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# Studies on gas adsorption in porous polymers via solid-state NMR( Digest\_要約 )

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# 学位論文の要約

題目     Studies on gas adsorption in porous polymers via solid-state NMR  
          (固体 NMR による多孔質高分子中のガス吸着に関する研究)

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## 序論

Over the past two decades, porous polymers represented by metal organic frameworks (MOFs) and covalent-organic frameworks (COFs) have attracted great research interest owing to their outstanding properties. They are porous crystalline polymers constructed by organic linkers and interconnected by metal clusters (MOFs) or covalent bonds (COFs). The superior surface area and the designability of the pores in nano-meter scale endow these two materials with unprecedented performance for adsorption and separation.

Solid-state NMR (SSNMR) spectroscopy is an excellent characterization method with both nuclide and site specificity. It can extract information about the local environment in the atomic range without the influence of long-range disorder. Therefore, SSNMR is an ideal method to study the gas adsorption process of porous materials to obtain insight into the host-guest interaction and molecular dynamics.

In this thesis, SSNMR spectroscopy was exploited to investigate the gas adsorption in MOFs and COFs from three aspects utilizing homemade NMR probes, gas loading setups, and hermetic rotors.

## **1. Sodium-Ion-Induced Discriminative C<sub>2</sub>H<sub>2</sub>/CO<sub>2</sub> Adsorption in a Covalent Organic Framework Studied by Solid-State <sup>23</sup>Na NMR**

The discriminative adsorption of acetylene (C<sub>2</sub>H<sub>2</sub>) over carbon dioxide (CO<sub>2</sub>) in Py-Na COF was analyzed using <sup>23</sup>Na MQMAS coupled with density functional theory calculations and molecular dynamics simulations. The Na<sup>+</sup> ion sites of Py-Na COF are confirmed to be interaction sites for both C<sub>2</sub>H<sub>2</sub> and CO<sub>2</sub> molecules. The stronger host-guest interaction developed between the C<sub>2</sub>H<sub>2</sub> and Py-Na COF than that of CO<sub>2</sub> is the origin of the discriminative adsorption.

## **2. Crystal-size effect on the kinetics of CO<sub>2</sub> adsorption in metal organic frameworks studied by NMR**

The crystal-size dependent adsorption kinetics of CO<sub>2</sub> in NDMOF was studied by <sup>13</sup>C spectra of CO<sub>2</sub> adsorbed in MOF crystals of sizes from μm to mm. The crystal-size dependence of the <sup>13</sup>C NMR lineshape of the guest CO<sub>2</sub> molecules reflects the core-surface nature of the crystallites in gas adsorption. The CO<sub>2</sub> exchange process between the motion-restricted core sites and hindrance-free surface sites inside the crystal was revealed and quantified using an isolated two-site exchange model. The populations of each site, the thickness of the surface layer, and the apparent exchange rate could be estimated using this model. The surface-to-volume ratio is the origin of the trend that the smaller the host crystal is, the faster the exchange is.

## **3. Probing dynamics of carbon dioxide in a metal organic framework under high pressure by high-resolution solid-state NMR**

The behavior of CO<sub>2</sub> molecules in Zn-MOF-74 at high pressure was investigated using high-resolution in-situ MAS <sup>13</sup>C spectroscopy. It is found that the guest-guest interaction between CO<sub>2</sub> molecules at high pressure resulted in abnormally low mobility of CO<sub>2</sub> molecules and thereby facilitated the stable adsorption of CO<sub>2</sub> in the pore of MOF at high pressure.

This thesis demonstrates that SSNMR is a powerful and versatile technique for studying gas adsorption in porous polymers that can probe the host-guest interaction, dynamics/kinetics, and guest-guest interaction. More and more molecular-scale insights are looking forward to being unraveled by SSNMR in the future.