Adsorption properties of benzene and water vapor on hyper-cross-linked polymers

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A series of hyper-cross-linked polymers (HCPs) was synthesized via a post-cross-linking reaction using low-cross-linked polydivinylbenzene (PDVB) as precursor and 4,4'-bis(chloromethyl)biphenyl (BCMBP) as cross-linking reagent. The effects of various amounts of BCMBP on the structures of the hyper-cross-linked polymers were discussed. The resultant typical HCP-1.3 possesses hierarchical micro/meso pore structures and a high stability up to 400 °C. The increased specific surface area and total pore volume of HCP-1.3, which reach 1231 m² g⁻¹ and 1.99 cm³ g⁻¹, respectively, imply the high cross-linking ability of BCMBP. In order to study the adsorption properties of HCP-1.3, benzene and water were selected as typical adsorbates for their non-polar and polar characteristics. The static adsorption amount of benzene on HCP-1.3 is 30.0 mmol g⁻¹, which is two times higher than the corresponding adsorbed water amount, suggesting a potential hydrophobic property of HCP-1.3. Dynamic adsorption was performed with a fixed-bed column to simulate the real situation under dry and 30% relative humidity conditions. The results show the dynamic adsorption amount under the 30% relative humidity condition is as high as 90% of the value under dry conditions, implying HCP-1.3 would be a promising adsorbent for VOC adsorption under both dry and humid conditions.

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Introduction

Volatile organic compounds (VOCs), including kinds of organic chemical, are one of the most important pollutants emitted from anthropical activities such as industrial processes.^{1,2} Most of them are hazardous to the environment, contributing to serious problems such as destruction of the ozone layer, photochemical smog and global warming. Also, long-term exposure to VOCs is harmful to human health, and may cause deformity, pathogenic and even fatal diseases.³ Because of the increasing concern on environmental protection and human health, research for VOCs abatement technology has been of great interest in recent years.

Among all methods in practical application to remove VOCs, adsorption technology has always been a prior choice for its efficiency, low cost and convenience,⁴⁻⁶ especially in the recovery of high-value adsorbates.^{2,3,5} The most important issue in adsorption technology is the choice of proper adsorbents, and an ideal adsorbent for VOCs adsorption is expected to possess a large adsorption capacity, favorable hydrophobic performance and an easy regeneration property.^{1,7} Until now, activated carbon has been most widely used as an adsorbent for its low cost and good adsorption capacity.^{7,8} However, some

intrinsic weaknesses such as its hydrophilic properties and pore blocking cause problems in various operational conditions.^{1,7} Thus, a new kind of adsorbent possessing high surface area and good hydrophobicity, as well as high thermal stability is in great need for VOCs removal.⁸

In recent years, a new kind of polymeric adsorbent, namely hyper-cross-linked polymers, which were first synthesized by Davankov,⁹ have gained great attention for the removal of organic compounds from industrial effluents.¹⁰⁻¹⁶ The hyper-cross-linked polymers possess high specific areas and large pore volumes, making them a possible kind of useful adsorbent. Long *et al.* used a hyper-cross-linked polymer as an adsorbent for the removal of chlorinated VOCs, the results showed that it had a good adsorption capacity.¹³ Pan *et al.* adopted a hyper-cross-linked polymer and activated carbon to investigate the adsorption performance of 4-nitrophenol, the results proved a higher adsorption capacity of the former.¹⁵ Besides, the hyper-cross-linked polymers are also much easier to regenerate using organic solvents, or even by a simple wash using hot water for their hydrophobic performance.^{15,17,18}

The hyper-cross-linked polymers are usually synthesized by Friedel-Crafts reaction from a low-cross-linked polymer through a post-cross-linking procedure. By adding some bi-functional cross-linking reagents and suitable Friedel-Crafts catalysts, such as 2,6-dichlorotoluene and ferric chloride, respectively, the low-cross-linked polymer, which was first dissolved completely in a good solvent, was further cross-linked to form high polymeric degree networks. Micro and/or meso pores

