

## HYPERCROSSLINKED SORBENTS AND THEIR ADSORPTION PROPERTIES

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(Received August 8, 2006; revised October 17, 2006)

**ABSTRACT.** Hypercrosslinked sorbents which have excellent adsorption capacities for organic compounds were prepared by cross-linking the polypropylene grafted styrene-divinylbenzene fiber according to the Friedel-Crafts reaction. As crosslinking agents, we have used monochloromethylether and bis-chloromethylated derivatives of benzene or biphenyl. We have performed detailed investigations of the preparation and the optimal synthesis conditions of hypercrosslinked sorbents were obtained. Compared with the initial fiber, hypercrosslinked fibers were remarkable materials exhibiting high specific surface area and exceptional adsorption properties for organic compounds. The adsorption capacities on the hypercrosslinked sorbents were related with the size of cross-linking agents, which increased by about 8 to 10 fold.

**KEY WORDS:** Hypercrosslinked sorbents, Fibers, Surfaces; Adsorption; Organic compounds

### INTRODUCTION

Three-dimensional polystyrene networks serve as the basis of various sorbents widely used both in laboratory practice and industrial technology. Simplicity of synthesis, availability of initial materials, the possibility of varying the physical structure within wide limits and therefore the operational properties of sorbents, have earned polystyrene networks much-deserved popularity. At present, the main types of polymeric networks can be subdivided into three large groups. The first group consists of homogeneous networks, which are styrene copolymers with divinylbenzene (DVB) or other divinyl monomers, obtained by the radical copolymerization of monomers in the absence of a solvent. The second group consists of heterogeneous networks, which have interpenetrating networks as well as macroporous structures [1]. They are obtained by the copolymerization of styrene with a relatively large amount of divinylbenzene in the presence of an inert diluent which dissolves the monomers but precipitates the growing copolymer. The third group consists of hypercrosslinked networks, the structure and properties of which differ in principle from the known types of homogeneous and heterogeneous networks. Such hypercrosslinked polymers have been obtained by crosslinking linear polystyrene chains in solution or in swollen state using bifunctional compounds which react with phenyl rings via a Friedel-Crafts reaction [2-5]. Three dimensional resins obtained in this way have been thoroughly studied. Compared with resins, ion exchange fibers are new materials which have been rapidly developed in recent years. They have a great deal of advantages: the greater exchange rate, the shorter reclaiming time, easier to elute can be made in a form of filaments, staple fiber, nonwoven fabrics, threads, cloths, bands, braids and plenty of other textile items. This creates new technological possibilities in arrangements of ion exchange processes as well as opens new fields for the applications of ion exchange processes. So ion exchange fibers have been widely used in the fields of scientific research and commercial production. The most important and realistic fields of their applications are water and air purification [6-8]. But, up to now, the studies on three-dimensional networks in the fibrous form obtained by introducing additional cross-linking bridges according to Friedel-Crafts reaction have not been reported. Therefore, the synthesis of hypercrosslinked fiber would be most desirable because the

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properties of their granular prototypes are well studied and fields of their applications are well defined [9, 10].

The present paper deals with a type of new hypercrosslinked sorbents which possess a principally different structure and therefore offer new possibilities for sorption procedure from gaseous and liquid media.

## EXPERIMENTAL

### *Materials*

The polypropylene grafted styrene-divinylbenzene (PP-ST-DVB) fiber was provided by the Research Institute of Organic Chemistry, Russia. It was extracted with benzene before it was used. Monochloromethylether (MCDE) was purified by distillation. 1,2-Dichloroethane was boiled over  $P_2O_5$  and distilled over fresh portion of the dryer. *p*-Xylyenedichloride (XDC) and 1,4-bis-chloromethyldiphenyl (CMDP) were used without additional purification. Nitrobenzene, methanol, ethanol, benzene, toluene and other chemicals were all grade reagents.

### *Measurement*

Specific surface area was measured by the high-speed surface area and pore size analyzer (American NOVA2000e) according to the Brunauer-Emmet-Teller (BET) theory. The average pore radius, total pore volume, and pore size distribution were calculated by using the instrument.

### *Synthesis*

#### *Hypercrosslinked sorbent 1*

A solution of quantitative MCDE in 30 mL of 1,2-dichloroethane was added to quantitative PP-ST-DVB fiber, and the mixture was held at room temperature for 12 h for swelling of the PP-ST-DVB fiber. Then the mixture was cooled to 273.15 to 275.15 K and the quantitative catalyst in 5 mL of 1,2-dichloroethane was added. The mixture was placed in a flask equipped with reflux condenser. The mixture was carefully stirred and it was heated at 313.15-353.15 K for 4-15 h, respectively. The fiber was then washed with acetone, a mixture of acetone and 0.5 M HCl, water, and was dried at 333.15 to 353.15 K. under vacuum.

