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IMPACT OF OXIDATION OCCURRED DURING DESOLVATION PROCESS ON THE MELTING PROPERTIES OF ZIF-62

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Zeolitic imidazolate frameworks (ZIFs), as a family of metal-organic frameworks (MOFs) which possess nanoporous structure, have been investigated intensively in the past two decades for a variety of applications. Recently, a subgroup of ZIFs including ZIF-62 ($Zn(Im_{2-x}bIm_x)$) has been demonstrated to form a new kind of glasses by melt-quenching, indicating that some ZIFs possess excellent melting properties. In this paper, ZIF-62 crystals were synthesized using solvothermal synthesis method. The impact of oxidation occurred in desolvation process on the melting properties of ZIF-62 was investigated by preheating the ZIF-62 samples under different conditions. From the results of T_m and T_g obtained from differential scanning calorimeter measurement (DSC), we found that the solvent removal of ZIF-62 in inert environment prior to the melting does not cause the structural collapse; however, oxidation occurred during the desolvation process under air atmosphere has a significant effect on the melting attributes of ZIFs. This result shows that the framework structure of ZIFs is quite sensitive to oxygen, giving us an enlightenment that preventing oxidation during pretreatment to remove solvent is crucial to the formation of ZIFs glasses.

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Key words: ZIF-62; Oxidation; Melting properties

1. Introduction

Metal-organic frameworks(MOFs) are a relatively new family of nanoporous materials which consist of metal nodes linked by organic ligands in infinite arrays and are heralded for their chemical versatility in being able to accommodate an enormous range of ligand- or metal-based functionalities[1-3]. They possess extremely large surface area, remarkably low density, nanoporosity, easily designed or modified to have different pore sizes and are regarded as promising candidates for storage, separation, catalysis, drug delivery, membranes and films in various nanotechnologies. Zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs that adopt zeolitic topologies [4-5], have been the focus of much attention, primarily because of their promising gas storage, separations, catalysis, and sensing properties [6-8]. They adopt porous crystalline structures composed of metal ions and organic linkers, ordered in an analogous fashion to that of silicon and oxygen in zeolite [9-10]. Architecturally, ZIFs are similar to the frameworks of

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zeolites in which the Si-O-Si bridges are replaced by Zn-Im-Zn bridges (or Co, Cu) and their bond angles are both close to 145° (Fig.1a) [11-13]. Remarkably, ZIFs combine the classical zeolitic traits of chemical and thermal stability with the rich topological diversity and pore size tunability characteristic to MOFs [14-16]. The retention of thermal stability derived from their zeolitic structures makes particularly attractive candidates for practical applications.

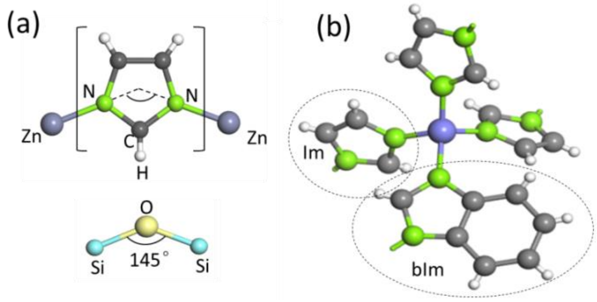


Fig.1 (a) Representations of the Zn-im-Zn and Si-O-Si linkages in tetrahedral ZIF and silicate networks, respectively; (b) Structural units of ZIF-62

Recently, an international research team found that some ZIFs are good glass formers which possess brilliant melting behavior. They succeeded in melting four MOF structures prior to decomposition, and obtained ZIF glasses by quenching [1]. Apparently, melting property is of great importance in the study of ZIFs crystals, but few scholars have focused on this aspect at the present stage. For ZIF synthesis, organic solvents such as N,N-dimethylformamide (DMF) are always required. These solvents are incorporated into the cages of ZIF crystals during solvothermal synthesis. In order to examine some unique properties, solvent remained in the frameworks must be removed. Therefore, our original goal was to study the impact of solvent removal on the melting behavior of ZIFs. However, during the preheating process under air atmosphere, we found that the frameworks of ZIFs are so sensitive to the ambient environment that they tend to be oxidized in the presence of oxygen.