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of hyper-cross-linked polymers are mainly formed after evaporation of solvents between the voids of the network structures. During the evaporation process, the interaction of the cross-linking reagents and polymer networks should be strong enough to avoid collapse of the polymeric structures, otherwise a large surface energy and capillary pressure would seriously affect the stability of the pore structures.¹⁹ Thus, the post-cross-linking stage is the key point and the cross-linking reagent plays an important role during the synthesis process. However, to the best of our knowledge, only a few studies have been carried out on how the cross-linking reagents take effect over the pore structures and then further affect the VOCs adsorption properties of the hyper-cross-linked polymers.^{10,20}

In this research, we successfully synthesized a series of hyper-cross-linked polymers from a low-cross-linked polydivinylbenzene (PDVB) by a post-cross-linking procedure with 4,4'-bis(chloromethyl)biphenyl (BCMBP) as cross-linking reagent and ferric chloride as catalyst. During the synthesis process, various amounts of BCMBP were used and the effects of them on the pore structure and morphology were discussed. Moreover, in order to investigate the adsorption property of the synthesized hyper-cross-linked polymers, a resultant typical polymer, HCP-1.3, was selected as an adsorbent. For comparison, benzene and water were selected as different adsorbates considering their non-polar and polar characteristics. The adsorption amounts were recorded under static and dynamic models, respectively.

Experimental

Synthesis of materials

Tetrahydrofuran (THF, $\geq 99.0\%$), azobisisobutyronitrile (AIBN, Chemical Pure), 1,2-dichloroethane (DCE, $\geq 99.5\%$), ferric chloride ($\geq 99.0\%$), acetone ($\geq 99.5\%$), and hydrochloric acid (36.0–38.0%) were purchased from Sinopharm Chemical Reagent Company and used as received without any further purification. Divinylbenzene (DVB, 80%) was purchased from Alfa Aesar and is a mixture of isomers stabilized with 1000 ppm 4-*tert*-butylcatechol liquid. BCMBP ($\geq 95.0\%$) was purchased from Tokyo Chemical Industry Company. In addition, distilled water was used during the extraction process.

The hyper-cross-linked polymers were synthesized by the following procedure. First, the low-cross-linked PDVB was synthesized by a solvothermal method with some changes modified by us.¹² In a typical procedure, 2 g DVB was completely dissolved in 20 ml THF, then 0.05 g AIBN was added as an initiator. After stirring for 4 h at room temperature, the mixture was transferred into a polytetrafluoroethylene autoclave for further reaction at 100 °C for 48 h. The resultant mixture was then cooled down to room temperature, and finally PDVB was synthesized after evaporation of the solvents.

The hyper-cross-linked polymers were synthesized *via* a post-cross-linking reaction of the above-mentioned PDVB. Typically, 4 g PDVB and 3.08 g BCMBP were added into 70 ml DCE successively. After completely swelling for 20 h, the solution was cooled to 0 °C, then 2.0 g ferric chloride was added as a catalyst. The solution was stirred for 2 h and then heated up to 80 °C for a

further reaction of 12 h. The resultant solid product was extracted using a Soxhlet extractor. Acetone, acetone–hydrochloric acid and distilled water were used as medium successively. The extraction process was not stopped until the extracted solvent was transparent. Finally, the hyper-cross-linked polymers were successfully synthesized after drying at 60 °C for 24 h under vacuum conditions. The resultant polymers were denoted as HCP-*x*, where *x* refers to the molar fraction of BCMBP to DVB. In the present study, 0, 0.4, 0.7, 1.0 and 1.3 were chosen as *x* values, respectively.

Characterizations and measurements

The textural properties of HCP-*x* were measured with a NOVA 1200 gas sorption analyzer at liquid nitrogen temperature (77 K). The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution curves were calculated by analyzing the desorption branches of isotherms based on the Barrett–Joyner–Halenda (BJH) method.²¹ The micropore surface area and micropore volume were calculated by a *t*-plot method. *In situ* Fourier Transform Infrared (FT-IR) spectra were measured on a Bruker Tensor 27 spectrometer in the range of 600–4000 cm^{−1}. Scanning electron microscopy (SEM) images were taken on Hitachi S-3000N equipment. The thermogravimetry (TG) and derivative thermogravimetry (DTG) analyses of samples were carried out on a Setaram Labsys-16 thermal analyzer. The heating rate was 10 K min^{−1} from 50 °C to 900 °C under a nitrogen flow of 30 ml min^{−1}.

