

Adsorption and Adsorbed Species of SO₂ during Its Oxidative Removal over Pitch-Based Activated Carbon Fibers

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Adsorption and adsorbed species of SO₂ in humid air during its oxidative removal were studied over pitch-based activated carbon fibers (ACFs) to clarify the reaction scheme of continuous removal of SO₂, influence of reaction variables, and origin of activity enhancement by the calcination in inert atmosphere. The temperature-programmed desorption of SO₂ adsorbed species suggests that when both oxygen and water were present, the main species on ACF was hydrated SO₃ (H₂SO₄), which desorbed in the form of SO₂ around 300 °C, and that the presence of both increased the amount of species by oxidizing and hydrating the adsorbed SO₂, which desorbed around 60 °C without oxidation and 200 °C with oxidation but without hydration. The amount of adsorbed H₂SO₄ over ACF stayed at the same level after 25 h of reaction by balancing elution and adsorption of H₂SO₄ to allow the steady removal of SO₂. More water enhanced the adsorption of SO₂ at the initial stage but reduced the amount of adsorbed H₂SO₄ at the steady state, eluting out H₂SO₄ faster than the adsorption of SO₂ to keep more active sites open over ACF at the steady state. Hence, complete removal was achieved. A higher calcination temperature significantly increased the rate and amount of both oxidative and oxidative/hydrating adsorption, explaining the largest activity of ACF calcined at 1100 °C. The amounts of adsorbed SO₂ and evolved CO from OG-20As by calcination at 500–1000 °C are well correlated, indicating that the evolved CO creates an adsorption site on the ACF surface. A similar but different correlation was obtained among ACFs of different surface areas calcined at different temperatures.

Introduction

We have proposed continuous oxidative removal of SO₂ over the activated carbon fibers (ACFs) where SO₂ in the gas phase is adsorbed, oxidized, and hydrated and continuously eluted in the form of aqueous H₂SO₄ from the ACF surface, achieving complete removal at the steady state.^{1–5} A pitch-based ACF of the largest surface area exhibited the highest activity for such an oxidative removal after calcination at 1100 °C.⁶ CO elimination

from the ACF surface by calcination appears to create active sites and enhance the hydrophobicity over the ACF surface for rapid elution of hydrated H₂SO₄.^{7,8}

In the present study, adsorption and adsorbed species of SO₂ during the oxidative removal were studied over pitch-based ACFs, using temperature-programmed desorption (TPD) analysis of SO₂ species adsorbed on the ACF surface.^{9,10} The reaction scheme, influence of reaction variables, and origin of activity enhancement

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Table 1. Properties of Pitch-ACFs

ACFs	elemental analysis					S.A. (m ² /g)
	C	H	N	O (diff)	ash	
OG-5A-as	89.6	1.1	0.7	8.2	0.3	563
-H900	92.3	0.9	0.7	5.6	0.5	539
OG-10A-as	91.6	0.9	0.6	7.4	0.2	977
-H1100	96.2	0.1	0.6	2.9	0.2	793
OG-15A-as	93.9	0.9	0.7	4.1	0.4	1162
-H1100	96.8	0.1	0.4	2.2	0.5	879
OG-20A-as	95.5	0.9	0.3	2.8	0.5	1894
-H500	95.7	0.9	0.3	2.6	0.5	1768
-H800	96.2	0.8	0.3	2.3	0.4	1734
-H1100	97.5	0.1	0.2	1.6	0.6	1460

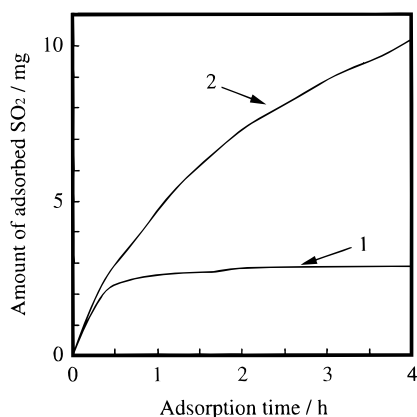


Figure 1. Adsorption profiles of SO₂ over OG20A-H1100 in a microbalance: flow rate = 150 mL/min (He balance), ACF = OG-20A-H1100 (200 mg), adsorption temperature = 30 °C. Flow gas: (1) SO₂ 1000 ppm, (2) SO₂ 1000 ppm, O₂ 5 vol %.

by calcination are discussed by correlating SO₂ removal with the amounts of adsorbed species under the reaction conditions.