Herein, we focus our attention on ZIF-62($Zn(Im_{2-x}bIm_x)$), research of which is hitherto scarce. We present a study on the impact of oxidation and the remaining solvent on the melting behavior of ZIF-62. Specifically the ZIF-62 crystals were prepared via solvothermal synthesis. Then the crystals were pretreated at different temperatures to remove the guest solvent under different conditions. The melting behavior of ZIF-62 is studied in detail by differential scanning calorimeter. Besides, we simply shed light on the impact of oxidation on the melting behavior of ZIFs, and make it clear that preventing oxidation during pretreatment to remove solvent is crucial to the melting of ZIFs.

2. Experimental

2.1 Synthesis of ZIF-62

The ZIFs were synthesized using solvothermal synthesis method. Highly crystalline materials were obtained by combining the specific metal salt (usually nitrate) and imidazole-type linkers in an amide solvent such as N,N-dimethylformamide (DMF). Specifically, as for ZIF-62 crystals, $Zn(NO_3)\cdot 6(H_2O)$(99%) was used as the metal source, imidazole (Im, 99.5%) and benzimidazole (bIm,99%) were used as the linkers, and DMF as the solvent. In the first place, the three reagents Zn, Im, bIm into DMF were dissolved to form three stock solutions. Before the experiment, we designed the solution concentration, and calculated the masses and volumes of Zn, Im, bIm and DMF solution. Then appropriate volumes of the stock solutions according to our calculation were mixed together. In a typical synthesis, 9.7ml 0.2mol/L Zn stock solution, 17.45ml 1.5 mol/L Im stock solution, 14.55ml 0.2mol/L bIm stock solution and 8.3ml DMF (molar ratio Zn:Im:bIm:DMF=1:13.5:1.5:333) were mixed for the solvothermal reaction. Subsequently, the solutions were mixed in a 100ml Teflon-lined autoclave and stirred for 1h, then placed in an oven at 110℃ for 96h. At the end of reaction, the Teflon-lined autoclave was cooled to ambient temperature along with the oven cooling. The solid was washed by DMF for three times, and dried at 100℃ for 4h. Thus we got the fresh ZIF-62 powders [17].

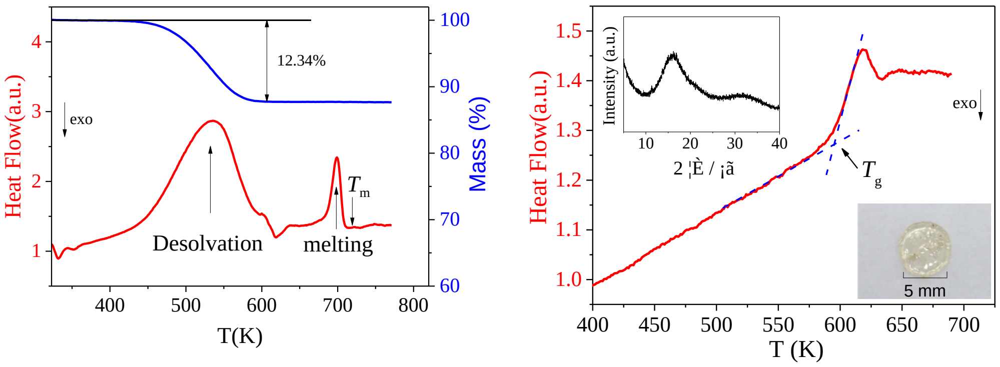
2.2 Characterizations

The melting behaviors including melting points (T_m) and glass transition temperatures (T_g) were obtained during upscanning in NETZSCH STA 449 F1 differential scanning calorimeter, with samples held in platinum pans in a continuous flow argon atmosphere. Each sample was previously heated to 773K at 10 K/min, and subsequent cooled to 523 K at 20 K/min, then naturally to room temperature. For details see the previous work in our lab [18-22]. X-ray diffraction measurement was performed using a diffractometer (RU-200B; Rigaku) with Cu Kα radiation.