Static adsorption measurements

Static adsorption measurements were performed on an Intelligent Gravimetric Analyzer (Model IGA-002, Hiden Isochema Instrument) with a high sensitivity of 0.1 μg. During the static adsorption procedure, the adsorbed amounts were recorded and used to evaluate the static adsorption property of the HCP-*x* samples. The instrument has an ultrahigh vacuum system precisely controlled by a computer allowing the accurate gravimetric changes to be recorded in gradually increased or decreased relative pressure values. Before the measurement, each sample was degassed overnight at 110 °C in a vacuum to remove the physically adsorbed water molecules and other impurities adsorbed in the pores. The constant weight of the sample was recorded as net weight for further analysis. 298 K, 308 K and 318 K were selected as static adsorption temperatures, respectively.

Dynamic adsorption measurements

Dynamic adsorption measurements were carried out on a fixed-bed column. The corresponding experimental set-up and method were described in our previous work.²² Before starting each experiment, the flow rate of the carrier gas and the temperature of the saturator were adjusted so that the required outlet concentration of benzene vapor was reached and kept stable. Then, about 100 mg of sample was packed into the fixed-bed column with an inner diameter of 6 mm and the

temperature was maintained at 298 K. The samples were degassed at 110 °C overnight to remove the physically adsorbed water molecules and other impurities, just as in the static adsorption procedure. The concentration of benzene was adjusted to 800 ppm and the total flow rate was 100 ml min⁻¹. In order to investigate the effect of water vapor on the adsorption behavior, 800 ppm of benzene under a relative humidity (RH) of 30% was passed through the adsorption bed. The benzene concentration was recorded on a gas chromatograph (GC) equipped with a flame ionization detector and breakthrough curves were collected. The breakthrough time is defined as the time when the outlet concentration is about 5% of the inlet concentration. The absorbed amounts were calculated by the following equation:

$$q = \frac{F}{Mw} \left(C_i t_s - \int_0^{t_s} C_o dt \right) \quad (1)$$

where q is the absorbed amount (mmol g⁻¹); F is the volumetric flow rate of the carrier gas (ml min⁻¹); w is the net weight of adsorbent (g⁻¹); M is the molar mass of benzene (g mol⁻¹); C_i represents the benzene concentration at the inlet (g ml⁻¹), while C_o is the benzene concentration at the outlet (g ml⁻¹) and t_s is the breakthrough time of the adsorbent (min).

Results and discussion

Characterization of hyper-cross-linked polymers

Fig. 1 depicts the nitrogen adsorption-desorption isotherms and pore size distributions of HCP- x with different BCMBP amounts. As shown in Fig. 1(A), isotherms b to e belong to type IV according to the IUPAC classification, and the existence of the typical hysteresis loops indicates the mesopore structures in HCP- x .²³ In contrast, isotherm a shows a non-typical hysteresis loop caused by the irregular mesopores of the low-cross-linked polymer. Furthermore, in the low pressure region ($P/P_0 < 0.1$), the amount of nitrogen adsorption increased from isotherms a to e. The accordance of the growing tendency suggested an increasing micropore volume as the x value increased from 0 to 1.3 after the post-cross-linking reaction. Similarly, in the high pressure region of $P/P_0 > 0.8$, the adsorption amounts show the same trend as the low pressure region, indicating the mesopore volume increased gradually. The hierarchical micro/meso pore structures after the post-cross-linking procedure are expected to be more favorable for VOCs adsorption than just the predominant mesopore structure in HCP-0. The pore size distribution curves are shown in Fig. 1(B). There is a wider pore size range for hyper-cross-linked polymers using more BCMBP as cross-linking reagent than the corresponding polymer with less BCMBP.

