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Synthesis of Zinc-Organic Frameworks Nano Adsorbent and their Application for Methane Adsorption

Mahnaz Aghajanloo¹, Ali Morad Rashidi^{2*} and Mohamad Ali Moosavian¹

¹Oil and Gas Processing Centre of Excellence, School of Chemical Engineering, College of Engineering, Tehran University, Tehran, Iran ²Research Institute of Petroleum Industry, Nanotechnology Research Center, West Blvd., Azadi Sport Complex, Tehran, Iran

Abstract

In the present work, MOF-5 consisting of Zn₄O inorganic vertices was hydrothermally synthesized. Three-step activation treatment including preservation in initial solvent, solvent exchange and drying under evacuated condition was performed and it was found that activation is efficient by increasing the methane adsorption capacity of samples. The final product was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), scanning electron microscopy (SEM) and pore size distribution (PSD). The corresponding pore size of MOF-5/DEF (sample A) and MOF-5/DMF (sample B) which was determined by nitrogen adsorption at 77 K, were equal to 31.27 Å and 42.65 Å and also BET surface area of samples were 2157 and 1532 m²/g, respectively. Methane adsorption equilibrium for both samples was measured in a volumetric adsorption unit and it was found that the adsorbent (A) and (B) in this work have methane adsorption capacity of 18.15 and 11.36 mmol/g at temperature of 298 K and pressure of 36 bar, respectively. Four different models (Langmuir, Unilan, Toth and Sips) were used to correlate the experimental equilibrium data. The root mean square error values demonstrated that the Toth and Sips equation provide better models for correlating adsorption isotherms.

Keywords: Adsorption; Metal-Organic Framework; Methane storage

Introduction

The drawbacks of fossil fuels are well known as increasing the environmental pollution, changing the climate, and instability in oil market. Therefore, the use of alternative energy sources has recently attracted special attention [1,2]. Over the past two decades, considerable efforts have been allocated to develop new fuel technologies to meet transport fuel demand and reduce reliance on conventional fuels [3]. Natural gas (NG) has significant advantages over other hydrocarbon fuels because of its natural abundance and higher hydrogen-to-carbon ratio, which leads to higher thermal efficiency. In addition, it offers lower emission of carbon monoxide and nitrogen oxides. In practice, no particulates are produced compared to gasoline [4-6]. Among the possible ways to storage the natural gas (methane is the primary component of natural gas), its storage in the form of adsorbed gas (adsorption at moderate pressure of 35 bar) is superior to the current compression technology because it offers some advantages such as low cost, high energy efficiency and safety [7,8].

Porous materials provide a suitable base for satisfying storage demands [5]. In comparison with the same tank without adsorbent, efficient porous adsorbents have the capability of storing natural gas in tanks at lower pressure (40 bar) [9,10]. Traditional adsorbents such as zeolites, activated carbons, and MWCNTs have problems including low adsorption capacity in industrial applications. In recent years, hybrid porous solids such as metal organic framework (MOF) have emerged as promising materials for different applications including small molecule storage [11], separation [12,13], catalysis [13,14] and biological imaging [15,16]. In order to better understand the usage of MOFs for these applications, incremental attempt is being put forth to investigate the synthesis condition, physical properties, chemical properties and morphology of MOFs [17]. Metal-organic frameworks (MOFs) are an intriguing class of 3D organic-inorganic hybrid materials [18]. They are constructed by organic ligands and metal clusters linked with coordination bonds of moderate strength [19,20]. Recently, there has been significant progress towards building of MOF-n structures (n as an integer assigned in roughly chronological order) with desirable materials features, including ultra high porosity in the range of micro and nano pore sizes, unsaturated metal coordination sites and fascinating structures [21,22]. The MOF family also has high thermal stability with decomposition temperatures in the range of 300°C to 500°C. Due to superior properties of MOFs, some research works have also been done in order to increase the adsorption capacity of natural gas by the use of MOFs and expand the ANG (Adsorbed Natural Gas) technology [23,24].

