ZEOLITIC IMIDAZOLATE FRAMEWORK MATERIALS FOR POTENTIAL ADSORPTION THERMAL BATTERY APPLICATIONS

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ABSTRACT

Adsorption thermal batteries utilize gas/vapor sorption on porous solids to transfer solar energy from summer to winter, potentially reducing fossil fuel consumption for residential space and water heating. The efficiency of this technology depends on the performance of the adsorbents, which is strongly influenced by their structural properties in combination with synthesis procedures. In this study, we have conducted a simple and sustainable synthesis of ZIF-90 for application in adsorption thermal batteries. ZIF-90 was synthesized using classical and microwave-assisted solvothermal methods with reaction times of 1.5 hours and 5 minutes, respectively. In both procedures, pure ZIF-90 was obtained with suitable structural and adsorption properties for the intended application.

Key words: ZIF, thermal batteries, water adsorption

INTRODUCTION

Intensive industrial activities and rapid population growth are increasing energy demands and consumption. As a result, countries around the world are facing major challenges such as fuel price fluctuations, energy shortages, energy crises and environmental pollution caused by fossil fuel consumption. The transition to renewable energy sources is becoming increasingly popular and affordable, especially in households where energy is mainly utilized for space heating and water heating. However, there is still a discrepancy between the energy produced from renewables and the actual demand. Therefore, thermal energy storage could be a solution to bridge the gap between energy supply and demand [1].

Thermal energy storage can be categorized into three groups: sensible, latent, and thermochemical energy storage (TCES). Among these, TCES is considered the most promising candidate for thermal batteries, possessing the highest energy storage density and the lowest heat losses compared to other methods. TCES utilizes sorption processes to generate and store heat, with the charging and discharging processes relying on reversible adsorption and desorption between adsorbents and adsorbates. The adsorbates can vary and include compounds such as water, methanol, ethanol, and ammonia, while the adsorbents encompass microporous materials like zeolites, aluminophosphates, metal-organic framework (MOF) materials, and composites [2, 3].

A major concern in utilizing MOFs for adsorption thermal batteries is their stability when exposed to water vapor. Therefore, the primary focus is on identifying MOFs with hydrophilic characteristics and water stability even after numerous cycles, making them potentially suitable for application as adsorption thermal batteries [4]. A promising study was conducted by Fröhlich et al [5], who prepared a hydrophilic MOF, CAU-10-H, exhibiting a breathing effect during the water sorption process. The material demonstrated high water stability, even after 700 cycles, making it a promising candidate for thermal battery applications [5].

Zeolitic imidazolate frameworks (ZIFs) belong to a subclass of MOFs. ZIFs are produced by the reaction of metal salts (*e.g.* Zn, Co) and imidazole linkers and form tetrahedral topologies similar to those of zeolites. While much research on ZIFs has focused on the adsorption of CO_2, heavy metals and volatile organic compounds, there are few studies on water adsorption and their application in thermal batteries [6]. Since most ZIFs are hydrophobic, the hydrophilic ZIF-

90 with the sodalite topology is usually chosen for research on water sorption processes. The hydrophilic character is due to the carbaldehyde groups in the structure of the material, making it suitable for water sorption [7].

Herein, we present the facile synthesis of ZIF-90 and its suitability for adsorption thermal battery applications. The synthesis of ZIF-90 was carried out by *via* two routes: conventional solvothermal and microwave-assisted solvothermal synthesis. Our objective was to prepare ZIF-90 by replacing the toxic solvent *N, N*- dimethylformamide (DMF) with an acetone and water mixture and to analyze its water adsorption capacity. Pure ZIF-90 was formed in 1.5 hours at 60 °C, whereas the microwave-assisted synthesis yielded ZIF-90 in only 5 minutes at 80 °C. The water sorption experiments were performed to gain insight into the application of the material for adsorption in thermal batteries. The cyclic tests proved the stability of the material, with the structure remaining intact after 20 cycles. The materials showed suitable adsorption properties, indicating their potential use as adsorption thermal batteries.

EXPERIMENTAL

1. Materials

1H-Imidazole-2-carbaldehyde (HICA, 97%) was purchased from Fluorochem (Hadfield, UK). Zinc acetate dihydrate (ZnAc, 98%) was purchased from Sigma Aldrich (Darmstadt, Germany). Acetone (≥99.5%) was purchased from Honeywell Riedel-de Haën AG (Berlin, Germany).

2. Synthesis of ZIF-90

ZIF-90 was synthesized by modifying a previously published procedure [8]. In both the conventional solvothermal synthesis and the microwave-assisted solvothermal synthesis, DMF was replaced by a mixture of acetone and water.

For the conventional solvothermal synthesis, zinc acetate was dissolved in water. In another beaker placed on a stirring plate, HICA, acetone, and water were mixed together. Once the HICA was completely dissolved, the zinc acetate solution was slowly added to the HICA solution and stirred at 60 °C for 1.5 hours. The resulting solution was filtered and washed with ethanol. The obtained ZIF-90 was dried in an oven at 60 °C overnight.