The texture properties of HCP- x are calculated from the isotherms and listed in Table 1. The BET surface area and total pore volume are considered as the most important characteristics for adsorbents and they increased from 209 m² g⁻¹ and 0.19 cm³ g⁻¹ to 1231 m² g⁻¹ and 1.99 cm³ g⁻¹ when the x value increased from 0 to 1.3, respectively. For HCP-1.3, these data are a little larger than those reported by others.^{14,15,18,24} The BET surface area and micropore volume of HCP- x increased with the enhanced quantity of BCMBP, as well as the hierarchical pore

structures in both the micro/meso pore range after the post-cross-linking reaction, suggesting the high post-cross-linking property of BCMBP and the high cross-linking degree of HCP-1.3.²⁰ The cross-linking reagent plays a very important role during the post-cross-linking reaction. It joins the low-cross-linked PDVB with a rigid linkage, forming a hierarchical structure of micro/meso pores instead of the predominant mesoporous structure, as shown in Fig. 1. Besides, it is interesting to notice that as the x value changes from 0 to 1.3, the micropore volume increases from only almost 0 to 0.17 cm³ g⁻¹ while the total volume changes from 0.19 to 1.99 cm³ g⁻¹. This implies the main development of mesopore structures during the post-cross-linking reaction. This would be reasonable if the molecule dimensions of BCMBP were taken into consideration as BCMBP molecules are almost two times larger than benzene molecules (327.7 × 662.8 × 773.7 pm),²⁵ so it is hard for BCMBP to penetrate into structure pores and form micropores even smaller than its own dimensions.

The FT-IR spectra of HCP- x are shown in Fig. 2. In general, the characteristic absorbance peaks of HCP- x are in accordance with each other, suggesting the persistence of skeleton structure. The absorbance peaks at 1600 cm⁻¹ and 1450 cm⁻¹ are identified as the vibration of the benzene ring.¹⁸ The peaks at 3050 cm⁻¹ and 2930 cm⁻¹ are assigned to the stretch vibration of the aromatic C-H and aliphatic C-H in HCP- x , respectively.²⁶ The newly detected absorbance bands around 1265 cm⁻¹ in curves b to e are attributed to the wagging vibration of CH₂Cl after the post-cross-linking reaction.^{18,24} This indicates the BCMBP was successfully grafted onto the skeleton structure. Also, the relatively low peaks of CH₂Cl reflect the low content of CH₂Cl after post-cross-linking. In addition, it is worthy to be noted that no peaks corresponding to oxygen-containing functional groups occur in the FT-IR spectra. As we know, the hydrophilic and hydrophobic properties of adsorbents interrelate closely with the surface oxygen-containing groups of adsorbents, and generally the higher the content of surface oxygen-containing groups, the more hydrophilic the adsorbent.²⁷ During the synthesis procedure in our experiments, most of the reagents such as DVB and BCMBP are non-polar organic chemicals. Thus the oxygen-containing functional groups, such as typical hydroxyl and carbonyl groups with FT-IR spectra located at 3100–3700 cm⁻¹ and 1700 cm⁻¹, respectively,^{18,28} were absent in our FT-IR measurement. The absence of oxygen-containing functional groups implies a better hydrophobic property of HCP- x .

The typical synthesized HCP-1.3, which has the biggest BET specific surface area and total pore volume in this study, and the corresponding low-cross-linked precursor HCP-0 were selected as representative polymers to study the stability of HCP- x . The corresponding TG and DTG curves are depicted in Fig. 3. A small degree of weight loss around 170 °C in HCP-0 can be assigned to the evaporation of organic solvents. With the temperature higher than 370 °C, an obvious loss in weight occurs which may be caused by the thermal decomposition of the organic skeleton. Compared with HCP-0, the post-cross-linked HCP-1.3 shows a higher thermal stability up to 420 °C, which is a little bit higher than others.²⁹

Fig. 1 Nitrogen adsorption-desorption isotherms (A) and BJH pore size distributions (B) of HCP-0 (a), HCP-0.4 (b), HCP-0.7 (c), HCP-1 (d) and HCP-1.3 (e). Isotherms (b)–(e) are shifted by 100, 400, 700 and 1000 cm³ g⁻¹, respectively.

Fig. 4 shows the SEM images of HCP-0 and HCP-1.3. It can be seen that their morphologies are quite different from each other. The low-cross-linked HCP-0 shows a relatively smooth and compact surface, which is typical for gel-type PDVB precursors,³⁰ while HCP-1.3 displays a more sophisticated and hierarchical porous structure after the Friedel-Crafts reaction. The SEM images intuitively reflect the high cross-linking function of BCMBP during the post-cross-linking reaction. Benefiting from the rigid-bridge effect, the branch chains of the skeleton structures joined together, forming a hierarchical pore structure.

