REGULAR ARTICLE

Tuning the adsorption properties of UiO-66 via acetic acid modulation

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Abstract. UiO-66 (Universitetet i Oslo) is one of the most known metal-organic frameworks with high hydrothermal stability. In this work, a series of UiO-66 were prepared using acetic acid as a modulator to produce linker defects. Samples were characterized by X-ray powder diffraction, nitrogen adsorption-desorption isotherms, thermogravimetric analysis and adsorptive desulfurization test. Results indicated that increasing the amount of acetic acid to 30% equivalent with respect to terephthalic acid did not have an obvious negative effect on the structure. At the same time, surface area and micropore pore volume are further increased from 988 m²/g, 0.34 cm³/g to 1424 m²/g, 0.54 cm³/g. Adsorptive desulfurization performance is also significantly improved from 6.0 mg/g to 7.9 mg/g. So, the linker defects produced by acetic acid can remarkably enhance the adsorption ability. Adsorptive desulfurization kinetics indicates that while indicating the monomolecular layer, chemical adsorption occupies the dominant position, and there is no special chemical force formed between the defects and dibenzothiophene.

Keywords. Desulfurization; dibenzothiophene; acetic acid; defects; adsorption.

1. Introduction

Metal-organic frameworks (MOFs) attract much more interest in the field of adsorption due to their unique property based on the molecular scale porous character. MOFs have not only high specific surface areas and porosity but also interesting and tunable topologies.¹ There are several interesting characteristics that make MOFs unique and different from other conventional porous solids. These include (1) simple and easy synthesis compared to zeolites;² (2) huge surface areas and tunable porosities;¹ (3) the presence of coordinatively unsaturated sites (CUSs or open metal sites, OMSs);³ and (4) the ability to incorporate specific functionalities or active species without altering the framework topology.⁴ The stability of the MOFs is a crucial issue and much attention has been given to enhance the water stability of MOFs because one of the important barriers to utilize several types of MOFs in practical applications is the instability toward water (both in liquid and vapor phase).⁴ UiO-66 consists of 12-connected cluster [Zr₆(O)₄OH₄(O₂C)₁₂], terephthalic acid and its isorecticular series.⁵ UiO-66 has excellent thermal stability and

high surface area, so it has been extensively studied among other various metal-organic frameworks.⁶ The exceptional stability of UiO-66 can be attributed to the strong Zr-O bonds as well as the compact structure.⁶ UiO-66 features an arrangement of secondary building units (SBUs) which is topologically equivalent to a cubic close-packing.⁷ It exhibits good thermal and chemical stability, that can remain in the crystalline state even after exposure to 400 °C for a short period of time.⁸ The high thermal stability makes the regeneration of saturated adsorbent simpler, and the application prospect wider.

Due to the above advantages, UiO-66 is chosen as an adsorbent to remove sulfur from fuels. Because of increasingly high pressure mounting on the refineries to produce cleaner sulfur-free fuel products, deep desulfurization from transportation fuels has become an urgent issue for the petroleum refining industries.⁹ Hydrodesulfurization (HDS) is used for the removal of aliphatic sulfur compounds such as mercaptanes, sulfides and disulfides. However, other sulfur compounds such as thiophene and its derivatives belong to aromatic refractory sulfur and are difficult to remove by HDS.¹⁰ In addition, it requires high operation temperature, pressure and high dosage of catalyst to achieve the desired

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level, which is not economical. To overcome the limitations of HDS, various alternative processes have been studied. Adsorptive desulfurization is considered to be one of the most promising methods owing to the high capacity and selectivity in removing thiophene sulfur compounds at room temperature and atmospheric pressure, with no need for hydrogen.^{11–13}

In this work, we synthesized a series of UiO-66 samples with different amounts of linker defects by varying the amount of acetic acid (AcOH, acting as a modulator) in the synthesis system^{14,15} and investigated the effect of defects on the adsorption properties. To eliminate the interference of competitive adsorption, to make the effect of defects prominent, model oil instead of real gasoline is used as an adsorptive object.