3. Results

Enthalpic responses and thermal gravity curves of ZIF-62 are shown in Fig.2a, which are similar to a previous work reported by a previous paper [2]. When heating under an inert atmosphere, the as-synthesized ZIF-62 undergoes two abrupt enthalpy changes. Specifically, it first exhibited an endothermic peak in the temperature range from 400K to 570K, with a gradual weight-loss of 12.34%, corresponding to the escape of solvent molecules DMF trapped in the pores. Upon further heating, another endothermic peak appears, with no weight-loss at all, ascribing to the melting of the ZIF-62 crystals. The offset temperature (708 K) of the melting peak is defined as the temperature at which the last crystallite vanishes. In addition, in the following second upscan, we observed the obvious endothermic effect representing glass transition (T_g) at about 595 K.

Above T_m by quenching the melt at 10 K/min in DSC, we got a compact and transparent bulk disk (inset in the bottom of Fig.2b). The obtained sample was fully amorphous, as evidenced by the XRD patterns in the top inset of Fig.2b, indicating that ZIF-62 is a good glass former, that is to say, ZIF-62 is able to melt before decomposition, enabling casting or shaping before vitrification of the melt upon quenching. Such result opens a new field, promising to provide exciting opportunities for a great number of practical applications in the future.

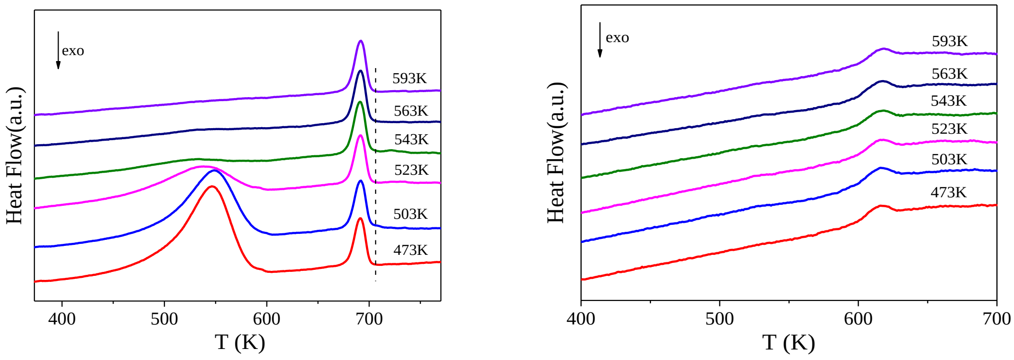


a) *b)*

Fig. 2. (a) Enthalpic responses and mass change of the as-synthesized ZIF-62 samples on the first DSC heating upscan at 10K/min. Desolvation and melting temperature(T_m) are indicated. T_m refers to the offset temperature of the melting peak; (b) Enthalpic responses of the as-synthesized ZIF-62 samples on the second DSC heating upscan at 10K/min. T_g was obtained from DSC measurements by the standard method. The top inset is the XRD pattern of the obtained ZIF-62 sample. The bottom inset illustrates the typical image of the transparent bulk glass after DSC upscans.

Solvents used during synthesis usually remain in the pores of the materials and for obtaining ZIF-62 glasses, activation by heating is usually required to remove these solvent molecules. These residual solvent DMF remained in the frameworks might have a considerable effect on its melting behavior [23]. Once, after we preheat the ZIF-62 samples at 493K in vacuum oven to remove the solvent, we accidentally observed some changes in its melting point in subsequent DSC upscans. This peculiar phenomenon brought a problem about whether the residual solvent have an effect on its melting behavior on earth. Next, a systematic study should be done to thoroughly explore the pretreatment effect on it.

