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Biomass and Coal Modification to Prepare Activated Coke for Desulfurization and Denitrification

Guangkui Liu [1], Liwei Wang [2,*], Yukun Li [3,*] and Xiaohan Ren [2,*]

[1] China Special Equipment Inspection & Research Institute, Beijing 100029, China; liuguangkui9527@163.com
[2] Institute of Thermal Science and Technology, Shandong University, Jinan 250061, China
[3] School of Chemical and Process Engineering, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK
* Correspondence: 201933886@mail.sdu.edu.cn (L.W.); pmyuli@leeds.ac.uk (Y.L.); xiaohan09126@gmail.com (X.R.)

Abstract: SO_2 and NOx in flue gas are serious environmental pollutants. As an excellent adsorbent, activated coke has good application potential in flue gas desulfurization and denitrification. In this study, different concentrations of NH_3 and K_2CO_3 solutions were used to modify the activated coke made from biomass and coal, and then separate and coordinated desulfurization and denitrification experiments were carried out. The adsorption efficiency of activated coke and the adsorption capacity of SO_2 and NO were compared, and the adsorption relationship between SO_2 and NO was clarified. The changes of the surface functional groups of activated coke before and after adsorption and the forms of SO_2 and NO after adsorption were analyzed by Fourier transform infrared spectrometer and X-ray diffractometer patterns. Results show that K_2CO_3 and NH_3 modification can promote the adsorption of SO_2 and NO in activated coke, and K_2CO_3 modification is more significant for improving the denitrification and desulfurization capacity. When the unmodified activated coke synergistically adsorbs SO_2 and NO, there is a competitive adsorption between NO and SO_2. However, when the activated coke modified with K_2CO_3 solution and NH_3 synergistically adsorbs SO_2 and NO, both have a promoting effect. After the adsorption of NH_3-modified activated coke, $CaSO_4$ and Na_2SO_4 crystals will appear. K_2SO_4 will exist after the adsorption of activated coke modified with K_2CO_3 solution.

Keywords: activated coke; desulfurization; denitrification; adsorption capacity; synergistically

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1. Introduction

Flue gas pollutes the atmosphere around residential areas, and its components are very complex, including steam, SO_2, N_2, CO, CO_2, O_2, hydrocarbon compounds, and nitrogen oxides. In flue gas, SO_2 and NOx are the most harmful to human health and the environment [1,2]. Activated coke is an excellent adsorbent, and its specific surface area, pore structure abundance, and functional group types can all affect its physicochemical properties and adsorption performance [3–6]. Due to the difference in adsorption medium (gas phase and liquid phase) and adsorbate, the properties of activated coke are also different. Usually, activated coke with developed granular and microporous structure is mostly used for gas phase adsorption. The adsorption of pollutants by activated coke is divided into physical adsorption and chemical adsorption [7,8]. Physical adsorption relies on the van der Waals force combined with activated coke's larger specific surface area and developed pore structure to adsorb pollutants in activated coke. Chemical adsorption relies on the defective carbon atoms and surface chemical functional groups on the surface of the activated coke to convert pollutants into non-polluting substances in a targeted manner. Activated coke desulfurization and denitrification have the advantages of strong reliability, low water consumption, high stability, no secondary pollution, and resource utilization, and has become the focus of research in recent years [9–14]. At present, the use of activated coke to desulfurize and denitrify flue gas is the most practical method for controlling the emission of polluting gases [10,15].

The essence of activated coke flue gas desulfurization is to use the abundant pore structure to adsorb and catalyze SO_2, O_2, H_2O, and other gases in flue gas, so as to convert SO_2 in the gas phase into H_2SO_4 [16,17], and store them in the pores of activated coke. Therefore, a flue gas desulfurization method using activated carbon to adsorb SO_2 was developed [10,11,18]. The essence of activated coke denitrification also mainly relies on the microporous structure and surface functional groups of activated coke for adsorption. First, NO is oxidized to NO_2, and then NO_2 is combined with H_2O and stored in the pore structure of activated coke in the form of HNO_3. Davini et al. [19] prepared activated coke with asphalt and polyacrylonitrile as raw materials, and carried out SO_2 adsorption experiments at an adsorption temperature of 360 °C to explore the effect of SO_2 concentration on desulfurization efficiency. They found that the basic functional groups on the surface of the activated coke were favorable for the adsorption of SO_2, and the adsorption amount was up to 87 mg/g. Raymundo-Pinero et al. [20] used ammonia to activate carbonaceous materials to prepare activated coke, and detected the functional groups on the surface of activated coke. It was found that nitrogen-containing functional groups can play a role in the desulfurization process. Shirahama N et al. [21] prepared activated coke to adsorb NO_2 using asphalt as raw material, and found that activated coke showed a higher adsorption efficiency (75%) at an adsorption temperature of 30 °C.