2. Experimental

2.1 Synthesis of UiO-66 samples

UiO-66 samples were prepared following a recipe reported by Behrens's group¹⁶ (a modulator approach), that generates relatively large crystallites (>200 nm) that are beneficial to diffraction studies. Briefly, ZrCl₄ and the linker precursor terephthalic acid (BDC) in the equivalent molar ratio were dissolved in N,N-dimethyl formamide (DMF) in a Teflon-capped glass jar by using ultrasound for about 10 min. Acetic acid (AcOH, acting as a modulator) was then added to the solution and dispersed by ultrasound for another 10 min. The tightly capped jars were kept in an oven at 120 °C under static conditions for 24 h. White precipitates were produced and were isolated by centrifugation. Final samples were gotten after the white precipitates were washed with DMF to remove unreacted precursors and solvent-exchanged with acetone for six times. According to the amount of acetic acid added to the synthesis system (0–30% equiv. with respect to terephthalic acid), the final samples are denoted as UiO-66-0, UiO-66-10, UiO-66-20 and UiO-66-30, respectively.

All reagents were obtained from Sinopharm Chemical Reagent Co. Ltd. of analytical grade and used without any further purification.

2.2 Characterization of sample

X-ray diffraction analysis of all the adsorbents in the powder state to characterize the crystal structure was carried out using a Siemens Model D-500 X-ray diffractometer equipped with Ni-filtered Cu K α radiation (40 kV, 100 mA). The patterns were recorded over a range of 2 θ angles from 5–80° in steps of 0.02°/s. The surface area and pore volume were obtained from nitrogen isotherms determined at liquid nitrogen temperature on JW-BK200C. Before testing, the samples were degassed under vacuum condition for 300 min at 150 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore volume was estimated from the last

point of the isotherm. Pore size distribution was determined by nonlocal density functional theory (NLDFT) with a slit pore model. Thermo-gravimetric (TGA) curves were obtained using a TA Instruments thermal analyzer. The samples were exposed to an increase in temperature of 10 °C/min up to 800 °C while the nitrogen flow rate was held constant at 100 mL/min.

2.3 Adsorption experiments

Dibenzothiophene (99%, Acros) and n-octane (ACS reagent grade, Fisher) were employed to be the model components for sulfur compound and saturated hydrocarbon in gasoline distillate, and sulfur concentration is 224 ppm.

Static tests were carried out to evaluate the adsorption desulfurization of the adsorbents at room temperature (25 °C) and atmosphere pressure (0.1 MPa). Adsorbent (0.1 g) was added to a 10 mL mixture sample in an airtight container operating at room temperature for 12 h. Then the concentration of sulfur was analyzed by TS-3000 fluorescence sulfur tester. The sulfur capacity of the adsorbent was calculated as follows:

$$\text{Sulfur capacity (mg S/g adsorbent)} = (C_0 - C_t) \cdot V / m \quad (1)$$

Where C_0 is the initial concentration of sulfur (mg/L), C_t is the final concentration of sulfur (mg/L), V is the volume of the mixture (L), m is the mass of the adsorbent (g).

2.4 Adsorption kinetics

An aliquot of 100 mg of UiO-66 materials was introduced into a conical beaker containing 10.0 mL of model oil. The beaker was placed in a water bath with magnetic stirring at a fixed temperature (25 °C). The mixture was sampled at specific intervals. To do this, 1 mL of the mixture was drawn out with a syringe and filtered by centrifugal forces. Then, each filtrate was analyzed by fluorescence sulfur tester to determine the remaining concentration.

2.5 Adsorption isotherms

UiO-66 adsorbents samples (100 mg each) were introduced into different conical beakers. Then, 10.0 mL of the model oil was added into each conical beaker. The conical beakers which contained those mixtures were placed in a water bath and stirred at a fixed temperature (25, 35 and 45 °C, separately) for 12 h. The mixtures were drawn out with a syringe and filtered by centrifugal forces. Then the filtrates were analyzed to determine the remaining concentration (C_e , mg/L) using fluorescence sulfur tester. The equilibrium adsorption capacity (Q_e , mg/g) was calculated according to the following equation:

$$Q_e = V \cdot (C_0 - C_e) / m \quad (2)$$

Where V (L) is the volume of model oil solution; m (g) is the weight of UiO-66 adsorbent.

