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Mono-dispersed dendritic mesoporous silica/carbon nanospheres with enhanced active site accessibility for selective adsorptive desulfurization

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Abstract

Mono-dispersed dendritic mesoporous silica/carbon nanospheres (DMS/CNs) with adjustable particle sizes and carbon contents were controllably fabricated via a facile method and were further loaded with silver nanoparticles by wet impregnation and thermal dispersion for adsorptive desulfurization of dibenzothiophene (DBT). The carbon substrate deposited on the mesoporous channels could alter the textural and chemical properties of materials, thus could improve the adsorptive performance. DMS/CNs with the unique center-radial pore structure and large surface area were favorable for the incorporation of active metals, and the adsorptive capacity could be significantly enhanced after the incorporation of AgNO₃. The results showed that Ag loaded on material treated with H₂SO₄ exhibited a superior adsorptive performance with the highest activity and selectivity for DBT, which might result from a good combination of its large center-radial pore channels and a synergistic effect between carbon substrate and silver species. Our contribution is to provide a promising silver-based adsorbent for selective adsorptive desulfurization.

Keywords: Silica-carbon composites; adsorptive desulfurization;

dibenzothiophene; synergistic effect; selectivity

1. Introduction

Transportation fuel occupies a large proportion of energy resources in many countries around the world. The combustion of sulfur compounds in commercial fuels emits a great deal of SO_x, which is one of the main sources of air pollution and makes seriously harm to people's health [1,2]. Therefore, the desulfurization of commercial fuels becomes an important worldwide issue. Hydrodesulfurization (HDS) process is considered to be the most effective method for the removal of most aliphatic sulfur compounds to produce clean fuel. Nevertheless, heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives are hard to be removed due to the steric hindrance of alkyl substitutes, thus making HDS process more complicated and inefficient [3]. In addition, the process requires severe operation conditions, high hydrogen consumption and high cost to achieve the desired product of clean fuel. Therefore, the alternative desulfurization technologies to produce clean fuel with high efficiency and low energy consumption have been widely developed [4,5].

Adsorptive desulfurization (ADS) is recognized to be one of the most promising technology among alternative methods, as its apparent advantages of mild operating conditions, easy availability, hydrogen-free consumption, low cost, less environmental pollution and so on. In the past decades, various types of adsorbents such as activated carbon [6, 7], zeolites [8, 9], metal oxides [10-12], metal-organic frameworks (MOFs) [13, 14], mesoporous materials [15-18] have been extensively investigated. Park et al. [19] studied Ni-based adsorbents Ni/KIT-6 and Ni/SBA-15 for sulfur adsorption in diesel and it was indicated that Ni/KIT-6 exhibited a larger total sulfur adsorption capacity (3.3 mgS/g) than that of Ni/SBA-15 (2.3 mgS/g), attributing to the superior three-dimensional pore structure and large pore volume of KIT-6. Thus, it is clear that the high surface area, large pore volume and pore size of adsorbents are crucial for improving adsorptive performance.

It should be noted that the existence of aromatic compounds in fuels has influences on sulfur adsorption capacity due to the competitive adsorption [20-23]. The adsorption

mode of aromatics is similar to that of sulfur compounds with the thiophene ring toward active sites through π electronic interaction. Therefore, the selectivity of adsorbents is a key factor for evaluating desulfurization performance. Mesoporous silica materials are usually used as supports due to their high specific surface area, large pore volume and abundant silanol groups on the surface which are beneficial for loading metal species, and the specific active sites can greatly enhance the selective desulfurization performance. Hence, many attempts have been focused on the modification of adsorbents with transition metals like Cu, Ag, Ni, Pd, Pt, which can form π -complexation or sulfur-metal interaction (S-M) with sulfur compounds [24-26]. Notably is that silver can form both π -complexation and sulfur-metal interaction [27]. Additionally, it is interesting to find that the hydrophobic nature of carbonaceous materials and synergistic effects with metal species would also promote the ADS selectivity [28], but unfortunately, to the best of our knowledge, few reports on the usage of carbon-silica composites as adsorbents for selective ADS until now.

Herein, mono-dispersed dendritic mesoporous silica and silica/carbon nanospheres (DMS/CNs) with various particle sizes and carbon contents were controllably fabricated and applied as adsorbents for selective removal of DBT at ambient conditions. The particle size of DMS/CNs could be easily controlled by simply adjusting the stirring rate in the synthesis process and the carbon content was varied under different post-treatment method. It is shown that the adsorptive capacity was increased with the increase of the carbon content of DMS/CNs, and the smaller the particle size, the faster the adsorption rate could be reached. Furthermore, AgNO_3 was introduced by wet impregnation and thermal dispersion methods, and also used for selective ADS in the presence of toluene. It was found that the ADS performance was significantly enhanced due to the π -complexation and S-Ag interaction between Ag species and DBT molecules, and AgNO_3 supported over DMS/CNs with high carbon content ($\text{Ag/S-100-H}_2\text{SO}_4$) showed the highest activity and selectivity for DBT, attributing to its large center-radial mesopore channels and a synergistic effect between carbon substrate and silver active species.

2. Experimental

2.1 Chemicals

All the chemicals were of analytical grade and used as received without further purification. Cetyltrimethylammonium bromide (CTAB), triethanolamine (TEA), tetraethyl orthosilicate (TEOS), cyclohexane, sulfuric acid (H_2SO_4), silver nitrate (AgNO_3), n-heptane, toluene, were purchased from Aldrich. Dibenzothiophene (DBT) was purchased from Alpha. H_2O used in all experiments was deionized water.

2.2 Methods

2.2.1 Synthesis of DMS/CNs

The as-synthesized DMS/CNs were prepared according to an oil-water biphasic stratification approach [29]. The synthesis of DMS/CNs with various particle sizes list as follows. Firstly, a mixture containing 3.125 g of CTAB and 9.375 g of H_2O was added into a 100-ml round bottom flask and stirred for 0.5 h at 60 °C, then 18 ml of H_2O and 0.09 ml of TEA were added into above solution and stirred for 1 h. Afterward, 10 mL of TEOS (20 v/v % in cyclohexane) was gently dropped and capped with a condenser pipe. The reaction was maintained at 60 °C for 20 h in an oil bath with reflux under different magnetic stirring speed (100, 300, and 350 rpm). After removing the upper oil layer, the products were collected by centrifugation and washed with ethanol and water for several cycles. The as-made samples were dried in vacuum at 40 °C all over the night. The obtained white powders with different particle sizes were denoted as S-X, in which X represented the stirring speed of 100, 300 and 350 rpm.

The typical preparations of the samples with various carbon contents were carried out according to the following procedures. By post-treating the above as-synthesized samples with different methods, the DMS/CNs with different carbon contents were obtained. The as-made samples S-100, S-300 and S-350 were calcined under air atmosphere at 600 °C for 3 h to produce samples S-100- O_2 , S-300- O_2 and S-350- O_2 without carbon. The samples with low carbon contents (S-100- N_2 , S-300- N_2 and S-350- N_2) were obtained by treating the as-made samples under N_2 atmosphere at 600 °C for

3 h. The samples with high carbon contents (S-100-H₂SO₄, S-300-H₂SO₄ and S-350-H₂SO₄) were produced via a pretreatment approach with H₂SO₄ before calcined under N₂ atmosphere. In brief, 1.5 mL of 10 wt. % H₂SO₄ was dropped on the white powder of the as-made samples and kept at room temperature for 2 h, followed by drying at 100 °C for 12 h, then at 160 °C for 12 h under ambient conditions. Then the powder was subjected to calcination at 600 °C for 3 h under N₂ atmosphere.

