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Ionothermal Synthesis and Proton-Conductive Property of NH_2-MIL-53 MOF Nanomaterials

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It is a big challenge for the construction of proton-conductive materials for practical applications operating at high temperatures and low humidity. Herein, we propose an ionothermal synthesis strategy for the preparation of highly stable NH_2-MIL-53(Al)$_{it}$ nanomaterials with high proton conductivity. The crystalline structure and the direct incorporation of 1-ethyl-3-methyl-imidazolium ionic liquid within NH_2-MIL-53(Al)$_{it}$ are identified by XRD, TG/DTA and IR techniques. As-prepared NH_2-MIL-53(Al)$_{it}$ exhibits high proton conductivity of 3.0×10^{-5} S cm^{-1} at 80 °C and low relative humidity of ~26%.

Proton-conductive solids have found their significance and applications in the solid-state devices, particularly in the fuel cells.[1] The development of proton-conductive materials operating at low humidity and high temperatures (≥ 80 °C) is a big challenge that needs to be met for practical applications in fuel cell technology. The solids with proton-conductive property have interested us from the perspective of diversified structures and transport dynamics. In general, these materials need proton carriers (e.g. H_3O^+, H^+ or NH_4^+ provided by acid, OH groups or bases), as well as require proton-conducting pathways. In recent years, organic polymers, inorganic oxides, and other inorganic-organic hybrids,[2] particularly for metal organic frameworks,[3] have been widely studied and applied to electrochemical devices.

Metal organic frameworks (MOFs) constructed from metal ions/clusters and organic ligands have received much attention in the syntheses of topologically pleasing structures and in the promising applications of gas storage/adsorption, separation, catalysis, conductivity and etc., thanks to distinguished features of structural diversity, pore-size tunability, high surface areas, and good thermal/chemical stability.[4-6] In the literature, three types of proton carriers have been introduced into MOFs including inherent unsaturated metal sites,[7-9] acid/base groups on the frameworks,[10-14] and counter-ions/acidic molecules incorporated in the voids.[15-20] Additionally, proton-transport pathways are generally composed of hydrogen-bond networks from water[21-25] or other molecules.[26-31] We are interested in the designed synthesis of highly stable MOFs with high porosity and high proton conductivity, which is rarely shown in the previous reports. Hence, we propose the use of ionothermal synthesis strategy to prepare proton-conductive MOFs due to its two merits of protocol greenness and intrinsic conductivity of ionic liquids. Ionothermal synthesis using ionic liquids has been recognized as green synthetic chemistry in inorganic nanomaterials. Ionic liquids possess interesting properties, such as high thermal stability, non-flammability, negligible vapor pressure, low toxicity, ability to dissolve various reactants, and recyclability. Recently, ionic liquids have been explored and utilized in the preparation of MOF materials with interesting physicochemical properties.[32-33]

Herein, we focus on the synthesis of NH_2-MIL-53(Al) in an ionothermal system in order to achieve the main goal of improved conductivity at low-humidity/anhydrous condition and high temperature. NH_2-MIL-53(Al), an analogue to MIL-53(Al), is composed of $AlO_4(OH)_2$ clusters with 2-amino terephthalate as linkers instead of terephthalate.[34-35] The framework of NH_2-MIL-53(Al) contains 1-D diamond shaped channels with free standing amino groups, having a free diameter close to 7.5 Å. The available and highly dense amino groups (4 NH_2 per unit cell) can be served as proton carriers. The voids offer space in which the carrier molecules can move. The high thermal stability (~400 °C) guarantees the desirable working condition for electrochemical tests. In addition, NH_2-MIL-53(Al) nanocrystals possess a minimized interfacial transport barrier for the carriers.

