Water Adsorption Characteristics and Microcalorimetric Studies of MOF-5 and MOF-199 Synthesized Using “Green” Sol-Gel

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In this study, types of porous metal-organic framework materials namely MOF-5 (robust framework), MOF-199 in the non-ion-exchanged condition were compared in terms of hydrophobicity-hydrophilicity of the surface. The investigations were done using microcalorimetric measurements of heat of immersions in water. MOF-5 and MOF-199 were synthesized using plant-based polymer of palm oil derived fatty alcohols (PODFA) as porous template using “green” sol-gel approach. The synthesis approach applied was environmental-friendly by eliminating the use of organic solvents and surfactants substituting with water and PODFA. X-ray diffraction patterns of MOF-199 exhibited prominent reflection peaks assigned to octahedral structure with small peak shift while MOF-5 exhibited truncated and full cubic morphology. PODFA with longer aliphatic carbon chain exhibited higher porosity and pore volume. The addition of PODFA increased the homogeneity of the cubic and octahedral single crystals typically observed in MOF-5 and MOF-199 morphology. This was due to the increased in immiscibility of metal oxide precursors and organic linkers hence allowing reactions to occur from all directions. PODFA molecules were suggested to form self-assemblies at the air-water interface governed by surface tension auto-oscillations and formed clusters on which metal oxide and organic linker precursors bind with. The water adsorption isotherms of MOF-5 and MOF-199 prepared in this study exhibited “gate-opening” effect at lower relative pressure not observed in other nanoporous framework structure made up of two-components such as organosilica materials.

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1. Introduction

The scarcity of clean water resources due to water pollution worldwide imposed a major threat to the survival of human and other life into the next century. Thus, activities towards effective and rapid reducing of the contaminants to an accepted level has become a major topic. Water pollutants especially heavy metals are overabundance and gradually enter our food chains by bioaccumulation [1]. There are several mitigation methods applied to reduce the heavy metal ions in water such as ion-exchange, membrane filtration, chemical deposition, electrochemical treatment as well as adsorption [2, 3].

Adsorption is the most widely used separation technologies owing to its effectiveness, economic value, reversibility and flexibility of the system for heavy metals separation [3]. Adsorption method requires the adsorbents to be having nanoscale features either nanosize or nanopores to impart high surface area for the adsorptive to adhere onto the solid surfaces [4]. Therefore, nanoporous solid requires a minimal intrinsic surface area at above ca. 1200 \text{m}^2/\text{g} combined with good textural porosity for high mechanical stability to capture the heavy metal ions [4]. Several adsorbents were considered as heavy metals capture including nanosized metal oxides (NMOs) due to its large active surface area [5]. However, NMOs faced several problems such as particle aggregations due to high reactivity and van der Waals interaction affecting the overall efficiency of the system. Another class of adsorbents are microporous aluminosilicate zeolites materials that are either man-made or naturally occurring [6]. Zeolites have moderate surface areas, uniform pores and excellent ion exchange capabilities given rise by the negative charge originating from silicate species. However, the microporosity of the channels making it difficult for easy adsorption and tend to cause pore-clogging decreasing the overall efficiency as well as the environmental effect due to acid-base treatment or ion exchange [6].

Metal-organic framework materials (MOFs) are one of the most studied materials of 21st century that emerged within the past three decades. MOFs are a class of organic–inorganic hybrid materials made of struts of metal ions clusters interconnected by organic

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ligands (linkers) forming a geometrically well-defined 3-dimensional pore framework structure [7–9]. They are classified as having dual pores of microporous (< 2 nm) and mesoporous (2–50 nm) under the IUPAC classifications of porous solid materials. MOFs have great potential as adsorbents and catalysts due to their extremely large surface area, well-ordered nanoporous structures and diverse surface functionalities given rise from the organic-inorganic framework that are available for further functionalizations. This is because of their secondary building unit (SBU) of metal clusters and organic-linker could be carefully chosen and tailored to design the targeted materials with specified nanoporous structure [1]. Due to these factors, MOF materials have extraordinary permanent porosity [8], large pore volume, very low density and high surface area [9]. A MOF material was reported to achieve up to ca. 7,000 m²/g as compared to the simulated value that can go up to ca. 14,600 m²/g [10]. Furthermore, the pore surfaces that consist of organic-inorganic parts resulted into flexible and permanent porosity. Based on these excellent structure-related properties, MOFs were widely studied for gases adsorption applications such as methane and hydrogen storage, carbon dioxide capture, gases or molecular separation and as heterogeneous catalysis [10, 11]. A series of MOFs with various structures were reported in the year 2000 by Yaghi and co-workers [7, 8]. Several types of MOFs such as MOF-5, MOF-74, MOF-177, HKUST-1, MIL-100 and MIL-101 are becoming potential solid materials as adsorbents to store substantial amounts of gases [10, 11]. These gases are either for energy utilization or pollutant gases storage. Non-polar molecules of gases such as hydrogen, carbon dioxide, methane or ethane molecules are adsorbed onto their surfaces through weak van der Waals interactions and electrostatic potentials. The applications of MOFs in adsorption and separation of heavy metal ions from drinking water are gaining increasing attention due to easy accessibility of adsorption sites (either on the metal oxide clusters or the organic linkers), on the outer textural pores and/or diffusion through the frameworks. However, at present, most of MOF materials were synthesized from non-renewable petroleum feedstocks, synthetic chemicals and transition metals. In 2014, Misran et al. reported on the successful attempts to synthesize MOF-5 as well as MOF-199 using renewable fatty alcohols derived from edible palm oil with various carbon chain length analogous to commercial surfactants [12]. Several stringent parameters must be controlled in order to produce MOF at room temperature and pressure. Thus, in this study, MOF-5 and MOF-199 were attempted to be synthesized using the “green” sol-gel method developed by Misran et al. [12] with some modifications. In addition, the hydrophilic and hydrophobic properties by water adsorption measurement and heat of immersions of surfaces towards water molecules were carried out and compared with hybrid organosilanes surfaces that consisted of organic-inorganic moieties as reported by Matsumoto et al. [4].