2.2.2 Preparation of supported Ag adsorbents over DMS/CNs

The supported Ag adsorbents were prepared by wet impregnation and thermal dispersion methods. In a typical process, 1 g of support materials were dissolved in 10 ml of deionized water with stirring, then 0.175 g of AgNO₃ (10 wt. %) were dissolved in 5 ml of H₂O, followed by adding the silver precursor solution into the above solution. After treated under the ultrasonic condition for 30 min at room temperature, the mixture was placed in a vacuum oven and evaporated at 80 °C for 12 h, then dispersed at 105 °C for 5 h under N₂ atmosphere. All processes were operated away from light. The obtained adsorbents were denoted as Ag/S-100-O₂, Ag/S-100-N₂, Ag/S-100-H₂SO₄, Ag/S-300-H₂SO₄ and Ag/S-350-H₂SO₄, respectively.

2.3 Characterization

Scanning electron microscopy (SEM) images were obtained using a FEI Quanta 200F microscope (USA) operated at 15 kV. Before analysis, the samples were coated with gold by cathodic sputtering. Transmission electron microscopy (TEM) was applied on a Philips Tecnai G2 F20 instrument (Netherlands) at an accelerating voltage of 200kV. N₂ adsorption-desorption measurements of the samples were performed on a Micromeritics ASAP 2002 instrument (USA) at -196 °C. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method and the pore size distributions were evaluated by the Barrett-Joyner-Halenda (BJH) method [30]. Fourier transform infrared spectroscopy (FTIR) spectra were performed on a Thermo Nicolet Nexus 470 FTIR instrument (USA) with wave numbers ranging from 4000 to 400 cm⁻¹. The transparent discs were prepared by mixing the samples with dry KBr and the weight ratio of the sample to dry KBr was around 1:100. The thermal decomposition

behaviors of the samples were carried out on a STA409PC thermogravimetric analyzer (Netzsch, Germany) from 25 to 800 °C under oxygen (50 mL/min) atmosphere with a heating rate of 10 °C/min. Powder X-Ray diffraction (XRD) analyses were conducted on a Philips X'Pert diffractometer equipped with a Cu K α radiation and operated at 40 kV and 30 mA with 2θ scanning speed at 10° per minute and diffraction lines of 2θ between 8 and 70°. Raman spectra of the samples were performed by in Via Raman spectrometer (Renishaw company) using a wavelength of 633 nm for the laser source.

2.4 Adsorptive test

Adsorptive desulfurization experiments were conducted by a batch method under ambient conditions with DBT as the model sulfur compounds. The model fuel I was prepared by mixing DBT and n-heptane with the initial sulfur content of 200 mg/L. For competitive adsorption experiments, the model fuel II was prepared by mixing DBT and a mixture of n-heptane and toluene (4 : 1 in volume ratio) while the sulfur content was kept the same. In a typical process, 0.25 g of adsorbent and 50 ml of model fuel were added into a glass flask. The mixture was magnetically stirred in a water bath at 30 °C for the contact time in the range of 5-120 min, then the liquid phase was separated from adsorbents by filtration. The sulfur contents of samples were measured with a sulfur analyzer (RPP-2000S, Taizhou Central Analytical Instruments Co. Ltd., P.R.China). The amount of sulfur adsorbed by the adsorbent, q_t (mgS/g), was calculated by using the following Eq. (1):

$$q_t = (C_0 - C_t) \cdot \frac{V}{W} \quad (1)$$

Where, C_0 and C_t (mg/L) are the sulfur concentrations of model fuel at contact time = 0 and t , respectively. V (L) is the volume of model fuel and W (g) is the weight of the adsorbent.

3. Results

3.1 Characterizations of DMS/CNs

3.1.1 Morphology and pore structure of DMS/CNs

The SEM images and particle size distributions of DMS/CNs are shown in Fig. 1,

revealing a uniform and mono-dispersed spherical morphology with adjustable particle sizes. It can be clearly seen that the average particle size decreases from around 145 (A1-A3) to 85 (B1-B3), then to 80 nm (C1-C3) with the increase of stirring speed from 100 to 350 rpm. The samples treated under N₂ atmosphere (A2-C2) and pretreated with H₂SO₄ before calcined under N₂ atmosphere (A3-C3) show a similar particle size as the corresponding samples calcined under O₂ atmosphere, indicating the different post-treating methods have almost no influence on the morphology. It should be noted that S-350 samples have wrinkled surface (C1-C3), different from S-100 and S-300 samples with the smooth surface, which may have impact on the structural properties and desulfurization performance.

The corresponding TEM images in Fig. 2 display highly uniform monodispersed nanospheres with dendritic center-radial oriented pore structure for S-100 (A1-A3) and S-300 (B1-B3). TEM images for S-350 (C1-C3) show an irregular “flower-like” pore structure with a large pore size. Notably, the pore structure can also be maintained by post-treated with different methods.

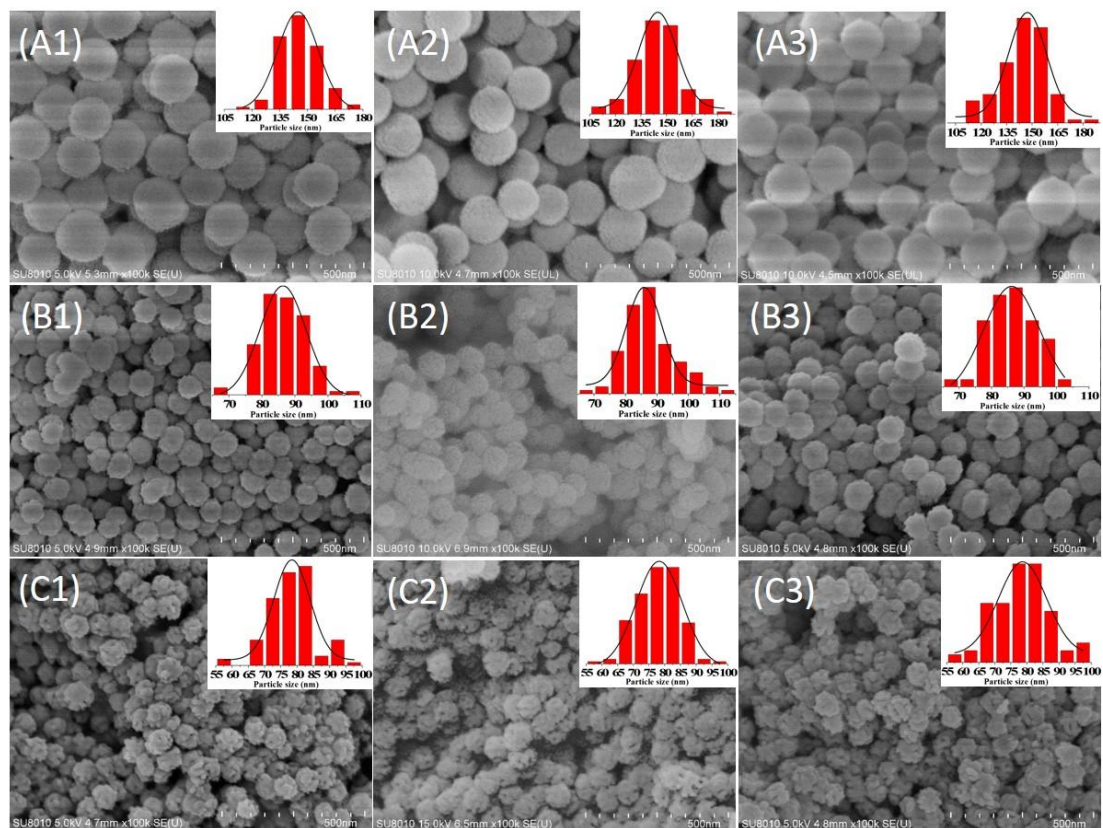


Fig. 1 SEM images and particle size distributions of DMS/CNs: (A1) S-100-O₂; (A2) S-100-N₂; (A3) S-100-H₂SO₄; (B1) S-300-O₂; (B2) S-300-N₂; (B3) S-300-H₂SO₄; (C1) S-350-O₂; (C2) S-350-N₂; (C3) S-350-H₂SO₄

