Study of the Influence of Pore Width on the Disposal of Benzene Employing Tunable OMCs

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ABSTRACT: By employing SBA-15 as a hard template and boric acid as a pore-expanding agent, we synthesized a series of tunable ordered mesoporous carbons (OMCs) with high specific surface areas and large pore volumes. The synthesized OMCs were used as adsorbents for benzene disposal to explore the influence of pore width on the adsorption of benzene. The XRD and nitrogen adsorption results revealed that the pore sizes of OMCs were contracted at certain values, within the range of 3.4−7.7 nm. The adsorption results for benzene on the OMCs showed that there was a gradual decrease in adsorption potential as the pore size of the adsorbent material increased. In addition, an evaluation of the dynamic adsorption of benzene per unit surface area indicated that the adsorption behaviors were strongly influenced by the pore width of the adsorbent material.

1. INTRODUCTION

Volatile organic compounds (VOCs) are a type of special gas pollutants emitted from different sources and processes. Considering the inherently hazardous effects of VOCs on the environment and human health, the control of VOC emissions has attracted much attention in recent years. Many technologies, such as adsorption, absorption, catalytic oxidation, and biofiltration, have been used in practical applications for the removal of industrial VOCs. Among these methods, adsorption technology has always been a prominent choice because of its efficiency and relatively low cost, especially in adsorption procedures for recovering high-value adsorbates. One of the most important issues in adsorption technology is the choice of proper adsorbent. To date, carbon materials such as activated carbon and activated carbon fiber have been widely used as efficient adsorbents for various types of VOCs. However, the irregularly shaped pores and relatively small pore sizes of such microporous adsorbents lead to pore blocking and a decrease of the adsorption/desorption rate during adsorption procedures, which limits the further improvement of their adsorption performances. Moreover, to prepare adsorbents with high adsorption efficiencies, further research and studies associated with the adsorption mechanism are still needed.

Ordered mesoporous carbon (OMC) is a type of special carbon material that has regular pore shapes and large specific surface areas and pore volumes and is quite different from traditional carbon adsorbents. Moreover, the pore size distributions of OMCs can be easily tuned by adding some pore-expanding agents or selecting different surfactant templates. Benefiting from these advantages, OMCs can be used as efficient adsorbents and model materials in the adsorption field. He and Hu investigated the adsorption properties of CMK-3 toward three different commercial anionic dyes. Their results indicated that CMK-3 can be used as an efficient adsorbent for the removal of anionic dyes, with adsorption capacities that are 90−200% higher than those traditional activated carbons. Saha and Deng employed OMC doped with metals as potential adsorbents for hydrogen storage and found that the adsorption capacity of hydrogen at 25 °C and 300 bar on nickel-doped OMC could reach 2.14 wt %. Recently, Yuan et al. studied the adsorption and separation properties of CO2, N2, and CH4 on OMC. The results revealed that OMC has high adsorption capacities for CO2 and CH4 and high selectivities for CO2/CH4, CH4/N2, and CO2/N2 mixtures simultaneously. All of the relevant research results confirm the superior adsorption properties of OMCs. However, to the best of our knowledge, little research has been performed on the adsorption properties of VOCs on OMCs, considering the inherently hazardous properties of VOCs and the urgent need for their disposal. Moreover, in view of adsorbent characteristics that influence adsorption properties, most studies have focused on pore volume whereas few have considered the effects of the pore size distribution of the adsorbent.

In this research, benzene was selected as a typical adsorbent for VOCs, and the main purpose of this study was to investigate the adsorption properties of benzene on OMCs with different pore sizes. OMCs were synthesized through the hard template method, using SBA-15 as the hard template and sucrose as the carbon precursor. SBA-15 is a type of mesoporous silica material with ordered concentrated pores, and it was widely used as a hard template because the silica can be removed by HF or NaOH solution. Furthermore, during the synthesis process, boric acid was added as a pore-expanding agent to produce OMCs with tunable pore size distributions without changing the primary pore structure. During the carbonization process, the boric acid is expected to form boron oxide and borosilicate nanolayers between the silica and carbon frameworks. Removal of these compounds leads to the enlargement of the pores in the resultant OMC materials. The adsorption properties of benzene on OMCs under static and dynamic conditions were systematically studied. Meanwhile, the effects of OMC pore size on the adsorption properties of benzene are also discussed.

