Synthesis, characterization, and catalytic properties of Metal Organic Frameworks containing cerium cations

ABSTRACT

The motivation to the research which are described in this dissertation, was the need for developing new materials to reduce the risks associated with increasing CO_2 emissions to the atmosphere. For this, materials are needed to allow the capture of CO_2 from exhaust gases (adsorbents) and then its conversion (catalysts) to useful chemicals. In my interests there was materials belonging to the group called Metal Organic Frameworks (MOFs).

These structures are an interesting group of crystalline materials with exceptional textural properties and an almost unlimited possibility of modifications, e.g., to enhanced sorption and catalytic properties. The presence of easily accessible metallic centers in MOF and its high porosity makes them promising adsorbents, sensors, and heterogeneous catalysts.

The aim of the study was to investigate how the modification (substitution of Zr cations in the structure with cerium; deposition of cerium / copper on MOF) of selected MOFs with the UiO-66, MOF-808 and HKUST-1 topology affects their crystallinity, textural properties, morphology, thermal stability, CO_2 sorption capacity and catalytic activity in CO_2 hydrogenation to methanol. Additionally, their catalytic activity in the CO oxidation reaction was also determined.

To achieve the goal, a series of materials with the UiO-66, MOF-808 and HKUST-1 topology were obtained, and then their chemical composition was modified by (i) partial or complete substitution of zirconium cations with cerium in UiO-66 and MOF-808 structures, and (ii) impregnation with copper and cerium salts of the UiO-66 / MOF-808 and HKUST-1, respectively. The physicochemical properties of the modified MOFs were determinate by X-ray diffraction (XRD), low-temperature N_2 sorption, X-ray photoelectron spectroscopy (XPS), scanning and transmission electron microscopy and thermogravimetric analysis.

The obtained results indicated that the synthesis parameters of the modified UiO-66 and MOF-808 structures with both zirconium and cerium clusters determine the crystal and textural properties as well as thermal stability of these materials. It was also observed that the substitution of zirconium cations with cerium results in improve of catalytic activity in CO_2 hydrogenation reaction. The studies of HKUST-1 structures and their composites with cerium oxide have shown a significant influence of the synthesis method on their morphology, chemical composition, thermal stability, and catalytic activity in the CO oxidation reaction.

The dissertation increases the knowledge of the synthesis as well as the adsorptive and catalytic properties of bimetallic and monometallic structures with the UiO-66, MOF-808 and HKUST-1 topology