For a long time, people have gradually realized that when SO_2 and NOx are treated separately, the investment and operating costs are high. In order to reduce the cost of flue gas purification and meet the needs of power plants, new technologies for synergistic desulfurization and denitrification need to be developed [22]. Lee et al. [23] used KOH modification to prepare activated coke to adsorb SO_2 and NO gas in flue gas. The study showed that the adsorption capacity of activated coke for NO was greater than that for SO_2 in the solo adsorption process, and SO_2 had more affinity than NO in the synergistic adsorption process.

The synergistic desulfurization and denitrification of activated coke has been widely studied, but the reaction mechanism of SO_2 and NO in the adsorption process remains unclear. The change of adsorption efficiency of activated coke obtained after modification with different modifying reagents and the change of activated coke before and after adsorption are also less studied. Biomass has low cost, large reserves, and less sulfur and nitrogen [24–26]. Coal has a high carbon content, is widely distributed and readily available, and is an excellent precursor material for the preparation of activated coke [27–32]. In this study, we used poplar bark and coal as raw materials to modify the activated coke and conducted solo and synergistic desulfurization and denitrification experiments. We compared the adsorption efficiency and adsorption capacity of activated coke and clarified the adsorption relationship between SO_2 and NO. The FTIR and XRD patterns were used to analyze the changes of the surface functional groups of the activated coke before and after the adsorption and the existing forms of SO_2 and NO after the adsorption, which provided a theoretical basis for the preparation and industrial application of the activated coke with specific adsorption properties.

2. Experimental

2.1. Preparation of Experimental Samples

The activated coke used in the experiment was the activated coke prepared in the previous modification experiments. The relevant data of modified activated coke are obtained from our previous experiments, see Table 1 [5]. The specific surface area value and pore size distribution were all measured and calculated by using the BSD-PS1/2 high-performance specific surface area analyzer (Beijing Beishide Instrument Technology, Beijing, China).

Table 1. Physical properties of modified activated coke [5].

Modification Reagent	Total Surface Area (m^2/g)	Micropore Specific Surface Area (m^2/g)	Average Hole Diameter (nm)	Micropore Ratio (%)
unmodified	585	334	3.40	57.1
5% NH_3	620	325	3.18	52.5
10% NH_3	626	328	3.28	52.4
15% NH_3	637	332	2.86	52.0
20% NH_3	652	330	3.38	50.6
3% K_2CO_3	627	517	2.67	82.4
6% K_2CO_3	602	540	1.94	89.8
9% K_2CO_3	484	469	1.94	96.9
12%K_2CO_3	438	427	2.20	97.5

2.2. Experiment Procedure

As shown in Figure 1, the system consists of three parts: simulated flue gas distribution system, fixed bed reaction system, and flue gas analysis system. The simulated flue gas used in the experiment was composed of SO_2, NO, N_2, O_2, and steam. The concentration of SO_2 and NO is controlled by a mass flow meter to be 400 ppm respectively, and the amount of activated coke is 0.5 g. The fixed bed reaction system is a quartz glass tube with an inner diameter of 18 mm and a length of 580 mm. After the gas entered the gas mixing bottle and was evenly mixed, it was mixed with the steam provided by the micro-injection pump and the heating cable and passed into the fixed bed reactor. A flue gas analyzer was used for gas distribution calibration. After the flue gas analyzer reading was stable, 0.5 g of activated coke was added into the middle of the fixed reaction bed for adsorption test. The fixed bed reaction temperature was set to 70 °C [33], the reaction time (1–2 h) was determined according to the adsorption efficiency, and the concentration of the gas at the outlet of the reactor was detected by a flue gas analyzer. The suction flow rate of the gas pump of the flue gas analyzer is 500 mL/min, so the total flow set for the adsorption experiment is 500 mL/min. When the SO_2 and NO outlet concentrations reached the expected value or reached the set time, the experiment was stopped, and the exhaust gas was completely treated by the gas washing bottle (containing NaOH solution) and then discharged into the air. After the experiment, the adsorbed activated coke was encapsulated for subsequent detection and use.