Static adsorption and desorption behaviors

Adsorption-desorption isotherms of benzene vapor on HCP-0 (A) and HCP-1.3 (B) at various temperatures are shown in Fig. 5. According to the IUPAC classification, all of the isotherms show a combination of type II and type IV.²³ The type II isotherms represent unrestricted multilayer adsorption of benzene onto non-porous parts of the HCP-0 and HCP-1.3, while the type IV isotherms represent the mesopore structures in HCP-0 and HCP-1.3. In the low pressure region ($P < 25$ mbar), the amount of benzene vapor adsorbed on HCP-1.3 is about four times that on HCP-0, verifying the larger micropore volume of HCP-1.3, which is consistent with the nitrogen adsorption-desorption isotherms in Fig. 1. The equilibrium adsorbed amounts of benzene under static conditions on some other

Fig. 2 FT-IR spectra of HCP-0 (a), HCP-0.4 (b), HCP-0.7 (c), HCP-1.0 (d) and HCP-1.3 (e).

adsorbents are also collected for a further comparison and the corresponding values are listed in Table 2. It can be seen that the amount of benzene adsorbed on HCP-1.3 is relatively higher than on the other adsorbents. As shown in Fig. 5, the highest adsorbed amount of benzene is about 30 mmol g⁻¹. It is reported that the kinetic diameter of benzene is about 5.85 angstroms, and the monolayer benzene adsorption is about 6.1 μmol m⁻².³⁵ The adsorbed amount in our paper is

Table 1 Textural properties of HCP-x

Material	BET surface area (m² g⁻¹)	Average pore diameter (nm)	Total pore volume (cm³ g⁻¹)	Micropore volume (cm³ g⁻¹)	Micropore area (m² g⁻¹)
HCP-0	209	3.7	0.19	—	—
HCP-0.4	881	5.9	1.29	0.09	189
HCP-0.7	1001	5.8	1.46	0.12	259
HCP-1.0	1073	6.0	1.60	0.14	307
HCP-1.3	1231	6.5	1.99	0.17	359

Fig. 3 TG and DTG curves of HCP-0 and HCP-1.3 materials.

Fig. 4 SEM images of HCP-0 (A) and HCP-1.3 (B).

Fig. 5 Adsorption-desorption isotherms of benzene vapor on HCP-0 (A) and HCP-1.3 (B) at various temperatures.

30 mmol g⁻¹, *i.e.* 24.4 μmol m⁻² (the specific surface area of HCP-1.3 is 1231 m² g⁻¹), which means almost 4 layers of adsorption of benzene on HCP-1.3. This corresponds to the inherent character of type II isotherms that a strong adsorbate–

Table 2 Equilibrium adsorption capacities (Q_e) of benzene on HCP-1.3 and some other adsorbents

Adsorbent	Q_e (mmol g ⁻¹)	Temperature (K)	Reference
HCP-1.3	20.3	298	Present work
MIL-101	16.7	298	31
Activated carbon	9.40	298	41
Silicalite-1	8.39	295	32
SBA-15	7.1	303	33
Hydrophobic aerogels	6.27	298	34

Fig. 6 Adsorption-desorption isotherms of water vapor on HCP-0 (A) and HCP-1.3 (B) at various temperatures.

adsorbent interaction plays an important role during the adsorption process. Generally speaking, the adsorbed amount of VOCs for an adsorbent closely relates with the following factors: the molecular weight, the structure similarity and the cohesive energy.³⁶ VOCs that have high molecular weights and high similarity of structure and cohesive energy with adsorbents are expected to give high adsorption amounts. In this paper, we chose PDVB as the precursor and BCMBP as the cross-linking reagent. Comparing with the benzene molecule, both of them possess high structural similarity. This may be the reason why the adsorbed benzene amount on HCP-1.3 reaches 30 mmol g⁻¹. There is also another interesting phenomenon which is irregular in Fig. 5, that the adsorbed amount of benzene on HCP-0 and HCP-1.3 increased with the increased temperature, because of the fact that most adsorption procedures are

Fig. 7 Adsorption kinetic profiles for benzene on HCP-0 (A, $P/P_0 = 0.4610$ – 0.6185) and HCP-1.3 (B, $P/P_0 = 0.0033$ – 0.0101) at 25°C , line is the LDF model.