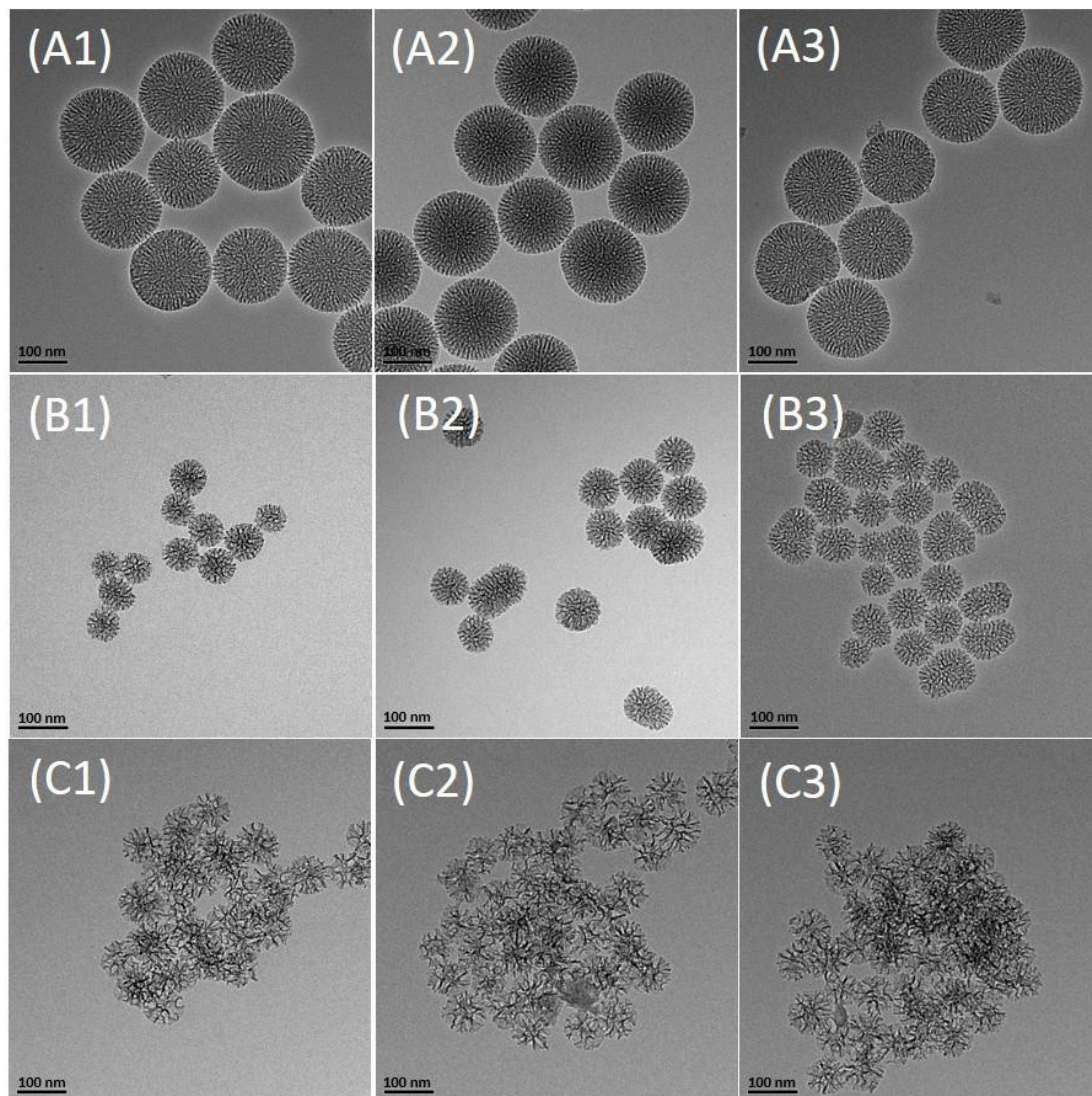


Fig. 2 TEM images of DMS/CNs: (A1) S-100-O₂; (A2) S-100-N₂; (A3) S-100-H₂SO₄; (B1) S-300-O₂; (B2) S-300-N₂; (B3) S-300-H₂SO₄; (C1) S-350-O₂; (C2) S-350-N₂; (C3) S-350-H₂SO₄

N₂ adsorption-desorption isotherms and the pore size distributions calculated from the adsorption branch of DMS/CNs are shown in Fig. 3. The corresponding textural characteristics (the specific surface area S_{BET} , total pore volume V_t and pore diameter D_p) are summarized in Table 1. All samples display a typical type IV curve, and the isotherms present a capillary condensation step in the relative pressure range of 0.45-0.78 with H1 hysteresis loop for the S-100 samples (Fig. 3A), indicating the existence

of uniform and large mesopores. The capillary condensation step of S-300 (Fig. 3C) occurs in the relative pressure range of 0.60-0.80 with H1 hysteresis loop, demonstrating its mesoporous structure with a larger pore size than that of S-100. As illustrated in Fig. 3E, the isotherms of S-350 exhibit H3 hysteresis loop with a sharp capillary condensation step in the high relative pressure range of 0.8-1.0, confirming the existence of large pores or stacking pores. Figs. 3B and D display intense and narrow mesopore size distributions for S-100 and S-300. The pore sizes are found to be increased from around 6.0 nm to 7.0 nm with the increase of stirring speed and affected by the different post-treated methods. S-350 samples show a much larger pore size around 30-40 nm. Furthermore, it can be seen from Table 1 that the specific surface areas, pore volumes and pore sizes of the samples pretreated with H₂SO₄ then calcined under N₂ atmosphere are higher than the other two post-treated processes. As for S-100 samples, S-100-O₂, S-100-N₂ and S-100-H₂SO₄ possess S_{BET} and V_t of 534, 539, 572 m²/g and 0.91, 0.98, 1.01 cm³/g, respectively. S-300 and S-350 samples follow the similar tendency. It should be noted that the stirring speed has little effect on the specific surface area of the samples, but it has a great influence on the pore volume: S-350 > S-300 > S-100.

