STUDY ON THE MODIFICATION OF METAL-ORGANIC FRAMEWORKS FOR ENHANCED WATER ADSORPTION

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論 文 名　：STUDY ON THE MODIFICATION OF METAL-ORGANIC FRAMEWORKS FOR ENHANCED WATER ADSORPTION (水分吸着性能の向上に資する有機金属構造体の改質に関する研究)

区　　分　：

論 文 内 容 の 要 旨

Utilizing water as the refrigerant for the cooling system is challenging but important for creating pollution-free environmental-friendly systems. An adsorption cooling system (ACS) is a green system that offers benefits over conventional compression cooling systems by utilizing water as a refrigerant and low-grade heat as energy sources. ACS utilizes refrigerant's evaporation enthalpy to induce a cooling effect directly proportional to the net refrigerant uptake onto the adsorbent. Therefore, the adsorbent material used in the adsorption bed has a crucial role in the overall performance of an adsorption cooling system. Porous materials with well-defined porosity, high surface area, high thermal stability, good thermophysical properties, low manufacturing cost, and higher affinity towards adsorbate are employed as adsorbents. Metal-organic frameworks (MOFs), a class of porous, organometallic compounds, are promising as adsorbents for ACS, mainly when water is used as a refrigerant. The tunability of MOFs makes them capable of being modified to achieve the targeted property and improve the system's overall performance. This thesis mainly emphasizes the synthesis and modification of metal-organic frameworks by the alternation of the secondary building unit and experimental investigation of the effect of modification on the structure, stability, thermophysical properties, and water adsorption properties. Finally, an energy-efficient synthesis procedure has been described for synthesizing the promising MOF-801. This thesis consists of seven self-explanatory chapters.

Chapter 1 describes a general introduction that provides the fundamental ideas regarding the components and working principles of ACS. Besides, it includes the motivation behind this work and the aims, objectives, and organization of the thesis.

In **Chapter 2**, a detailed review of the literature relevant to the current study has been discussed. The historical background and structural features of MOFs, the types of modifications that can be attained in metal-organic frameworks, and the effect of the modification on the application of the MOFs have been studied in detail.

In **Chapter 3**, a series of bivalent (M^{2+}), trivalent (M^{3+}), and tetravalent (M^{4+}) metal ion substituted mixed-metal HKUST-1 samples were synthesized, and the effect of metal doping on the structure and water adsorption capacities were investigated. Structural characterizations indicated that the bivalent metal incorporated in MM (mixed metal)-HKUST-1 samples were isostructural with the parent HKUST-1, and the presence of metals other than Cu in the structure affects their water affinity. It was found that the moisture

stability of the Co-HKUST-1, the MM-HKUST-1 possessing the highest water uptake capacity, was partially enhanced as well as the specific cooling effect of the Co-HKUST-1 and Mg-HKUST-1 was improved within the stability map of HKUST-1.

Chapter 4 includes the study of the effect of mixed-valence metal doping on the thermophysical properties of a trivalent metal ion Al^{3+} containing MOF, aluminium fumarate through the synthesis of transitional metal-doped aluminium fumarate MOFs. The partial substitution of Al^{3+} with transitional metals resulted in a decrement in the specific heat capacity and enhancement in thermal conductivity, rendering the materials beneficial as adsorbents for ACS. The thermodynamic properties of MOF/water pairs were also rigorously analyzed from the water adsorption isotherms. The isosteric heat of adsorption and the adsorbed phase specific heat capacity were analyzed theoretically as a function of adsorbate uptake. The specific cooling effect and coefficient of performance were calculated for varying evaporative conditions for a range of desorption temperatures.

To provide cooling below 10°C, a Zr-based highly hydrostable MOF, MOF-801, with a short hydrophobic length, was studied extensively in **Chapter 5** from the viewpoint of structure and water adsorption properties. The water sorption capacity of MOF-801 was enhanced by the partial incorporation of Ni or Co into the framework. The structure of the synthesized materials was investigated through various experimental techniques (porosity analysis, PXRD, SEM, TEM, XPS, and TGA), and the bimetallic MOFs were found to be isostructural with the parent single metallic MOF. The synthesized bimetallic MOFs exhibited an increased affinity to water vapor within the working pressure region of ACS and improved thermophysical properties. The mixed valency of the SBU, as well as the electronegativity of the nickel or cobalt might have increased the affinity of the bimetallic MOFs towards water vapor. Higher electronegativity of Ni as well as of Co caused an increase in polarity in metal-OH bonds, which resulted in a large number of water cluster formations in the metal cluster, consequently an increase in the step of S-shaped adsorption isotherm. The Co-MOF-801 provided 43% higher specific cooling effect than the pristine MOF-801.

In **Chapter 6**, a novel energy-efficient, environment-friendly, rapid, and ultrasonication-assisted room temperature-green synthesis procedure for the synthesis of MOF-801, omitting the use of organic solvent DMF (N, N-dimethylformamide), a hazardous organic solvent commonly used in the conventional synthesis of this MOF. Moreover, optimum synthetic condition for hydrothermal synthesis of this MOF was suggested. The structural properties and their applicability as adsorbents were studied by experimental investigations and thermodynamic analysis, respectively. The MOF-801 synthesized from the proposed optimized conditions exhibited the highest water uptake capacity among the reported MOF-801 hitherto.

Finally, **Chapter 7** provides a brief review of the work done during the study and concludes with the primary findings, including the author's uniqueness and contribution and suggestions for future improvement.

To summarize, several novel MOFs have been synthesized, exhibiting outstanding water sorption performances. These MOFs could be employed to design and construct highly efficient adsorption cooling systems.