3. Results and Discussion

3.1 Morphology analysis

UiO-66 is a highly important prototypical zirconium metal-organic framework compound because of its excellent stabilities not typically found in common porous MOFs. In its ideal crystal structure, each Zr metal center is fully coordinated by twelve organic linkers to form a highly connected framework. Once the organic linker separates from the core Zr, a defect site is formed, and the increase in defect sites usually results in a large increase of the catalytic activity. Schaate¹⁶ and Fredrik¹⁵ discussed the method in which the use of specific synthesis modulators allow for a high level of control over the number and nature of the defect sites in the zirconium terephthalate MOF UiO-66. They introduce acetic acid or trifluoroacetic acid to partially substitute originally terephthalic acid linker. Acetic acid has typically similar chemical functionality as the acetic acid linker, but it is monofunctional rather than bifunctional, resulting in the missing of linker and creation of functionalized pores. By varying the concentration of the acetic acid modulator, the linker vacancies can be tuned systematically, leading to dramatically enhanced porosity and defect sites. We investigated the possibilities of systematically tuning porosities and adsorption ability of UiO-66 by varying the addition amount of acetic acid (AcOH) modulator, which transferred the defect sites into adsorption active sites. XRD patterns (Figure 1) of all the samples were in good agreement with the previous reports,¹⁷ confirming that the formation of pure crystalline UiO-66 phase. However, their relative crystallinities were different and the samples prepared with adding more acetic acid had lower crystallinities. The weight of UiO-66 samples that were derived also decreased with the increasing amount of acetic acid. This result is in agreement with that observed by Shearer and his co-workers.¹⁵

The N₂ adsorption-desorption isotherm analysis results of the different UiO-66 samples are displayed in Table 1. Pore size distributions in Figure 2 were derived using the NLDFT model for these samples with missing-linker defects. Despite the fact that the missing-linkers represent a type of ‘imperfect’ structure, one good consequence is that of boosting the porosity of the MOF material. Indeed, for a perfect UiO-66 crystal, the theoretical pore volume and surface areas are 0.426 cm³/g and 954 m²/g.¹⁷ While, for an imperfect crystal, for example, after one of the twelve linkers is artificially removed for every metal center in the unit cell (i.e., a hypothetical model structure with ordered defects), the theoretical pore volume and surface area increase

Figure 1. XRD patterns of UiO-66 prepared with different acetic acid addition level.

significantly to 0.502 cm³/g and 1433 m²/g. We found that by increasing the amount of AcOH, the surface area and micropore pore volume is further increased from 988 m²/g and 0.34 cm³/g to 1424 m²/g and 0.54 cm³/g (similar with the theoretically calculated value). From the pore size distributions, it is seen that micropores with a diameter of about 1.1 nm dominate in all the UiO-66s, and the pores around 1.4 nm are in a decided minority.

The specific surface area and pore volumes increase in the following order: UiO-66-0 < UiO-66-10 < UiO-66-20 < UiO-66-30. The use of AcOH during the synthesis results in partial substitution of terephthalates. AcOH is much easier to be removed from the hexanuclear Zr cluster. The following thermal activation results in a more open framework with a large number of open sites. Consequently, the addition of AcOH leads to a highly surface area and pore volume UiO-66 material. For porous material, higher porosity is generally preferred and beneficial for most applications, thus UiO-66-30 may be a more favorable adsorbent for dibenzothiophene (DBT) removal.

3.2 Effect of the amount of AcOH on desulfurization property

The sulfur capacities of different UiO-66s are displayed in Figure 3. The adsorption capacity for DBT is in the order UiO-66-10 < UiO-66-20 < UiO-66-30. It is evident that more the amounts of AcOH, the larger is the capacity of DBT adsorption. In comparison to the results of N₂ adsorption-desorption isotherms analysis, we can find that the missing linkers are beneficial to the desulfurization performance. So in the subsequent

Table 1. Structural properties of UiO-66s samples.

Sample	Surface area (m ² /g)	Micropore volume (cm ³ /g)	Total pore volume (cm ³ /g)
UiO-66-0	987.95	0.369	0.495
UiO-66-10	1169.50	0.422	0.541
UiO-66-20	1326.36	0.515	0.566
UiO-66-30	1424.03	0.537	0.567

Figure 2. N₂ isotherms and pore size distributions of different UiO-66 samples. **Figure 3.** Effect of AcOH amount and calcination temperature on desulfurization.

work, we primarily focus on the adsorption behavior of UiO-66-30.