Fig. 8 Desorption kinetic profiles for benzene on HCP-0 (A, $P/P_0 = 0.003$ – 0.0002) and HCP-1.3 (B, $P/P_0 = 0.7390$ – 0.6141) at 25°C , line is the LDF model.

exothermal and the adsorbed amount would be expected to decrease with increasing temperature. However, this may be reasonable if we notice the intrinsic swelling property of rubbery polymers. Comparing with the classical rigid adsorbents such as zeolites and activated carbons, new organic framework materials show structure flexibility aroused by rotation and vibration of chemical bonds.^{37,38} During the adsorption procedure, adsorbates will exist in a liquid state on

Fig. 9 Breakthrough curves of benzene on HCP-0 and HCP-1.3. The filled symbols are under dry conditions and the open symbols are under wet conditions (30% RH).

Table 3 Dynamic adsorption capacities of benzene on HCP-0 and HCP-1.3 under dry and wet conditions

Sample	Dynamic adsorption capacity Q (mmol g^{-1})		
	Q_{dry}	$Q_{30\%RH}$	$Q_{30\%RH}/Q_{\text{dry}}$ (%)
HCP-0	0.96	0.88	92
HCP-1.3	1.76	1.59	90

Fig. 10 Dynamic adsorption capacities of benzene on HCP-1.3 for four consecutive adsorption cycles under dry conditions.

the adsorbents according to the adsorption theory. With the existence of liquid state adsorbates and the increased temperature, the polymer will swell to a certain degree, resulting in a gradual increase in the free pore volume. This may be the reason for the apparent concave shapes and gradually larger hysteresis loops in Fig. 5.

The adsorption properties of water vapor on the synthesized HCP-1.3 and HCP-0 were investigated by static measurements and the corresponding isotherms at different temperatures are depicted in Fig. 6. It is obvious that all the isotherms are of type III, *i.e.* the adsorbate–adsorbent interactions are smaller than the adsorbate–adsorbate interactions during the adsorption process. This is in good coincidence with the non-polar and polar properties of benzene and water. The adsorbed amounts of water at different temperatures are much less than those of benzene, implying that the synthesized HCP-*x* are inclined to showing a

more hydrophobic feature than hydrophilic. Compared with the post-cross-linked HCP-1.3, HCP-0 shows a much lower adsorbed amount of water, indicating the larger pore volume of HCP-1.3 than HCP-0. This corresponds with the values shown in Table 1. Similarly, the increased absorbed amount of water on HCP-1.3 at higher temperatures, as well as the enlarged hysteresis loops, might be caused by the swelling property of HCP-1.3, just as the adsorption behavior of benzene vapor was.

Adsorption and desorption kinetics

Adsorption and desorption kinetics are important in practical applications for their prediction of the change of process rate and until now the linear driving force (LDF) model is the most widely used uptake rate approximation.^{39,40} Studies show that adsorption kinetics of various gases or vapors on porous materials, such as activated carbon, metal–organic framework materials and carbon molecular sieves, can be well fitted to the LDF model.^{25,41–43} In this study we choose the LDF model to simulate the adsorption–desorption kinetics of benzene onto the synthesized typical HCP-1.3 and HCP-0. The specific equation of the LDF model for the adsorption process can be described as follows:⁴⁴

$$M_t/M_e = 1 - e^{-kt} \quad (2)$$

where M_t is the adsorbed amount at time t , M_e is the equilibrium adsorbed amount for the given pressure increment, and k is the rate constant. For the desorption process, the corresponding specific equation can be described as follows:

$$M_t/M_e = e^{-kt} - 1 \quad (3)$$

where M_t is the desorbed amount at time t , M_e is the equilibrium desorbed amount for the given pressure increment, and k is the desorbed rate constant.