Numerous studies on properties and chemical structures of MOFs have been done [25]. One of the most interesting structures of metal organic frameworks is MOF-5 or $Zn_4O(bdc)_3$ (bdc=1,4-benzenedicarboxylate), which is a highly porous material consisting of Zn_4O -cluster that has a decisive role in the final shape and the pore size of the crystals, linked to the terephthalate anion forming a cubic network (Figure 1) [26-28]. The initial findings of reversible gas adsorption of MOF-5 (also widely known as IRMOF-1) have made it one of the most studied metal–organic frameworks [29]. These MOFs have pore sizes ranging from microporous (<2 nm) to mesoporous (2-50 nm) [30]. Typically, the synthesis of MOFs is frequently performed by mass transfer methods (*e.g.* diffusion of amine in to a solution containing a metal salt and organic acid), hydrothermal and solvothermal methods [31].

In the present study, MOFs have been synthesized from two different solvents with same procedure. The samples of octahedral cluster of MOF-5/DEF and MOF-5/DMF are named as sample (A) and

*Corresponding author: Ali Morad Rashidi, Research Institute of Petroleum Industry, Nanotechnology Research Center, West Blvd., Azadi Sport Complex, Tehran, Iran, Tel: +98-21-48252323; Fax: +98-21-48257676; E-mail: rashidiam@ripi.ir

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sample (B), respectively (Figure 2). After vacating their pores by using a three-step activation process, methane adsorption measurements of samples were performed at temperature of 298 K and pressure up to 36 bar.

Experimental

Materials

The solvents N,N-diethylformamide (DEF, 99%) and N,N-demethylformamide (DMF, 99%) were purchased from Fluka. 1,4-Benzene dicarboxylic acid (H_2BDC) as a ligand and zinc nitrate tetrahydrate ($Zn(NO_3)_2$ '4 H_2O) as a metal were purchased from Merck. All materials were used without further purification.

Synthesis of MOFs

During synthesizing the metal-organic frameworks, several factors should be considered. For instance, the type of solvent and its concentrations have essential role in process of the synthesis.

Synthesis of MOFs from DEF (sample A): Optimum conditions for the MOF synthesis were determined through experimental design. Consequently, for synthesis of MOF-5 at first, 0.34 g of terephthalic acid and 1.78 g of $Zn(NO_3)_2$ ·4H₂O were dissolved in 45 mL of pure N,Ndiethylformamide (DEF) solvent. After sufficient stirring at ambient temperature and formation of a white precipitate, the mixed solution was transferred into a Teflon-lined autoclave and heated at 105°C for 24 h to yield MOF-5 as cubic crystals. It is important to note that heating slowly decomposes the mixed solution and helps to deprotonate the organic ligand. The yellow crystals formed on the wall of reaction container, were repeatedly washed with DEF and soaked in anhydrous chloroform for 72 h followed by filtration. Finally, the resulting solid product was dried under vacuum at 120°C for 8 h.

Page 2 of 6

Synthesis of MOFs from DMF (sample B): The same procedure of sample (A) was used for synthesis of sample (B). The only difference was solvent type, which in this case, N, N-dimethylformamide (DMF) was used as solvent and the ligand concentration was doubled. After removal of sample from autoclave, a white product was filtered off and washed for three times with DMF, then treated with CHCl₃.

Activation method

Three step activation: (1) As-synthesized MOF-5 was washed with DEF/DMF three times (2) solvent exchange of DMF/DEF \leftrightarrow CHCl₃ was performed in which the sample was washed with a lower boiling point solvent for removal of the first solvent from the pores. For implementing this exchange, the mixture was immersed in CHCl₃ for 4 days and then the solvent removed under mild conditions. (3) After solvent exchange process, the sample was filtered and then the product was dried under vacuum at 120°C for 8 h.

Characterization

The structure of MOF-5, which was characterized by Fourier transform infrared spectrum of the samples, was recorded on a Bruker Vector 22 FT-IR spectrometer. The X-ray diffraction analysis was done on a Philips diffractometer with Co-K radiation source. The thermal stability of the sample was performed using thermogravimetric analysis (TGA/SDTA851e Mettler, Swiss) where 5.53 mg of sample was heated up to 700°C with a heating rate of 10°C/min in air atmosphere. To examine the morphology, the crystal structure and size of samples were analyzed by a CamScan S360 MV2300 scanning electron microscope (SEM) Cambridge with prior gold deposition. The nitrogen physical adsorption–desorption isotherm of MOF-5 adsorbent was measured at 77 K using a Micrometrics ASAP₂₀₁₀ analyzer and pore size distribution was obtained by built-in software of the mentioned device. Prior to the measurement, the sample was out-gassed at 250°C for 3 h.

