

Abstract

Strong requirements for consumption of clean energy sources and for global reduction of greenhouse gases emissions induced the intensive research towards the development of efficient H₂ and CO₂ adsorbents. Metal-organic frameworks (MOF's) are promising materials for successful storage of these gases, but the effectiveness of hydrogen storage in particular, is still low due to the weak interaction between H₂ and framework. The suitable sorption capacity is reached only at very low temperatures, thus the improvement of the sorbent-sorbate interactions is the main goal of the researchers and that is also the purpose of this work. This work is based on the preparation and *postsynthetic* modification (PSM) of metal-organic framework's, which are based on iron, zirconium and titanium, with incorporation of nickel and magnesium salts as possible agents for additional unsaturated metal sites to improve their sorption properties of H₂ and CO₂.

Different structural parameters have a great impact on improved H₂ and CO₂ capacity, especially coordinatively unsaturated sites, which can be optimally prepared by a suitable activation process. Sorbed gas capacity is usually lower if the trapped solvent molecules within the pores of frameworks are less volatile and are difficult to remove. Furthermore, the specific surface area, pore size, pore volume and free amine sites have a crucial role for the CO₂ sorption properties. I have systematically studied the activation process in MIL-101(Fe) and successfully created the coordinatively unsaturated metal sites. Additionally, I have studied the effect on the sorption of gases with further impregnation with different salts; nickel nitrate and magnesium chloride for MIL-101(Fe) and with nickel nitrate and nickel acetylacetonate in the case of an aminoterephthalic structure of MIL-101(Fe)-NH₂, containing additional amine sites on the organic ligand. Furthermore, I have observed the impact of PSM in materials that in principle don't possess the open metal sites and furthermore, have smaller pore size and pore volume compared to the structure of MIL-101, as both zirconium UiO-66-NH₂ and titanium MIL-125-NH₂ that contain amine groups on the ligand. I have modified both materials by PSM using three similar organometallic complexes containing either different cations (nickel or magnesium acetylacetonate) or different ligands (acetylacetonate or tetramethylheptanedionate).

It was shown that MIL-101(Fe)-NH₂ has a larger capacity of stored CO₂ compared with MIL-101(Fe) due to open metal sites and free amine groups. However, the PSM of MIL-101(Fe) by selected nickel salts does not significantly affect the CO₂ sorption properties. On the other hand, the hydrogen adsorption enthalpy increased in case of impregnation of UiO-66-NH₂ with nickel acetylacetonate (modification in toluene in vacuum), where the distorted tetrahedral geometry of nickel centers offers additional accessible sites. The hydrogen adsorption enthalpy has also increased in case of exposure of the tetramethylheptanedionate complex to the H₂ atmosphere and the sample preparation during the supercritical fluid reactive decomposition procedure (SFRD), resulting in the formation of elemental nickel particles. Detailed NMR spectroscopy investigations showed that the interactions of incorporated Ni- and Mg- acetylacetonates with the frameworks of UiO-66-NH₂ and MIL-125-NH₂, are established only by weak interactions and are not covalently bonded to -NH₂ sites. The strength of complex bonding with the MOF framework does not play significant role in improvement of hydrogen-to-framework interactions, while the type of the deposited metal within the MOF pores (Ni > Mg) and the type of ligand (preferable the Ni-tetramethylheptanedionate) seem to have more important role, which can be mainly assigned to the solubility properties of complex molecules in the supercritical fluid.

Keywords: metal-organic frameworks, *postsynthetic* modification, hydrogen and carbon dioxide sorption