

論文の内容の要旨

論文題目 Infrared spectroscopy of water during adsorption and
desorption processes in metal-organic frameworks
(金属有機構造体の吸着及び脱着過程における水の赤
外分光分析)

氏 名 高 嬌

Cooling is one of the most energy-consuming aspects of our modern life. According to the International Energy Agency, the use of air conditioners (AC) and electric fans to stay cool currently account for more than 10% of the total electricity used in housing around the world. In 2050, the energy demand for space cooling is expected to increase to around 37%, which is almost three times than today. The increased use of the conventional AC units will be harmful to the environment, as the flammable and toxic hydrogenated chlorofluorocarbons are always used as refrigerants. Moreover, more electricity will be consumed with the increased AC units, resulting in more CO₂ emissions to the atmosphere.

Recently, due to the potential of high refrigeration efficiency and energy efficient property, the sorption-desorption cycle of water on porous materials is being considered as the cutting-edge replacement for the conventional compression-evaporation cycle used in the air-conditioning systems. In the sorption-desorption cycle, evaporation of the water is induced by the adsorption of porous adsorbent material, and this endothermic process is used to achieve the desired refrigeration effect. Noticeably, for the sorption-based AC units, the property of porous adsorbent and the interaction with adsorbed water molecules are the crucial factors to the whole system performance and energy consumption, thus becoming the focus of studies and have been widely discussed.

Zeolites and silica gel are two commercial porous materials commonly used in the sorption-based AC units. However, these two adsorbents are not so ideal for this application. For zeolites, a strong interaction between the structures and water molecules is always formed, and therefore a high driving

temperature ($> 150^{\circ}\text{C}$) is needed when water is desorbed from the material. With this high driving temperature, the desired low-grade energy sources cannot be used. For silica gel, it processes an unwanted linear shape water isotherm, limiting the exchangeable amount of water in the cycle and the refrigeration efficiency of the whole system. To address the problems of these two adsorbents, activation treatment, acid treatment, and some other methods are always used, which are time and energy-consuming. New energy-saving porous materials must be developed.

Lately, metal-organic frameworks (MOFs) are proposed and have become widely studied as candidates for separation processes, catalytic processes, and gas storage due to their peculiar coordination structures, controllable organic ligands, tailor-made porous morphologies, and large Langmuir surface areas. For metal-organic frameworks, metal means the metal sites, and organic means the organic ligands. The combination of different metal sites and organic ligands forms these MOFs materials with various cages structures and cages properties. As the potential materials used in the sorption-based AC units, the water uptake capacities of different MOFs have been researched, and among all these materials, a MOF called MIL-101(Cr) is the most attractive. This chromium terephthalate-based solid is unique in terms of hierarchical cages with large diameters of 29 Å and 34 Å (window aperture of 12 Å and 16 Å), and corresponding huge pore volume of 12,700 Å³ and 20,600 Å³. Moreover, MIL-101(Cr) possesses high hydrothermal stability that can retain structural integrity up to 240°C, which is higher than other similar porous materials, implying that this material is more suitable for hydrothermal applications. Based on these physical properties, MIL-101(Cr) is the most potential material to become an ideal porous adsorbent used in the sorption-based AC units.

The sorption-desorption property of water adsorbed in the MIL-101(Cr) has been discussed. However, among these current studies, researchers mainly focus on how to enhance the water adsorption property of the MIL-101(Cr) and how to reduce the energy requirement in the desorption process by adding various functional groups, optimizing the pore structures, and adjusting the component elements. Although directly improving the performance is essential, the research of the water sorption-desorption mechanism of the MIL-101(Cr), especially the dynamic phase transitions of water molecules confined in the cages, is also an indispensable part that needs to be comprehensively analyzed not only for its real industrial applications but also for the further development of superior materials used in the sorption-based AC units.

In this thesis, MIL-101(Cr) and two functional MIL-101(Cr) are prepared using a scaled-up version of the reported hydrothermal reaction. The synthesized MIL-101(Cr) is a solid material that has a regular octahedral structure with smooth surfaces. The XRD patterns of it are in good agreement with the previous reports and simulation, indicating that the MIL-101(Cr) has been successfully synthesized. Two characteristic peaks in the Raman spectrum are observed revealing a relatively weak intensity ratio, thus confirming that the structure of the MIL-101(Cr) crystallite has no significant disorder. For N₂ adsorption isotherm, as expected, MIL-101(Cr) processes two size cages with the diameter of 2.6 and 3.2 nm in the

structures, and it exhibits a large pore volume equals to $2.9 \text{ cm}^3/\text{g}$ with a specific surface area equals to $3601 \text{ m}^2/\text{g}$. In the type-V water isotherm, a significant water adsorption/desorption occurs in a stepwise manner within a narrow pressure variation range in both the adsorption and desorption processes. The total water uptake is 1.3 g/g , which is 2.5 to 5 times higher than that of the zeolites and silica gel. The narrow step-wise sorption manner and superior water uptake indicate that the demand for energy-saving and efficiency improvement could be satisfied using the MIL-101(Cr) as the sorption-desorption material.