Experimental Section

OG series pitch-based ACFs were supplied by Osaka Gas Co. They were heat-treated in argon gas at several temperatures. Their properties are summarized in Table 1.

SO₂ adsorption was performed under flowing helium containing SO₂ (1000 ppm) and O₂ (5%) at a flow rate of 150 mL/min over the ACF (200 mg) suspended in a quartz basket in a microbalance (Cahn 1000).

Temperature-programmed desorption analysis of the ACFs as-received, heat-treated, and after SO₂ adsorption and elution was carried out using a quartz-glass apparatus equipped with a mass spectrometer (AQA-200; Nichiden-Anelva Inc.). The 0.1 g sample was heated in helium flow up to 400 °C at 10 °C/min to measure continuously the desorbed SO₂.

Results

Adsorption of SO₂ over OG-20A-H1100. Figure 1 illustrates SO₂ adsorption over OG-20A-H1100 at 30 °C in a Cahn balance. SO₂ alone was adsorbed rapidly to reach saturation after 30 min. In the experiment, 2.5 mg of SO₂ was adsorbed over 200 mg of the ACF. O₂ (5 vol %) enhanced the adsorption, increasing the amount adsorbed to 10 mg in 4 h. No indication of saturation was observed.

Figure 2 illustrates the adsorption and desorption profiles of SO₂ at 30 °C where SO₂ adsorbed to saturation was desorbed by purging with He alone and O₂ (5 vol %) in He, respectively. O₂ in He desorbed 0.5 mg of SO₂ within 1 h and left the remaining 1.5 mg of SO₂ on

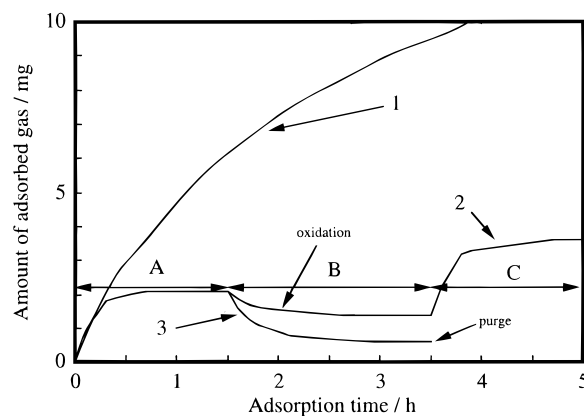


Figure 2. Adsorption and desorption of SO₂ over OG-20A-H1100 in a microbalance: flow rate = 150 mL/min (He balance), ACF = OG-20A-H1100 (200 mg), adsorption temperature = 30 °C. (1) Adsorption by SO₂, 1000 ppm, O₂ 5 vol %; (2) A. Adsorption by SO₂ (1000 ppm in He), B. Desorption by O₂ (5 vol % in He), C. Adsorption by SO₂ (1000 ppm in He), (3) A. Adsorption by SO₂ (1000 ppm in He), B. Desorption by He purge.

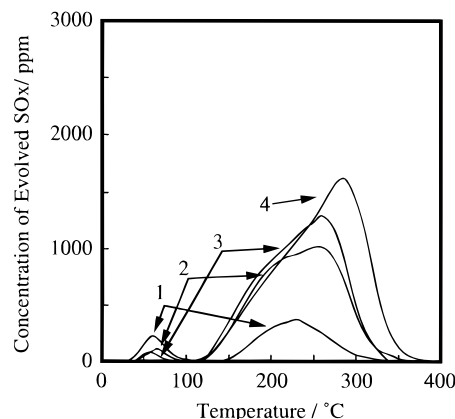


Figure 3. TPD profiles of adsorbed SO₂ species over OG-20A-H1100: flow rate = 100 mL/min, ACF = OG-20A-H1100 (100 mg), adsorption of SO₂ (2000 ppm) + O₂ (5 vol %) followed by purge with He for 1 h. Adsorption temperature of SO₂ = 30 °C. Adsorption time: (1) 1, (2) 5, (3) 15, (4) 25 h.

the ACF, whereas He alone removed 1.5 mg within 1.5 h. More SO₂ desorption was observed. Such results indicate that two-thirds of the adsorbed SO₂ is reversible while one-third stays undesorbed, probably oxidized by the surface oxygen. Oxygen in the purging gas oxidizes the adsorbed SO₂ and competes with desorption of SO₂. The adsorbed SO₂ species in the presence of O₂ was desorbed by purging with He, whereas SO₃ produced from SO₂ did not desorb at 30 °C.