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2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) triblock copolymer Pluronic 123 was purchased from Sigma-Aldrich. Ethyl silicate (SiO₂, >28.4%), hydrochloric acid (36.0–38.0%), ethanol (>99.7%), boric acid (>99.8%), sucrose (>99.0%), sulfuric acid (95.0–98.0%), hydrofluoric acid (>40.0%) were purchased from Sigma Chemical Reagent Company. All chemicals were used as received without any purification process. Distilled water was used in all of the experiments.

2.2. Synthesis of OMC. The hard template method was employed to synthesize the OMCs according to the reported procedure with some modifications. During the synthetic procedure, SBA-15 was selected as the hard template, and sucrose was used as the carbon precursor. First, the soft template synthesis method was employed to synthesize siliceous template SBA-15. The triblock copolymer P123 and ethyl silicate were employed as the sources of template and silica, respectively. Typically, 32 g of Pluronic 123 was first dissolved in 1000 g of distilled water and 200 g of HCl, and the mixture was stirred at 40 °C for 4 h to form a template solution. Then, 68.8 g of ethyl silicate was added to the solution with vigorous stirring at 40 °C for 15 min. After that, the solution was aged at 40 and 100 °C for 24 h each. Afterward, the sediment was washed thoroughly with ethanol, and SBA-15 was obtained by calcination at 550 °C in air for 2 h.

The synthesized mesoporous siliceous SBA-15 material was then used as a template for the synthesis of OMCs. Sucrose and boric acid were used as the carbon source and pore-expanding agent, respectively. In a typical synthesis process, 0.141 g of sulfuric acid, 1.25 g of sucrose, and a certain amount of boric acid were dissolved into 5 mL of distilled water, and then 1 g of SBA-15 was added to the solution and dispersed by the supersonic method. The resultant pasty sample was dried at 70 °C for 1 h and then precarbonized at 100 and 160 °C for 6 h each. The obtained dark-brown solid sample was then ground into a powder, and the above immobilization and carbonization processes were repeated. The quality of the impregnation liquor for the second time was 66% of that of the first time, with the same mass ratio of sulfuric acid, sucrose, boric acid, and water. The obtained composites were carbonized at 900 °C for 10 h to remove the physically adsorbed water molecules and other impurities. The inner diameter of the adsorption column was 6 mm. In each experiment, 50 mg of OMC was loaded, and the total gas flow rate was maintained at 50 mL min⁻¹. During the whole experimental procedure, the concentration of benzene at the outlet of the reactor was determined intermittently using a photoionization VOC detector. The breakthrough time is defined as the time when the outlet concentration was about 5% of the inlet concentration. The adsorbed amounts were calculated by the equation

\[ q = \frac{F}{M_w} (C_f - \int_0^t C_o \, dt) \]

where \( q \) is the adsorbed amount (mmol·g⁻¹), \( F \) is the volumetric flow rate of carrier gas (mL·min⁻¹), \( w \) is the net weight of adsorbent (g), \( M \) is the molar mass of benzene (g·mol⁻¹), \( C_f \) represents the benzene concentration at the inlet (g·mL⁻¹), \( C_o \) is the benzene concentration at the outlet (g·mL⁻¹), and \( t \) is the saturation time of adsorbent (min).

The isosteric heats of adsorption are usually used as a measure of the surface heterogeneity of a solid adsorbent. The values can be calculated by the Clausius–Clapeyron equation, which can be written in the form

\[ Q_{st} = -R \left( \frac{\partial \ln P}{\partial T^{-1}} \right)_{\theta} \]

where \( Q_{st} \) is the isosteric heat of adsorption at a given uptake \( \theta \), \( P \) is the vapor pressure, \( T \) is the temperature, and \( R \) is the gas constant.