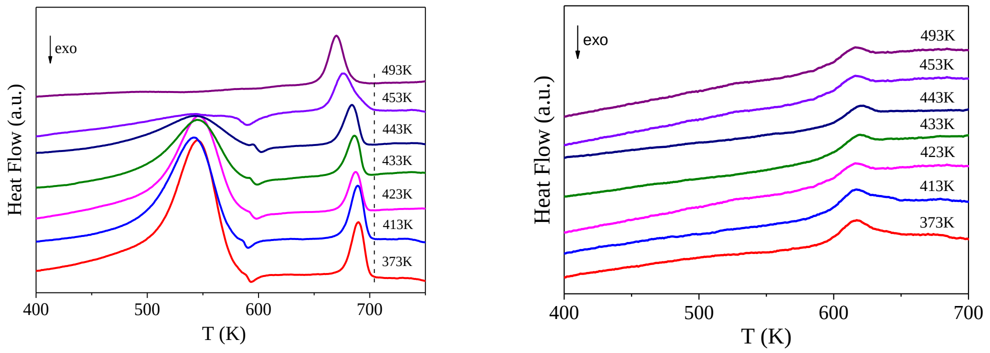
We dynamically heated and annealed the as-synthesized samples in a DSC (NETZSCH STA 449 F1) in Ar. A series of samples (molar ratio Zn:Im:bIm=1:13.5:1.5:111) were heated to the selected maximum temperatures (T_{max}=473, 503, 528, 548, 558, 593K) at 10 K/min, and then cooled down to 523K at 10 K/min, finally naturally to room temperature. DSC upscans were again taken to characterize the melting and glass forming of ZIF-62. The DSC curves of as-prepared ZIF-62 samples after pretreated in differential scanning calorimeter to different maximum temperature (T_{max}) are shown in Fig.3. Upon dynamic heating to different temperatures, the T_m and T_g both stay unchanged, making it clear that solvent release have no effect on the melting behavior of the as-synthesized ZIF-62 specimens. In addition, after twice cycling DSC upscans, the obtained ZIF-62 glass is transparent, perfectly just as shown in Fig.2b inset. This phenomenon strongly indicates that solvent removal prior to the melting does not give rise to the structural collapse.



a) *b)*

Fig.3 The DSC curves of as-prepared ZIF-62 samples after pretreated in differential scanning calorimeter to different maximum temperature (T_{max}). (a) First upscans showing both desolvation and melting; (b) Second upscans showing glass transition. The up- and downscans were performed at 10 K/min in argon.

Secondly, prior to the study of melting behavior in DSC, the effect of oxidation on the melting behavior was probed by varying the heat-treatment temperature from 373K to 493K under air atmosphere. Specifically, the as-synthesized ZIF-62 product (molar ratio Zn:Im:bIm=1:13.5:1.5:111) were preheated at the temperatures (T_{max}) of 373, 393, 413, 433, 453, 473, 493 and 523K for 18h under air atmosphere to remove the solvent. Fig.4 shows the DSC curves of as-prepared ZIF-62 samples after pretreated under air atmosphere at different heat-treated temperatures. It is crucial to note that, after pretreatment at higher temperatures, the melting peaks of ZIF-62 product acquired from the subsequent DSC upscans slightly move to lower temperatures, while the glass transition point (T_g) stay unchanged. This study manifests that the stability of ZIF-62 in open air was much lower than that in an inert atmosphere, indicating that the framework structure of ZIFs was quite sensitive to oxygen. This finding also indicates that the melting properties of ZIFs can be changed by oxidation occurred in the process of solvent removal under air atmosphere, so pretreatment prior to melting must be done in high inert atmosphere to avoid oxidation.



a) *b)*

Fig.4 The DSC curves of as-prepared ZIF-62 samples after pretreated in air conditions at different maximum temperature (T_{max}). (a) First upscans showing both desolvation and melting; (b) Second upscans showing glass transition. The up- and downscans were performed at 10 K/min in argon.

