



Metal-Organic Frameworks and Their Composites for Water-Alcohol Separation Applications
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Summary

Metal-organic frameworks form a special class of materials which is highly suitable for molecular separation processes. One of the key properties of MOFs relevant to separation is their defined pores that can be tailored specifically to enable size and shape selectivity toward guest molecules. Other types of porous materials usually have a limited range of pores size or do not possess uniform pore size distribution. For example, the pore size of zeolites is limited by the small size of inorganic crosslinking anions which make them suitable only for a limited number of separation applications. In contrast, there is almost no such limitation for MOFs due to their modular synthesis and the wide variety of inorganic and organic building-blocks. MOFs have been widely used in various separation applications, but their potential in water-alcohol adsorptive separation is less studied. This is mainly due to the reduced stability of many MOFs in the presence of water as well as the similarity in the chemical properties of water and alcohol molecules. Therefore, the main goal of this thesis was to develop synthetic strategies for the design of water stable MOFs which can be used in water-alcohol adsorptive separations.

Chapter 1 gives an overview of the synthetic strategies used for designing MOFs and MOFs-based composites studied for their application in water-alcohol adsorptive separations. It shows that various organic linkers, including flexible ligands, hydrophobic ligands and zwitterionic ligands have been used for the synthesis of MOFs with flexible frameworks, highly hydrophobic MOFs as well as MOFs with unique electronic distribution in the pores. Due to their specific properties, all these materials show different adsorption behaviors in the presence of water and alcohols, being able to separate water-alcohol mixtures. Several studies aimed at using microporous MOFs to separate water-alcohol mixtures on the basis of the difference in the molecular size of water and alcohols. Furthermore, combining MOFs with organic polymers into composites is viewed as a viable alternative to tackle some problems powder MOFs may cause in industrial applications. Indeed, the research so far shows that MOFs embedded in polymer matrixes have led to improved efficiency and mixture permeability when comparing with the performance of pristine polymer membranes. Nevertheless, the swelling of the polymer matrix as well as the difficulties in retaining the matrix integrity while increasing the MOF loading make it challenging to design membranes with high permeability, selectivity and stability.

In Chapter 2, a new series of alkaline-earth-metal based MOFs were synthesized by using the 2,5-H₂pzdc ligand under hydrothermal conditions. These compounds show a variety of structural topologies, reflecting the variable coordination geometries

of the alkaline-earth ions as well as the key role of the metal precursor salts. Ca^{2+} , Sr^{2+} , and Ba^{2+} give porous three-dimensional compounds, namely $[\text{Ca}(2,5\text{-pzdc})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$, $[\text{Sr}(2,5\text{-pzdc})(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$, $[\text{Ba}(2,5\text{-pzdc})(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$ and $[\text{Ba}(2,5\text{pzdc})(\text{H}_2\text{O})_2]$, that feature one-dimensional hydrophilic channels which are filled with water molecules. Sr^{2+} compound retains its structure when the lattice water molecules are removed while the other compounds undergo a structural rearrangement. The hydrophilicity of the Sr^{2+} compound combined with its high stability even in the absence of guest molecules are the key characteristics that determine its good water adsorption and proton conductivity properties.

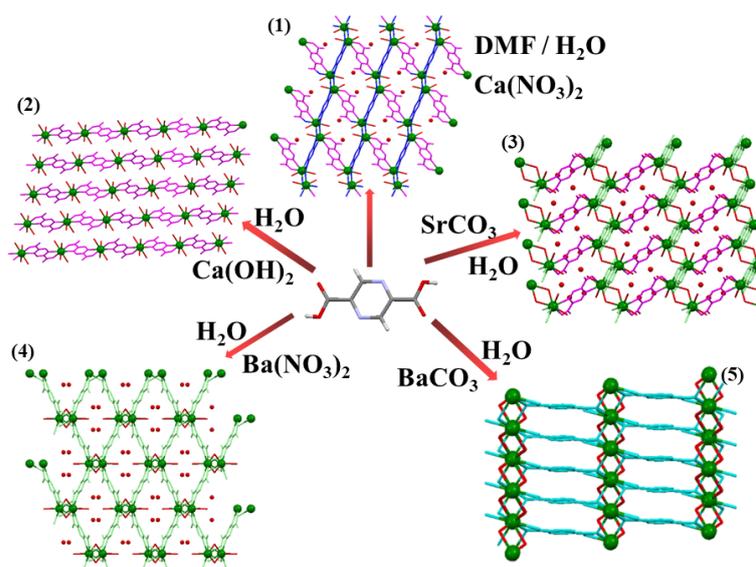


Figure 1 Synthetic routes used for crystallizing a series of MOFs by using alkaline-earth metal ions and 2,5- H_2pzdc .

