamine by itself, however, it should exert influence on the ZSM-5 crystal formation. This novel structure has some similar features of twinned crystals. It has been reported that the increase of twinned crystals is one of the evidence of isomorphous heteroatom substitution [9], therefore, this novel structure may be correlated with the existent state of zinc in zeolite.

The coordination states of the synthesized samples were investigated by diffuse reflectance UV–vis spectrum as depicted in Fig. 3. As a reference, pure ZnO exhibits a large broad absorption band around 360 nm, which can be assigned to the $\text{O}^{2-} \rightarrow \text{Zn}^{2+}$ ligand to metal charge transfer (LMCT) transition [11,12]. The Zn-ZSM-5 samples exhibit quite different absorption bands from that of ZnO, with peaks or shoulders at about 280, 230, 195 nm, respectively. This result indicates the great difference of coordination environment between the zinc species in ZSM-5 and that in pure ZnO. The appearance of absorption bands below 230 nm are generally considered as the distinguishing proof of incorporation of metal atoms into the framework of zeolite by isomorphous substitution. Therefore, it can be concluded that most of zinc species should have entered the zeolite framework and the absorption band of 195,230 nm may be assigned to the charge transfer transitions of framework zinc species with lattice O^{2-} , whereas the detailed zinc coordination states are not confirmed.

Furthermore, pyridine adsorption IR spectrum was employed to examine the change of acidic property after zinc introduction as shown in Fig. 4. Previous researches [13,14] showed that the introduction of zinc by ion-exchange and impregnation caused the decrease of B-acidic site number and corresponding increase of L-acidic site number through the proton exchange of acidic OH-groups by Zn^{2+} ions. But our results show that the acidic amount of B-acidic site (1547 cm^{-1}) is slightly declined, while that of L-acidic site (1454 cm^{-1}) is increased remarkably. Considering that zinc species outside framework can only offer small amount of acidic sites, this result may further indicate that zinc species have incorporated into the framework of ZSM-5, and similar results have been reported on Ti and V-ZSM-5 zeolite [15].

From the above results, we tentatively consider that the zinc species from $[\text{Zn}(\text{NH}_3)_4]^{2+}$ might take part in the nucleation process [16] of ZSM-5 and thus the framework zinc species affected the crystal growth and therefore caused the appearance of this special crystal structure. Further studies on the formation mechanism are in process.

4. Conclusions

In summary, a novel Zn-ZSM-5 structure has been firstly synthesized in a one-step route. This novel structure has a strong correlation with the introduction of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ aqueous solution to the initial gel stage of ZSM-5 zeolite. The characterizations on these materials show that most zinc species have entered into the framework of ZSM-5. This work can be beneficial to the synthesis and application of zinc-containing ZSM-5 zeolite.

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