3.3 Adsorption behaviors over UiO-66-30

Thermal analysis was performed in nitrogen with a heating rate of 10 °C/min, and TGA/DSC curves are shown

in Figure 4. The TGA curve of three main weight losses can be divided into three stages: (i) from room temperature to 100 °C, (ii) from 100 °C to 300 °C, (iii) from 400 °C to 600 °C. The weight was maintained as nearly constant when the temperature was over 600 °C. In the first stage, the minor weight loss is attributed to the thermal desorption of water. In the second stage, the obvious weight loss is associated with the removal of DMF that had not been washed thoroughly by filtering. The final weight loss in the third stage is mainly attributed to the thermal desorption of linkers.

The influence of calcination temperature ranging from 120 °C to 500 °C on the performance of the desulfurization over UiO-66-30 was studied. As shown in Figure 3-B, the best calcination temperature of UiO-66-30 is 300 °C. Combined with the results of XRD patterns and TGA/DSC curves, it can be concluded that the skeletal structure had collapsed when the temperature was over 400 °C. We believe it was caused by the thermal desorption of the linkers, so the structure has been destroyed. When the temperature is lower than 300 °C, the residual DMF couldn't be removed efficiently and caused poor sulfur capacity.

Figure 4. Effect of calcination on UiO-66-30.

Figure 5. Adsorption kinetic and adsorption isotherms of dibenzothiophene on UiO-66-30 at different temperature.

3.4 Adsorption kinetics of DBT on UiO-66-30

The kinetic curve of DBT adsorption on UiO-66-30 is shown in Figure 5. All the profiles are similar in adsorption tendency: the adsorption amount increases rapidly at the beginning till 50 min, and then gradually levels off; saturated adsorption is achieved after 2 h. To understand the adsorption kinetics further, the pseudo-first-order model and pseudo-second-order model are applied to fit the kinetic data.

The pseudo-first-order and pseudo-second-order model can be represented by Eq. 3 and Eq. 4

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{q_e k_2} \quad (4)$$

And their error calculation formula (Eq. 5) is as followed.

$$SE = \sqrt{\frac{1}{n} (q_{ep} - q_e)^2} \quad (5)$$

Where q_t and q_e (mgS/g) are the amounts of sulfur adsorbed on UiO-66-30 at time t (min) and equilibrium. q_e (mgS/g) is fitting equilibrium capacity. k_1 (min^{-1}) and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the pseudo-first-order and pseudo-second-order adsorption rate constant.

As given in Table 2 and Table 3, both the pseudo-first-order and pseudo-second-order model fit well in the adsorption data, but the pseudo-second-order model fits much better in the adsorption data. It is assumed that weak chemical interactions are the main forces involved in the adsorption processes. Thus, it can be speculated that by increasing the specific surface area, the microporous structures promote adsorption capacity of UiO-66s toward DBT, which is in good accordance with the N_2 adsorption-desorption isotherms analysis results.

3.5 Adsorption isotherm of DBT on UiO-66-30

The saturation adsorption capacities of UiO-66-30 toward DBT were determined at different DBT concentrations and temperatures. The saturation adsorption data were fitted with the Langmuir (Eq. 6) and Freundlich (Eq. 7) isothermal equations to estimate the adsorption features of UiO-66-30.

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (6)$$

$$\lg q_e = \lg K_0 + \frac{1}{n} \lg C_e \quad (7)$$

Where q_e (mgS/g) and C_e (ug/g) are adsorption amount and concentration of sulfur at adsorption equilibrium; q_m (mgS/g) represents maximum adsorption; b (g/ug) is the Langmuir constant, which is related to the affinity of binding sites; K_0 (mg/g) and n are both Freundlich constants that represent the adsorption capacity and adsorption favorability, respectively.

Table 2. The pseudo-first-order equations and parameters.

Presudo-first-order equations	q_e (mg-S/g)	k_1 (min ⁻¹)	SE	R^2
$dq_t/dt = 0.0203(26.01 - q_t)$	16.087	0.0203	3.310	0.964

Table 3. The pseudo-second-order equations and parameters.

Presudo-second-order equations	q_e mg S/g	K_2 g.mg ⁻¹ .min ⁻¹	u mg/(g.min)	$T_{1/2}$ min ⁻¹	SE	R^2
$dq_t/dt = 0.0023(26.01 - q_t)^2$	26.981	0.0023	1.659	16.256	0.328	0.997

Table 4. Langmuir thermodynamic fitting parameters of adsorption isotherm.