For the microwave-assisted synthesis, HICA and acetone were mixed in a Teflon autoclave for 15 minutes at room temperature. The zinc acetate solution was slowly added to the HICA solution and left to stir for 5 minutes. The Teflon autoclave was then placed in the microwave reactor and heated at 80 °C for 5 minutes. The resulting mixture was centrifuged at 6000 rpm and washed with ethanol. The obtained ZIF-90 was dried overnight in the oven at 60 °C.

3. Characterization

Powder X-ray diffraction (PXRD) was performed using a PANalytical X'Pert PRO diffractometer (Malvern Panalytical, Almelo, The Netherlands) with Cu Kα radiation (λ = 1.5418 Å). The 2θ range was 5 - 55° with a step size of 0.033°. The patterns were evaluated using the X'Pert HighScore Plus program package. Nitrogen physisorption was performed using Autosorb iQ3 (Quantachrome Instruments, Boynton Beach, FL, USA). The isotherms were collected at 77 K. Prior to this, the ZIF-90 samples were degassed at 150°C in a vacuum for 10 hours. The specific surface areas were determined using the Brunauer-Emmett-Teller equation (BET). The total pore volume was estimated based on the amount of adsorbed nitrogen at a relative pressure of 0.95. The micropore volume of the samples was determined using the built-in algorithm based on the t-plot method. Thermogravimetric analysis (TGA) was performed with the TA Instruments Q5000IR. Prior to the analysis, the samples were placed in a desiccator with 75 % relative humidity for 24 hours. Measurements were performed in continuous flow (25 mL/min air) from 25 °C to 250 °C, with heating rate of 5 °C/min. The water uptake was determined using a Hiden IGA100 electronic microbalance. After the sample was placed in the reactor, the system was evacuated to vacuum and the sample was degassed at 150 °C for 5 hours. During the sorption experiments, the sample temperature was 25 °C and was controlled by the thermo-regulated water bath and the vapor pressure was step-wise increased up to saturation pressure. The cyclic tests for ZIF-90 were performed using a Hiden IGASorptX. The test consisted of pre-treatment of the sample in a nitrogen flow at 150 °C for 5 hours under atmospheric pressure, followed by cooling the sample to 30 °C. The water vapor sorption tests were conducted under atmospheric pressure, where the adsorption took place at 30 °C with the relative humidity of 80 %, while the desorption temperature was 100 °C.

RESULTS AND DISCUSSION

1. Structural properties of ZIF-90

The powder XRD patterns of ZIF-90 and microwave synthesized ZIF-90 were compared with the simulated XRD pattern of ZIF-90, revealing the presence of pure crystalline phases in both materials. Furthermore, the structures were preserved after activation in vacuum at 150 °C.

SEM analysis was used to determine the morphology and the particle size of the as-synthesized materials. SEM pictures showed the phase purity of the materials with prismatic nanoparticles ranging in size from 100 to 500 nm.

The nitrogen physisorption isotherms show a mixture of Type I and Type IV isotherms, indicating the presence of micropores and mesopores. The specific surface areas are well correlated with the particle size, with values above 1100 m^2/g. Total pore volume of the conventional ZIF-90 is 0.571 cm^3/g, whereas for the microwave synthesized it is 0.576 cm^3/g. However, the conventional ZIF-90 exhibits a slightly higher micropore volume compared to the microwave-synthesized sample.

In order to estimate the thermal stability of the prepared materials and the activation temperatures, thermogravimetric studies were performed on the as-synthesized materials. In addition, the analysis was also performed on the activated samples to ensure that the solvent was completely removed. After activation in a vacuum oven at 150 °C overnight, the materials showed a slight weight loss, due to the solvent residues on the material surface, which means that activation of these materials, is not necessary.

2. Water sorption on ZIF-90

The use of ZIF-90 in adsorption thermal batteries was assessed by examining its sorption capacities under different conditions.

Preliminary experiments were conducted by thermogravimetric analysis, where the water content of the ZIF-90 materials was investigated in the temperature range from 25 °C to 150 °C. The water loss determined at 150 °C was 30 % for both materials.

Both samples showed a sigmoidal shape of the water sorption isotherms, with an initial low water uptake followed by a sharp increase at relative pressure of 0.5 P/P_0 for conventional and 0.4 P/P_0 for microwave-synthesized ZIF-90. Furthermore, microwave-synthesized ZIF-90 shows a slightly higher water uptake at lower relative pressures. These observations suggest that the adsorbent prepared by the microwave-assisted synthesis is favorable for the adsorption thermal batteries, by shifting the water uptake towards lower relative pressures.

The cycle tests are an important indicator of material stability and usability as adsorption thermal batteries. After 20 cycles of adsorption and desorption between 30 and 100 °C at 12 mbar, a slight reduction in water uptake (2 %) was observed after the last cycle, confirming that ZIF-90 is a promising candidate for use in low-temperature thermal battery.

CONCLUSION

ZIF-90 was successfully synthesized using a mixture of water and acetone as the solvent and further improved by microwave-assisted synthesis, resulting in rapid production within minutes. The ZIF-90 samples prepared by both conventional and microwave methods exhibited promising water sorption properties, suggesting their viability for application in adsorption thermal batteries. Furthermore, no degradation of the material was observed after 20 cycle tests, which is crucial for the application of adsorption thermal battery.

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