#### *Hypercrosslinked sorbent 2*

A solution of quantitative PP-ST-DVB fiber in 20 mL of nitrobenzene was added to a solution containing of *p*-xylyenedichloride (XDC) and catalyst in 10 mL of nitrobenzene. The mixture was carefully stirred and it was heated at 353.15-393.15 K for 10-20 h, respectively. Upon accomplishing the reaction, the fiber was washed with acetone, a mixture of acetone and 0.5 M HCl, water, and was dried at 333.15 to 353.15 K under vacuum.

#### *Hypercrosslinked sorbent 3*

To a solution containing quantitative PP-ST-DVB fiber in 25 mL of 1,2-dichloroethane was added a solution containing CMDP and catalyst in the 5 mL of 1,2-dichloroethane. The mixture was placed in a flask equipped with reflux condenser. The mixture was carefully stirred and it was heated at 333.15-383.15 K for 4-15 h, respectively. Upon accomplishing the reaction, the

fiber was washed with acetone, a mixture of acetone and 0.5 M HCl, water, and was dried at 333.15 to 353.15 K under vacuum.

### Adsorption of organic vapours

The adsorption capacities of organic vapours on the hypercrosslinked sorbents at equilibrium were calculated according to the weight changes of sorbents in the gas-solid adsorption plant. The adsorption experiments were conducted at 298.15 K and the pressures in the gas-solid adsorption plant were their saturated vapor pressures.

## RESULTS AND DISCUSSION

The cross-linking reagents MCDE, XDC and CMDP react with phenyl rings via a Friedel-Crafts reaction forming a bridge between two polymeric chains (Figure 1). The cross-linking bridges formed in the reaction have a long and rigid structure. They are capable of retaining the polypropylene chains at a significant distance from each other. Its length is two phenyl rings larger than the length of the crosslinking agents. Thus, the three-dimensional networks were formed and the specific surface area of fiber was greatly increased.

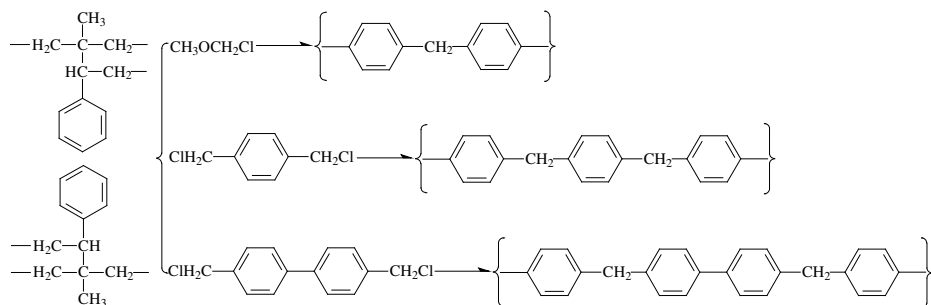


Figure 1. The structures of the sorbents.

The temperature dependence of the specific surface area of hypercrosslinked sorbents is shown in Figure 2. The reaction conditions were as follows: when the cross-linking agent was MCDE, the described results were obtained in experiments where the molar ratio of PP-ST-DVB/MCDE/catalyst = 1:0.60:0.45 with stannic tetrachloride as catalyst, were kept for 12 h; when the cross-linking agent was XDC, the results were achieved in experiments where the molar ratio of PP-ST-DVB/XDC/catalyst = 1:0.75:1.125 with aluminum trichloride as catalyst, were maintained for 18 h; when the cross-linking agent was CMDP, the results were gained in experiments where the molar ratio of PP-ST-DVB/CMDP/catalyst = 1:0.5:0.625 with stannic tetrachloride as catalyst, were maintained for 15 h. According to the Figure 2, the temperature has a remarkable effect on the Friedel-Crafts reaction. The specific surface area of sorbents increased with the growing temperature, approaching to 202.27 m<sup>2</sup>/g, 150.54 m<sup>2</sup>/g and 217.58 m<sup>2</sup>/g at 333.15, 373.15, 358.15 K, respectively, then, began to decrease slowly. With increasing temperature of the Friedel-Crafts reaction, the reaction rate increased and the degree of crosslinking of hypercrosslinked structures was enhanced, and, therefore, the specific surface area grew gradually. When the reaction temperature exceeded to 333.15, 373.15 and 358.15 K,

respectively, the breaking rate of the polymer chains tended to increase which induced the decreasing of the specific surface area.

