

# PREPARATION AND PROPERTY OF SURFACE-MOLECULARLY IMPRINTED POLYMER ON CARBON MICROSPHERES

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## Introduction

To date, molecularly imprinted polymers (MIPs) have been developed as biosensors, separation media and affinity supports for the recognition of target molecules. The main limitations in traditional molecular imprinting technology are its low selectivity, low response kinetics and large template size. So, the surface molecular imprinting technique, which improves the binding rate between recognition sites and imprinted molecules and the adsorption efficiency of the molecular imprinted materials by designing the molecular recognition sites on the surface of imprinted materials, has been explored by grafting a very thin polymer film onto a support, such as polymer beads [1], silica-based materials [2, 3] and carbon nanotubes [4-5]. Carbon microspheres (CMSs) are promising for surface imprinting because of their large surface area, good mechanical and thermal stabilities. In this paper, MIPs on the surface of CMSs, which were modified by acid and silylation treatment, were obtained by using dibenzothiophene as template, methacrylic acid (MAA) as functional monomer, ethylene glycol dimethacrylate (EDMA) as cross-linking agent and azoisobutyronitrile (AIBN) as initiator. This novel surface molecular imprinted material with priority recognition and adsorption is of importance for deep desulfurization of oils.

## Experimental

**Oxidization of CMSs:** 1 g of CMSs with ~350 nm in diameter prepared by chemical vapor deposition was added to 100 mL of mixed solution of 0.1 M  $\text{KMnO}_4$  and 1.5 M  $\text{H}_2\text{SO}_4$  in a flask. Then the mixture was refluxed at 80°C for 6 h under vigorous magnetic stirring, filtered, washed with distilled water several times to remove residual  $\text{KMnO}_4$ , and then dried at 40°C in air. Subsequently, the composite was washed with 200 mL of 0.1 M  $\text{H}_2\text{C}_2\text{O}_4$ , filtered, washed with distilled water, and dried at 40°C to give the sample oxidized-CMSs.

**Silanization of oxidized-CMSs:** 0.5 g of oxidized-CMSs was added to 200 mL of a mixed solvent of ethanol and water (v/v=1:1) followed by the addition of 10 mL of KH-570. The mixture was refluxed in  $\text{N}_2$  atmosphere at 55°C for 14 h under

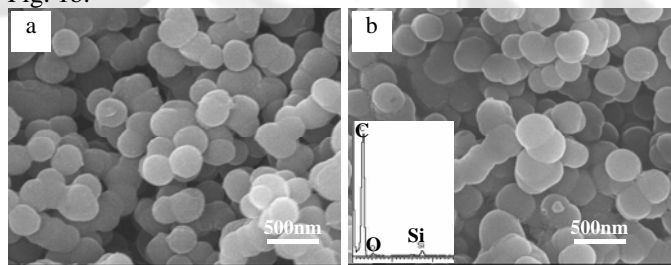
magnetic stirring. The samples were extracted with ethanol repeatedly to remove excess KH-570 and dried, resulting in the formation of the surface-modified silanized-CMSs.

**Preparation of imprinted material MIP-CMSs:** 0.369g of dibenzothiophene was dissolved in 20 ml of chloroform in a flask, and then 1 ml of MAA and 0.3 g of silanized-CMSs were added with continuous stirring, followed by the addition of 0.065 g of AIBN and 4 mL of EDMA. The flask was sealed after the mixture solution was stirred under  $\text{N}_2$  atmosphere at 60°C for 24 h. Afterwards, the samples were washed successively by ethanol to remove the polymer on the surface of CMSs and the mixed solvent of methanol and acetic acid (v/v=9:1) to remove the template. Ethanol was then used to remove the residual acetic acid. After drying, MIP-CMSs were obtained. For comparing, NIP-CMSs were also prepared in the same way but without the addition of the template by the same technique.

**Characterization and absorption experiment:** The morphology and structure of the products were characterized by field emission scanning electron microscopy (FESEM) and Fourier transformation infrared spectroscopy (FTIR). The behavior of the absorption thermodynamics and kinetics of MIP-CMSs for dibenzothiophene was studied in a 25 ml solution by UV absorbance spectra at 273 nm.

## Results and Discussion

Fig. 1 shows the FESEM images of oxidized-CMSs and silanized-CMSs. It is observed that the oxidized-CMSs with uniform size were well dispersed in spherical shape with bare surfaces (Fig. 1a) and silanized-CMSs kept homogeneous spheres (Fig. 1b). The covering layer on the surface of silanized-CMSs is suggested to be grated KH-570 from X-ray energy dispersive spectroscopy (EDS) in lower-left corner of Fig. 1b.