Methane adsorption measurement

To examine the methane adsorption capacity of MOF-5, we have used volumetric method under the equilibrium condition. A schematic diagram of experimental apparatus is shown in Figure 3. Before each experiment, 1 g of sample was loaded in the adsorption cell and degassing pretreatment process of the adsorbent was carried out by vacuum pump at 433 K for 1.5 h. After de-gassing, the system was cooled to ambient temperature and then the temperature was kept fixed by a water bath.

Methane (99.9% purity) adsorption measurements were performed at constant temperature of 298 K, which was made by water bath. For investigating the effects of solvent type and activation process on gas adsorption capacity of samples, the pressure was increased up to 36 bar. By using Helium (99.99% purity) as a test gas for measuring the dead volumes (including hollow space and the connected tubes), the exact pressure decrease because of gas adsorption was obtained. By applying the SRK equation of state and MATLAB software, the adsorption rate was calculated at each pressure.

Results and Discussion

FT-IR spectra

FT-IR spectra for both samples (Figure 4) confirmed the presence of all functional groups and MOF-5 bonds forming. Two sharp peaks







at 1600 cm⁻¹ and 1405 cm⁻¹ in sample (A) and 1606 cm⁻¹ and 1409 cm⁻¹ in sample (B) were allocated to C-O linked to Zn. Small peaks, which take place in the range of 1330 cm⁻¹ to 895 cm⁻¹ in sample (A) and 1313 cm⁻¹ to 827 cm⁻¹ in sample (B), related to the C-H group present in the benzene ring of terephthalic acid. The bands between 2566 cm⁻¹ and 3095 cm⁻¹ in both samples which are due to methyl and $-CH_2$ - groups in DEF and DMF molecules, confirm the removal of guest molecules from the structure [32].

X-Ray diffraction

The X-ray diffraction of both sample A and B that were crystalline in nature, are represented in Figure 5. Sample (A) and (B) showed a sharp peak at 10.31° and 10.29°, respectively. Based on these results the crystals size of the sample A and sample B that have been obtained from scherrer equation, was 2491 Å and 2785 Å, respectively. The peak positions and relative intensities of synthesized samples were in good agreement with reported XRD patterns for MOF-5 [33].

Page 3 of 6

Thermo-gravimetric analysis

Figure 6 shows the TGA result for activated MOF-5/DEF. The result indicates a thermal stability up to 400°C, where decomposition of the framework starts. The TGA curve experiences only one main weight loss around 450°C, meaning that guest molecules like DEF, were evacuated completely. Although due to the humidity, about 3.8 wt% loss was still observed on the activated sample curve.

Scanning electron microscopy

The morphology of MOF-5 (sample A and B) was studied by scanning electron microscopy (SEM) after gold deposition (Figure 7). Figure 7(A), shows three dimensional cube-like microcrystals of sample (A), synthesized under the same conditions with sample (B), but in DEF as a solvent and molar ratio of H_2BDC and zinc nitrate (H_2BDC :Zn) 1:6. Figure 7(B) shows sample (B) as hexahedron crystals from a simple reaction of zinc nitrate and H_2BDC in DMF and molar ratio of H_2BDC and zinc nitrate (H_2BDC :Zn) of 1:3. Moreover, comparing Figure 7(A) and (B), it is obvious that MOF/DEF crystalline is smaller than MOF/DMF.

Nitrogen adsorption-desorption isotherm

The nitrogen physical adsorption–desorption isotherm of MOF-5 was measured at 77 K by using a Micrometrics $ASAP_{2010}$ analyzer. Prior to gas adsorption analysis, the samples were heated at 250°C for 3 h. From N₂ adsorption isotherms, PSD was evaluated using the Barrett–Joyner–Halenda (BJH) method. At 77 K the isotherm (Figure 8) shows a typical type II isotherm based on the IUPAC classification which corresponds to mono- and multilayer physical adsorption.















Figure 9 shows the pore volume and pore size distribution of samples as an important parameter of adsorbents. Clearly, Figure 9 demonstrated that the pore size distribution of MOF-5/DEF displays sharper and higher peak. The BET surface area of sample A and B were 2157 and 1532 m^2/g , respectively.

Methane adsorption capacity of samples

Figures 10 and 11 compare the methane adsorption isotherms of two MOF-5 samples synthesized by two different solvents of dimethyl formamide (A) and diethyl formamide (B), at temperature of 298 K and different pressures in the range of 0-36 bar. The presence of solvent molecules in the crystal cavities prevents entering the methane gas in holes. Thus, the pore volume of the material and consequently the adsorption capacity are significantly reduced. To solve this problem, a three-step activation process was performed to remove the guest solvent molecules from the frameworks.

