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Effect of mechanochemical grinding on stability, morphology, and adsorption properties of MIL-101(Fe)-NH_2

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Porous metal-organic frameworks (MOFs) represent a class of crystalline micro-/mesoporous materials constructed by self-assembly of metal cations or their clusters as connectors and usually anionic organic ligands as linkers. The final structure and dimensionality of MOFs depend on several factors, such as the molar ratio of reactants, composition and the ratio of the mixture of solvents, choice of the organic linker and inorganic salt, pH value, reaction temperature, etc. One of the most important properties of porous MOFs is their high specific surface area, which may lead to applications in the fields of gas storage and separation, achiral and chiral catalysis, drug delivery, sensor technology, and polymerization reactions in the channels.

The presented study deals with the effect of mechanochemical milling on the well-known MOF material, MIL-101(Fe)-NH_2. We expect that milling has an influence on the stability, particle size, and adsorption properties of the prepared material. The crystal structure of MIL-101(Fe)-NH_2 is built from 2-aminoterephthalate molecules as linkers and Fe(III) ions as nodes. Fe(III) ions are arranged in a trigonal planar cluster with composition [$Fe_3(\mu_3\text{-}O)(\mu_2\text{-}COO)_6(H_2O)_2Cl$] (COO = carboxylate) and a trigonal prismatic secondary building unit. Four [$Fe_3(\mu_3\text{-}O)(\mu_2\text{-}COO)_6(H_2O)_2Cl$] clusters are bridged with six BDC-NH_2 anions under the formation of the structural unit, so-called supertetrahedron. The final crystal structure of MIL-101(Fe)-NH_2 contains different cages with different sizes: a microporous cage and two different mesoporous cages. The resulting cubic structure exhibits several unprecedented features: extraordinary cell volume, a hierarchy of extra-large pore sizes, large cage volumes, and enormous sorption capacity toward different gases and large surface area. The MIL-101(Fe)-NH_2 was ground through a planetary mill at different speeds, times, and balls of different diameters and numbers of pieces. The structure and stability of the material were studied after the milling process using infrared spectroscopy, thermal analysis, and powder X-ray diffraction. The change in particle size of ground MOF materials and their textural properties were also investigated. The surface area (S_{BET}) of samples was calculated based on the nitrogen/argon adsorption measurements, and the maximum storage capacity of CO_2 at 0 °C and 1 atm was also determined. The effect of MIL-101(Fe)-NH_2 milling on stability, particle size, textural properties, and impact on CO_2 storage will be presented in detail at the conference via a poster presentation.

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