Synthesis and adsorption property of hypercross-linked sorbent

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A novel hypercross-linked fiber sorbent (HFS) was prepared by cross-linking polypropylene grafted styrene-divinylbenzene (PP-ST-DVB) fiber with p-xylylenedichloride using Friedel-Crafts (F-C) reaction. A series of synthesis tests were conducted and effects of reaction temperature, reaction time, catalyst type, and material ratio on F-C reaction were investigated. Compared with PP-ST-DVB fiber, HFS has an excellent adsorption capacity for benzene vapor. Adsorption equilibrium for benzene vapor on HFS was measured at 298, 323 and 348K by a static volumetric technique. Isosteric heat curve, derived from equilibrium data, indicated that HFS has an energetically heterogeneous surface. HFS showed faster adsorption rate and higher adsorption capacity than that of PP-ST-DVB fiber.

Keywords: Adsorption, Benzene, Kinetics, Sorbent, Thermodynamics

Introduction

Three-dimensional polystyrene networks (homogeneous, heterogeneous, and hypercross-linked) serve as the basis of various sorbents widely used in laboratory practice and industrial technology[1-3]. Hypercross-linked polymers have been obtained by cross-linking linear polystyrene chains in solution or in swollen state using bifunctional compounds, which react with phenyl rings via Friedel-Crafts (F-C) reaction. Compared with resins, ion exchange fibers as new materials, have greater exchange rate, shorter reclaiming time, easier to elute and can be made in a form of filaments, staple fiber, nonwoven fabrics, clothes, bands, and plenty of other textile items. This creates new technological possibilities in arrangements of ion exchange processes as well as opens new fields for applications of ion exchange processes[4-8]. Most important and realistic fields of their applications are water and air purification[9-11]. However, studies on three-dimensional networks in fibrous form obtained by introducing additional cross-linked bridges according to F-C reaction have been reported rarely[12,13].

This study presents synthesis of a new hypercross-linked fiber sorbent (HFS) using F-C reaction and its adsorption properties for adsorption of benzene vapor.

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Materials and Methods

Materials

Polypropylene grafted styrene-divinylbenzene (PP-ST-DVB) fiber, provided by Research Institute of Organic Chemistry, Russia, was extracted with benzene before use. Nitrobenzene was distilled within boiling ranges. p-Xylyenedichloride (XDC) was used as such. Benzene, acetone and other chemicals were analytical reagents.

Methods

(a) Preparation of Hypercross-linked Sorbent

HFS was prepared by cross-linking PP-ST-DVB fiber with cross-linking agent using F-C reaction. A solution of quantitative PP-ST-DVB fiber in nitrobenzene (20 ml) was added to a solution containing XDC and catalyst in nitrobenzene (10 ml). Mixture was placed in a flask equipped with reflux condenser, stirred and heated at 353K~393 K for 10~20 h. After completion of reaction, fiber was washed with acetone, a mixture of acetone and 0.5 N HCl, and water, and then dried at 333~353 K under vacuum.

(b) Study of Static Adsorption

Isotherm measurement apparatus is based on static volumetric method, wherein total quantity of gas admitted to system and amount of gas in vapor remaining after adsorption equilibrium is determined by appropriate pressure, volume, and temperature measurements. Pressure was recorded using a Baratron absolute pressure

transducer (range, 0-133 kPa) with an accuracy of 0.05%. Adsorption cell was placed in a water bath with maintaining constant temperature (±0.02 K) by a refrigerated circulating thermostat. Experimental temperature was measured with a T-type thermocouple. HFS was kept in a drying oven at 373 K for >24 h, to eliminate any trace of pollutant. Sorbent mass was determined with an accuracy of ±10 μg. Before each isotherm measurement, sorbent was regenerated at 423 K at high vacuum for 12 h. An oil diffusion pump combined with a mechanical vacuum pump provided a vacuum down to 10^{-3} Pa. A convection gauge monitored pressure with a vacuum gauge controller. Volume of adsorption cell was determined by expansion of helium gas at the experimental temperature.

