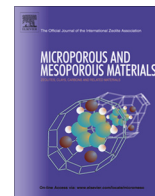




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Enhancement of hydrogen storage capacity and hydrostability of metal–organic frameworks (MOFs) with surface-loaded platinum nanoparticles and carbon black



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ABSTRACT

Metal–organic frameworks (MOFs) have generated considerable interest as a potential candidate for hydrogen storage, owing to their extremely high surface-to-volume ratio and low density. However, practical applications have been limited because of low hydrogen storage capacity at room temperature, and of moisture sensitivity of MOFs. To improve hydrogen storage capacity at room temperature and hydrostability under ambient conditions, platinum (Pt) nanoparticles were introduced on the outer surface of MOF-5, $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$ that was then coated with hydrophobic microporous carbon black (CB) to generate a CB/Pt/MOF-5 composite. To study the chemical composition, morphology, crystallinity, and properties of the synthesized material, various techniques were employed including wide-angle X-ray diffraction, X-ray photoelectron spectroscopy, inductively coupled plasma emission spectrometry, high-resolution transmission electron microscopy, and N_2 adsorption–desorption analysis. The characterization analyses confirmed the formation of a novel composite designated as CB/Pt/MOF-5 with a highly crystalline structure, and large specific surface area and pore volume. The hydrogen storage capacity (0.62 wt.%) of CB/Pt/MOF-5 was superior to that of pristine MOF-5 (0.44 wt.%) by 41%; furthermore, CB/Pt/MOF-5 displayed excellent hydrostability under ambient conditions. Overall, these findings indicate that MOF-5 with improved hydrogen storage capacity and hydrostability was successfully synthesized by introducing Pt nanoparticles and a carbon black layer.

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1. Introduction

Hydrogen (H_2) has attracted growing attention in recent years as a clean and renewable energy resource. Moreover, it is the most promising candidate among the clean energy sources to overcome the current energy-related issues and global warming owing to the high energy density, and zero emission of greenhouse gases when it is used as a fuel. However, hydrogen storage is a major challenge to using hydrogen as a clean energy source for practical applications such as hydrogen-powered vehicles [1,2]. The use of porous materials, such as carbon materials and zeolites, is one possible method for hydrogen storage; it is the most suitable technique for transport applications. This method is advantageous owing to the use of lightweight materials with high surface areas and porosities [3].

Metal–organic frameworks (MOFs) are promising hydrogen storage materials because of their high surface area, easy synthesis, and low density. MOFs are crystalline porous materials composed of metal ions, such as Zn^{2+} , Mn^{2+} , and Cu^{2+} , coordinated by organic ligands such as carboxylate and imidazolate. MOFs have unique properties, enabling application in broader areas when compared with other porous materials [4]: luminescence owing to conjugated organic linkers; structural tunability in response to molecular adsorption or changing environmental conditions; charge transfer (ligand-to-metal or metal-to-ligand); high thermal stability owing to the presence of many organic polymers; electronic and conducting properties; and pH-sensitive stability. However, despite the remarkable advantages of MOFs, two major drawbacks must be overcome for use as a hydrogen storage material.

The first drawback is the considerably lower hydrogen storage capacity at room temperature when compared with that at 77 K. In general, hydrogen binds to the surface of substrates by weak van der Waals interactions, with an adsorption enthalpy between

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4 and 10 kJ/mol – the required binding energy for hydrogen storage is between 20 and 30 kJ/mol [5]. Hence, at room temperature, hydrogen adsorption is significantly low because the adsorption enthalpy is too low to bind hydrogen. Hydrogen storage in MOFs is also dominated by weak van der Waals interactions, with a hydrogen binding energy of 4–6 kJ/mol, which is insufficiently high to retain hydrogen on the surface [6]. For example, MOF-5, composed of zinc clusters coordinated by 1,4-benzene dicarboxylate (BDC), displays hydrogen storage capacities of 1.25 wt.% at 77 K and 0.4 wt.% at room temperature. For practical applications, it is necessary to increase hydrogen storage capacity at room temperature. A promising approach is the introduction of metal nanoparticles into the materials. Metal nanoparticles act as a catalyst for the so-called spillover process [7,8]. Hydrogen spillover involves the dissociation of a hydrogen molecule to hydrogen atoms on a metal catalyst followed by migration of a hydrogen atom from the metal to the substrate. The hydrogen gas adsorption enthalpy can be improved by the hydrogen spillover effect. The hydrogen spillover effect has been studied for carbon materials, zeolites, and MOFs [9–21]. Hydrogen storage capacity could be increased by the introduction of metal nanoparticles. In general, the hydrogen spillover effect on MOFs can be facilitated by building carbon bridges between the dissociation (metal nanoparticles) and acceptor (MOFs) sources [12–16]. Recently, direct doping of metal nanoparticles in MOFs has been studied [17–21]. It has been reported that the particle size and dispersion of the metal nanoparticles on MOFs influence the hydrogen spillover process [17]. The direct metal doping method affords better control than the MOFs-bridging method over the particle size and dispersion, resulting in an improved hydrogen storage capacity through efficient hydrogen spillover processes [17,18]. However, the introduction of metal nanoparticles leads to a decrease in the specific surface area. Many studies have shown that the loading of metal nanoparticles in the inner pores considerably decreases the specific surface area [19,20].