TPD of SO₂ Adsorbed over OG-20A-H1100. Figure 3 illustrates TPD profiles of adsorbed SO₂ in the presence of O₂ for 1–25 h. The adsorbed SO₂ exhibited two desorption peaks, one at 60 °C and the other at 220–300 °C. Longer adsorption times reduced desorption at 60 °C and increased desorption at a higher temperature, also raising the temperature of the peak. The increase of desorption was very large for the first 1 h and almost approached saturation by 25 h. The major adsorbed species appeared to be SO₃, which was desorbed in the form of SO₂ at higher temperatures after reduction on the carbon surface as described later.

Figure 4 illustrates the TPD profiles of SO₂ adsorbed for 1–25 h with O₂ (5 vol %) and H₂O (10 vol %). H₂O

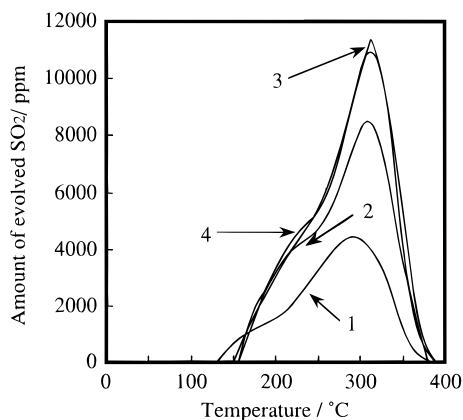


Figure 4. TPD profile of SO_x species adsorbed over OG-20A-H1100 after 1–25 h exposure: flow rate = 100 mL/min (N_2 balance), ACF = OG-20A-H1100 (100 mg) feed = SO_2 (1000 ppm), O_2 (5 vol %), H_2O (10 vol %) in N_2 , $\text{W/F} = 1.0 \times 10^{-3} \text{ g min mL}^{-1}$, reaction temperature = 30 °C. Reaction time: (1) 1, (2) 5, (3) 15, (4) 25 h.

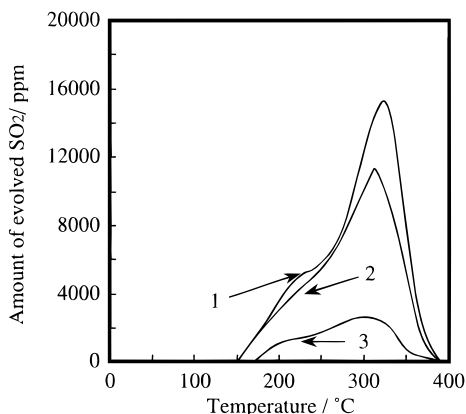


Figure 5. TPD profiles of SO_x species adsorbed over OG-20A-H1100 after 15 h of exposure at different H_2O concentrations: ACF = OG-20A-H1100 (100 mg), feed = SO_2 (1000 ppm), O_2 (5 vol %), and H_2O in He, $\text{W/F} = 1.0 \times 10^{-3} \text{ g min mL}^{-1}$, reaction temperature = 30 °C. H_2O : (1) 5, (2) 10, (3) 15 vol %.

increased the amount of desorption around 300 °C. The absence of desorption at 60 °C ruled out physical adsorption of SO_2 under the present conditions. The desorption at 220 °C was a shoulder of the main desorption peak. The amount desorbed rapidly increased with the adsorption time for the initial 5 h and then gradually to saturation by 15 h. Saturation was approached. After 15 h, no further significant increase was observed over another 5 h.

Figure 5 illustrates TPD profiles of SO_2 adsorbed with variable amounts of water for 15 h when adsorption approached the saturation. The amount of desorption decreased with more water. The decrease was marked when the water increased from 10% to 15%. The amount of adsorbed H_2SO_4 at the steady state, where both continuous adsorption of SO_2 and continuous elution of aqueous H_2SO_4 took place, appeared to be governed by the amount of H_2O . Faster elution than adsorption reduces the stationary amount of adsorbed SO_2 on ACF. Although H_2O increased SO_2 adsorption by oxidation and hydration of adsorbed SO_2 , more rapid elution of aqueous H_2SO_4 reduces the stationary amount of adsorbed SO_2 under the conditions of complete SO_2 removal.

