SO$_2$ removal from flue gas by activated semi-cokes 2. Effects of physical structures and chemical properties on SO$_2$ removal activity

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Abstract

This paper deals with the effects of physical structures and chemical properties of the catalysts, activated semi-cokes, on SO$_2$ removal activity. The catalysts were characterized in terms of physical structures—specific surface area, pore volume and pore size—and chemical properties—acidity and basicity. Results show that the presence of basic groups on the catalyst surface is a precondition for SO$_2$ removal at 90 °C. For catalysts containing copper species, there is no relation between chemical properties and sulfur retention. For catalysts without copper species, sulfur retention shows no correlation with the content of acidic groups, but it nonlinearly increases with increasing the content of basic groups, and there is a good linear relationship between SO$_2$ capture capacity and Brunauer–Emmett–Teller surface area and pore volume. These results indicate that for catalysts without copper species in this work, physical structure dominates SO$_2$ capture capacity while chemical properties have a smaller influence on SO$_2$ removal efficiency.
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1. Introduction

Carbonaceous materials have been proven as promising adsorbents for SO$_2$ removal. At temperatures of flue gas releasing from a precipitator (60–150 °C), SO$_2$ is adsorbed onto the surface of carbonaceous material and converts to SO$_3$ by oxidation with O$_2$, then it exists as sulfuric acid [1]. In this process, SO$_2$ capture capacity has been shown to be in close relation to the general characteristics of carbon materials and, in particular, to the physical structures and chemical properties. However, which factor plays the decisive role in SO$_2$ removal is still debated. According to several researchers [2–7], the chemical nature is considered as the main factor, influencing the adsorption and desorption of SO$_2$. An increase of basicity leads to an increase of sulfur capacity and strengthening of SO$_2$ bonding with the surface. A less important role is attributed to the pore structure characteristic. However, Rubio

and Izquierdo [8–10] proposed that SO$_2$ removal efficiency mainly depended on the surface area, in particular in the presence of O$_2$ and H$_2$O, while the basicity of the carbons influenced the adsorption of SO$_2$ less than the physical properties. Moreno-Castilla et al. [11] also reported that an adequate microporosity in the activated carbons was the most influential parameter for SO$_2$ removal.

Our previous work [12] has proven that the catalysts made from lignite semi-coke and prepared through HNO$_3$ oxidation and calcination showed a good performance for SO$_2$ removal at 90 °C. However, for these catalysts, the determinant factor for SO$_2$ removal efficiency is not clear. Lisovslii et al. [13,14] have reported an activated carbon prepared through HNO$_3$ activation for SO$_2$ removal and proposed that oxidation treatment by HNO$_3$ did not significantly change the pore structure but increased the amount of oxygen. In other words, the chemical nature is considered as the main factor. It is important to point out that the Brunauer–Emmett–Teller (BET) surface area of the catalyst employed by Lisovslii et al. [13,14] was 1200

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m^2/g. Whether the conclusion drawn by Lisovslii et al. [13,14] is applicable to the catalysts in this work (BET surface area of less than 500 m^2/g) needs further study. The purpose of the present work is to study the critical factor affecting desulfurizing properties of activated semi-cokes with BET surface areas of less than 500 m^2/g.

2. Experimental

2.1. Preparation and characterization of catalysts

Lignite semi-coke was selected as raw material and the preparation process was described in detail elsewhere [12]. Briefly, the raw material was pre-activated in an autoclave, followed by oxidizing with HNO_3, modifying by $CuSO_4$ or not and calcining at 700 °C. The resulting catalysts were termed B-nHN-N or B-nHN-Cu-N (n stands for the concentration of HNO_3 used and N represents calcination). In addition, the catalysts prepared through pre-activation and oxidizing with H_2O_2 (termed B-HO) were also investigated for comparison. In this work, an amount corresponding to 4.0 wt.% CuO is used.

The total content of surface sites of acidic nature or basic nature was estimated comparatively through a neutralization technique. Activated semi-cokes of 0.2 g (80–120 mesh) were mixed with 20 ml of 0.01 M NaOH solution for the acidic nature test or 20 ml of 0.01 N trichloroacetic acid (TCA) for the basic nature test. The mixed suspensions were stirred at ambient temperature for 16 h and deposited for 2 h. Then, 10 ml of the filtrated NaOH and TCA solutions was re-titrated with 0.01 M HCl and 0.01 M NaOH, respectively. For raw material, the contents of the basic groups and acidic groups are 0.214 and 0.153 mmol/g, respectively.