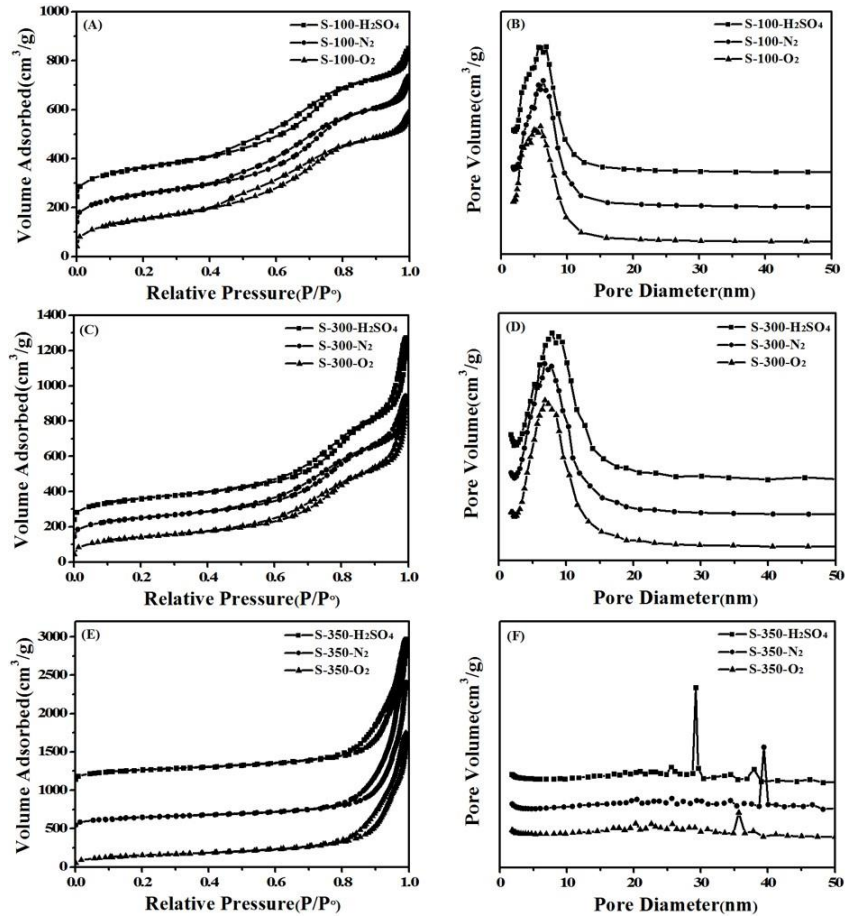


Fig. 3 N₂ adsorption-desorption isotherms of DMS/CNs: (A) S-100; (C) S-300; (E) S-350, and pore size distribution curves calculated from adsorption branches: (B) S-100; (D) S-300; (F) S-350

Table 1. Textural properties of DMS/CNs with various particle sizes and carbon contents

Absorbents	S_{BET} (m ² /g)	V_t (cm ³ /g)	D_p (nm)
S-100-O ₂	534	0.91	6.0
S-100-N ₂	539	0.98	6.4
S-100-H ₂ SO ₄	572	1.01	6.8
S-300-O ₂	490	1.33	6.9
S-300-N ₂	521	1.30	6.9
S-300-H ₂ SO ₄	555	1.66	7.8
S-350-O ₂	525	2.70	—
S-350-N ₂	516	2.90	—
S-350-H ₂ SO ₄	576	2.89	—

3.1.2 Chemical compositions of DMS/CNs

As confirmed by FTIR spectra in Fig. 4, the as-prepared sample S-100 without calcination (Fig. 4a) displays two absorption bands around 2920 and 2849 cm^{-1} originating from the C-H bonds of the surfactant CTAC [31]. While these two absorption bands disappear for the calcined samples S-100- O_2 (Fig. 4b), S-100- N_2 (Fig. 4c) and S-100- H_2SO_4 (Fig. 4d), indicating the CTAC can be completely removed by calcination at 600 $^\circ\text{C}$. But as shown in Fig. 5, the samples calcined under N_2 atmosphere show a more weight loss than those calcined under O_2 atmosphere from TG analysis, which is derived from the partial carbonation of CTAC inside the mesopore channels. The carbon contents in S-100- N_2 , S-300- N_2 and S-350- N_2 can be calculated to be 3.0, 2.5 and 2.5 wt. %, respectively. The pretreated process using H_2SO_4 carbonization before calcination under N_2 atmosphere is intended to improve the carbon contents, which can be successfully increased to be 5.0, 4.5 and 5.5 wt. % for S-100- H_2SO_4 , S-300- H_2SO_4 and S-350- H_2SO_4 , respectively. In addition, the powder samples are changed from white to gray and then to black in color (Fig. S1), demonstrating the increase of carbon contents.

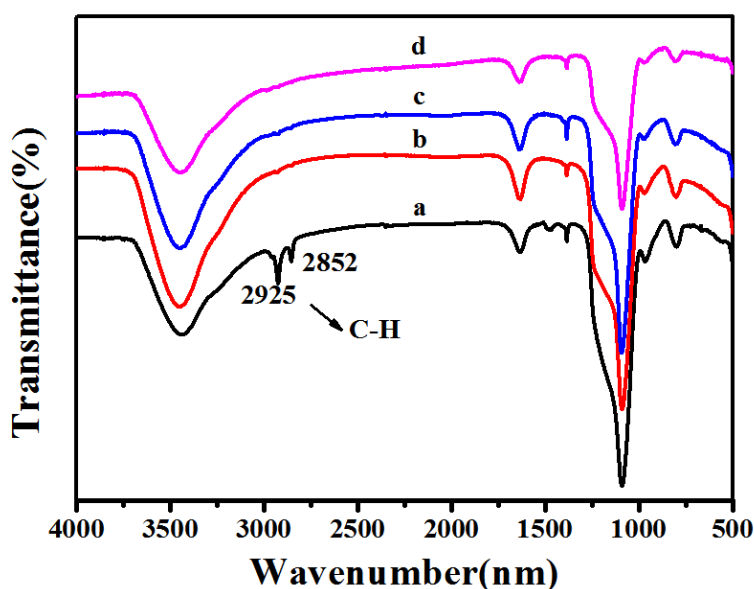


Fig. 4 FTIR spectra of the S-100 samples: (a) S-100 without calcination; (b) S-100- O_2 ; (c) S-100- N_2 ; (d) S-100- H_2SO_4