(c) *Study of Dynamic Adsorption*

Measurement apparatus of adsorption capacity is based on weight method, wherein gas-solid adsorption plant is used. Sorbent mass was determined with an accuracy of ±0.1 mg, and sorbent was introduced into quartzose spring balance. Prior to measurement, to eliminate any trace of pollutants, sorbent was desorbed at constant temperature under a high vacuum for 2 h. Total quantity of gas admitted to the system at saturated vapor pressure. During adsorption, temperature was maintained at 293.15±0.02 K. From the beginning to adsorption balance, adsorption capacity of benzene vapor on sorbent was calculated according to the weight changes of sorbent on quartzose spring balance in gas-solid adsorption plant at regular intervals.

Results and Discussion

Cross-linking of styrene in polypropylene (PP) fiber chains in swollen state was obtained by introducing large amount of bridges using XDC, which alkylates two phenyl rings in presence of F-C catalyst. Cross-linking bridges have a long and rigid structure, and are capable of retaining PP chains at a significant distance from each other. Thus, three-dimensional networks were formed and specific surface area (SSA) of fiber was greatly increased.

During synthesis of HFS, reaction temperature, reaction time, catalyst types and material ratio affected SSA of fiber. Optimum parameters were found as follows: temperature, 373 K; reaction time, 18 h; and molar ratio, PP-ST-DVB/XDC/catalyst =1:0.75:1.125. During synthesis reaction (with optimum reaction time and molar ratio), SSA of HFS increased with increasing
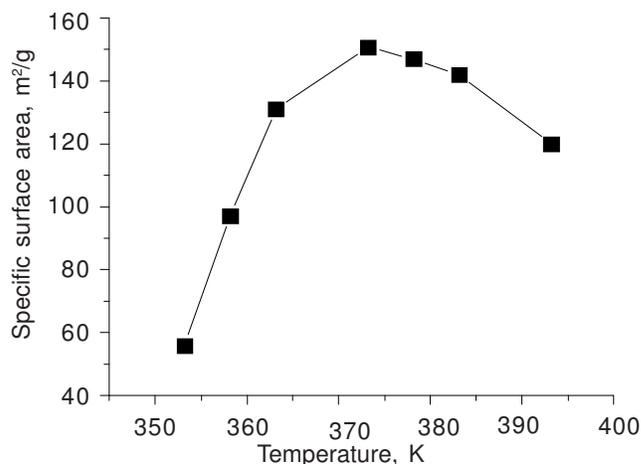

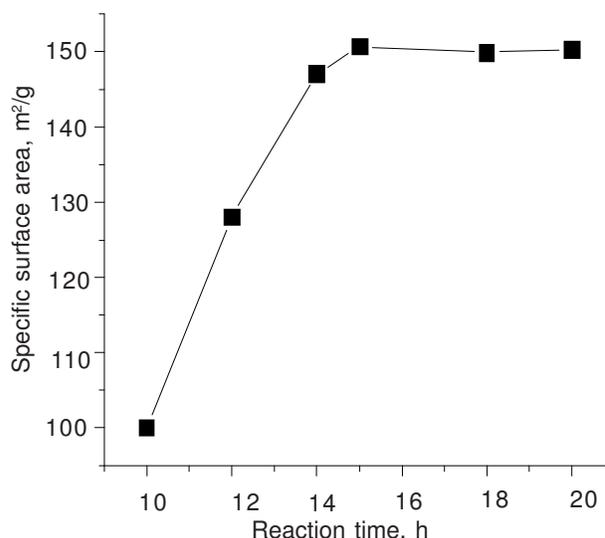Fig. 1—Dependence of specific surface area of hypercross-linked sorbent on reaction temperature

Fig. 2—Dependence of specific surface area of hypercross-linked sorbent on reaction time

temperature, approaching a maximum at 373 K, then began to decrease slowly (Fig. 1). With increasing temperature of F-C reaction, reaction rate increased and degree of cross-linking got enhanced. Therefore, SSA grew gradually. When reaction temperature exceeded threshold value, breaking rate of polymer chains tended to increase, inducing a decrease in SSA. During synthesis reaction (with optimum temperature and molar ratio), SSA of HFS increased with increasing time, reaching maximum at 15 h, and remained constant afterwards (Fig. 2). During synthesis reaction (with optimum temperature, reaction time and molar ratio),

SSA of HFS for catalysts was found as follows: $AlCl_3$, 150.64; $SnCl_4$, 130.69; and $ZnCl_2$, 40.11 m²/g. Thus, $AlCl_3$ was optimal catalyst. At optimal conditions (catalyst, $AlCl_3$; temperature, 373 K; reaction time, 18 h), SSA of HFS increased with increasing levels of cross-linking agent, approaching a maximum, then began to decrease (Table 1).