4. Discussion

As a fascinating glass former which possesses ultra-high glass-forming ability [1-2, 24], the oxidation occurred during the desolvation process under air atmosphere has a significant effect on the melting behavior of ZIF-62. On the contrary, simple solvent removal under inert atmosphere has no effect on its melting properties. As mentioned above, through DSC characterization, the melting point of ZIF-62 was found to decrease with the increase of pretreatment temperature under air atmosphere.

However, why and how the framework oxidation affects the melting behavior of ZIFs is unknown so far. Firstly, we should have a preliminary understanding on the structure of ZIF-62, which is shown in Fig.1b. ZIF-62 is a mixed-linker framework of nominal composition $Zn(Im)_{1.75}(bIm)_{0.25}$ in which Zn^{2+} is coordinated to Im ($C_3H_3N_2^-$) and bIm ($C_5H_7N_2^-$) ligands whose orientation alternates along tetrahedral lines[24].

Secondly, the melting mechanism of ZIFs is referenced to help us better understand the melting. Take ZIF-62 for example. In a molecular level of the melting process, the ideal four-fold coordination (Fig.1b) is maintained at low temperatures, where more than 94% of the Zn ions are coordinated by three imidazolate groups and one benzimidazole but another 6% of Zn ions are under-coordinating. In this regime, the under-coordination of Zn^{2+} can be seen as a defect in the solid, which act as nucleation sites for melting. Then when melting occurs, the proportion of undercoordinated Zn^{2+} increases dramatically [23], which demonstrates that melting process involves the breaking of Zn-N bonds. Therefore, based on the detailed structural characterizations of network topologies of the melt-quenched glass and the as-prepared crystals, together with the relatively weaker Zn-N bonds compared to other bonds, the melting process can be viewed as a process involving Zn−N bond breaking and reformation [2, 23-25].

In view of these, the lowering of the melting point should be explained from the weakening of the Zn-N bonds. So we proposed several interpretations to explain the reason for the change of melting point. First of all, the organic components are reported to be very unstable [26-28]. When oxygen exists, the organic linkers (imidazole and benzimidazole) in the skeleton of ZIFs are much easier to be destroyed than the Zn-N bonds. Hence upon heating, the organic components firstly oxidized prior to Zn-N bonds, destroying the balance of ZIFs to some extent. So it becomes much easier for the breaking of Zn-N bonds, inducing the shift of melting point to lower temperatures. Another possibility is that during the process of oxidation, the relatively weak Zn-N coordination bonds are somehow firstly destroyed, and then the oxygen atoms are incorporated into the frameworks, resulting in the formation of Zn-O bonds replacing the Zn-N ones. This can also lead to a drop in melting point.

In addition, further investigation are required to elucidate the detailed origins for the change of melting properties by clarifying the oxidation mechanism of ZIFs, which is undergoing in our lab. Nevertheless, the change of melting properties of ZIFs which is caused by oxidation during desolvation process suggests that the framework structure of ZIFs is quite sensitive to oxygen atmosphere.

5. Conclusions

The strong effect of oxidation on the melting properties of ZIFs was clearly observed in this investigation. Detailed comparison of preheat-treating processes under different atmospheres indicates that solvent remained in the frameworks of ZIFs has no impact on the melting properties while on the contrary, oxidation occurred during the process of solvent removal has a significant effect on the melting properties of ZIFs.

Furthermore, we carefully study the melting mechanism of ZIF-62 and give several explanations about why oxidation causes the decrease of melting point. This finding also gives us enlightenment that preventing oxidation during pretreatment to remove solvent is crucial to the formation of ZIFs glasses, promising to be an extremely exciting step forward in producing chemically functionalizable hybrid glass materials.

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