The second drawback is the very high sensitivity of MOFs to moisture. When exposed to air, the organic ligands substitute for moisture in air, resulting in partial destruction of the MOF structure and decrease in the specific surface area [22]. The moisture sensitivity of MOFs is a significant problem that hinders their practical application. Besides high hydrogen storage capacity being a key factor, high hydrostability is important for practical application. However, relatively few studies report on the improvement of stability under ambient moisture. Hydrostability has been mainly improved by using hydrophobic materials. For instance, Yang et al. introduced hydrophobic methyl groups on BDC moieties [23]. Yang et al. synthesized composite MOF-5/hydrophobic carbon nanotubes [24]. Nguyen et al. obtained moisture-resistant MOFs via post-synthesis modification [25]. However, these approaches required pre-functionalization that makes the synthesis complex.

In this study, in an attempt to increase hydrogen storage capacity through hydrogen spillover effects, Pt nanoparticles were loaded on the outer surface of MOF-5 using two solvents exhibiting different polarities in the inner and outer pores, without significant decrease in the surface area of MOF-5. Pt-loaded MOF-5 samples were prepared with various Pt contents to determine the amount of Pt required to achieve small Pt particles and high Pt dispersion. A hydrophobic carbon black layer was formed on the Pt-loaded MOF-5 samples to improve hydrostability. The formed carbon black layer facilitated the exclusion of moisture and selective infiltration of hydrogen. MOF-5 featuring Pt nanoparticles and a carbon black layer exhibited improved hydrogen storage capacity at room temperature and hydrostability under ambient moisture when compared with pristine MOF-5. Our approach can be applied to pre-synthesized MOFs requiring no pre-functionalization.

2. Experimental

2.1. Reagents and chemicals

Zinc acetate (Aldrich), 1,4-benzene dicarboxylate (BDC; Junsei), *N,N*-dimethylformamide (DMF; Junsei), chloroform (Junsei), chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$; Aldrich), carbon black (Columbian Chemical Company), and sucrose (Aldrich) were used as purchased.

2.2. Synthesis

2.2.1. Preparation of MOF-5

In this study, MOF-5 was synthesized using a modified direct mixing approach based on the method reported by Tranchemontagne et al. [26]. It has been reported that addition of H_2O_2 favors the growth of cubic MOF-5; however, with an increased particle size from 100 nm to 1 μm . Because large crystals are unfavorable for loading on MOF-5, the synthesis of MOF-5 was conducted in the absence of H_2O_2 . First, DMF was degassed for 1 h. Zinc acetate (0.82 g, 3 mmol) and BDC (0.24 g, 1 mmol) were separately dissolved in 30 mL and 10 mL of degassed DMF. The respective mixtures were stirred for 2 h at room temperature. The solution of BDC/DMF was directly added to the solution of zinc acetate/DMF and then stirred for 2 h at room temperature. Following addition, small white particles started to form. After 2 h of stirring, the reaction was complete and the solution became opaque. The small particles were washed, centrifuged thrice with DMF, and finally washed with chloroform. The particles were aged at 60 °C in chloroform for 3 days; during aging, the chloroform solution was replaced with a fresh solution daily. Finally, the particles were centrifuged and dried at 90 °C for 24 h. Then, small white crystalline particles were obtained and stored in a desiccator.

2.2.2. Introduction of Pt nanoparticles into MOF-5

Solvent-exchanged MOF-5 (SMOF-5), whose pores are fully filled with non-polar solvent, chloroform, was used as the starting material. First, SMOF-5 (0.5 g) was added to DMF (5 mL), and the mixture was sonicated for 3 min. To introduce Pt nanoparticles into MOF-5, $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ was dissolved in DMF at varying contents. The Pt precursor solution was directly added to the SMOF-5/DMF solution and reduced under UV light ($\lambda = 312 \text{ nm}$) for 24 h. Subsequently, a thick solution was obtained and centrifuged thrice with DMF. The resulting composite Pt/MOF-5 was stored in chloroform at 60 °C for 3 days. Then, guest molecules were removed by heating Pt/MOF-5 at 70 °C under vacuum. The prepared Pt/MOF-5 composites with varying Pt loadings of 1, 4, 7, and 10 wt.% on the outer surface of MOF-5 are denoted as 1Pt/MOF-5, 4Pt/MOF-5, 7Pt/MOF-5, and 10Pt/MOF-5, respectively.

2.2.3. Formation of carbon black layer (CB) on Pt/MOF-5

First, carbon black (0.15 g) and sucrose (0.8 g) in chloroform were mixed in a 50-mL vial with stirring for 2 h. Then, Pt/MOF-5 (0.5 g) in chloroform was added to the mixture. The colloidal suspension was heated at 200 °C with stirring for 12 h for carbonization of sucrose. The obtained CB/Pt/MOF-5 was dried under vacuum.

2.3. Characterization

The crystal structures of MOF-5, Pt/MOF-5, and CB/Pt/MOF-5 were analyzed by X-ray diffraction (XRD; M18XHF-SRA) at room temperature using a MAC/Science MXP 18XHF-22SRA diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$, 50 kV, 100 mA) as the X-ray source. The crystallinity

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