Thus, HFS can optimally be synthesized with a molar ratio of PP-ST-DVB/XDC/catalyst=1:0.75:1.125 and $AlCl_3$ as catalyst at 373 K for > 15 h. Physical properties of PP-ST-DVB and HFS, both nonpolar, were found as follows, respectively: BET surface area, 0.10, 150.64 m²/g; and total pore volume, 0.00061, 0.17229 ml/g. Results show that SSA and pore volume of fiber increased significantly after F-C reaction, may be due to network structure of fiber differs from that of initial fiber, and may provide different sorption properties.

Adsorption isotherm data for benzene on HFS at 298, 323, and 348 K were obtained at pressure up to 6.04 kPa (Table 2). Adsorption level tended to decrease with increasing temperature. Experimental data were further analyzed with respect to Langmuir [Eq. (1)] and Freundlich [Eq. (2)] models as

$$N = \frac{mbP}{1 + bP} \qquad \qquad \ldots(1)$$

$$N = kP^n \qquad \qquad \ldots(2)$$

where N, amount adsorbed; P, equilibrium pressure; m, maximum adsorbed amount with respect to complete monolayer coverage; b is a coefficient related to strength of adsorption [$b=k_a/k_d$ (where k_a, rate constant of adsorption; k_d, rate constant of desorption)]; k and n are two universal constants.

R_L and R_F are fit coefficients of Langmuir and Freundlich models, respectively (Table 3). According to fit coefficients (R_F and R_L), Freundlich model was in better agreement with experimental data than Langmuir model. Isotherms fitted by using Freundlich model (Fig. 3).Isosteric enthalpies of adsorption were calculated by Clausius-Clapeyron equation as

$$\frac{q_{st}}{RT^2} = \left[\frac{\partial \ln P}{\partial T} \right]_N \qquad \ldots(3)$$

where q_{st}, differential enthalpy of vaporization (isosteric enthalpy); P, pressure; T, temperature; and R, gas constant.

Plotting isosteric enthalpy data for benzene vapor on HFS (Fig. 4), isosteric heats varied with respect to loading, indicating heterogeneity of HFS, as a property of the surface are assumed to be independent of adsorbate used[14]. HFS having an energetically heterogeneous surface is reflected through variation of isosteric heat (Fig. 4).

Table 1—Effect of material ratio on Friedel-Crafts reaction at optimum temperature (373 K) and reaction time (>18 h)

Amount of crosslinking agent mol/mol PP-ST-DVB	Amount of catalyst mol/mol crosslinking agent	Specific surface area m²/g
0.50	1.50	139.52
0.75	1.50	150.21
1.00	1.50	143.76
1.25	1.50	109.81

Table 2—Experimental isotherm data for benzene vapor on the sorbent

298 K		323 K		348 K	
P, kPa	N, mmol/g	P, kPa	N, mmol/g	P, kPa	N, mmol/g
0.13	0.91	0.09	0.39	0.17	0.27
0.35	1.46	0.27	0.70	0.64	0.56
0.5	1.69	0.48	1.07	1.34	0.89
0.76	1.99	0.81	1.50	2.08	1.18
0.952	2.13	1.27	1.66	2.56	1.47
1.236	2.67	1.56	1.89	3.23	1.99
2.472	3.54	2.83	2.37	4.09	2.21
3.394	3.89	3.57	2.95	4.67	2.52
3.911	4.33	4.08	3.30	5.11	2.74
4.207	4.44	4.98	3.54	6.04	2.86

Table 3—Adsorption Langmuir and Freundlich parameters for benzene vapor on the sorbent