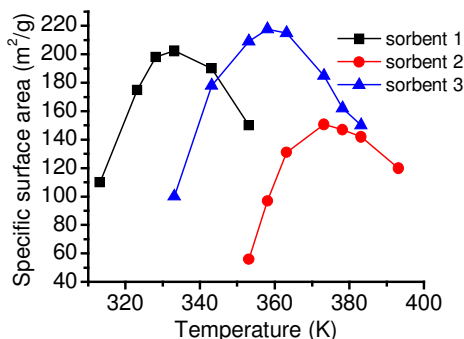


Figure 2. Dependence of the specific surface area of the hypercrosslinked sorbents on reaction temperature.

In Figure 3 the dependence of the specific surface area of the hypercrosslinked sorbents on reaction time is depicted. The reaction conditions were as follows: when the cross-linking agent was MCDE, the reactions were completed at 333.15 K, with a molar ratio of PP-ST-DVB/MCDE/catalyst = 1:0.60:0.45 and with stannic tetrachloride as catalyst; when the cross-linking agent was XDC, the reactions were completed at 373.15 K, with a molar ratio of PP-ST-DVB/XDC/catalyst = 1:0.75:1.125 and aluminum trichloride used as catalyst; when the cross-linking agent was CMDP, the reaction were completed at 353.15 K, with a molar ratio of PP-ST-DVB/CMDP/catalyst = 1:0.5:0.625 and stannic tetrachloride used as catalyst. As can be seen from the Figure 3, an increase in specific surface area with the prolonging time becomes clear. But, after 8, 10, 15 h, respectively, the specific surface area of the sorbents tends to 202.28 m<sup>2</sup>/g, 217.54 m<sup>2</sup>/g and 150.49 m<sup>2</sup>/g, respectively.

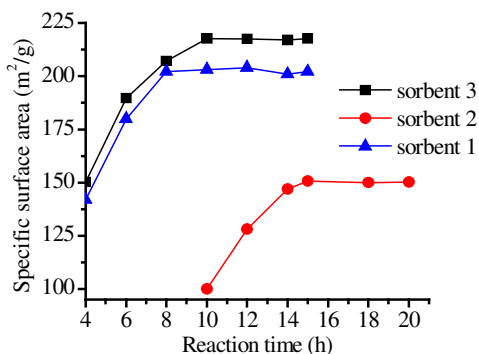


Figure 3. Dependence of the specific surface area of the hypercrosslinked sorbents on time.

The Lewis acids  $\text{AlCl}_3$ ,  $\text{SnCl}_4$ , and  $\text{ZnCl}_2$  were used in all cases as the Friedel-Crafts catalysts. The molar ratios were the same as above described and detailed experiments are described in Table 1. When the cross-linking agents are MCDE and CMDP, the catalytic activity

of  $\text{SnCl}_4$  was superior to that of  $\text{AlCl}_3$  and  $\text{ZnCl}_2$ ; On the other hand when the cross-linking agent is XDC,  $\text{AlCl}_3$  was the optimal catalyst.

Table 1. Effect of catalyst on Friedel-Crafts reaction.

Crosslinking agent	Catalyst	Temperature (K)	Time (h)	Specific surface area ( $\text{m}^2/\text{g}$ )
MCDE	$\text{AlCl}_3$	333.15	10	98.15
	$\text{SnCl}_4$	333.15	10	202.31
	$\text{ZnCl}_2$	333.15	10	120.74
XDC	$\text{AlCl}_3$	373.15	18	150.64
	$\text{SnCl}_4$	373.15	18	130.69
	$\text{ZnCl}_2$	373.15	18	40.11
CMDP	$\text{AlCl}_3$	358.15	12	153.37
	$\text{SnCl}_4$	358.15	12	217.69
	$\text{ZnCl}_2$	358.15	12	134.91

The material ratio in the synthesis of hypercrosslinked sorbents also has an important effect on Friedel-Crafts reaction. When the optimal catalyst was selected, respectively, the reaction conditions of the synthesis are briefly summarized in Table 2. From the Table 2, it can be observed that the specific surface area of sorbents increased with the growing amount of crosslinking agent, approaching a maximum, respectively, then, began to decrease. When the crosslinking agent was added too much, it was not help for increasing of the specific surface area.

Table 2. Effect of material ratio on Friedel-Crafts reaction.