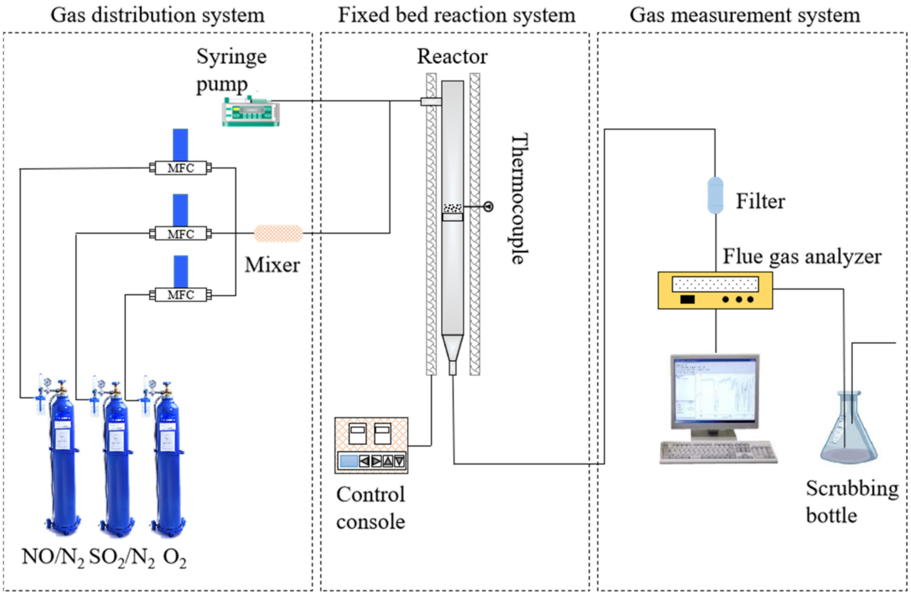


Figure 1. System diagram of activated coke adsorption experiment device.

2.3. Material Characterization

Field emission scanning electron microscopy (Zeiss Sigma 300) produced by Zeiss, Germany was used to observe the microscopic morphological changes of the activated coke before and after adsorption. A Fourier transform infrared spectrometer (Thermo Scientific Nicolet iS50) produced by Thermo Fisher Scientific Co., Ltd. (Waltham, MA, USA) in the US was used to detect the changes of activated coke functional groups before and after adsorption. X-ray diffractometer (Ultima IV) produced by Shanghai Xinghe Instrument Co., Ltd. (Shanghai, China) was used to analyze the phase of activated coke to detect the phase change before and after adsorption of activated coke.

2.4. Performance Evaluation Method

The desulfurization and denitration performance of activated coke is mainly reflected by SO_2 adsorption efficiency, NO adsorption efficiency, SO_2 adsorption capacity, and NO adsorption capacity. The calculation method is as follows:

Desulfurization efficiency of activated coke:

$$\eta_{SO_2} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \tag{1}$$

Denitration efficiency of activated coke:

$$\eta_{NO} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \tag{2}$$

In Equations (1) and (2), η represents the adsorption efficiency (%), C_{in} is the gas concentration at the inlet of the fixed reaction bed (ppm), and C_{out} is the gas concentration at the outlet of the fixed reaction bed (ppm).

The SO_2 and NO adsorption capacity of activated coke refers to the SO_2 and NO adsorption capacity per unit mass of activated coke within a certain period of time.

SO_2 adsorption capacity of activated coke:

$$V_{SO_2} = \int_0^t \frac{(C_{in} - C_{out}) \times M \times Q \times 10^{-6}}{22.4 \times m_{AC}} dt \tag{3}$$

NO adsorption capacity of activated coke:

$$V_{NO} == \int_0^t \frac{(C_{in} - C_{out}) \times M \times Q \times 10^{-6}}{22.4 \times m_{AC}} dt \tag{4}$$

In Equations (3) and (4), V represents the cumulative adsorption capacity of activated coke per unit mass (mg/g), M represents the molar mass of SO_2 and NO (g/mol), Q is the simulated flue gas flow (L/min), t represents the total time required for adsorption (min), and m_{AC} is the mass of activated coke in the fixed bed (g).

