STRUCTURAL FEATURES AND PHYSICOCHEMICAL PROPERTIES OF THE METAL-ORGANIC FRAMEWORK Ni-MOF-74

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Abstract. This paper examines the structure of the metal-organic framework Ni-MOF-74, Ni_2(dobdc), and the physicochemical properties that follow from it. The honeycomb-like arrangement of the metal rods, the one-dimensional channels, and the coordinatively unsaturated nickel sites are considered as the main structural features. The role of these sites in the adsorption of carbon dioxide, methane, and hydrogen is discussed, together with the influence of the metal in the framework. The importance of activation conditions and of the combined use of several experimental methods for a reliable evaluation of the material is emphasized.

Keywords: Ni-MOF-74, open metal sites, gas adsorption, carbon dioxide, physicochemical properties.

Introduction. Metal-organic frameworks combine metal ions and organic

linkers into ordered porous solids and are widely studied for gas storage, separation, and catalysis [1, 2]. Within this large group, the MOF-74 family is distinguished by its regular channels and by the high concentration of metal centers that can interact directly with guest molecules. The structural type was first reported for a zinc-based framework built from rod-shaped building units [3]. The nickel analogue, Ni-MOF-74, is also known as CPO-27-Ni and has been investigated as an adsorbent with accessible metal sites [4].

Structure of the framework. In Ni-MOF-74 the Ni^{2+} ions are connected by the $dobdc^{4-}$ linker, and the metal centers are arranged in rods that are packed in a honeycomb-like pattern. This arrangement produces one-dimensional channels that run through the whole crystal and are lined with metal sites and aromatic parts of the linker [3, 4]. Such a geometry provides open and easily accessible pore space, which is favorable for the transport of small gas molecules.

Open metal sites. After synthesis, the nickel centers are coordinated by solvent molecules. Heating under vacuum or in a flow of inert gas removes these molecules without destroying the framework, and coordinatively unsaturated nickel sites become available on the surface of the channels [4]. These sites act as centers of stronger interaction with polar and polarizable molecules. The studies of the iron analogue of MOF-74 show that the open metal sites can also discriminate between hydrocarbon molecules, which demonstrates the general importance of this structural feature [5].

Adsorption of gases. The adsorption behavior of Ni-MOF-74 is governed by a combination of the accessible metal sites and the dispersion interactions with the channel walls. For carbon dioxide, the interaction with the open metal sites is especially significant, while for methane the dispersion interactions and the available pore volume play a more important role [6]. The adsorption of hydrogen on the open nickel sites has also been investigated for this material [4]. A comparison of such data helps to understand which properties of the adsorbent are responsible for selectivity.

Influence of the metal. The properties of MOF-74 can be modified by changing the metal in the framework while keeping the same topology. It has been shown that the replacement of the metal leads to a pronounced change in the carbon dioxide uptake [7]. A systematic comparison of frameworks with different metals confirms that the nature of the metal center affects the strength of the interaction with carbon dioxide and the overall adsorption behavior [8]. Therefore, nickel should be considered as one of several possible options, and the choice of the metal should depend on the intended application.

Stability and sensitivity to activation. The framework is able to keep its structure after the removal of coordinated solvent, which is an important condition for gas adsorption studies [4]. At the same time, polar molecules such as water can bind to the open metal sites and compete with the target gas, so the exposure of the activated material to moisture should be controlled. In general, the stability of metal-organic frameworks in the presence of water and under repeated use remains a key question for practical applications [2].

Experimental evaluation. A complete picture of the material is obtained only by combining several techniques. Powder X-ray diffraction is used to confirm the structure, infrared spectroscopy and thermal analysis show the state of the linker and the removal of solvent, and adsorption isotherms measured at different temperatures provide information on capacity and interaction strength. Measurements with gas mixtures and repeated adsorption and desorption cycles are necessary to estimate the practical performance [6, 8].

Conclusion. The properties of Ni-MOF-74 result from the combination of its honeycomb-like channel structure, the accessible nickel sites, and the conditions of activation. The role of the metal center and the competition of different molecules for the open sites must be taken into account when the material is evaluated. A consistent

experimental approach makes it possible to compare the results of different studies and to define realistic areas for the use of this framework.

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