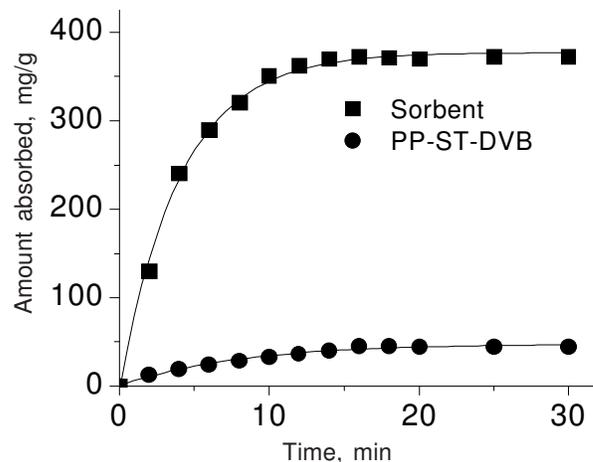| T, K	M, mmol/g	b, kPa^{-1}	R_L	k, mmol/g	n	R_F
298	3.616	2.397	0.965	2.304	0.453	0.998
323	2.633	1.834	0.982	1.492	0.541	0.996
348	2.330	0.739	0.978	0.812	0.695	0.994
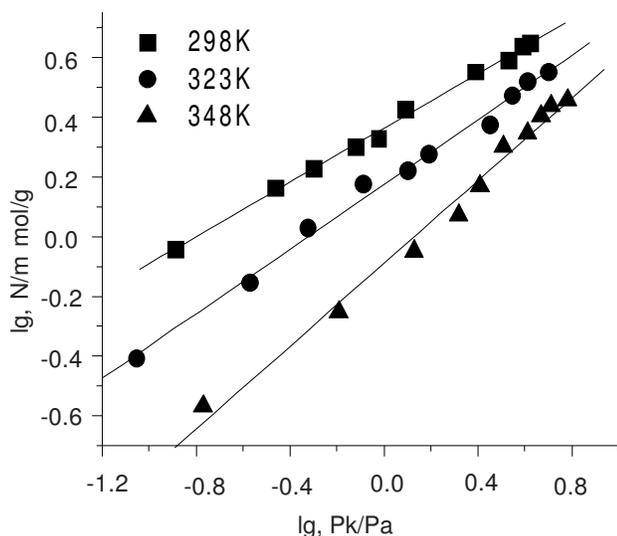
Fig. 3—Freundlich curves for benzene on sorbent
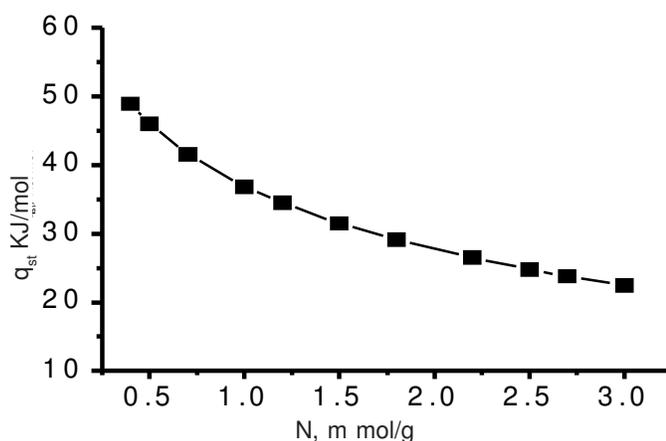

Fig. 5—Adsorption kinetics of benzene on sorbent

Fig. 4—Isoteric heat of adsorption for benzene on sorbent

Adsorption speed is directly related to adsorption efficiency. HFS showed faster adsorption kinetics and larger adsorption capacity than PP-ST-DVB fiber (Fig. 5). It was only 8-10 min for benzene vapor on the sorbent to attain adsorption equilibrium. Maximum uptake of sorbent was about 8-9 times larger than that of PP-ST-DVB fiber, mainly due to its larger surface area.

Conclusions

A novel HFS was obtained by introducing additional cross-linking bridges using F-C reaction, which was obviously affected by reaction temperature, reaction time, catalyst, and material ratio. HFS resulting from cross-linking reaction has a high specific surface area, a large total pore volume and a high average pore radius. Therefore, HFS is characterized by having a high adsorption capacity for organic vapour. Adsorption equilibrium data of benzene on a HFS at 298, 323 and 348 K were obtained at pressures up to 6.04 kPa. Experimental equilibrium data were satisfactorily correlated using Freundlich equation. Isosteric enthalpies of adsorption imply that HFS has an energetically heterogeneous surface. Kinetic study for benzene on HFS lead to conclude that sorbent showed higher adsorption rate and capacity. Maximum uptake of sorbent was about 8-9 times larger than that of PP-ST-DVB fiber. Adsorption for benzene vapor on sorbent can attain adsorption equilibrium within 8-10 mins, but adsorption equilibrium on PP-ST-DVB fiber needed about 20 min.

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