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Superior adsorption capacity of film typed carbon for the abatement of sulfur dioxide

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ABSTRACT

In this study film typed carbons (FTC) are chemically modified to effectively adsorb SO_2 with an excellent capacity, even at very high temperatures (200–300 °C). The FTC has an adsorption capacity of around 1.4 mmol/g at 300 °C, which is 460% more than the commercial activated carbons (0.25 mmol/g). The morphology, surface properties, and porous structure of the FTC were characterized using TEM, FTIR and physisorption analyses, correspondingly. From the interpretation of FTIR spectra of FTC before and after SO_2 adsorption, it is believed that the carboxylate group plays an important role in the adsorption affinity of SO_2 molecules. It is also found that the porous structure is kept intact after the SO_2 adsorption. The FTC is therefore a promising adsorbent for SO_2 abatement.

1. Introduction

Sulfur dioxide discharged as a combustion product of fossil fuels is a major air pollutant causing ecological damages and health problems to humans. Over the last decades, scientists have devoted lots of efforts in the control of SO_x emission by a conventional method called flue gas desulfurization [1–3]. However, it is a costly process particularly involving complex unit operations and designs and “throw-away sorbents”. Catalytic reduction of SO_x is another alternative way, where active reducing agents like carbon monoxide, methane, and syn-gas will be used [4–6]. This method is not substantially used in the industrial practice because of its evolved toxic byproducts in the effluent. At a high reduction temperature, gaseous sulfur (S_2) produced after the reduction process will react with the carbon monoxide to form carbonyl sulfide (COS) which is more toxic than SO_2. Adsorption is a cheaper process that can be simply applied in industry. Activated carbon is a well-known adsorbent, which is not only efficient for volatile organic compounds but also suitable for capturing acidic gases like SO_2, CO_2, CO and NO_x [7–11]. However, there are drawbacks to use activated carbon as an adsorbent. Since most exhausts after combustion process are at high temperatures (higher than 373 K), activated carbon has a comparatively lower adsorption affinity at this temperature. Even a cooling system has been installed in the exhaust, some secondary organic pollutants will still be condensed at such temperature and further separation process will be necessary. Here, we address a novel adsorbent that highly favors the SO_2 adsorption, demonstrating an extraordinary high adsorption capacity even at a relatively high adsorption temperature.

2. Experimental

The film typed carbon (FTC) was fabricated using a templating method which can be found elsewhere in the literature [12]. Briefly, a colloidal silica (Ludox AS-40) of spherical shape with an average diameter of around 40 nm was used as the template, whereas the crotonaldehyde was used as the carbon source. Followed by drying and carbonization, the carbon–silica composite was treated in a mixture of sodium hydroxide and ethanol in a ratio of 1:1 for 2 h at 100 °C. This step was repeated for 6 times and the samples were dried again at 70 °C. Such a critical step is different from the literature. It is believed that this modifying step can dissolve the templated silica and at the same time chemically modify the surface of the carbon.

The blank and chemically modified FTCs were characterized using TEM, FTIR, and physisorption techniques in order to study their morphology, surface properties, and porous structure, correspondingly. To further understand the changes after the SO_2 adsorption, the used FTC was regenerated at 350 °C under vacuum for overnight and then it was used again for the SO_2 adsorption to study the change in the corresponding adsorption capacity.

3. Results and discussion

Fig. 1 shows the TEM images of the developed FTC. The overall view of FTC-1 is shown in Fig. 1a. It can be seen that the FTC is structured with a stack of round-shaped carbon. In a magnified image as displayed in Fig. 1b, the FTC has a diameter of around