BET surface area was determined by nitrogen adsorption at 77 K using an ASAP2000 volumetric adsorption analyzer (Micromeritics, Norcross, GA, USA). The total pore volume was calculated from the amount of nitrogen adsorbed at $P/P_0 = 0.98$ and the average pore size was obtained from the formula of $4V$/BET surface area (V stands for the total pore volume).

Fourier transform infrared (FT-IR) measurement was carried out on FTIR-8100 spectrometer (Shimadzu) at ambient temperature. The samples were mixed with potassium bromide at a mass ratio of 1:100, ground, and then pressed into a thin slice. Forty scans were made to yield a spectrum with a resolution of 2 cm^{-1} over the spectral ranges of 4000–400 cm^{-1}.

2.2. Activity test

An activity test was carried out with fixed-bed equipment described elsewhere [12]. The reactor with the catalyst (25 ml estimated on the bulk density) was heated to 90 °C by an electric heater at a given N_2 flow. After the temperature reached a steady state, SO_2, O_2 and balance N_2 were introduced into the reactor. H_2O was introduced into the feed stream by passing N_2 and O_2 through water bath (controlled at 50 °C by a thermostat) and its content was confirmed by the consumed amount of water. In all runs, the flow rate of simulated flue gas was controlled at 340 ml/min by flow-meters. The concentrations of SO_2 and O_2 in the inlet and outlet were simultaneously measured through an on-line Flue Gas Analyzer (Dräger).

3. Results and discussion

3.1. Effects of oxidation and calcination

Table 1 summarizes the sulfur retention, physical structure and chemical properties of various catalysts in this work. It should be pointed out that in this work, sulfur retention is expressed as the amount of SO_2 captured (by weight) per 100 g catalyst before SO_2 conversion decreases to 50%. As can be seen, the content of basic groups considerably decreases from 0.485 mmol/g for the precursor to zero after being treated by HNO_3 regardless of its concentration, while the content of acidic groups

Table 1
Sulfur retention, physical structure and chemical properties of various catalysts

Sample	Sulfur retention (g SO_2/100 g C)	Basicity (mmol/g)	Acidity (mmol/g)	Surface area (m^2/g)	Pore volume (cm^3/g)	Average diameter (nm)
B-30HN	0	0	0.702	292.15	0.112	1.53
B-30HN-N	4.32	0.602	0.051	314.22	0.168	2.13
B-45HN	0	0	0.608	217.02	0.148	2.73
B-45HN-N	8.51	0.695	0.098	482.62	0.244	2.02
B-45HN-Cu-N	9.66	0.532	0.072	/	/	/
B-20HO	3.02	0.251	0.142	250.41	0.132	2.10
B-20HO-Cu	3.44	0.202	0.110	/	/	/
B-30HO	3.62	0.358	0.212	283.02	0.156	2.20
Precursor*	3.58	0.485	0.196	292.07	0.126	1.73

* Semi-coke that was pre-activated in autoclave and not further treated.

increases from 0.196 mmol/g to 0.702 and 0.608 mmol/g for B-30HN and B-45HN, respectively. These phenomena were also extensively described in the literature [13,15–18], i.e., the basicity on the carbon surface decreases while the acidity increases during oxidation by HNO_3. In contrast, for B-30HN and B-45HN, calcination largely increases their basicity and decreases their acidity, which is possibly due to the destruction of most of the acidic groups to form basic groups during the calcination step [19]. The decomposition of acidic groups is confirmed by FT-IR spectra (Fig. 1). The band at 1710 cm^{-1} assigned to carboxyl (showing acidic nature) [20] greatly fades and the double band around 1550 cm^{-1} assigned to cyclic conjugate alkone (acidic surface group) changes to a weak single band at 1550 cm^{-1} after heat treatment.