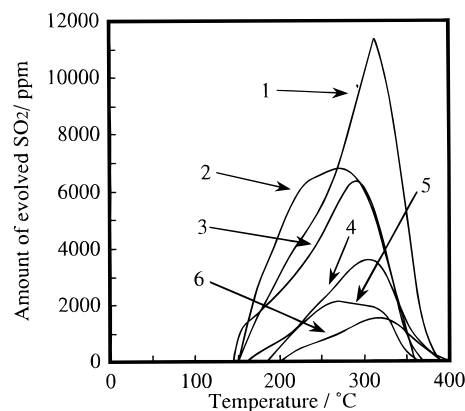


Figure 6. TPD profile of SO_x species adsorbed over pitch-ACFs soon after the removal and successive washing with air of 10 vol % H_2O : SO_2 1000 ppm, O_2 5 vol %, H_2O 10 vol %, $\text{W/F} = 1.0 \times 10^{-3} \text{ g min mL}^{-1}$, reaction temperature = 30 °C. ACF: (1, 4) OG-20A-H1100, (2, 5) OG-20A-H800, (3, 6) OG-10A-H1100. (1, 2, 3) Soon after SO_2 removal for 15 h. (4, 5, 6) After successive washing with air of 10 vol % H_2O for 10 h.

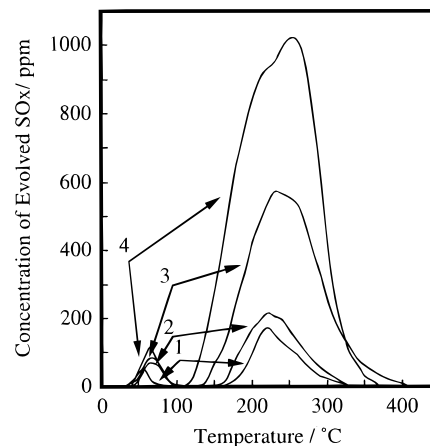


Figure 7. TPD profile of adsorbed SO_x species over pitch-ACFs: flow rate = 100 mL/min, adsorption = SO_2 (2000 ppm) + O_2 (5 vol %) in He for 5 h followed by purging with He for 1 h, adsorption temperature = 30 °C. ACFs: (1) OG-20A as received, (2) OG-20A-H500, (3) OG-20A-H800, (4) OG-20A-H1100.

Elution of Adsorbed H_2SO_4 by Air with 10 vol % H_2O . Figure 6 compares the amounts of evolved SO_2 from OG-20A-H1100 soon after SO_2 removal over 15 h in air with 10 vol % H_2O and after successive elution in air with 10 vol % H_2O without SO_2 supply for 10 h. The successive elution reduced SO_2 evolution in TPD. About 67% of adsorbed H_2SO_4 on ACF after 15 h of removal was eluted by a 10 h flow of air with 10 vol % H_2O .

TPD Profiles of Adsorbed SO_2 over OG-20A Calcined at Various Temperatures. Figure 7 illustrates the TPD profiles of SO_2 adsorbed in the presence O_2 for as-received and calcined OG-20A at 500–1100 °C. All ACFs exhibited similar profiles with two peaks at the same temperature except for the ACFs of lower temperature calcination and as-received. However, the amount of desorption at the higher temperature increased markedly with the calcination temperature.

Figure 8 illustrates the TPD profiles for SO_2 adsorbed with O_2 and H_2O (10 vol %) for 15 h over ACFs calcined at 500–1100 °C. The amount observed, which is considered to reflect the stationary amount over respective

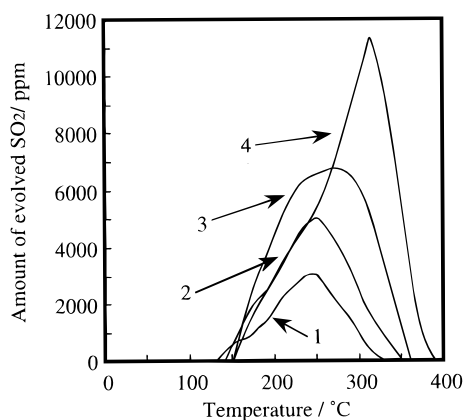


Figure 8. TPD profiles of SO_x species adsorbed over OG-20A heat-treated at different temperatures after 15 h of exposure: feed = SO_2 (1000 ppm), O_2 (5 vol %), H_2O (10 vol %) in N_2 , $\text{W/F} = 1.0 \times 10^{-3} \text{ g min mL}^{-1}$ reaction temperature = 30°C . ACFs: (1) OG-20A as received, (2) OG-20A-H500, (3) OG-20A-H800, (4) OG-20A-H1100.