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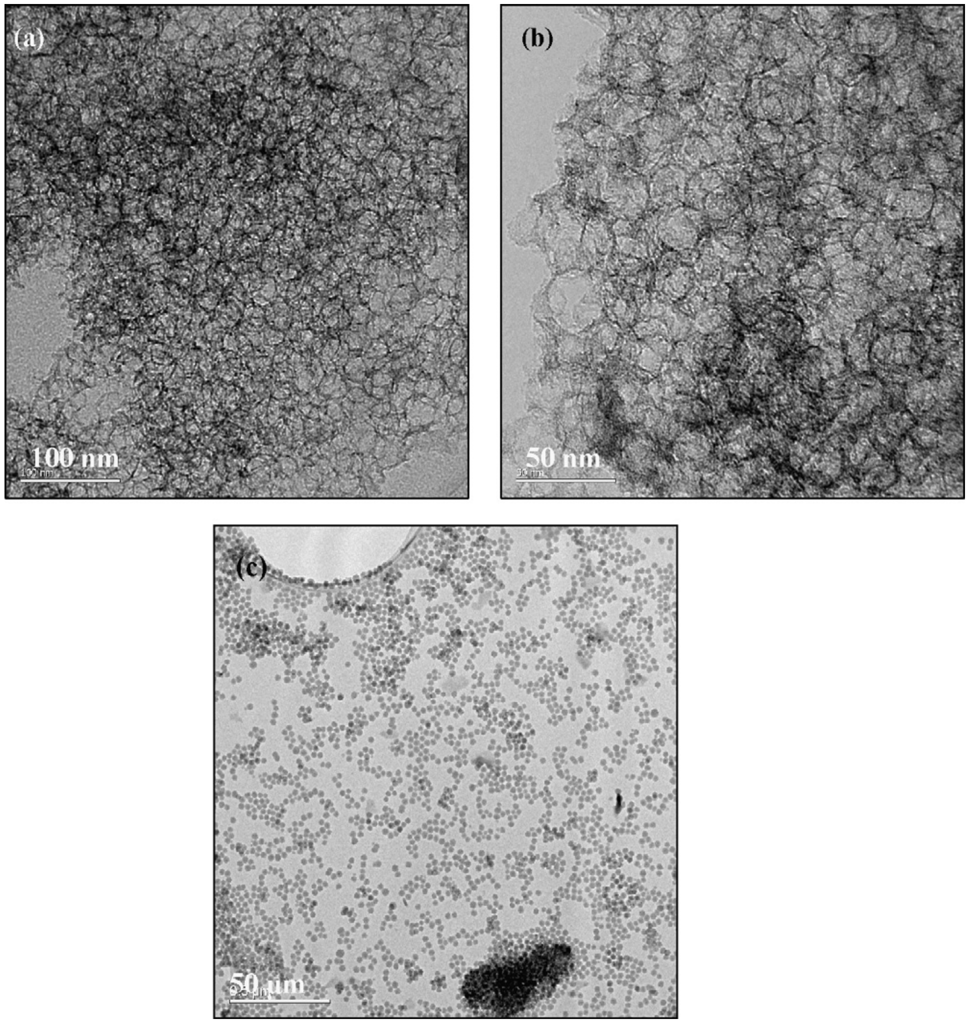

Fig. 1. TEM images of blank FTC-1 (a and b) and Ludox AS-40 template (c).

30–40 nm in average. This particle size is comparable to the Ludox AS40 which has an average silica particle size of around 40 nm, as shown in Fig. 1c. Such a little difference in dimensions between the observed TEM image and the original silica particle could be due to both carbonization and silica dissolution processes during the FTC preparation. In the carbonization step, the carbon atom which is coated on the silica particle is carbonized and finally polymerized to form a carbon shell on the silica particle. In the silica dissolution step, not only the silica particle is dissolved to form the hydroxyl complex ions but also the carbonized carbon is chemically modified to form the carboxylated surface. Therefore, by using this dissolution method, the FTC can be chemically modified and used as an adsorbent.

The synthesized film typed carbon, together with a commercial Norit activated carbon, and a commercial ZSM-5 zeolite, were analyzed by N_2 adsorption measurement to characterize their surface area, pore size and volume. The results were shown in Table 1.

Table 1
Physical properties of FTC, Norit carbon and ZSM-5 zeolite.

	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Norit AC	1052	1.1	0.62
ZSM-5	330	0.8	0.25
FTC-1	775	3.6	1.16

The Norit carbon and ZSM-5 mainly contain micropores (1.1 and 0.8 nm) with pore volumes of around 0.65 and 0.25 cm^3/g, respectively, while the developed FTC-1 adsorbent has a larger pore size and a larger pore volume of around 3.6 nm and 1.16 cm^3/g, respectively.

The three adsorbents were then evaluated for the SO_2 adsorption using a volumetric measurement rig [11].

Fig. 2a shows the adsorption isotherms of SO_2 at different temperatures ranging from 100 to 300 °C. At an adsorption temperature of 100 °C, FTC (solid circle) has the highest adsorption capacity of about 1.6 mmol/g at a SO_2 pressure of 10 kPa. This is followed by ZSM5 (solid diamond). The Norit AC (blank inverted triangle) has the least adsorption capacity. As temperature increases to 200 °C, FTC (blank circle) demonstrates a similar adsorption capacity as that at 100 °C of about 1.5 mmol SO_2/g at a pressure of 10 kPa. While for the other two adsorbents at this temperature, the adsorption capacities significantly drop for 50% to 0.49 and 0.5 mmol/g for Norit AC and ZSM5, respectively. At an even higher adsorption temperature of 300 °C, FTC (solid inverted triangle) performs much better (460%) than Norit AC (blank square), achieving capacity of around 1.4 mmol SO_2/g at a pressure of 10 kPa, compared with 0.25 mmol/g for Norit AC. The adsorption capacity of SO_2 on film typed carbon is not sensitive to the temperature change in the range of 100–300 °C, which suggests that this is a chemisorption process. Such a good adsorption efficiency of FTC-1 may be due to its chemically modified surface. It is important to retain a high adsorption