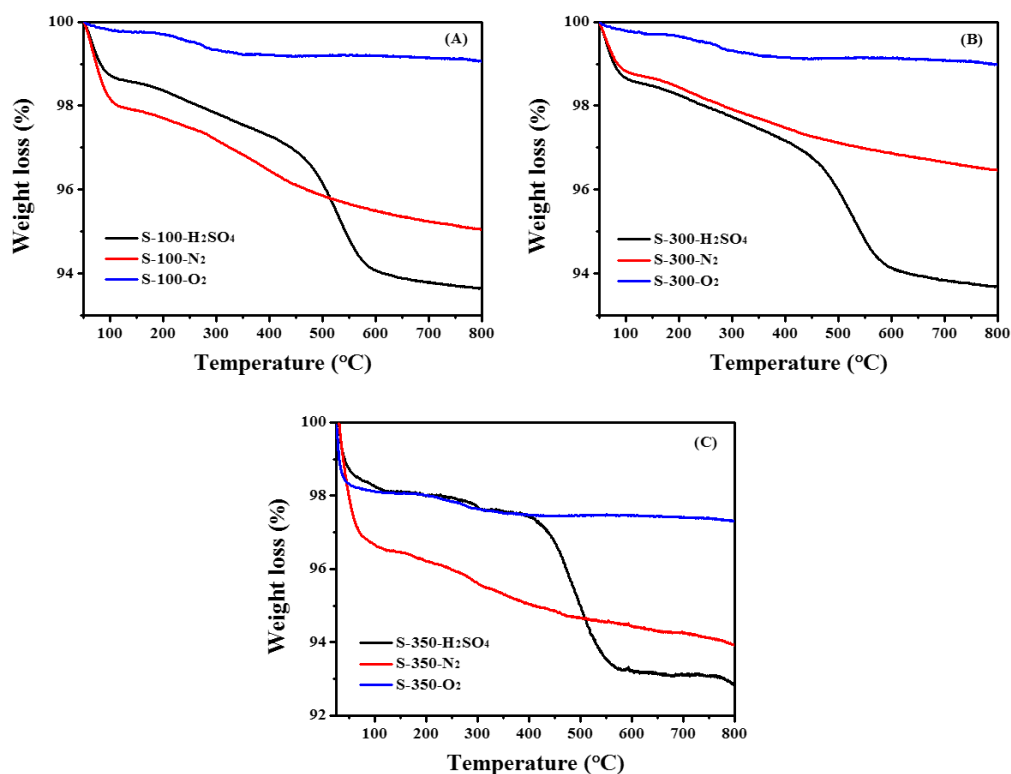


Fig. 5 TG curves of DMS/CNs: (A) S-100; (B) S-300; (C) S-350

Moreover, Raman spectrum in Fig. 6 displays two obvious adsorption bands D (1360 cm^{-1}) and G (1590 cm^{-1}) for S-100-H₂SO₄, deriving from the band stretching of sp² carbon [32]. The results indicate that those samples treated with H₂SO₄ carbonization before calcination under N₂ atmosphere possess sp² carbon with a certain degree of graphitization, which may provide adsorption active sites for the thiophenic compounds [31]. Additionally, all the samples show a broad peak at $2\theta=23^\circ$ in XRD spectra (Fig. S2), confirming the amorphous structure.

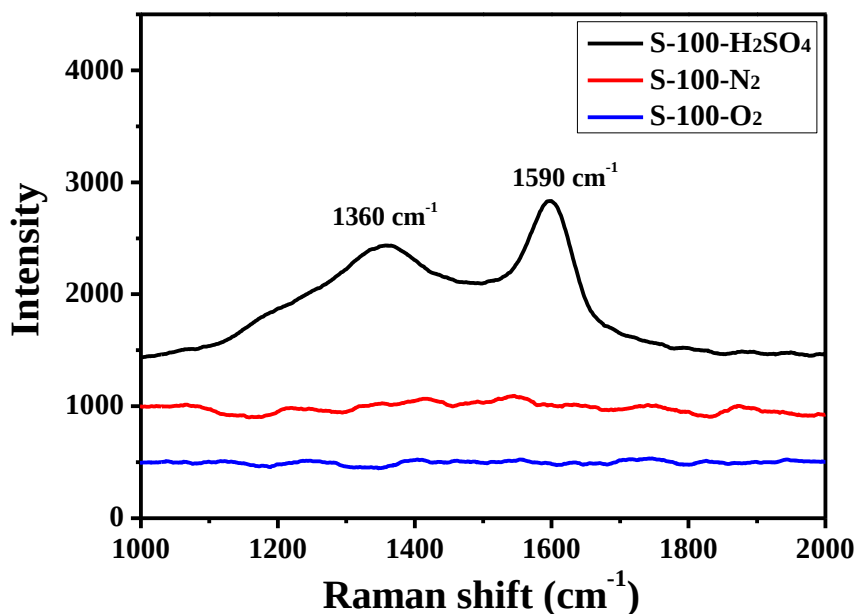


Fig. 6 Raman spectra of the S-100 samples

3.2 Adsorption of DBT on the DMS/CNs

Fig.7 shows the DBT adsorption kinetics on different materials under ambient conditions and the equilibrium adsorption capacity are summarized in Fig. S3. As can be seen from Fig. 7A (S-100 samples), the equilibrium can be reached within 60 min for all samples, indicating the different post-treatment methods have almost no influence on the adsorption rate. Yet, the equilibrium situation for S-300 samples (Fig. 7B) and S-350 samples (Fig. 7C) can be achieved at around 40 min and 30 min, respectively, and the adsorption amount of S-350 reaches 80% of equilibrium adsorptive capacity within 10 min, demonstrating the smaller the particle size and the larger the pore size, the faster the adsorption equilibrium can be attained. It is notable that the different post-treatment methods have a similar effect on the adsorption amounts for DBT, and the adsorption amounts follow the order of $S-X-H_2SO_4 > S-X-N_2 > S-X-O_2$ at the same stirring speed, which is consistent with the carbon content of DMS/CNs. In addition, the adsorption amounts of samples treated with H_2SO_4 carbonization before calcination under N_2 atmosphere are almost two times higher than the samples calcined under O_2 due to the high carbon content of $S-X-H_2SO_4$ samples.

It is also found that the adsorption capacities of the DMS/CNs with different particle sizes at the same post-treatment condition have a little change, ascribing to the complicated factors of carbon contents and pore structure properties. As to the samples S-X-H₂SO₄ and S-X-N₂, the carbon content and structural properties are responsible for the ADS performance. But for the samples S-X-O₂, the adsorption amounts are simply associated with the surface area and pore volume.

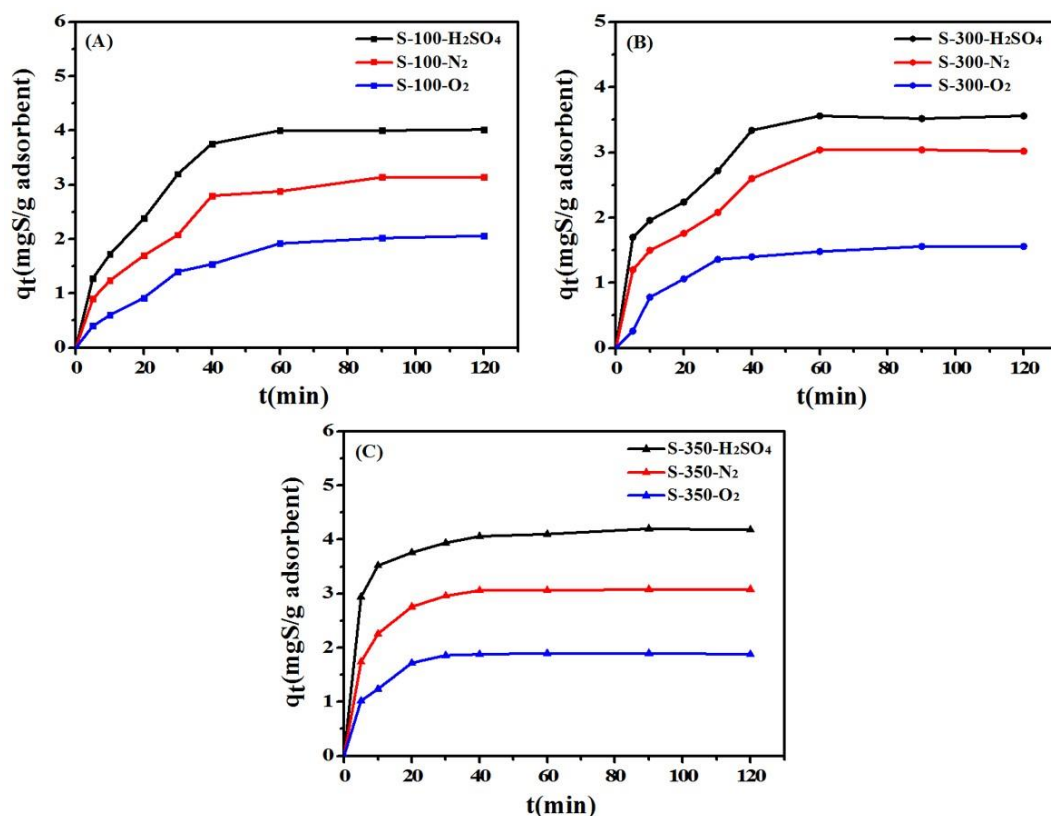


Fig. 7 Adsorption kinetic curves of the DMS/CNs with different particle sizes and carbon contents for adsorption of DBT: (A) S-100; (B) S-300; (C) S-350