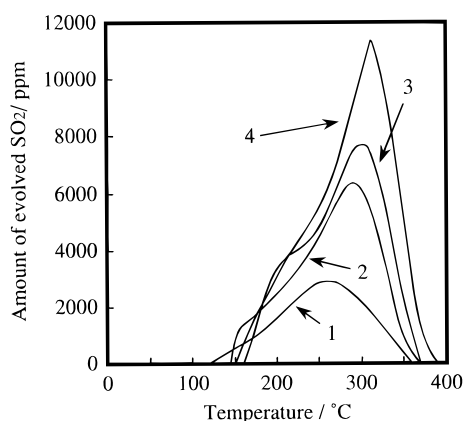


Figure 9. TPD profile of SO_x species adsorbed over pitch-ACFs after 15 h of exposure: feed = SO_2 (1000 ppm), O_2 (5 vol %), H_2O (10 vol %) in N_2 , $\text{W/F} = 1.0 \times 10^{-3} \text{ g min mL}^{-1}$, reaction temperature = 30°C . Sample: (1) OG-5A-H900, (2) OG-10A-H1100, (3) OG-15A-H1100, (4) OG-20A-H1100.

ACFs, also increased with calcination temperature. It is noted that the peak temperature over OG-20A-H1100 was considerably higher than those over ACFs calcined at lower temperatures. Adsorbed H_2SO_4 appears to be reduced to SO_2 at higher temperatures over the ACF calcined at 1100°C . It should also be noted that the largest amount of SO_2 in the gas phase was fixed as aqueous H_2SO_4 over OG-20A-H1100. This result indicates the rapid elution of aqueous H_2SO_4 from the ACF surface.

Figure 6 compares the evolution of SO_2 from OG-20A-H800 with that from OG-20A-H1100 soon after SO_2 removal for 15 h and successive elution for 10 h. The amount of eluted adsorbed H_2SO_4 from OG-20A-H800 was 81% of that from OG-20A-H1100. The rate of adsorbed H_2SO_4 elution was smaller on OG-20A-H800 than that on OG-20A-H1100.

TPD Profiles of SO_2 Adsorbed over ACFs of Different Surface Areas. Figure 9 illustrates the TPD profiles of SO_2 adsorbed with O_2 and H_2O (10 vol %) for 15 h over the pitch ACFs of different surface areas. The amount of desorbed SO_2 increased in the order OG-5A-H900 < OG-10A-H1100 < OG-15A-H1100 < OG-20A-H1100, in accordance with the order of the increasing surface area.

The desorption temperature peak increased with the calcination temperature. The lower calcination temperature of 900°C provided a desorption peak at 250°C , while a 1100°C calcination temperature gave a desorption peak at 300°C , reduction of adsorbed H_2SO_4 at a higher temperature again being suggested by the higher calcination temperature regardless of the surface areas of pitch ACFs.

Figure 6 compares the evolution of SO_2 from OG-10A-H1100 with that from OG-20A-H1100 soon after SO_2 removal for 15 h and successive elution for 10 h. The amount of eluted adsorbed H_2SO_4 from OG-10A-H1100 was 67% of that from OG-20A-H1100. The rate of H_2SO_4 elution from OG-10A-H1100 was faster than that from OG-20A-H800 but lower than that for OG-20A-H1100. The heat-treatment temperature had the most influence on the rate of elution. The amount of adsorbed H_2SO_4 that is proportional to the surface area also influenced the rate: the larger the adsorption amount gave the more rapid elution of the acid.

Discussion

The present study used TPD to clarify the species and amount of adsorbed SO_2 over pitch-based ACFs. Adsorbed SO_2 desorbed at two temperatures, indicating the presence of basically two species, physically adsorbed SO_2 and oxidatively adsorbed SO_3 . The latter species can be hydrated, making it more difficult to reduce, and thus desorbing at a higher temperature. It should be noted that the detected species is always SO_2 , even though it is desorbed at a high temperature. Some reduction of SO_3 to SO_2 may take place to account for the smaller amount of SO_3 desorbed at a higher temperature as discussed in previous papers.^{1-3,11}

The species and amount of SO_2 adsorbed over the ACF are strongly influenced by the adsorption conditions and kinds of ACFs. Oxygen and water with oxygen in the gas phase increased the amounts of SO_3 and hydrated SO_3 species markedly over ACF, although a limited amount of oxidized species was present without oxygen in the gas phase. Adsorbed oxygen or some of the surface oxygen functional groups on ACF are responsible in the latter case.

