

ABSTRACT

Metal-organic frameworks (MOFs) are one of the most promising materials for CO₂ capture and conversion. In my research, I have focused on three systems with high CO₂ capture capabilities – HKUST-1, ZnBDC and MOF-74.

The first part of my research was focused on the studies of HKUST-1 framework functionalization with ethylenediamine (ED) and the impact of the modification process on the CO₂ capture parameters relevant for the post-combustion process. In the case of the modified materials, the isosteric heat of adsorption and CO₂/N₂ selectivity was improved by almost 85 %. Both parameters are closely related to the materials porosity and pore accessibility. The increase of ED loading caused the formation of hierarchical structure expanded over micro-, meso- and macropore range, which further improved the adsorption kinetics and diffusion of CO₂ molecules within the framework of modified materials.

In the second part of this research, I investigated the effect of cation exchange on the CO₂ capture and conversion performances of the negatively charged ZnBDC framework, which was initially compensated by di- and trimethylammonium cations located within the material pores. The cation exchange was performed using sodium, potassium, lithium and magnesium cations to improve sorption and catalytic properties of the pristine material. In comparison with the pristine ZnBDC, all modified materials exhibited higher CO₂ adsorption capacities, and the sorption properties are improved by decreasing the cation radius. The ionic exchange also had a positive effect on catalytic activity in comparison with the pristine ZnBDC, which was almost catalytically inactive, the exchanged materials exhibit significant improvement. Namely, Mg-modified material exhibited a 40% higher conversion of propylene oxide to propylene carbonate without the use of co-catalyst.

The final part of the thesis is dedicated to the shaping of MOF materials by secondary recrystallization of metal-oxide initially incorporated in a polymeric matrix (polyHIPE) into M-MOF-74 (M=Zn, Co, Mg). All metal oxide precursors were efficiently recrystallized to MOF-74. Furthermore, incorporated MOF-74 phases exhibit unobstructed accessibility for the CO₂ adsorption reaching up 98.6 % for the case of Mg-MOF-74@polyHIPE. All immobilized MOF-74 phases also showed an improvement in adsorption kinetics and temperature swing adsorption regeneration efficiency performed at 150 °C (up to 95 % for Zn-MOF-74@polyHIPE).

KEYWORDS: metal-organic frameworks, post-synthetic modification, cation-exchange, CO₂ adsorption and conversion, secondary recrystallization, polyHIPE