Table 1 also shows that B-30HN and B-45HN display no activity for SO_2 removal, however, the calcination step allows them (B-30HN-N and B-45HN-N) to exhibit a relatively high desulfurizing activity. Combining sulfur retention with the content of basic groups and that of acidic groups, it may be concluded that there is no SO_2 capture capacity at 90 °C when no basic groups are present on the surface. This observation suggests that the presence of basic groups on the catalyst surface is a precondition for SO_2 removal and the acidic groups show not any contribution to SO_2 capture at 90 °C.
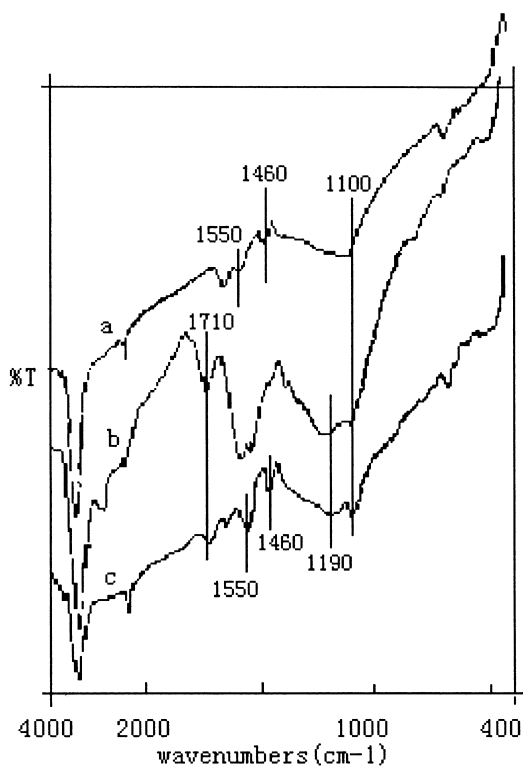

Fig. 1. FT-IR spectra of (a) B-45HN-Cu-N, (b) B-45HN and (c) B-45HN-N.

3.2. Effect of loading copper species

Table 1 shows that both acidic groups and basic groups in the catalysts loaded with copper species are less numerous than those in the corresponding catalysts without copper species. Theoretically, copper species exhibit basicity and therefore loading copper into the catalysts should increase their basic properties. However, the result is the reverse. On the one hand, the measurement method of basicity in this work probably cannot detect copper species [in the form of metallic Cu confirmed by X-ray diffraction (XRD) measurement]. On the other hand, the FT-IR spectrum of B-45HN-Cu-N (see Fig. 1a) shows that the band at 1190 cm^{-1} assigned to the stretching vibration of C–O–C–O–C group (showing basic nature) disappears in comparison with that of B-45HN-N (see Fig. 1c), which possibly accounts in part for the lower content of basic groups in B-45HN-Cu-N than in B-45HN-N. The reason why the C–O–C–O–C group disappears is not clear, and maybe copper species cover them. The FT-IR spectrum also shows that for the B-45HN-Cu-N sample, the band at 1710 cm^{-1} assigned to carboxyl (showing acidic nature) completely disappears and the band at 1550 cm^{-1} greatly fades in comparison with those for the B-45HN-N sample, which possibly accounts for the lower content of acidic groups in B-45HN-Cu-N than in B-45HN-N. This result suggests that copper species may promote the decomposition of carboxyl.

Sulfur retentions in Table 1 indicate that catalysts containing copper species show better performances for SO_2 removal than the corresponding catalysts without copper species. That the changes of functional groups on the surface after loading copper species (as mentioned above) give rise to the positive or negative effect on sulfur retention is not fully understood. However, loading metal oxides creates a new active site (copper species) for SO_2 removal, which is supported by XRD patterns before and after desulfurization (see Fig. 2). After desulfurization, diffraction peaks of metallic copper strongly decrease and some peaks of $CuSO_4$ appear. The formation of a small amount of bulky $CuSO_4$ can explain that copper, as an active site, takes part in SO_2 oxidation to enhance SO_2 removal. On the whole, loading copper species increases sulfur retention, however, reduces the functional groups on the catalyst surface (compare line 4 with 5 and line 6 with 7). These results suggest that for catalysts containing copper, SO_2 capture capacity has no correlation with the content of basic and acidic groups.