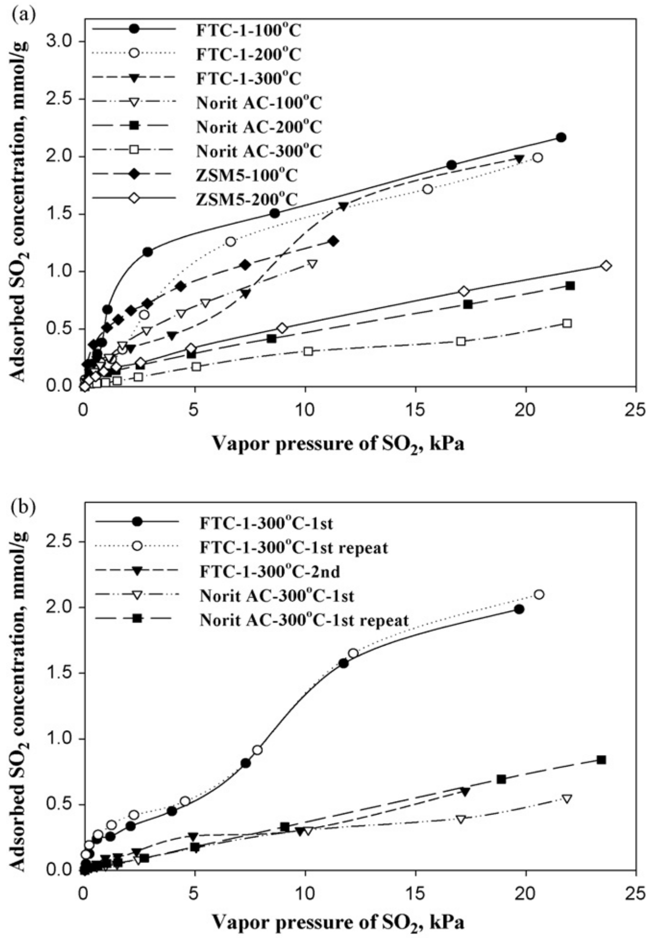

Fig. 2. (a) Adsorption isotherms of SO_2 on FTC-1, Norit AC, and ZSM5 at different temperatures; (b) repeatabilities of adsorption isotherms of SO_2 on FTC-1 and Norit AC.

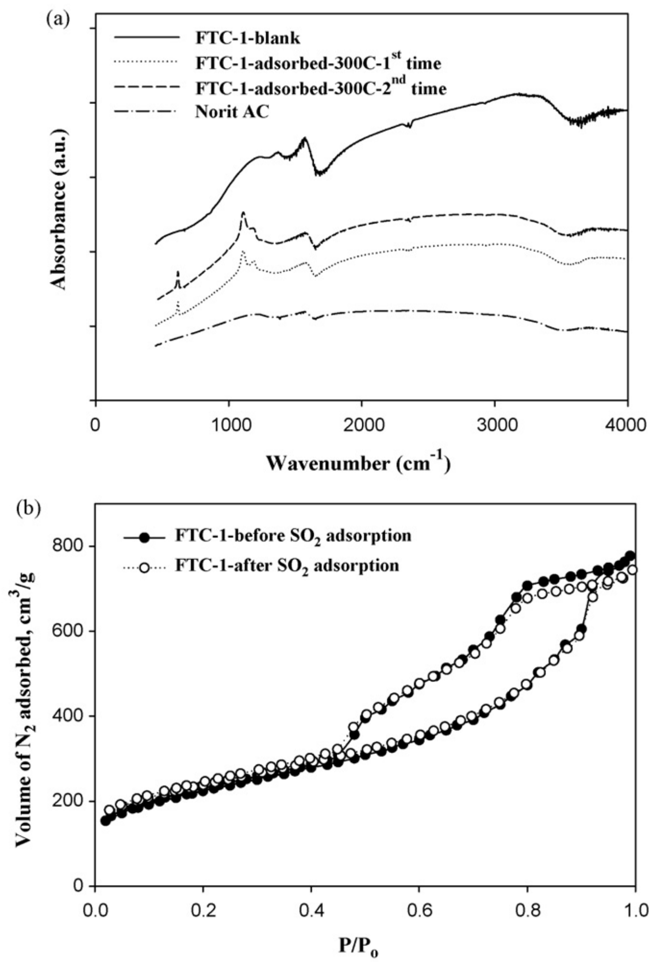

Fig. 3. (a) FTIR spectroscopy and (b) full sorption isotherm of N_2 of FTC-1 before and after SO_2 adsorption.

capacity at the temperature range of 200–300 °C, because most SO_2 generated from the industry, especially that from the combustion process, is emitted within this temperature range.