3. RESULTS AND DISCUSSION

3.1. Characterization of OMC. The XRD patterns of SBA-15 and the OMCs are depicted in Figure 1. The three diffraction peaks in the range 0.5–2° can be indexed to the (100), (110), and (200) reflections of SBA-15 in the dimensional hexagonal space group p6mm, implying the successful synthesis of SBA-15. All of the OMCs exhibited diffraction peak at 2θ = 1–1.2°, which corresponds to the two-dimensional hexagonal crystal structure (100) diffraction,
indicating that the OMCs reproduced the mesoscopic structure of SBA-15. For these OMCs, there was a slight shift to lower angle for the diffraction peak at $2\theta = 1^\circ - 1.2^\circ$. This might be due to the increased pore width of the OMCs, caused by the increased dosage of boric acid. In addition, a small diminution of intensity for the characteristic peaks occurred with increasing boric acid dosage, indicating a slight decrease of the long-range order of the OMCs.18

To further illustrate the pore structures of the materials, nitrogen adsorption/desorption measurements were employed. The isotherms of SBA-15 and OMCs are presented in Figure 2. As shown in Figure 2, only small amounts of nitrogen adsorbed on the OMCs in the low relative pressure range, and the adsorbed nitrogen was mainly contributed by mesopores, implying the mesoporous nature of the materials. With an increase in the relative pressure, typical type IV isotherms appeared according to the IUPAC classification, indicating the presence of a concentrated distribution of mesopores.30 Moreover, all of the OMCs demonstrated an H1-type hysteresis loop. With increasing boric acid dosage, the OMCs’ hysteresis loops shifted to higher relative pressure, indicating a gradual increase in the concentrated mesopores of the OMCs, which agrees well with the XRD results. Additionally, the inflection point of each isotherm where capillary condensation occurs grew gradually to a higher relative pressure value as the dosage of boric acid increased. The pore size distribution curves of the OMCs obtained from the BJH model are also shown in Figure 2. They are mainly in the range of 2–12 nm, as the larger parts of the pore size can be neglected. The pore size distributions of the OMCs were concentrated at certain widths. The most probable distributed pores were 3.5, 4.0, 4.5, 5.2, 6.0, and 7.0 nm, respectively, when the pore-expanding agent was increased from 20% to 75% in sequence. It is clear that an increase in the central pore diameter occurred as the amount of pore-expanding agent rose, indicating the successful synthesis of pore-width-tunable OMCs.

The texture properties of the samples are summarized in Table 1. Generally, the pore volumes and micropore volumes of the OMCs were almost the same. The micropore volume of SBA-15 accounted for about 7% of the total pore volume; this value is similar to that obtained in previous research, confirming the successful synthesis of SBA-15.51 With increasing amount of boric acid, an increase in the average pore diameter was observed, and thus, the specific surface area decreased accordingly. Corresponding data revealed that, as the average pore diameter increased from 3.4 nm for OMC-20% to 7.7 nm for OMC-75%, the specific surface area decreased by about 42%.

To investigate the pore structure of the materials more intuitively, transmission electron microscopy TEM images of SBA-15 and OMCs were recorded and are shown in Figure 3. Clearly, all of the samples exhibited an ordered two-dimensional hexagonal mesoporous structure. Meanwhile, a slight decrease in the long-range ordered structure can be seen, as the amount of boric acid increased, which is consistent with the XRD patterns in Figure 1.

### Table 1. Texture Properties of SBA-15 and OMCs

| sample       | surface area (m²/g) | pore volume (cm³/g) | micropore area (m²/g) | micropore volume (cm³/g) | average pore size (nm) |
|--------------|---------------------|--------------------|-----------------------|--------------------------|------------------------|
| SBA-15       | 844.2               | 0.98               | 134.7                 | 0.07                     | 5.7                    |
| OMC-20%      | 1120.8              | 1.00               | 199.9                 | 0.09                     | 3.4                    |
| OMC-35%      | 893.5               | 0.94               | 210.3                 | 0.10                     | 3.9                    |
| OMC-45%      | 792.7               | 0.97               | 294.1                 | 0.15                     | 4.9                    |
| OMC-55%      | 698.8               | 1.02               | 200.3                 | 0.10                     | 5.4                    |
| OMC-75%      | 640.9               | 1.22               | 223.6                 | 0.11                     | 7.7                    |