Another series of alkaline-earth metal-based MOFs were built from the flexible H_4L ligand using solvothermal methods, as reported in Chapter 3. A variety of three-dimensional frameworks were obtained when employing different alkaline earth ions with the formula $[\text{Mg}_2(\text{L})(\text{H}_2\text{O})(\text{DMA})]\cdot\text{DMA}$, $[\text{Ca}_4(\text{L})_2(\text{DMA})_3]$, $[\text{Ca}_4(\text{L})_2(\text{H}_2\text{O})_2(\text{DMA})_2]\cdot(3\text{DMA})$ and $[\text{Sr}_4(\text{L})_2(\text{DMF})_4]\cdot(2\text{DMF})$ reflecting again the variation in the ionic radius of alkaline-earth ions as well as the key role of the synthetic conditions used. By removing the guest molecules, a framework shrinking was observed driven by the structural flexibility of the H_4L ligand. This resulted in large diffusional resistances towards N_2 over CO_2 molecules, therefore leading to a good CO_2/N_2 separation selectivity. Both Ca^{2+} -based MOFs were very stable up to 98% relative humidity, while Mg^{2+} - and Sr^{2+} -based MOFs were much less stable.

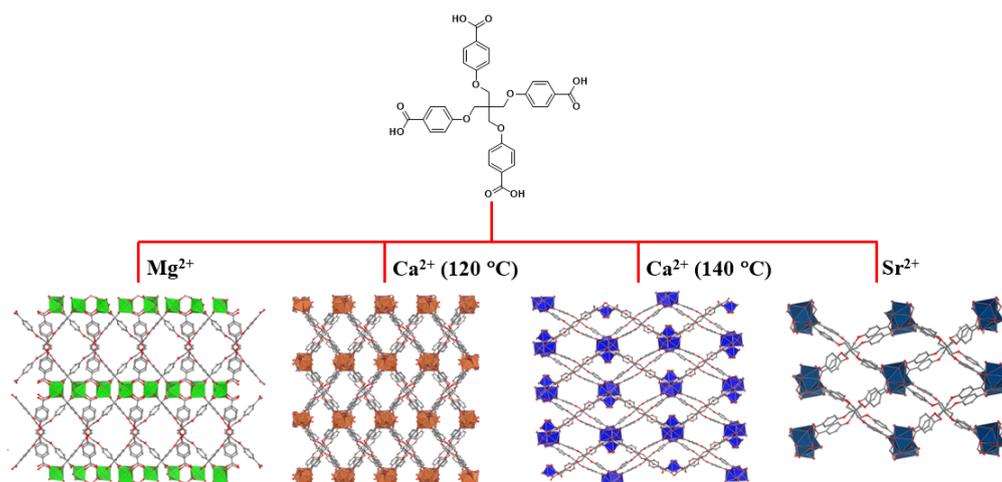


Figure 2 Alkaline-earth metal-based MOFs with different 3D crystal structures by using H₄L as organic linker.

Chapter 4 reports a new approach for the synthesis of a zeolitic imidazolate framework (ZIF-8) composite. It employs the direct growth of the crystalline ZIF-8 on a mixed-metal oxide support TiO₂-SiO₂ (TSO) which mimics the porous structure of *populous nigra*. Using the natural leaf as a template, the TSO support was prepared using a sol-gel method. The growth of the ZIF-8 layer on the TSO support was carried out by *seeds and second growth* method. This method facilitates the homogeneous dispersion of ZIF-8 crystals at the surface of the TSO composite. The ZIF-8@TSO composite adsorbs methanol selectively, mainly due to the hierarchical porous structure of the mixed oxide support. As compared with the as-synthesized ZIF-8, a 50% methanol uptake is achieved in ZIF-8@TSO composite, with only 25 wt.% ZIF-8 loading. IAST simulations show that the ZIF-8@TSO composite has a preferential adsorption towards methanol when using an equal molar methanol-ethanol mixture. An opposite behavior is observed for the as-synthesized ZIF-8. The results show that combining MOFs and mixed-oxide supports with bio-inspired structures open opportunities for synthesizing new materials with unique and enhanced adsorption and separation properties.