To test the reliability of the synthesis technique of FTC, the SO_2 adsorption measurement was done under the same condition with another batch of synthesized adsorbent. The result is illustrated in Fig. 2b as open circle and denoted with (-1st-repeat), which is almost superimposed to that of the first batch. This means that using the methodology developed here, we are able to produce stable FTC products.

To further investigate the adsorption nature of FTC, the used FTC adsorbent is regenerated under vacuum overnight at 350 °C and then used again for SO_2 adsorption. The result is shown in Fig. 2b as solid inverted triangle. It is noted that the adsorption capacity of the regenerated FTC is significantly lower than the fresh developed FTC. The main reason for this phenomenon is that some SO_2 molecules have been chemically bonded to the FTC surface during the first time adsorption, which is irreversible and cannot be regenerated. Therefore, the new adsorption can only happen through the physisorption mechanism. This leads to a huge difference in the adsorption capacity of FTC between the first and second time adsorption processes.

Since the developed FTC behaves as a chemisorption process, the surface group of FTC could have a change before and after the SO_2 adsorption. Fig. 3a shows the FTIR spectra of freshly developed FTC (solid line), FTC after the first adsorption (dotted line), FTC after the second adsorption (dashed line), and Norit AC (dash dotted line). In view of the freshly developed FTC, there is an indicative peak at 1530 cm^{-1}, indicating the presence of carboxylate group (COO^-). The carboxylate group mainly comes from the modification of oxidizing agent. As mentioned, the final step of FTC fabrication involved the ethanolic NaOH solution. It not only dissolves the silica but also modifies the interfacial carbon surface which may be oxidized to be carboxylate group. After the first adsorption process, the peak of 1530 cm^{-1} slightly shifts to 1535–1540 cm^{-1} with a smaller intensity and at the same time a peak at 1100 cm^{-1} appears with a little shoulder at 1150 cm^{-1}. The peak at 1100 cm^{-1} indicates the presence of surface group of $(CH_3)_2S{=}O$, while the peak at 1150 cm^{-1} indicates the surface group of $CH_3{-}S{=}O$. After the second adsorption process, the surface group of $CH_3{-}S{=}O$ has increased in intensity from a shape of shoulder to be a peak. From this information, it is believed that the SO_2 molecules are chemically bonded to the FTC surface and most likely on the carboxylated surface group. The adsorbed SO_2 on the carboxylated group may slightly change the FTIR pattern. Therefore there is a little shift for the peak at 1550 cm^{-1}. For the second time adsorption process, the peak generation of 1150 cm^{-1} may be due to the further adsorption of SO_2 molecules which may change the bond type from geminal posture ($(CH_3)_2S{=}O$) to $CH_3S{=}O$. In the case of Norit AC, there is no peak indicating the presence of carboxylate group. It means that the Norit AC mainly performs the physisorption for SO_2 molecules. Therefore, at a high adsorption temperature, its adsorption capacity is significantly reduced.

The role of carboxylate group may provide an electron-rich surface for the adsorption of SO_2. Since SO_2 is a polar molecule, it may have a dipole–dipole interaction on the carboxylated surface. It is critically important to this adsorption process by building a strong interaction between SO_2 molecule and carboxylated surface.

Fig. 3b illustrates the N_2 adsorption isotherms of FTC before and after SO_2 adsorption. It is seen that there is no significant change in the porous structure which forms similar hysteresis loops. Only a slight decrease in total adsorption volume of nitrogen is observed, suggesting that the adsorption of SO_2 on FTC is a monolayer chemisorption.

4. Conclusions

The chemically modified film typed carbon demonstrates a much superior adsorption capacity of SO_2 compared to those conventional commercial adsorbents. It has an adsorption capacity of 1.4–1.6 mmol/g at high adsorption temperatures between 100 and 300 °C. From the FTIR spectra, the chemically modified FTC has a carboxylated surface. It is believed that the carboxylate group is mainly responsible for the SO_2 adsorption. From the adsorption isotherm of the regenerated FTC, it implies that the SO_2 adsorption on FTC follows the chemisorption mechanism. Therefore, it can have a high adsorption capacity of SO_2 at 300 °C, which is about 460% more than that of commercial activated carbon. Until now, there are no carbonaceous materials that can have such a high adsorption capacity at that temperature. Therefore, it is promising to use the chemically modified FTC for the abatement of SO_2 from combustion emissions.

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