3.2. Static Adsorption of Benzene on OMCs.

Adsorption isotherms are important because they can be regarded as the primary source of information on a particular...
3.3. Isoteric Heats of Adsorption. The corresponding $Q_e$ values of benzene on the OMCs were calculated and are shown in Figure 5. Sample OMC-20% exhibits the highest isoteric heats of adsorption, especially in the beginning of the adsorption process. In comparison with that of OMC-20%, the variations of the isoteric heats of the other OMCs seem to be less obvious, because the curves are more stable. Considering that the pore diameter of OMC-20% is much smaller than those of the other OMCs, it can be concluded that OMCs with narrower pore widths are more accessible for benzene. In addition, although the isoteric heats of OMC-35%, OMC-45%, and OMC-55% are close to each other, it can be concluded that, overall, the isoteric heat decreased with increasing pore size, as the values of the isoteric heat for OMC-20% are the highest and the corresponding values for OMC-75% are the lowest. Thus, one can speculate that an adsorbent with a narrower pore diameter has a higher adsorption potential for the benzene adsorption, that is, that benzene molecules are more likely to be adsorbed onto an adsorbent with a narrower pore diameter.

3.4. Dynamic Adsorption of Benzene on OMCs. In practical applications, adsorbents are usually loaded in a fixed-bed apparatus and used for adsorption. Thus, the dynamic adsorption of benzene vapor onto the OMCs was performed to simulate the real situation, and the results are shown in Figure 6. As can be seen from Figure 6, there is a clear regularity in dynamic breakthrough curves among the various OMCs. For the OMCs with larger average pore diameters, the breakthrough times are correspondingly shorter. Generally, the longer the breakthrough time is, the higher the dynamic adsorption capacity of an adsorbent will be. Thus, the gradually increased breakthrough time from OMC-75% to OMC-20%, implies higher adsorption amounts of benzene in the same sequence. The dynamic breakthrough times and adsorption amounts of benzene in the OMCs are reported in Table 2. As the pore size of the OMCs increased from 3.4 to 7.7 nm, the breakthrough time decreased from 32 to 6 min, and the corresponding adsorption amount decreased from 0.114 to 0.041 mmol/g.

It is meaningful to reveal how the microscopic structure of an adsorbent is reflected in the macroscopic characteristics of adsorption by employing a single type of adsorbent. In this study, the prepared OMCs had similar total pore volumes and micropore volumes, but the tunable pore sizes and BET specific surface areas exhibited greater variations (the BET specific surface area decreased from 1120.8 to 640.9 m²/g). To eliminate the influence of the surface area and pore volume, normalized adsorption amounts, namely, the adsorption amounts per unit surface area and unit pore volume, were determined (see Table 2). The trend that the dynamic adsorption capacity decreased with the enlargement of the pore size still holds. Furthermore, the amounts adsorbed per unit surface area and per unit pore volume for different samples are depicted in Figure 7, to reveal the relationships between adsorption characteristics and the pore width more intuitively.

Figure 3. TEM images of (a) SBA-15, (b) OMC-20%, (c) OMC-35%, (d) OMC-45%, (e) OMC-55%, and (f) OMC-75%.
Figure 4. Adsorption isotherms of benzene vapor on (a) OMC-20%, (b) OMC-35%, (c) OMC-45%, (d) OMC-55%, and (e) OMC-75% at 25, 35, and 45 °C and (f) collective adsorption isotherms of benzene at 25 °C on OMCs.

Figure 5. Variation of isosteric heats for benzene adsorption onto OMCs.

Figure 6. Experimental dynamic breakthrough curves of benzene vapor onto OMCs.
This figure helps to conceptualize the relationship between pore width and dynamic adsorption capacity. Clearly, the benzene adsorption amounts per unit surface area and pore volume decreased with increasing average pore diameters of the OMCs. Thus, this figure is able to clarify the relationships between the adsorption characteristics and the textural property unequivocally that, in the mesoporous range, a narrower pore size effectively increases the utilization of the adsorbent’s surface area and pore volume. In a word, the pore size distribution is the dominant factor that influences the adsorption characteristics of benzene on the OMCs.

4. CONCLUSIONS

In this work, OMCs were synthesized by a hard template method, and boric acid was added during the synthetic procedure to tune the pore sizes in the small mesopore range of 3–8 nm without changing the main texture of the OMCs. The resultant OMCs were used as adsorbents to evaluate their adsorption properties for benzene. A study of the isosteric heats of adsorption revealed that the OMCs with narrower pore sizes have higher adsorption potentials. The static and dynamic adsorption amounts of benzene no the OMCs indicate that the pore size distribution is the dominant factor influencing the adsorbed amounts of benzene and that, in the mesoporous range, a narrower average pore size is preferred for adsorption and results in a higher adsorbed amount.

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