Adsorption kinetics data and the corresponding simulative curves are shown in Fig. 7. According to the experimental results and the simulations, the adsorption kinetics of both HCP-0 and HCP-1.3 obey the LDF model, suggesting that diffusion through the barrier at the pore entrance is the rate-determining step during the adsorption process.²⁵ This result seems to be inaccurate since we consider the fact that the average pore sizes of HCP-0 (3.7 nm) and HCP-1.3 (6.5 nm) are much bigger than the dimensions of the benzene molecule ($327.7 \times 662.8 \times 773.7$ pm). This surprising phenomenon may have resulted from the pore structures of the cross-linked polymers. According to the nitrogen adsorption–desorption isotherms in Fig. 1, we would speculate the existence of pores characterized by the “ink-bottle” structure. This particular structure inhibits the diffusion of benzene molecules into the inner part of the mesopores as the neck of the pores is relatively narrower than the body part.²³ Similarly, the desorption kinetics data of benzene on HCP-0 and HCP-1.3 in Fig. 8 obey the LDF model.

Dynamic adsorption

The dynamic breakthrough curves of benzene on HCP-0 and HCP-1.3 under dry and wet (30% relative humidity) conditions

are depicted in Fig. 9. The dynamic adsorption breakthrough curves reveal the time-dependent change of benzene concentration during the adsorption procedure. According to Fig. 9, it can be obtained that under dry conditions, the breakthrough time of benzene on HCP-1.3 is 46 min, with a relatively low value of 41 min under the 30% relative humidity wet condition. Compared with the post-cross-linked HCP-1.3, the breakthrough times of benzene on HCP-0 under dry and wet conditions are 25 and 23 min, respectively. The dynamic adsorption amounts calculated by eqn (1) are shown in Table 3. The total dynamic adsorption amounts of benzene on HCP-0 are 0.96 mmol g^{-1} and 0.88 mmol g^{-1} under dry and wet conditions, respectively. The corresponding values on HCP-1.3 are 1.76 mmol g^{-1} and 1.59 mmol g^{-1} . The enhanced adsorbed amounts of benzene on HCP-1.3 compared to HCP-0 verify the increased pore volume after the post-linking procedure. Also, the adsorbed amounts of benzene under wet conditions reach up to 90% of the corresponding values under dry conditions for both HCP-1.3 and HCP-0, indicating a good hydrophobicity of the synthesized materials. Adsorption experiments with four consecutive cycles were performed to investigate the regeneration and re-use properties of HCP-1.3. After each adsorption cycle, the saturated HCP-1.3 was heated to 105°C under vacuum for 10 h so that the adsorbed benzene can be desorbed. The desorbed HCP-1.3 was then re-used for the next adsorption procedure. The corresponding adsorption capacities of benzene on HCP-1.3 for four consecutive cycles are shown in Fig. 10 for comparison. As can be seen from Fig. 10, the adsorption capacities gradually decrease with the increased number of adsorption cycles. The results indicate that regeneration under the chosen experimental conditions was unsuccessful in desorbing the adsorbed benzene from some of the adsorption sites and thus the adsorption capacity decreased. However, it is worthy to note that after 4 cycles of adsorption, the adsorption capacity of benzene remains almost 75% of the corresponding 1 cycle value.

Conclusions

In this paper, we successfully synthesized a series of hyper-cross-linked polymers *via* a post-cross-linking reaction using BCMBP as cross-linking reagent and ferric chloride as catalyst. The chosen BCMBP joins the low-cross-linked PDVB efficiently and the typical resultant polymer has new hierarchical micro/meso pore structures, together with a high BET specific surface area and total pore volume up to $1231 \text{ m}^2 \text{ g}^{-1}$ and $1.99 \text{ cm}^3 \text{ g}^{-1}$, respectively. Benefiting from the high similarity in structure between HCP-1.3 and benzene molecules, the adsorption amount of benzene on HCP-1.3 reaches a high value of up to 30 mmol g^{-1} . Dynamic adsorption studies show that the adsorbed amount of benzene on HCP-1.3 under the 30% relative humidity condition is about 90% of the corresponding value under dry conditions. In general, the high BET surface area, together with the high stability up to 420°C and relatively high adsorption amount of benzene under certain humidity conditions imply the synthesized HCP-1.3 would be a promising VOC adsorbent under both dry and humid conditions.

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