2. Experimental procedure

Zinc-based MOF-5 and copper-based MOF-199 were synthesized by “green” sol gel method approach using water and fatty alcohol derived from palm oil at room temperature with low temperature heat treatment at ca. 333 K. Zinc (II) nitrate hexahydrate (> 99%, Zn(NO₃)₂·6H₂O), Copper (II) nitrate (> 99%, Cu(NO₃)₂·3H₂O), Benzene dicarboxylic and tri-carboxylic acid (BDC and BTC, both > 99%) were purchased from Sigma Aldrich, ethanol (99.8%, C₂H₅OH) were purchased from Merck. Palm oil derived fatty alcohol (PODFA) was purchased from Emery Oleochemical (M) Sdn Bhd. Generally, there were two precursors solution comprised of organic linker in a co-solvent of ethanol (EtOH). The second solution consisted of metal salt in water. Both metal and organic precursor solutions were mixed and stirred thoroughly. Then, modification in the synthesis was done by adding an amount of PODFA as a modulating agent was added into the solution to promote the formation of “pre-Ouoz” effect in the surfactantless mixture. The synthesis method was cheap and facile by substituting hazardous solvents with only water with the aid of palm oil derived fatty alcohols (PODFA) as renewable template to help the formation of porous framework at the water-fatty alcohols interfaces. Then, the resulting powder were washed and dried to obtain non-ion-exchange MOF-5 (robust pores) and MOF-199 (flexible pores) materials for subsequent water adsorption measurements and heat of immersions measurements.

Water adsorption measurements and heat of adsorption of water on MOF-5 and MOF-199 were conducted using a twin conduction microcalorimeter MPC-11 (Tokyo Riko) that was attached to a volumetric adsorption apparatus. The non-ion exchanged MOF materials were pretreated under 1mPa at 323 K for 24 h. The water adsorption isotherms were measured at liquid nitrogen temperature of 298 K. MOF-5 was selected for robust pore structure while MOF-199 was selected for flexible pores with readily accessible adsorption sites.

3. Results and discussion

The representative SEM images of non-ion exchanged of MOF-199 synthesized without and with the addition of palm oil derived fatty alcohol (PODFA) of octyl alcohol (C₈) are shown in Fig. 1a and b. The various morphology observed in this study was due to the hydrogen bond donation ability of solvent molecules that governed the crystallization rates. Higher crystallization rate resulted in less faceted structure. Furthermore, the various solvents used gave different capabilities to dissolve and to solvate Zn²⁺, Cu²⁺ and NO₃⁻ ions as well as the organic ligand because of their different dielectric constants, dipole moment and van der Waals volume [13]. Figure 2 shows the water adsorption isotherms of MOF-5 (robust pores) and MOF-199 (flexible pores). The water adsorption isotherm for non-ion-exchanged MOF-5 exhibited interesting and unusual behaviour at
relative pressure $P/P_0 = 0.4$. In most nanoporous materials, at relative pressure of $P/P_0 = 0.4$, a steep uptake of water was observed due to capillary condensation of water vapor. Condensed water vapor decreased the effective pore diameter by a multilayer adsorption of water molecules on the surface. Thus, the phenomena observed in this study may be related to structural change of MOF-5 by water uptake and removal of occluded liquid inside the pores of non-ion exchanged materials. However, for MOF-199 the pores were easily accessible to water molecules sorption with Type IIa in the IUPAC classifications often associated with monolayer-multilayer adsorption on an open and stable external surface suggesting MOF-199 flexible and stable porous structure towards water adsorption [4]. The smooth non-stepwise character of the isotherms was also associated with energetic heterogeneity in the adsorbent-adsorbate interactions of MOF-199 surface given rise from metal and organic moieties in the framework.

The corresponding heat of immersion of MOF-199 elucidated in Fig. 3 suggested stable adsorption of water molecules on the surface at 40 kJ/mol. However, MOF-5 exhibited gate-opening effect.

4. Conclusion

MOF-5 and MOF-199 materials were successfully synthesized at room temperature in the presence of palm oil derived fatty alcohol (PODFA). Monodispersity increased with the addition of PODFA that increased the
Fig. 3. Heat of immersions of non ion-exchanged MOF-5 and MOF-199 prepared using “green” sol-gel synthesis.

immiscibility of precursor mixtures. Non-ion-exchanged MOF-199 exhibited hydrophilicty and stable towards water vapor while MOF-5 exhibited unique behavior without capillary condensation.

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References