The crystalline structure of ionothermally synthesized NH_2-MIL-53(Al) (designated as NH_2-MIL-53(Al)$_{it}$) is investigated using powder X-ray diffraction (XRD).

a. *Department of Materials Science, Key Laboratory of Mobile Materials, MOE, and State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China. E-mail: wtzheng@jlu.edu.cn.*
b. *Faculty of Chemistry, Northeast Normal University, Changchun 130024, P.R. China. E-mail: xiaoqinzou123@gmail.com.*
c. *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China.*

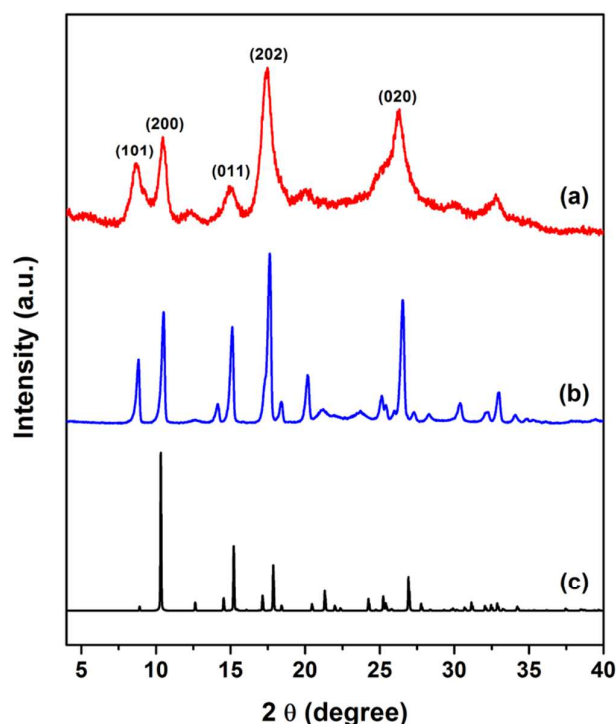**Fig. 1** XRD patterns of (a) prepared NH_2-MIL-53(Al)$_{it}$, (b) as-synthesized reference sample of NH_2-MIL-53(Al)$_{ref(as)}$, and (c) simulated from single crystal.[35]

Fig. 2 TG-DTA curves of as-synthesized NH_2-MIL-53(Al)$_{it}$ sample.

Fig. 1 shows XRD patterns of (a) NH_2-MIL-53(Al)$_{it}$ sample and (b) a reference one (NH_2-MIL-53(Al)$_{ref(as)}$) prepared according to the reported procedure.[34,36] As shown in Fig. 1a, as-prepared NH_2-MIL-53(Al)$_{it}$ exhibits several characteristic peaks of NH_2-MIL-53 type MOF, similar to the ones from Al(OH)[NH_2-BDC]·0.3NH_2-H_2BDC (Fig. 1c).[34-35] Also, the peak positions in Fig. 1b for NH_2-MIL-53(Al)$_{ref(as)}$ are identical to the ones from MIL-53(Al) single crystal (Fig. 1c). No other peaks are observed, indicating that as-prepared crystals in both samples are in a pure phase. To be noted, the peaks in Fig. 1a are much broader than the ones in Fig. 1b, which sheds lights on small crystallites of NH_2-MIL-53(Al)$_{it}$. Besides, the crystalline structure of NH_2-MIL-53(Al)$_{ref}$ is retained (Al(OH)[NH_2-BDC]·H_2O) after removing guest molecules in the pores (Fig. S2).[34] The morphology of NH_2-MIL-53(Al)$_{it}$ nanocrystals was studied by using scanning and transmission electron microscopes (SEM, TEM). Fig. S3a and b show representative SEM and TEM pictures of NH_2-MIL-53(Al)$_{it}$. Small ellipsoid-like crystals with particle size around 30 nm are obtained, which is contrast to the micronsized crystals (~1.0 μm) of NH_2-MIL-53(Al)$_{ref(as)}$ (Fig. S3c). The nanosized crystals are highly beneficial to the membrane processing in fuel cells as well as to enhance the proton transport at interfaces between crystals.

The thermal stability of NH_2-MIL-53(Al)$_{it}$ was examined by simultaneous thermal gravimetric (TGA) and differential thermal analyses (DTA), a typical technique for studying the thermal behaviors of solid materials. Fig. 2 presents TGA/DTA