3.3. Determination of the decisive factor influencing SO_2 removal activity

To better understand the influences of the chemical properties and physical structure on sulfur retention, it is necessary to avoid the effect of copper species. Consequently, after explaining the specific properties of Cu-
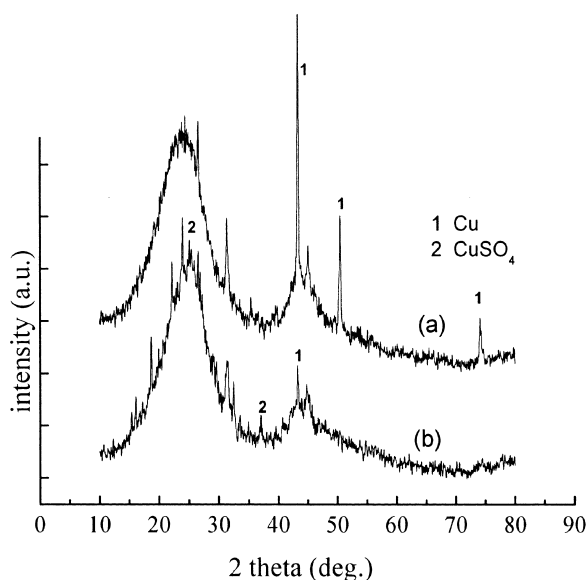
Fig. 2. XRD patterns of B-45HN-Cu-N (a) before desulfurization, (b) after desulfurization.

loaded activated semi-cokes, the discussion could be explicitly restricted to the catalysts without copper species. For clarity, sulfur retention versus the contents of acidic and basic groups are plotted in Fig. 3. As can be seen, for all catalysts investigated here, the content of basic groups is greater than that of acid groups, indicating that the catalysts render basicity. In addition, sulfur retention nonlinearly increases with increasing the content of basic groups, however, no relationship can be found between sulfur retention and the content of acidic groups, which indicates that basic groups on the surface are more important for SO_2 removal efficiency in comparison to acidic groups. These observations further confirm that acidic functional groups show no contribution to SO_2 removal and only basic groups serve as the active sites for
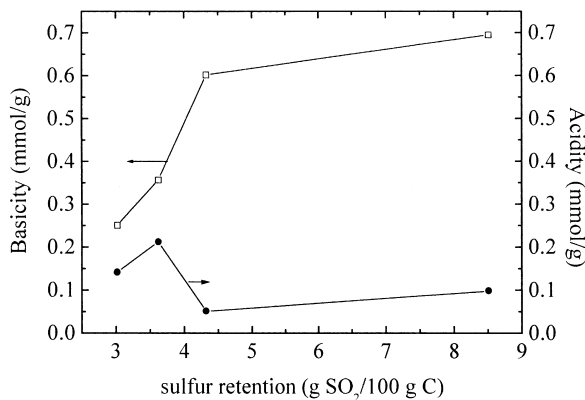
SO_2 adsorption, as stated in Section 3.1. The conclusion disagrees with the viewpoint of Lisovslii et al. [14] who proposed that SO_2 capture capacity has a relation to certain oxygenated groups of acidic nature.

Due to the reason mentioned above, Cu-loaded samples are also excluded from the discussion of the effect of physical structures on sulfur retention. Table 1 indicates that the average pore diameters for catalysts investigated here range from 2.02 to 2.20 nm, implying that the pores are easily accessible for SO_2 and O_2 because the diameters of SO_2 and O_2 are 0.41 and 0.28 nm, respectively. In order to illustrate more clearly the dependence of SO_2 removal efficiency on physical structures, sulfur retention versus surface area and pore volume are plotted in Fig. 4. As can be seen, sulfur retention linearly increases with increasing BET surface area and pore volume of the catalysts, indicating that SO_2 removal efficiency is greatly dependent on the physical structures of the catalysts.