In order to better understand the adsorption kinetic process, the kinetic models of pseudo-first-order and pseudo-second-order models as displayed in Eq. S1 and Eq. S2 were used to evaluate the experimental results and deduce the kinetic parameters for the adsorption of DBT over DMS/CNs [33]. The plots of $\ln(q_e - q_t)$ vs. t for the pseudo-first-order model and t/q_t vs. t for the pseudo-second-order model are shown in Fig. S4 and Fig. S5, respectively, and the calculated parameters together with the corresponding R^2 values are given in Table 2. The linear correlation coefficients for pseudo-second-

order model are all higher than those for pseudo-first-order model, indicating the adsorption processes of DBT over all adsorbents are fitted well with the pseudo-second-order model, that is, the adsorption is a chemical adsorption process [33]. Additionally, the rate constants k_2 of S-350 is ten or five times higher than those for S-100 or S-300, respectively, indicating that the smaller the particle size and the larger the pore size, the faster the adsorption rate can be achieved. Therefore, the fast-kinetic equilibrium behaviors for DBT adsorption over DMS/CNs originated directly from its unique features of open pore channels and large pore sizes.

Table 2. Pseudo-first-order and pseudo-second-order kinetic model for the adsorption of DBT

Sorbent	Fuel	Pseudo-first-order				Pseudo-second-order			
		C_0	$q_{e,exp}$	$q_{e,calc}$	k_1	R^2	$q_{e,calc}$	k_2	R^2
		(mg S/L)	(mgS/g)	(mgS/g)	(min ⁻¹)		(mgS/g)	(g/mg·min)	
S-100-O ₂	206	2.06	2.67	0.04535	0.9048	2.47	0.01225	0.9834	
S-100-N ₂	206	3.14	2.95	0.04275	0.9056	3.71	0.01435	0.9892	
S-100- H ₂ SO ₄	206	4.02	4.29	0.06754	0.8881	4.59	0.01593	0.9908	
S-300-O ₂	206	1.56	1.32	0.05048	0.9025	1.84	0.02281	0.9722	
S-300-N ₂	206	3.02	2.12	0.04401	0.8902	3.43	0.02142	0.9871	
S-300- H ₂ SO ₄	206	3.56	2.59	0.04744	0.9041	3.89	0.02687	0.9925	
S-350-O ₂	206	1.88	0.33	0.02924	0.4073	1.96	0.1020	0.9981	
S-350-N ₂	206	3.08	1.63	0.08427	0.8799	3.18	0.1548	0.9994	
S-350-H ₂ SO ₄	206	4.18	0.88	0.03377	0.9306	4.28	0.09939	0.9999	

3.3 Characterizations of silver loaded DMS/CNs

In order to further improve the desulfurization performance, Ag(I) species were introduced into the selected DMS/CNs by wet impregnation and thermal dispersion methods. The samples of S-100-O₂, S-100-N₂, S-100-H₂SO₄, S-300-H₂SO₄ and S-350-H₂SO₄ with favorable textural characteristics were selected for introducing guest species. As presented in Fig. S6, the morphology of all materials after incorporating AgNO₃ preserves well and the silver species are uniformly loaded on the surface of DMS/CNs which can be observed from SEM-EDX spectra (Fig. S7). The structural

features and morphologies of Ag/DMS/CNs can be identified from TEM images as shown in Fig. 8. Most of the silver species are highly dispersed inside the dendritic mesopores for the samples Ag/S-100-O₂ and Ag/S-100-N₂ (Fig. 8A and B) but the other three samples with high carbon contents (Fig. 8C, D and E) emerge sporadically aggregated Ag nanoparticles on the surface of DMS/CNs, indicating that the high content carbon is unfavorable for the dispersion of active metals due to the hydrophobic feature.

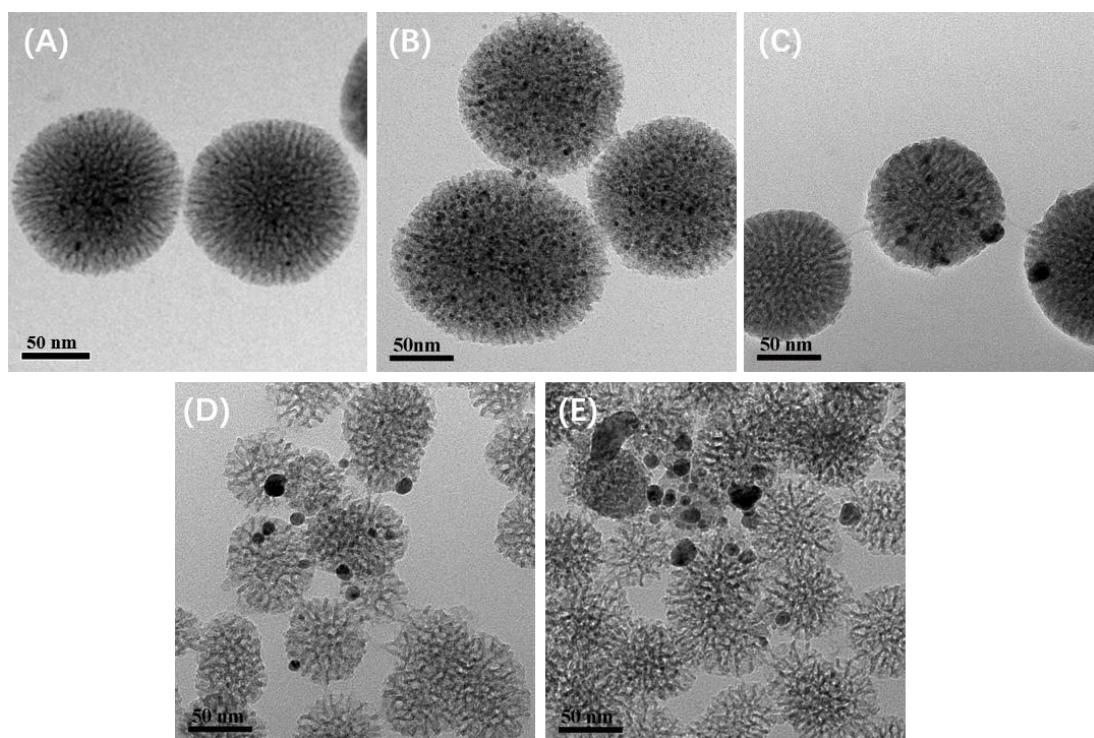


Fig. 8 TEM images of Ag/DMS/CNs: (A) Ag/S-100-O₂; (B) Ag/S-100-N₂; (C) Ag/S-100-H₂SO₄; (D) Ag/S-300-H₂SO₄; (E) Ag/S-350-H₂SO₄

The X-ray diffraction (XRD) patterns in Fig. 9 display that all the DMS/CNs after modification of AgNO₃ show a broad peak at $2\theta=23^\circ$ assigned to the amorphous structure. In addition, no characteristic diffraction peaks of Ag nanoparticles and AgNO₃ can be observed for Ag/S-100-O₂ and Ag/S-100-N₂ (Fig. 9a and b), indicating the good dispersion of Ag species. However, the characteristic peaks assigned to the metallic silver are observed at $2\theta = 38.12^\circ, 44.30^\circ, 64.44^\circ, 77.40^\circ$ for the samples Ag/S-100-H₂SO₄, Ag/S-300-H₂SO₄ and Ag/S-350-H₂SO₄, corresponding to (111),

(200), (220), (311) reflections from the face-centered cubic structure of Ag nanoparticles (JCPDS NO. 00-004-0783) [34]. The results reveal that the silver species consisting of metallic silver and active silver phase (Ag^+) disperse better on the samples S-100- O_2 and S-100- N_2 . It has been proved that Ag(I) can improve the adsorptive capacity through π -complexation (π -Ag interaction) and S-Ag interaction between Ag^+ and DBT [23,35], thus the dispersion state of silver species can influence the ADS performance. Moreover, the characteristic peak intensities of metallic silver for Ag/S-300- H_2SO_4 and Ag/S-350- H_2SO_4 with higher carbon contents are much stronger than Ag/S-100- H_2SO_4 , which may be because the higher surface area of S-100- H_2SO_4 favors the loading and dispersion of Ag species. These results are in good agreement with the above TEM results.