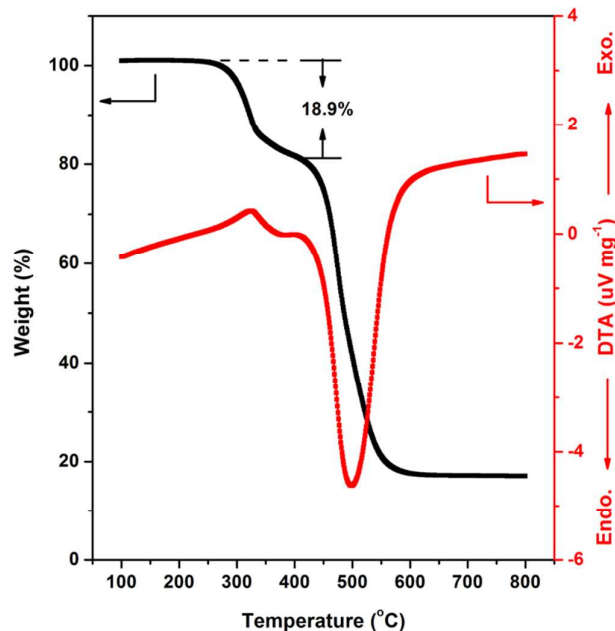curves of NH_2-MIL-53(Al)$_{it}$ collected at air condition. The TG curve displays a two-step weight loss in the temperature range of 100-800 °C. An initial weight loss of 18.9% starts from 250 °C and continues up to 415 °C, which corresponds to the combustion of encapsulated ionic liquid of 1-ethyl-3-methyl-imidazolium bromide ($C_6H_{11}BrN_2$). The presence of ionic liquid molecules in NH_2-MIL-53(Al)$_{it}$ is confirmed by a distinct endothermal band at 380 °C. This finding is very different from that of NH_2-MIL-53(Al)$_{ref}$ with a small weight loss of ~2% around 120 °C, ascribed to water release (Fig. S4). Based on the weight loss (18.9%) and the pore volume of NH_2-MIL-53 (0.167 cm^3 g^{-1}, assuming cylinder pores with diameter of 7.5 Å in Fig. S1, the detailed calculation is described in the supporting information), the pore filling factor is calculated to be 0.87, namely that nearly 90% of voids are occupied by the ionic liquid molecules. The high occupancy guarantees the very close stacking of 1-ethyl-3-methyl-imidazolium molecules in the one-dimensional pore of NH_2-MIL-53(Al)$_{it}$, offering an efficient proton transport pathway. A second weight loss of 63.8% is measured above 415 °C, which is attributed to the decomposition of organic ligands in the NH_2-MIL-53(Al)$_{it}$ framework. These results reveal that as-prepared NH_2-MIL-53(Al)$_{it}$ sample is thermally stable up to 400 °C, which can meet the basic requirement for practical application in fuel cells at high temperatures. Further, NH_2-MIL-53(Al)$_{it}$ was characterized by infrared (IR) measurement and elemental analysis. Fig. S5 shows the IR spectra of NH_2-MIL-53(Al)$_{it}$, NH_2-MIL-53(Al)$_{ref}$ and 1-ethyl-3-methyl-imidazolium bromide. An IR band associated with C–N stretching vibration in the imidazole ring appears at 1312 cm^{-1} in NH_2-MIL-53(Al)$_{it}$. Elemental analysis data in Table S1 shows that the nitrogen content in NH_2-MIL-53(Al)$_{it}$ (6.7%, 0.17 for N/C) is larger than in NH_2-MIL-

53(Al)$_{ref}$ (5.4%, 0.14 for N/C). Both results confirm the presence of 1-ethyl-3-methyl-imidazolium entity in NH$_2$-MIL-53(Al)$_{it}$ crystals. Besides, a decrease in aluminum content (~19%) validates the amount of ionic liquid within NH$_2$-MIL-53(Al)$_{it}$, which is consistent with TG result (18.9%).

The co-existence of amino groups and ionic-liquid chains makes NH$_2$-MIL-53(Al)$_{it}$ appropriate to be used as proton-conducting materials in fuel cell technology. Thus, the proton conductivity of the solid sample was investigated by AC impedance spectroscopy at high temperature and low humidity from the perspective of practical application. Fig. 3a shows Nyquist plot of NH$_2$-MIL-53(Al)$_{it}$ at 80 °C and ~26% RH (relative humidity). It is found that NH$_2$-MIL-53(Al)$_{it}$ displays a proton conductivity of 3.0×10^{-5} S cm^{-1}, while a reference sample of MIL-53(Al)$_{it}$ prepared at the same condition[33] shows a conductivity of 1.3×10^{-7} S cm^{-1}. The two-magnitude higher conductivity is owing to the abundance of amino groups as proton carriers. The individual role of ionic liquid was also studied on NH$_2$-MIL-53(Al)$_{ref}$, and the measured conductivity is 2.5×10^{-7} S cm^{-1}. The huge enhancement in the conductivity for NH$_2$-MIL-53(Al)$_{it}$ in comparison to that for NH$_2$-MIL-53(Al)$_{ref}$ can be explained with closely packed 1-ethyl-3-methyl-imidazolium molecules as proton-conducting pathways in NH$_2$-MIL-53(Al)$_{it}$. The above results suggest that amino groups and ionic liquid molecules interplay in a synergic manner, consequently function as carriers and pathways in proton transfers.