**Fig. 1** FESEM images of (a) oxidized- and (b) silanized-CMSs. (Inset is EDS spectra)

FTIR spectra were used to detect the surface functional groups of all samples, as shown in Fig. 2. After various treatments of CMSs, remarkable changes occurred in CMSs. The stronger bands of oxidized-CMSs at about 3433  $\text{cm}^{-1}$  than original CMSs indicate the introduction of  $-\text{OH}$  groups after the oxidization of CMSs. Compared with oxidized-CMSs, silanized-CMSs show weaken bands at about 3433  $\text{cm}^{-1}$ , suggesting the reaction of KH-570 and  $-\text{OH}$  groups of oxidized-CMSs. Compared with silanized-CMSs, new adsorption bands at 1153  $\text{cm}^{-1}$ , 1627  $\text{cm}^{-1}$ , 1727  $\text{cm}^{-1}$  and stronger 3433  $\text{cm}^{-1}$  can be found in the FTIR spectra of MIP-CMSs, which can be identified as the characteristic peaks of

the polymer of the monomer and the cross-linker, similar to those shown in NIP-CMSs. This result supports that the polymer was grafted onto the surfaces of the CMSs.

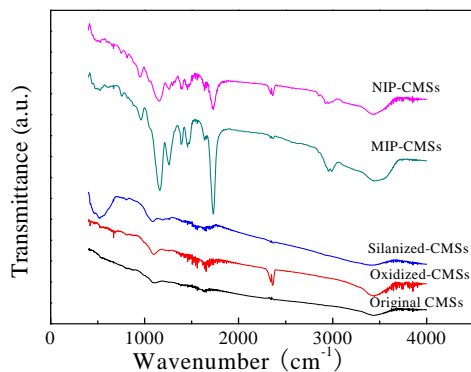


Fig. 2 FTIR spectra of the samples

The behavior of the absorption thermodynamics of MIP-CMSs for dibenzothiophene was explored at room temperature for 6 h, as shown in Fig. 3. The adsorption amount ( $Q$ , mmol/g) was calculated based on the difference in dibenzothiophene concentration before and after the adsorption in a constant volume of *n*-hexane and a constant weight of the MIP-CMSs or NIP-CMSs, according to:

$$Q = (C_0 - C)V/M$$

where  $C_0$  is the initial dibenzothiophene concentration (mmol/L),  $C$  is the dibenzothiophene concentration after adsorption,  $V$  is the volume of dibenzothiophene solution (mL), and  $M$  is the weight of the MIP-CMSs or NIP-CMSs (g).

The adsorption amount increased with increasing concentration of dibenzothiophene, and a saturation value was achieved at a dibenzothiophene concentration of 4 mM, which represents the saturation of the active binding cavities on the MIP-CMSs or NIP-CMSs. Furthermore, a saturation value of dibenzothiophene concentration on the NIP-CMSs was faster to arrive at than that on the MIP-CMSs. Maximum adsorption capacity of MIP-CMSs (0.595 mmol/g) was higher than that of NIP-CMSs (0.425 mmol/g) for dibenzothiophene.

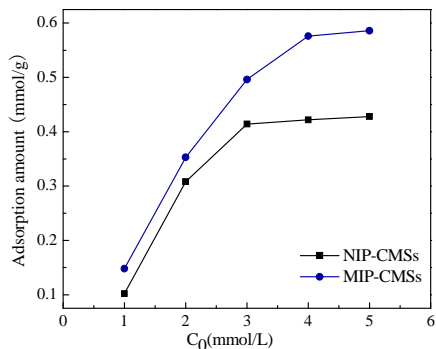


Fig. 3 Adsorption thermodynamics curves of MIP-CMSs and NIP-CMSs at room temperature for 6 h

The adsorption kinetics processes of dibenzothiophene on MIP-CMSs and NIP-CMSs were studied in 8 mmol/L of dibenzothiophene at room temperature, and the results are

shown in Fig. 4. It can be clearly observed that the adsorbance  $Q$  of dibenzothiophene increased with time and that a higher amount was absorbed by MIP-CMSs compared with NIP-CMSs. The adsorption kinetics data showed that the adsorption rate was fastest in the first 1.5 h and that equilibrium was reached in 5 h.

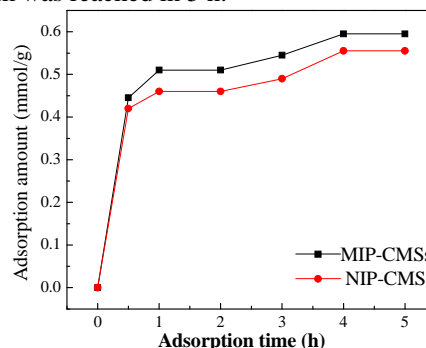


Fig. 4 Adsorption kinetic curves of MIP-CMSs and NIP-CMSs in 8 mmol/L of dibenzothiophene at room temperature

## Conclusions

Surface molecular imprinting polymers were prepared on the surface of CMSs, which were oxidized by a mixed solution of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  and silanized by KH-570, using dibenzothiophene as template, MAA as functional monomer, chloroform as solvent, azobisisobutyronitrile as initiator, and ethylene glycol dimethacrylate as crosslinking agent. The adsorption behavior of MIP showed that the adsorption equilibrium time was about 5 h and the equilibrium adsorption amount was 0.595 mmol/g. Compared with NIP-CMSs, MIP-CMSs possessed a better adsorption property toward dibenzothiophene.

**Acknowledgment.** The authors acknowledge financial support from National Natural Science Foundation of China (20971094), International S&T Co-operation Program (2007DFA50940), International S&T Co-operation Program of Shanxi Province (2009081018), Natural Science Foundation of Shanxi Province (2009011012-4), and Shanxi Research Fund for Returned Scholars (2008-31).

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