Crosslinking agent	Temperature (K)	Time (h)	Amount of crosslinking agent (mol/mol PP-ST-DVB)	Amount of catalyst (mol/mol crosslinking agent)	Specific surface area ( $\text{m}^2/\text{g}$ )
MCDE	333.15	10	0.40	0.75	110.33
	333.15	10	0.50		189.46
	333.15	10	0.60		201.37
	333.15	10	0.70		180.37
XDC	373.15	18	0.50	1.50	139.52
	373.15	18	0.75		150.21
	373.15	18	1.00		143.76
	373.15	18	1.25		109.81
CMDP	358.15	12	0.30	1.25	166.91
	358.15	12	0.50		215.38
	358.15	12	0.70		174.32
	358.15	12	0.90		117.42

From the above studies, the optimal synthesis conditions of sorbents can be obtained. When the cross-linking agent was MCDE, the sorbent 1 can be synthesized at 333.15 K for more than 8 h, with the molar ratio of PP-ST-DVB/MCDE/catalyst = 1:0.60:0.45 and stannic tetrachloride as catalyst; when the cross-linking agent was XDC, the sorbent 2 can be synthesized at 373.15 K for more than 15 h, with the molar ratio of PP-ST-DVB/XDC/catalyst = 1:0.75:1.125 and aluminum trichloride as catalyst; when the cross-linking agent was CMDP, the sorbent 3 can be synthesized at 358.15 K for more than 10 h, with molar ratio of PP-ST-DVB/CMDP/catalyst = 1:0.5:0.625 and stannic tetrachloride as catalyst. Their relevant parameters are showed in Table 3. The results show that the synthesized sorbents show a significant difference in the pore

structure. In contrast to the initial PP-ST-DVB, the sorbents have high specific surface area, the great total pore volume and the high average pore radius. Because of the network structure of the sorbents which differs in principle from the initial fiber, it can offer different sorption property. The adsorption capacities of organic vapours on the sorbents are listed in Table 4.

Table 3. The structure parameters of sorbents.

Sorbent	Cross-linking agent	Specific surface area (m <sup>2</sup> /g)	Total pore volume (mL/g)	Average pore Radius (nm)
PP-ST-DVB	-----	0.10	0.00061	0.00115
Sorbent 1	MCDE	202.31	0.15172	1.79742
Sorbent 2	XDC	150.64	0.17229	2.29392
Sorbent 3	CMDP	217.69	0.20210	2.85672

Table 4. The adsorption capacities (mg/g) for organic vapours on the sorbents.

Sorbent	Methanol	Ethanol	Benzene	Toluene
PP-ST-DVB	32.0	39.1	48.9	42.2
Sorbent 1	428.6	316.6	202.3	175.4
Sorbent 2	284.4	375.6	471.9	297.5
Sorbent 3	251.8	267.9	368.2	491.1

It follows from Table 4 that the adsorption capacities of hypercrosslinked sorbents are very high. The adsorption capacity of initial fiber only amounts to 30-50 mg/g, but the adsorption capacities of hypercrosslinked sorbents are in the range of 200-500 mg/g. The adsorption capacities for organic vapours increased to about 10 fold, and they were related with the size of cross-linking agents. With increasing size of organic vapours, the adsorption capacity of hypercrosslinked sorbent 1 tends to decrease; while, the result of sorbent 3 is contrary. The adsorption capacity on the sorbent 1 for methanol is the largest; however, the adsorption capacity on the sorbent 3 for toluene is the largest among the four kinds of organic vapours. When the cross-linking agent is XDC, the adsorption capacity for benzene is larger than that of the other organic vapours studied.

These results can make the following explanation: The specific surface area of hypercrosslinked sorbents is greatly increased and is about more than 1500 times of original fibers. So the contact area between the adsorbates and the hypercrosslinked sorbents is greatly increased in the course of adsorption. Therefore the high adsorption amount can be gained. The networks were formed during the Friedel-Crafts reaction. The sizes of the network pores were different because the sizes of cross-linking agents were different. The CMDP chains are longer than the XDC chains and the XDC chains are longer than the MCDE chains, so the more the network pores are large, the more it is helpful for adsorbing the big size organic vapour.

## CONCLUSION

Three kinds of hypercrosslinked sorbents can be obtained by introducing additional cross-linking bridges according to the Friedel-Crafts reaction. The effects of several important factors on the Friedel-Crafts reaction, including reaction temperature, reaction time, catalyst type, and material ratio were investigated in detail and the optimal synthesis conditions of sorbents were achieved.

The specific surface area of sorbents, when calculated formally in terms of the BET theory, reaches a value of 150-200 m<sup>2</sup>/g which is more than 1500-2000 times of original fibers, and, the hypercrosslinked sorbents possess high pore volume and average pore radius. So the hypercrosslinked fibers are characterized by high adsorption capacity for organic vapours, which is related to the size of cross-linking agents. The adsorption capacity for organic vapours on the hypercrosslinked sorbents is increased by 10 fold. The amounts absorbed on sorbent 1, sorbent 2, and sorbent 3 reached up to 428.6 mg/g for methanol, 471.9 mg/g for benzene, 491.1 mg/g for toluene, respectively.

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