The chart shows that methane adsorption capacity in the sample (A) is higher in comparison with sample (B). The higher CH_4 adsorption capacity of MOF-5/DEF can be ascribed to its smaller crystal size, smaller mean pore diameter and larger pore volume.

Table 1 represents methane adsorption capacity of MOF-5 synthesized in this work with other adsorbents reported in the literature. The temperature in all works is at room temperature and the maximum pressure is around 30 bar. As it is indicated from this table our adsorbents have the highest methane storage capacity of 18.15 and 11.36 mmol/g for samples synthesized by DEF (A) and DMF (B) in comparison with the data reported in the literature.

Correlation of Isotherms: The data fitting was performed by using Langmuir, Toth, Unilan and Sips adsorption models, which are generally used for micro porous adsorbents. Table 2 shows the equations and correlated parameters. From this study, we conclude that Toth and Sips models lead to good correlation of the data for both samples. On the other hand, the Langmuir model and the Unilan model did not produce satisfactory results for correlating the isotherms of methane adsorption at 298 K.

Conclusions

In summary, MOF-5 was hydrothermally synthesized by employing two different solvents. These MOFs structure were obtained from the Zn(BDC) system by DEF (sample A) and DMF (sample B) as solvents. Resulting components were characterized by FT-IR, XRD, SEM, TGA and ASAP analysis. Three-step activation mechanism of MOF-5 including repeatedly washed sample with initial solvent, solvent exchange, and drying under vacuum, enhance the capacity for methane adsorption by removal of almost all guest molecules (solvent and





Sample	Storage capacity Gravimetric (mmol/g)	Conditions pressure/ temperature	reference
Coconut shell-AC	7.4	35 bar / 300 K	[35]
CMK-3	5.2	35 bar / 298 K	[36]
MOF-5	14	30 bar / 298 K	[37]
SOC-MOF	4	27 bar / 298 K	[38]
MIL-53(AI) AI(OH)(bdc)	10.2	35 bar / 298 K	[39]
MOF-5/DMF	11.36	36 bar / 298 K	this study
MOF-5/DEF	18.15	36 bar / 298 K	this study

 $\label{eq:table_transform} \ensuremath{\text{Table 1: Comparison of the methane adsorption capacity of MOF-5 with other adsorbent.}$

Volume 5 • Issue 5 • 1000203

lsotherm	leatharm acuation	Isotherm constant		
Name	isotherm equation	sample (A)	sample (B)	
Langmuir	$Q_e = \frac{q_m b P}{1 + b P}$	q _m =30.23	20.69	
		b=0.045	0.041	
		R-square=0.995	0.986	
		RMSE=0.435	0.487	
Unilan Q_e =	$q_{m,i}\left(1+be^{s}P\right)$	q _m =30.24	20.44	
		b=0.045	0.041	
	$Q_e = \frac{1}{2s} ln \left(\frac{1}{1 + be^{-s}P} \right)$	s=0.0002	0.0008	
		R-square=0.995	0.986	
	-	RMSE=0.456	0.512	
Q_e Toth		q _m =20.4	11.77	
	$Q_e = \frac{q_m bP}{\left(1 + \left(bP\right)^n\right)^{\frac{1}{n}}}$	b=0.049	0.05	
		n=2.212	3.825	
		R-square=0.998	0.998	
		RMSE=0.258	0.158	
Sips	$Q_e = rac{q_m b P^{rac{1}{n}}}{1 + b P^{rac{1}{n}}}$	q _m =24.22	13.21	
		b=0.035	0.015	
		n=0.792	0.575	
		R-square=0.997	0.999	
		RMSE=0.336	0.123	

 Table 2: Isotherm equations used to model the adsorption experimental data and their parameter.

water) and vacating the pores. The measurements of methane storage at temperature of 298 K and 36 bar, indicated that the sample (A) can adsorbed 18.15 mmol/g, so it showed better methane storage behavior than sample (B) with 11.36 mmol/g at the same pressure. Experimental data for the methane adsorption of both samples were modeled by isotherms of Langmuir, Toth, Sips, and Unilan equations. It was finally found that the Toth and Sips models provide better correlation of adsorption isotherms.

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Page 5 of 6

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