SOLVOTHERMAL PREPARATION AND POST-SYNTHETIC ACTIVATION OF A Ni-MOF-74-TYPE COORDINATION MATERIAL

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Abstract. A nickel-containing coordination material targeted as Ni-MOF-74 was prepared using a solvothermal procedure based on nickel nitrate hexahydrate and 2,5-dihydroxyterephthalic acid (H4DOBDC). The nickel-to-ligand molar ratio was 1.42:1, and a mixture of N,N-dimethylformamide (DMF), ethanol and distilled water (15:1:1 by volume) served as the solvent. Crystallization was carried out at 100 °C for 24 h in a sealed, Teflon-lined autoclave. The isolated product was washed with DMF, treated with methanol, vacuum-dried at 80 °C and activated at 150 °C. The synthesis sequence and the rationale for solvent exchange and activation are discussed. FTIR observations reported for the product are consistent with nickel–ligand coordination, but additional diffraction and porosity measurements are required for independent structural confirmation.

Keywords: Ni-MOF-74; nickel coordination material; solvothermal synthesis; H4DOBDC; solvent exchange; activation.

Introduction

Metal–organic frameworks (MOFs) are coordination solids constructed from metal ions or metal-containing units and bridging organic ligands. Their chemical

composition and preparation conditions determine how the resulting frameworks form and which functional properties can subsequently be investigated. MOF-74-family materials attract attention because the established framework structure contains channels and metal coordination sites that can become accessible when coordinated guest molecules are removed. Nickel-based members have therefore been studied in adsorption, catalysis and other materials applications [1–3].

Materials and methods

Parameter	Experimental condition
Organic ligand	H4DOBDC: 6.72 mmol
Nickel precursor	Ni(NO3)2·6H2O: 9.52 mmol
Nominal Ni:ligand ratio	1.42:1
Solvent composition	DMF:ethanol:water = 15:1:1 (v/v/v)
Solvothermal treatment	100 °C, 24 h, sealed 200 mL autoclave
Product treatment	DMF wash ×3; methanol exchange; 80 °C vacuum drying (12 h); 150 °C vacuum activation

The starting compounds were 2,5-dihydroxyterephthalic acid (H4DOBDC, 6.72 mmol) and nickel(II) nitrate hexahydrate (Ni(NO3)2·6H2O, 9.52 mmol). Thus, the nominal Ni:ligand molar ratio was 1.42:1. N,N-Dimethylformamide, absolute ethanol and distilled water were mixed at a volume ratio of 15:1:1 to form the solvothermal reaction medium. The experimental procedure employed a 200 mL autoclave fitted with a Teflon liner.

First, DMF, ethanol and water were combined. H4DOBDC was introduced and dispersed by magnetic stirring for 20 min at room temperature. Nickel nitrate hexahydrate was then added and stirring continued for a further 60 min. The resulting reaction mixture was transferred to the sealed autoclave, which was heated to 100 °C and maintained at that temperature for 24 h. After the solvothermal treatment, the

vessel was allowed to cool naturally to room temperature, and the solid product was separated from the mother liquor by filtration.

The solid was rinsed three times with fresh DMF. A subsequent methanol treatment was used for solvent exchange, with the aim of displacing DMF and other residual species in the product. The washed solid was vacuum-dried at 80 °C for 12 h and subsequently activated under vacuum at 150 °C. Quantitative activation yield, residual-solvent content and pore volume were not reported.

Results and discussion

The described procedure produced a solid nickel-containing material after heating, cooling and filtration. The combination of a metal salt and a multidentate aromatic ligand supplies the components needed for the formation of a nickel–organic coordination network. In the proposed synthetic pathway, dissolution and mixing precede metal–ligand coordination, followed by growth of the insoluble product during solvothermal treatment. No time-resolved nucleation or crystallization data were reported; therefore, these steps are interpreted rather than directly measured.

Post-synthetic treatment is essential in interpreting the prepared sample. Washing with DMF removes readily soluble residual components, while the methanol exchange step is intended to displace higher-boiling solvent molecules. Vacuum drying and activation are intended to reduce the amount of volatile guests retained by the product. The effectiveness of these operations should ideally be assessed through thermogravimetric measurements, surface-area analysis and complementary spectroscopy before quantitative statements concerning pore accessibility are made [3, 5].

FTIR spectroscopy provided evidence of changes in the ligand environment: the product displayed bands associated with carboxylate stretching at approximately 1556 and 1411 cm−1. These features are compatible with coordination between nickel and the deprotonated ligand. Nevertheless, FTIR cannot on its own confirm the Ni-MOF-

74 crystal structure or establish phase purity. Powder X-ray diffraction would be needed to compare the product with a reference structural pattern, followed by nitrogen sorption or other measurements to characterize its accessible porosity.

Conclusion

A reproducible set of stated conditions for preparing an Ni-MOF-74-targeted coordination material has been summarized: Ni:ligand = 1.42:1, DMF/ethanol/water = 15:1:1, solvothermal treatment at 100 °C for 24 h, and subsequent solvent exchange and vacuum activation. The procedure yielded a nickel-containing solid with FTIR features consistent with metal–ligand coordination. Phase identification, activation efficiency and adsorption performance remain subjects for further experiments; no unmeasured structural or sorption properties are assigned to this sample.

References

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