Instead of conventional infrared transmission and adsorption spectroscopy, diffused reflectance infrared spectroscopy (DRIFTS), which can carry more information of the powdered analytes and determine their polymorphic forms, is selected to be used. Noticeably, a water sorption-desorption machine is prepared and connected to this DRIFTS spectrometer so that the desired water amount applied to the samples can be precisely controlled. With this great measurement system, the phases and transitions of water molecules in the MIL-101(Cr) and two functional MIL-101(Cr) as a function of water amount at different temperatures are elucidated in detail. To further understand the relationship between the water molecules and the MIL-101(Cr) as well as functional MIL-101(Cr), molecular dynamics (MD) simulations under the same conditions as experiments are performed, and particular emphasis is given on localizing the position of the water molecules and identifying the main vibrations that contribute to the dominant peaks obtained in the spectra. The combination of the experimental DRIFTS spectroscopy with the theoretical MD simulation enables a better understanding of water molecule dynamics in the MIL-101(Cr) and functional MIL-101(Cr) cages.

Water molecules confined in the MIL-101(Cr) and two functional MIL-101(Cr) exhibit unique phases and dynamic behaviors at various sorption-desorption stages. For the original MIL-101(Cr), in the adsorption process, the water molecules first coordinate with metal sites and form 1-D water chains from the unsaturated Cr^{3+} . As the water amount increases, the 1-D water chains grow in length and connect together, gradually forming a water monolayer on the inner surfaces of the cages. This monolayer changes the property of the surface from hydrophobic to hydrophilic, which induces the beginning of water condensation in the medium and large cages. The entire pores are filled with condensed water in the end. In the desorption process, a reverse process is observed with hysteresis. The condensed water is first desorbed from the structures, followed by the water monolayer, and finally the 1-D water chains as well as single water molecule bonded to the Cr^{3+} site are desorbed from the MIL-101(Cr).

Compared to the MIL-101(Cr), when the MIL-101(Cr)- SO_3H adsorbs water, water molecules first coordinate with metal sites and form small water clusters from the Cr-bonded water molecules. As relative humidity increases, water molecules bond to the $-\text{SO}_3\text{H}$ functional groups to form more water clusters in the structures. There is no condensed water formed in the end. When the MIL-101(Cr)- SO_3H desorbs water, water clusters bonded to Cr^{3+} sites and $-\text{SO}_3\text{H}$ groups are gradually desorbed from the structures, followed by the desorption of single water molecule coordinated with the Cr^{3+} site. Different from the MIL-101(Cr)- SO_3H , when the MIL-101(Cr)- NO_2 adsorbs water, water molecules first

coordinate with metal sites and form water chains from the Cr-bonded water molecules. As relative humidity increases, the water chains grow in length and connect together, gradually forming highly bonded water in the structures, and the entire cages are filled with this type of water in the end. When the MIL-101(Cr)-NO₂ desorbs water, highly bonded water that originated from the -NO₂ groups and Cr³⁺ sites are first desorbed from the structure, followed by the desorption of water chains from the Cr-bonded water molecules, and finally all water molecules are desorbed from the MIL-101(Cr)-NO₂. The strong water peaks obtained in the DRIFTS spectra and the reverse process observed with hysteresis confirm the possible applications of these three materials in the future developed sorption-based AC units.

To further understand the confinement effect of cages in the MIL-101(Cr) and two functional MIL-101(Cr) on the adsorbed water molecules, water freezing behaviors are analyzed at high and low pressure conditions. For the original MIL-101(Cr), as temperature decreases, two new types of water form in the cages structures: the rigid ice-like water and ice-I_c. When the temperature decreases -60°C, ice-I_c mainly appears at the free layer for large cages under high pressure condition, and it forms at the interlayer both for large and medium cages under low pressure condition. When the temperature decreases -140°C, rigid ice-like water forms at the free layer for large cages, and it only appears at high pressure condition. For the MIL-101(Cr)-SO₃H, at high pressure condition, no formation of rigid ice-like water can be decided, but ice-I_c may form in the cages structures due to the strong polar force from the acidic -SO₃H groups. At low pressure condition, rigid ice-like water and ice-I_c form at the interlayer for the medium and large cages because of the weakest host-guest interaction and no curvature effect. In addition, ice with another specific structure may form within the cages. For the MIL-101(Cr)-NO₂, both at high and low pressure conditions, the formation of rigid ice-like water cannot be confirmed as the represented peak also appears when this material adsorbs water at 25°C. In addition, ice with another specific structure may form within the cages. All these systematic analyses of water and porous absorbents suggest the further development of superior materials of high-efficiency sorption-based AC units.