T/°C	Langmuir equations	q_m /mg/g	b /(ug/g) ⁻¹	R^2
25	$y=0.0278x+7.8875$	35.9712	0.003524	0.9933
35	$y=0.0323x+9.0037$	30.9598	0.003587	0.9994
45	$y=0.0411x+10.284$	24.3309	0.003996	0.9989

Table 5. Freundlich thermodynamic fitting parameters of adsorption isotherm.

T/°C	Freundlich equations	K_0 /mg/g	n	R^2
25	$y=0.5429x-0.1064$	0.8991	1.8420	0.9971
35	$y=0.5478x-0.1792$	0.8359	1.8255	0.9856
45	$y=0.5155x-0.1825$	0.8332	1.9399	0.9786

As shown in Figure 5, the isotherm is an L-shaped convex shape, indicating that there is a force that promotes adsorption. The adsorption capacity increased gradually when the concentration of DBT at adsorption equilibrium increased. When the temperature changed, the amount of increase of the capacity also became different. The calculated parameters of the curve-fitting equations for Langmuir and Freundlich models are listed in Table 4 and Table 5.

Both Langmuir and Freundlich models fit well with the experimental data. Actually, both the models have some limitations of presenting different (covalent or noncovalent) adsorption processes on UiO-66-30 at different concentration ranges. The Langmuir isotherm model refers to the system with one kind of binding site, whereas the Freundlich equation does not model the saturated portion in the adsorption isotherm curves. The high R^2 values for Langmuir fittings approved that the Langmuir models are suitable to simulate the adsorption behavior of UiO-66-30. The b values are related to the affinity of binding sites. The b values are positive and increased with the increase of temperature. The rising temperature is unfavorable to the

adsorption, indicating that the adsorption desulfurization process is the exothermic process. However, the values of Freundlich constant n are all larger than 1, representing the favorable adsorption conditions. The K_0 values decreased with the increase of temperature, indicating that the forces between DBT and adsorbents are weakened. On the whole, the R^2 values of Langmuir models are higher than those of Freundlich models, indicating that monomolecular layer chemical adsorption occupies the dominant position.

Previously, people focused on the adsorptive desulfurization by Cu-modified materials including SBA-15, MCM-48, SiO₂, KIT-6, respectively, and drew the conclusion that the active species for desulfurization is cuprous species. The cuprous species is derived from the autoreduction of CuO under heating in helium. Cu⁺ can form σ bonds with their empty s-orbital and in addition, their d-orbitals can back-donate electron density to the antibonding π -orbitals of sulfur rings through the π -complexation between thiophene derivatives and Cu⁺ achieving adsorptive desulfurization. This is the widely recognized π -complex mechanism and we think UiO-66 in this work also follow the same mechanism. In the structure of UiO-66, the positive electrical charge of Zr is divided by twelve linkers, during the calcination, some linkers are separated from the core Zr cluster, charge balance is disequilibrated and the positive charge of Zr becomes more and more enhanced. A weak chemical force formed between positive Zr and DBT and desulfurization by adsorption is realized. This weak chemical force is not definite now, maybe it is Van der Waals force, or hydrogen bond or π -complexation force, but what is

certain is that this chemical force is very weak, as the desorption occurs when the temperature is only higher than 60 °C.

4. Conclusions

A series of UiO-66 samples with different amounts of linker defects were prepared by varying the amount of acetic acid in the synthesis system. X-ray powder diffraction results indicated that increasing the amount of acetic acid to 30% equivalent with respect to terephthalic acid did not have an obvious negative effect on the structure. The effect of defects on the adsorption properties is investigated by both nitrogen adsorption-desorption isotherms and adsorptive desulfurization test. Experimental data showed that the surface area and micropore pore volume is further increased from 988 m²/g, 0.34 cm³/g to 1424 m²/g, 0.54 cm³/g. Adsorptive desulfurization performance is also significantly improved from 6.0 mg/g to 7.9 mg/g. So the linker defects produced by acetic acid can remarkably enhance the adsorption ability. Adsorptive desulfurization kinetics indicate that indicating the monomolecular layer chemical adsorption occupies the dominant position, and there is no special chemical force formed between the defects and dibenzothiophene.

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