

審査の結果の要旨

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Infrared spectroscopy of water during adsorption and desorption processes in metal-organic frameworks

Ph.D. thesis defended by Gao Jiao

The sorption-desorption cycle of water vapor on porous materials is being considered as a replacement for the conventional liquid-vapor compression cycle used in cooling and air-conditioning systems. Although the thermal performance of sorption-based heat exchangers can be estimated using the amount of water loaded in the porous material as determined from water vapor sorption isotherms, the interaction of water with the material pores is still not fully elucidated and hampers further improvements of porous materials under development. Mesoporous metal-organic frameworks (MOFs) are among the promising materials considered for use in heat exchangers based on sorption cycles. Particularly, the phases of the water incorporated in the matrix of the mesoporous material are not well understood and the freezing process of water in mesoporous materials not investigated.

Gao proposes to perform infrared vibrational mode analysis of the porous material together with incorporated water during the sorption/desorption cycles. For this purpose, a gas cell containing the mesoporous material is mounted in a diffuse reflectance Fourier transform infrared spectrometer and connected to a water vapor sorption analyzer. The mesoporous materials are analyzed during the sorption-desorption cycles, and interaction of water with the MOF cage surface as well as water condensation processes in the porous material under different conditions of pressure and temperature are investigated using the water infrared vibrational spectra. The assignment of the observed vibrational mode energies is confirmed by molecular dynamic simulations. Furthermore, the water freezing process in mesoporous materials is also investigated by infrared spectroscopy.

In Chapter One, a review of the current research on heat exchange systems based on sorption-desorption cycles in porous materials is presented. The general properties of porous materials such as silica gels, zeolites, and MOFs are introduced, and the review concludes on the high potential of the MOF MIL-101(Cr) when used in sorption-desorption heat exchange systems due to the high water intake within a narrow range of water pressure.

In Chapter Two, the synthesis of the MOF MIL-101(Cr) material, detailed microstructures, as well as the conventional characterization of this mesoporous material, are presented. Particularly, the sorption techniques used to determine the pore distribution and the amount of water exchanged during isotherm adsorption cycles are described and used to characterize the MOF materials investigated in this study, namely, MIL-101(Cr) and the two related functional MOFs, MIL-101(Cr)-SO₃H and MIL-101(Cr)-NO₂.

In Chapter Three, the proposed diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique used to monitor water interaction with the mesoporous materials is presented together with a discussion of the major advantages of the technique (material can be analyzed in the form of powder, high sensitivity to adsorbed water molecules, and wide energy range of

molecular vibrational modes). For the present study, it is expected to reveal bondings of the MOF metal with water molecules as well as liquid water bonds of different natures (four typical bounds used to characterize liquid water using infrared spectroscopy). A complete description of the setup is given as well as the detailed procedure to operate the system with particular emphasis on sample pre-processing to avoid contamination effects. Finally, the molecular dynamic simulation used to identify the type of molecular bounds observed by DRIFTS is presented.

In Chapter Four, the water sorption and desorption processes in the MOF MIL-101(Cr) are reported. Water molecules first coordinate to the unsaturated Cr^{3+} metal sites and then form one-dimensional water chains. As the water partial pressure increases, the one-dimensional water chains grow in length and connect gradually forming a water monolayer on the inner surfaces of the cages. This monolayer changes the property of the cage surface from hydrophobic to hydrophilic, which triggers the start of water condensation in the MIL-101(Cr) 29 and 34 Å cages. The cages are filled with condensed water as the pressure gradually reaches saturation pressure. In the desorption process, the condensed water molecules desorb first from the MIL-101(Cr). As the highly confined water molecules in the monolayer desorb, the one-dimensional water chains gradually become the main existing type of water molecules inside the pore structure. As the pressure further decreases, the desorption process comes to an end when the single water molecules bonded to Cr^{3+} sites desorb. The functional MOFs reveal different behaviors due to the change in their pore surface properties. Particularly, the hydrophobic functional group $-\text{SO}_3\text{H}$ is found to suppress the formation of liquid-like water so that water condensation is severely hampered in this type of functional MOF.

In Chapter Five, the formations of glassy states of water in the investigated MOFs at low temperatures are reported for the first time. For the MIL-101(Cr), it is found that the glassy state proceeds through the formation of some new bounds around -60°C at low partial pressure and reaches a glassy state at high partial pressures for a temperature of -120°C . The type of ice has been tentatively indexed to that of the Ic type.

The conclusions of the manuscript are given in Chapter Six.

In summary, Gao develops a system consisting of a diffuse reflectance infrared Fourier transform spectroscopy connected to a gas adsorption analyzer to monitor the water sorption/desorption processes in porous materials in a view to support the development of materials for use in sorption/desorption heat exchangers. This system makes it possible to observe the evolution in time of the sorption/desorption processes in mesoporous materials in terms of water phases including the icing process. The collected information is of critical importance for the future development of materials for use in sorption/desorption systems. One of the most promising mesoporous materials, metal-organic framework MIL-101(Cr) together with the $-\text{SO}_3\text{H}$ and $-\text{NO}_2$ functional MIL-101(Cr)s are investigated. The water coordination with the unsaturated Cr^{3+} sites of the MIL-101(Cr) as well as the formation of water chains and water condensation in the MIL-101(Cr) cages are revealed by the absorption variations of water-related vibrational infrared absorption modes, and the mode energies are confirmed by molecular dynamic simulations. Also, the icing process of the MIL-101(Cr) is observed for the first time so that the technologically important icing temperatures are identified and can be used in the design of heat exchanger systems.

よって本論文は博士（工学）の学位請求論文として合格と認められる。