It should be noted that increasing the amount of H_2O in the gas phase over 5% reduced the amount of adsorbed SO_2 at the stationary state. The rapid elution of aqueous H_2SO_4 is suggested by the larger amount of condensed H_2O and may allow the opening of more active sites for SO_2 or SO_3 adsorption. This may account for the complete removal of SO_2 in the gas phase.

Calcination at temperatures up to 1100°C increased the amount of adsorbed aqueous H_2SO_4 under the same conditions at the stationary state, indicating more adsorption sites and hence more activity caused by the calcination at higher temperatures. The ACF of the largest surface area calcined at 1100°C showed the largest amount of adsorbed H_2SO_4 at the stationary state among the ACFs. It should be noted that calcination at 1100°C shifted the peak of desorption to higher temperatures, indicating less reactivity of aqueous

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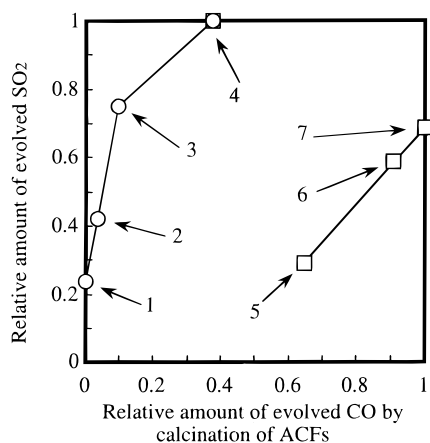


Figure 10. Relation between relative amounts of evolved SO_2 and CO from ACFs calcined at different temperatures. Bases of evolution of SO_2 and CO_2 : OG-20A-H1100 and OG-20A-H1100, respectively. ACF (○) 1. OG-20A as received, 2. OG-20A-H500, 3. OG-20A-H800, 4. OG-20A-H1100; (□) 5. OG-5A-H900, 6. OG-10A-H1100, 7. OG-15A-H1100.

H_2SO_4 for reduction because of larger adsorption over the ACF surface.

The calcination removes CO from the ACF surface, increasing the number of adsorption sites. Figure 10 illustrates a correlation between the relative amounts of evolved CO at 120–400 °C from OG-20A up to the calcination temperature and the amount of adsorbed H_2SO_4 under the same reaction conditions over the same calcined ACFs. A monotonic correlation is found in the figure, as observed with the activities of the ACFs.^{10,11}

The rate of H_2SO_4 elution from the ACF was also estimated by measuring the amounts of desorbed SO_2

after SO_2 removal and after the treatment of adsorbed H_2SO_4 over ACF with humid air. Calcination at high temperature was found to enhance the elution of adsorbed H_2SO_4 , as shown in Figure 6.

Among the OG-A series of ACFs, OG-20A with the largest surface area shows the largest activity, adsorption capacity, and rate of H_2SO_4 elution when it calcined at 1100 °C. The ACF of a smaller surface area shows a low adsorption capacity and rate. Calcination at higher temperatures always enhanced both. Relative amounts of evolved CO_2 from ACFs up to the respective optimum temperature are plotted against the relative amount of adsorbed H_2SO_4 on the same ACF. There is a monotonic correlation among OG-5A, -10A, and -15A, although OG-20A-H1100 is certainly out of the correlation. Some of the active sites might be already introduced at the activation stage, where some of the oxygen functional groups are decomposed at high temperature, leaving the active site on the particular ACF.

In conclusion, the calcination of OG-20A of the largest surface area at 1100 °C created the largest number of active sites for adsorption of SO_2 , which is oxidized, hydrated, and then eluted in aqueous H_2SO_4 at the highest rate. The surface, for which oxygen functional groups are completely removed by calcination up to 1100 °C, carries the largest number of active sites and exhibits a hydrophobic property, causing rapid elution of aqueous H_2SO_4 . Such ACF exhibited the largest activity for SO_2 removal. Calcination at temperatures higher than 1100 °C reduces the surface area and, hence, the active site of the ACF.^{9,11}

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