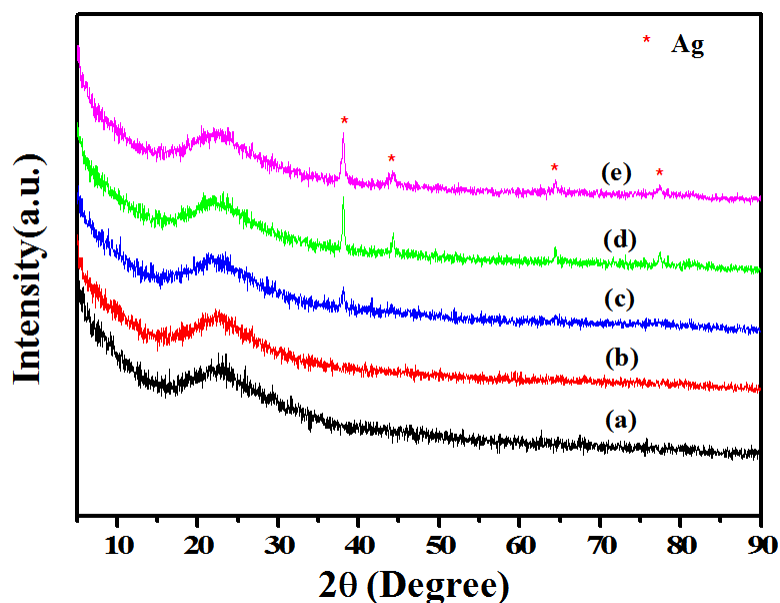


Fig. 9 Wide angle XRD patterns of Ag/DMS/CNs: (a) Ag/S-100- O_2 ; (b) Ag/S-100- N_2 ; (c) Ag/S-100- H_2SO_4 ; (d) Ag/S-300- H_2SO_4 ; (e) Ag/S-350- H_2SO_4

3.4 Adsorption of DBT on the silver supported DMS/CNs

Fig.10 shows the ADS performance of the selected Ag/DMS/CNs and it is indicated that for the Ag/S-100-X samples (Fig. 10A), the ADS performance increases with the increase of carbon content, consistent with the corresponding S-100 adsorbents

before loading AgNO_3 . But for $\text{Ag/S-X-H}_2\text{SO}_4$ samples (Fig. 10B), the adsorption behaviors display different trend with the corresponding samples without loading AgNO_3 . S-350- H_2SO_4 presents the highest adsorption capacity (4.18 mgS/g) due to its highest surface area and carbon content among the samples and S-100- H_2SO_4 with the similar surface area but lower carbon content shows a slightly lower ADS capacity (4.02 mgS/g). However, it is surprising that $\text{Ag/S-100-H}_2\text{SO}_4$ (6.88 mgS/g) is better than $\text{Ag/S-350-H}_2\text{SO}_4$ (6.48 mgS/g), which may be because S-100- H_2SO_4 with high surface area and low carbon content is favorable for the dispersion of Ag species, thus more active sites can be exposed to the DBT molecules resulting in the better ADS performance. As a whole, the introduction of AgNO_3 results in a sharp increase in the adsorption capacity for all the samples as shown in Table S1, and the increased percentage of the adsorption capacity follows the order of S-100- O_2 (146%) > S-100- N_2 (92%) > S-100- H_2SO_4 (71%) > S-300- H_2SO_4 (69%) > S-350- H_2SO_4 (55%). It is noteworthy that the increased percentages for samples S-100- O_2 and S-100- N_2 after loading of silver are about two or three times higher than the samples pretreated with H_2SO_4 , indicating the utilization efficiencies of silver active sites are higher for the formers. It is worth noting that the adsorption capacity of Ag/DMS/CNs is prior to the other reported adsorbents under the same conditions [36,37].

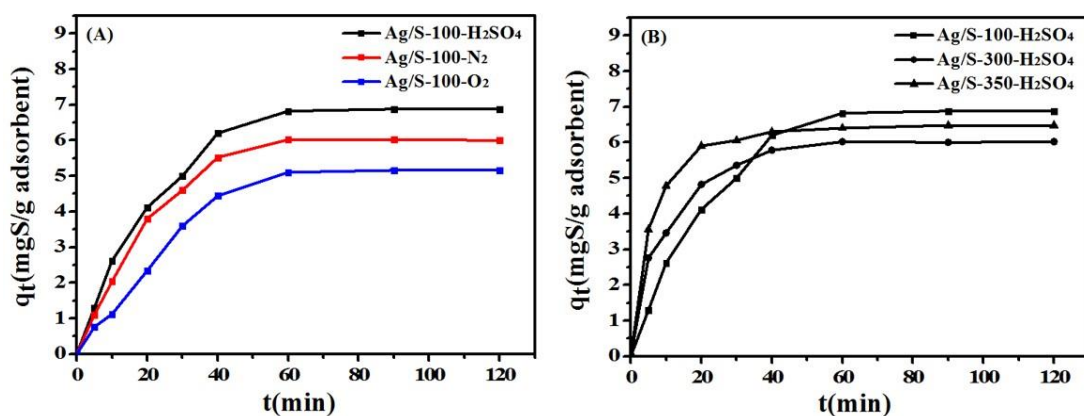


Fig. 10 Adsorption kinetic curves of Ag/DMS/CNs for adsorption of DBT: (A) S-100 series samples; (B) absorbents pretreated with sulfuric acid

3.5 Selective ADS performance

The aromatic compounds in fuels can compete with sulfur compounds in ADS process, therefore toluene was taken as a probe molecule to evaluate the selective ADS performance of Ag/DMS/CNs and the results are shown in Fig. S8 and Table 3. As can be seen from Fig. S8, the adsorption capacities for all the samples decrease after the addition of toluene. The selectivity factor K was calculated from $K = (q_{e1}-q_{e2})/q_{e1}$ and applied to describe the selective adsorption ability, and the smaller the K value, the better the selective ADS performance is exhibited. Table 3 shows that K value of the samples before loading AgNO_3 decreases with the increase of the carbon contents and changes in the sequence of $\text{S-100-H}_2\text{SO}_4(K=32.6\%) > \text{S-100-N}_2(K=34.4\%) > \text{S-100-O}_2(K=39.3\%)$, demonstrating the carbon substrate can improve the ADS selectivity. Besides, the K value of the DMS/CNs decreases after the introduction of AgNO_3 and $\text{Ag/S-100-H}_2\text{SO}_4$ possesses the lowest K value of 29.7%, indicating the Ag species enhance the selectivity. Among all the DMS/CNs, $\text{Ag/S-100-H}_2\text{SO}_4$ shows the highest adsorptive capacity (6.88 mgS/g) and selectivity ($K=29.7\%$), which is superior to the other reported results with K value in the range of 50-75% in the presence of aromatics [12,38,39].