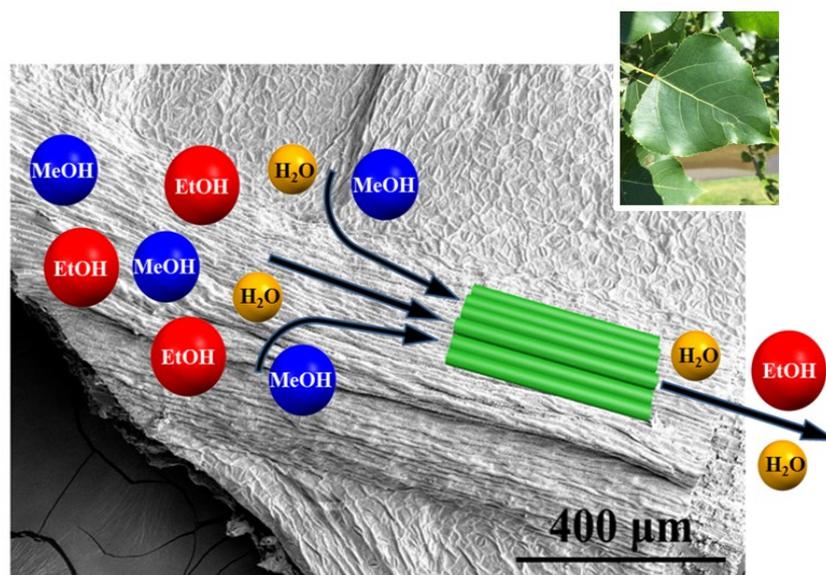


Figure 3 The ZIF-8@TSO composite adsorbs selectively methanol and ethanol from methanol-ethanol and water-ethanol mixtures.

Chapter 5 presents a straightforward approach for the *in situ* polymerization of PNIPAM chains in the 1D pores of the five-coordinated zinc-based metal-organic framework DMOF in order to obtain new MOF-based composites. The loading amount of PNIPAM within DMOF \supset PNIPAM composites can be tuned by changing the initial weight ratio between PNIPAM, which is the monomer of PNIPAM, and DMOF. The guest PNIPAM chains in the composites block partially the 1D pores of DMOF, thus leading to a narrowed nano-space. The water adsorption studies reveal that the water uptakes increased by increasing the loading of PNIPAM in the final DMOF \supset PNIPAM composites, indicating that the exposed amide groups of PNIPAM gradually alter the hydrophobicity of pristine DMOF and lead to hydrophilic DMOF \supset PNIPAM composites. DMOF \supset PNIPAM-3, which has the highest loading of PNIPAM among the composites studied, displays a selective adsorption for water and methanol over ethanol when using equimolar mixtures of methanol-ethanol and water-ethanol. This is confirmed by the single-component adsorption measurements as well as IAST molecular simulations. Additionally, the water stability of pristine DMOF has been greatly improved after the incorporation of PNIPAM in its pores. PNIPAM can undergo a phase transition between hydrophobic and hydrophilic phases in response to a low temperature change. This property can be used for DMOF \supset PNIPAM-3 in order to control the desorption of water and methanol molecules, therefore enabling an efficient and cost effective regeneration process.

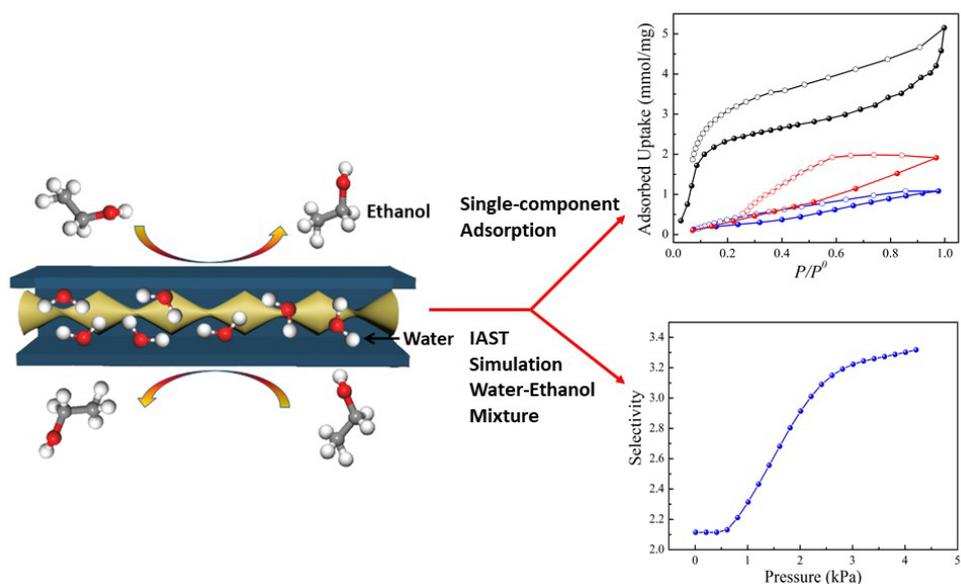


Figure 4 Combined single-component adsorption measurements and IAST simulation studies show that the DMOF-PNIPAM-3 has potential in water-alcohol adsorptive separation.

The work described in this thesis shows that combining alkaline-earth ions and specific organic linkers, *e.g.* either small and rigid ligands or flexible polycarboxylate ligands, is an appropriate approach to design MOFs with good water stability but it is still difficult to tailor their pore size for selective water or alcohol adsorption. However, introducing organic polymers as guests in MOFs with specific pores' structure enables not only to tune finely the pore size for selective molecular uptake but also increases the water stability of the host MOF. This thesis also shows that an alternative approach for optimizing MOF materials for industrial applications is by growing them at the surface of porous oxide structures. It leads to robust composite materials which have improved adsorption capacity as compared with the pristine MOF.