To be mentioned, the large value of NH$_2$-MIL-53(Al)$_{it}$ in conductivity makes it a superior candidate as proton conductors among MOF materials applied in anhydrous fuel cells (Table S2). The temperature dependence of proton conductivities of NH$_2$-MIL-53(Al)$_{it}$ are shown in Fig. 3b, which were measured at a narrow temperature range of 26-42 °C and under a relative humidity of 33%. The conductivity of NH$_2$-MIL-53(Al)$_{it}$ increases smoothly as the temperature is slowly elevated. The activation energy (E$_a$) for the proton transfer derived from conductivities data for NH$_2$-MIL-53(Al)$_{it}$ nanocrystals is calculated to be 0.37 eV according to arrhenius plots [ln(σT) vs 1000T^{-1}] (Fig. 3b), implying that the proton conduction process follows the Grotthuss mechanism (0.1-0.4 eV).[37]
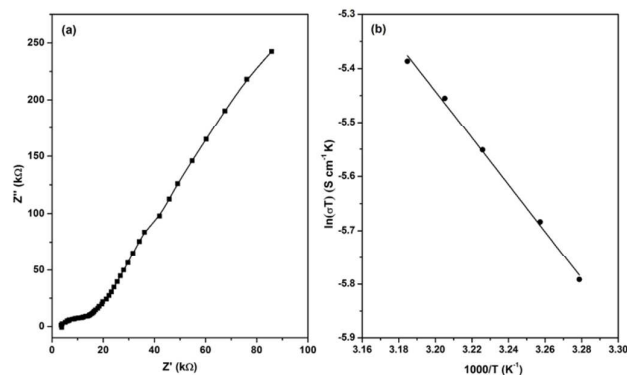
Fig. 3 (a) Nyquist plot of as-synthesized NH$_2$-MIL-53(Al)$_{it}$ sample at 80 °C and ~26% RH (relative humidity), and (b) Arrhenius-type plot of the conductivity at various temperatures and under ~33% RH.

Meanwhile, the low value of 0.37 eV suggests that ionic liquid plays a great contribution to the proton conduction because a considerable number of 1-ethyl-3-methyl-imidazolium molecules are participating in the formation of effective proton transfer networks.

Conclusions

In conclusion, we have successfully synthesized NH$_2$-MIL-53(Al) MOF nanocrystals *via* an ionothermal approach. Experimental results reveal that as-prepared NH$_2$-MIL-53(Al)$_{it}$ bears two features of free amino groups as intrinsic proton carriers and assembled 1-ethyl-3-methyl-imidazolium ionic liquid networks served as proton-conducting pathways. In addition to its structurally thermal stability (>400 °C), NH$_2$-MIL-53(Al)$_{it}$ possesses amazingly high proton conductivity of 3.0×10^{-5} S cm^{-1} at high temperature of 80 °C and low humidity of ~26% RH, showing that this MOF can be considered as a potential candidate for proton-conductive materials at anhydrous conditions. It has been also found that the proton conduction in NH$_2$-MIL-53(Al)$_{it}$ follows the Grotthuss mechanism. This study presents a new and universal strategy in constructing highly stable MOF materials with high proton conductivity.

Acknowledgements

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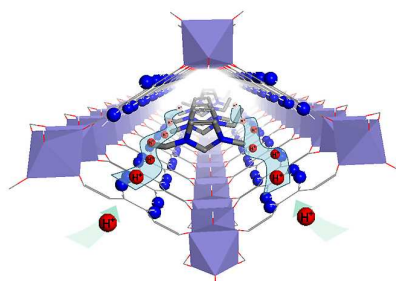
Highly stable and proton-conductive NH_2-MIL-53 metal organic framework nanomaterials have been successfully synthesized in an ionothermal system.