According to the above results, it seems that for catalysts without copper species, SO_2 capture capacity increases with increasing both BET surface area and basic groups on the surface, and the two factors are of importance during desulfurization. If the content of basic groups determines SO_2 removal activity, i.e., one basic active site can absorb a certain sulfur species, sulfur retention should have a linear or proportional relationship with the content of basic groups. However, by analyzing Fig. 3 in detail, it can be found that when the content of basic groups greatly increases from 0.3 to 0.6 mmol/g, sulfur retention weakly increases from 3 to 4.3 g SO_2/100 g C, however, when the content of basic groups only increases from 0.6 to 0.7 mmol/g (16% increase), sulfur retention greatly increases from 4.3 to about 8.5 g SO_2/100 g C (110% increase). This indicates that the chemical characteristics cannot determine desulfurizing activity, although basic groups are very necessary for SO_2 removal. SO_2 retention versus surface area/pore volume (see Fig. 4) shows that there is a good linear relationship between them. It is important to point out that considering the industrial application, sulfur
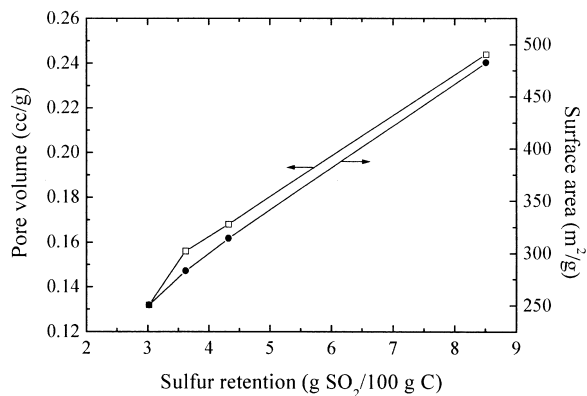

Fig. 3. Effect of chemical property on sulfur retention.

Fig. 4. Effect of physical structure on sulfur retention.

retention in this work is defined as the amount of SO_2 adsorbed before SO_2 conversion decreases to 50%, not the saturated value. Hence, the lines in Fig. 4 cannot pass through the origin, and even the sulfur retention is a negative value if the surface area extends to zero. However, compared with the nonlinear relationship between sulfur retention and the content of basic groups, the good linear relationship between sulfur retention and surface area/pore volume (in spite of disproportion) can prove that for catalysts without copper, physical properties have to be considered as the determinant factor. Also, as can be seen in Table 1, the precursor and B-30HO have similar surface areas but different contents of acidity and basicity, however, the two catalysts show similar SO_2 removal activities, which further confirms that the chemical properties are not the decisive factors influencing SO_2 removal efficiency.

By comparing the surface areas of the carbons employed by researchers holding different viewpoints, we found that carbons (including carbon fibers) used in Refs. [2–7] have higher surface areas (more than 1000 m^2/g), and therein, chemical properties were considered as the main factor influencing SO_2 removal efficiency. However, carbons used by Rubio et al. [8–10] have surface areas of less than 50 m^2/g, the surface areas of activated carbons in the literature [11] are not more than 700 m^2/g, and the surface areas of activated semi-cokes in this work are less than 500 m^2/g. The last three cases support the theory that physical structures play a key role in SO_2 removal. Herein, the mechanism of SO_2 removal by carbon materials is proposed to explain the different conclusions. SO_2 removal by carbonaceous catalysts in the presence of oxygen and water consists mainly of three steps [1,13,18]:

(a) Adsorption of SO_2, O_2 and H_2O.
(b) Catalytic conversion of SO_2 to SO_3 and then to adsorbed H_2SO_4.
(c) Desorption of H_2SO_4 from the surface.

Step (a) depends on the catalyst's surface area, steps (b) and (c) depend on active sites and the pore volume accessible for H_2SO_4 storage, respectively. When surface area is too small to meet the requirement of adsorption of reactants (according to the existing data, surface area of less than 700 m^2/g), the whole desulfurizing process is controlled by step (a), so the surface area determines sulfur capture capacity. When carbon materials have a higher surface area, step (b) becomes determinant and, as a result, SO_2 capture capacity is essentially determined by the content of active sites, i.e., surface chemical properties.

4. Conclusions

1. No SO_2 removal activity is observed when no basic groups are present on the surface of activated semi-cokes.
2. For catalysts loaded with copper species, copper takes part in the oxidation of SO_2 to form $CuSO_4$ and increases sulfur retention, and there is no relation between chemical properties (including acidity and basicity) and sulfur retention.
3. For catalysts without copper, sulfur retention nonlinearly increases with the contents of basic groups, but shows no relation with the content of acidic groups. There is a good linear relationship between this retention and BET surface area (or pore volume) of the catalysts. These results indicate that for catalysts without copper species in this work, physical properties are the main factors influencing SO_2 removal activity.
4. Physical structures determine SO_2 capture capacity when the BET surface area of carbonaceous catalysts is less than 700 m^2/g, while surface chemical properties has a greater influence on SO_2 removal when the BET surface area is more than 1000 m^2/g.

Acknowledgements

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