Table 3. The selectivity factor K and the corresponding equilibrium adsorption capacities

Samples	K (%)	Adsorption capacity (mgS/g)	
		Without toluene	With toluene
S-100-O ₂	39.3	2.06	1.25
S-100-N ₂	34.4	3.14	2.06
S-100-H ₂ SO ₄	32.6	4.02	2.71
Ag/S-100-O ₂	30.4	5.16	3.59
Ag/S-100-N ₂	29.9	6.02	4.22
Ag/S-100-H ₂ SO ₄	29.7	6.88	4.84

Note: $K = (q_{e1}-q_{e2})/q_{e1}$

q_{e1} : Sulfur capacity without toluene

q_{e2} : Sulfur capacity with toluene

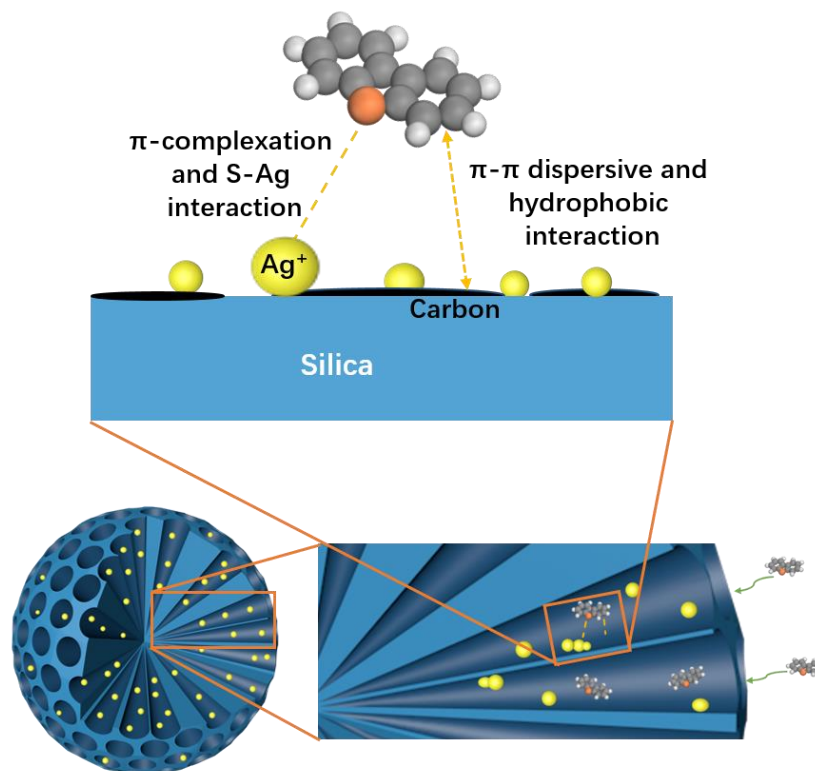
4. Discussion

Based on the above results, the unique center-radial pore structure, carbon species located on the mesopore channel of DMS/CNs, and the loaded silver species play important roles in the ADS performance. As to the DMS/CNs without loading of silver, it is found that the surface area has little effect on the adsorption rate. The adsorption rate is depended on the particle size and pore size, and the smaller the particle size and the larger the pore size, the faster the adsorption rate could be received. Yet the adsorption capacity increases dramatically upon the carbon content of the DMS/CNs, and the higher the carbon content, the better the ADS performance is achieved. The open pore channels of DMS/CNs with large pore size can facilitate the diffusion of sulfur compounds. Thus, the faster adsorption process can be reached for small-sized S-350 with larger open dendritic-like pore channel. Besides, the carbon species located on the pore channels of DMS/CNs can not only optimize the textural of materials such as the increased specific surface area (Table 1), but also can increase the adsorption active sites because the graphitized carbonaceous species could provide the aromatic carbon structure which will interact with the benzene ring of DBT through π - π dispersive interaction and hydrophobic interaction as shown in Scheme 1 [28]. Thereby the superior ADS performance can be achieved for the S-X-H₂SO₄ with high carbon contents.

While, after the introduction of silver species, the adsorption capacity and selectivity dramatically increased for all DMS/CNs (as demonstrated in Table S1 and Table 3), ascribing to the interaction between Ag⁺ and DBT molecules as indicated in Scheme 1. Ag(I) species can form the usual s-bonds with the empty s-orbitals, meanwhile, their d-orbitals can back-donate electron density to the antibonding π -orbitals (π^*) of the sulfur rings to form a π -complexation bond [40]. In addition, the thiophene can as an n-type donor by donating the lone pair electrons that lie in the plane of molecule ring to the metal, thus forming sulfur-metal bond (S-Ag). Furthermore, molecular orbital calculations have shown that both π -complexation and S-M bond between thiophenic compounds should be stronger than that with benzene [41]. Hence,

1 the enhanced selective ADS performance is obtained for the supported silver adsorbents.
2 Additionally, it should be noted that the increased percentage of ADS capacity has a
3 strong dependence on the dispersion state of silver species, thus is varied differently
4 with the change of carbon content.
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8 In view of the above results, the carbon matrix located on the pore channels is
9 double-faced. For one thing, the higher the carbon content, the stronger the π - π
10 dispersive interaction and hydrophobic interaction between carbon species and DBT.
11 On the other hand, the hydrophobic nature of carbon is not conducive to the loading of
12 active metals, thereby resulting in the aggregation of silver species and the decrease of
13 active sites when the carbon content increases. Hence, a proper carbon content is
14 favorable for the enhancement of ADS performance of the DMS/CNs loaded with silver.
15 Furthermore, the good adsorption selectivity of Ag/S-100-H₂SO₄ would be attributed
16 to the formation of synergistic effect between carbon substrate and silver active species,
17 as illustrated in Scheme 1. The DBT molecules can be easily diffused into the open pore
18 channels and adsorbed on the carbon matrix via the π - π dispersive interaction and
19 hydrophobic interaction. Besides, the dendritic pore channels could enhance the
20 accessibility of well-dispersed active silver sites with the DBT molecules. In this way,
21 the thiophene ring of DBT could form π -complexation and S-Ag interaction with silver
22 species, and the benzene ring of DBT could form π - π dispersive and hydrophobic
23 interaction with carbon matrix. By functioning cooperatively in this pattern, the strong
24 adsorption between DBT and adsorbents can be achieved, thereby the higher adsorption
25 capacity and selectivity are gained.
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Scheme 1 The exhibition of the synergistic effect in DBT adsorption on the Ag/DMS/CNs.

5. Conclusion

DMS/CNs with various particle sizes and carbon contents have been successfully fabricated and the adsorption capacity increases with the increase of carbon contents in DMS/CNs and the adsorption dynamics simulation indicates that the smaller the particle size, the faster the adsorption rate can be achieved. After loading silver, the ADS performance is improved for all absorbents due to the π -complexation and S-Ag interaction, and Ag/S-100-H₂SO₄ exhibits the preferable activity and selectivity for DBT. The significantly enhanced sulfur selectivity could be ascribed to its ordered dendritic mesoporous silica/carbon nature which enhances the accessibility of active metals in the pore channel and the synergistic effect between carbon substrate and supported silver species. In general, the design of the silver modified DMS/CNs in this work might be helpful for developing novel efficient adsorbents.

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