3. Results and Discussion

3.1. Study on the Desulfurization and Denitrification Performance of NH_3-Modified Activated Coke

3.1.1. Effect of Modified Activated Coke with Different NH_3 Concentrations on SO_2 Adsorption Efficiency

Figure 2 shows that the process of SO_2 adsorption by activated coke can be divided into fast adsorption stage, transition adsorption, and slow adsorption stage [34]. The fast adsorption stage refers to the stage where the SO_2 adsorption efficiency is above 99%; the slow adsorption stage refers to the stage where the SO_2 adsorption efficiency is stable; the transition stage refers to stage between the slow adsorption stage and the fast adsorption stage. Figure 2 shows that the activated coke modified with 15% NH_3 has the longest fast adsorption stage, whereas the activated coke without NH_3 modification has no fast adsorption stage. In the transition and slow adsorption stages, the adsorption efficiency curves under these five modified conditions have similar linearity and changing trends, but the magnitude of the adsorption efficiency is obviously different. In the slow adsorption stage, the adsorption efficiency of activated coke modified with 5% NH_3 was stable at about 40%, and the adsorption efficiency of activated coke without NH_3 modification was the lowest at about 22%.

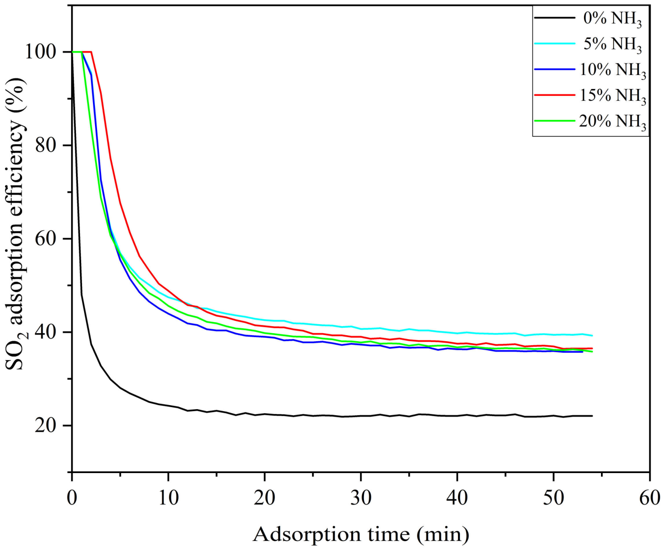


Figure 2. Effect of modified activated coke with different NH_3 concentrations on SO_2 adsorption efficiency.

Activated coke plays a dual role of adsorbent and catalytic oxidant in the process of adsorbing SO_2. The process is to first adsorb O_2, SO_2, and steam in the flue gas on the surface of the activated coke and then react O_2 (adsorbed state) and SO_2 (adsorbed state) to oxidize SO_2 to SO_3. Finally, SO_3 reacts with steam (adsorbed state) to form H_2SO_4. The basic steps of the activated coke desulfurization reaction are as follows [35]:

$$\frac{1}{2}O_2 + \sigma \rightleftharpoons O^* \tag{5}$$

$$SO_2 + \sigma \rightleftharpoons SO_2^* \tag{6}$$

$$SO_2^* + O^* \rightarrow SO_3^* + \sigma \tag{7}$$

$$H_2O + \sigma \rightleftharpoons H_2O^* \tag{8}$$

$$H_2O^* + SO_3^* \rightleftharpoons H_2SO_4 + \sigma \tag{9}$$

where σ is the adsorption activated site and the superscript * on the right represents the adsorption state. Activated coke adsorption is further divided into physical adsorption and chemical adsorption. Physical adsorption is caused by the balance of intermolecular attractive and repulsive forces; chemical adsorption is mainly achieved by chemical reactions between gas molecules and the activated sites on the adsorbent interface. Equations (5), (6) and (8) are chemical adsorption, in which gas molecules react with the activated sites on the surface of the activated coke to form gas molecules (adsorbed state). Equations (7) and (8) show that when SO_2 is oxidized to SO_3, it reacts with steam to form H_2SO_4, which will release new activated sites.

3.1.2. Effect of Modified Activated Coke with Different NH_3 Concentrations on NO Adsorption Efficiency

Figure 3 shows the denitration process curves of activated coke modified with different NH_3 concentrations. There is almost no fast adsorption stage in the denitration process of activated coke, and the transition stage enters the slow adsorption stage soon after the experiment starts. The NO adsorption efficiency of activated coke prepared under different modification conditions showed the same trend, but the final adsorption efficiency was different. The final adsorption efficiency of the activated coke without NH_3 modification treatment is the lowest at about 10%, whereas the final adsorption efficiency of the activated coke modified with 15% NH_3 concentration is about 17%. From the whole denitration process, the adsorption efficiency of activated coke to NO has been improved after NH_3 modification.

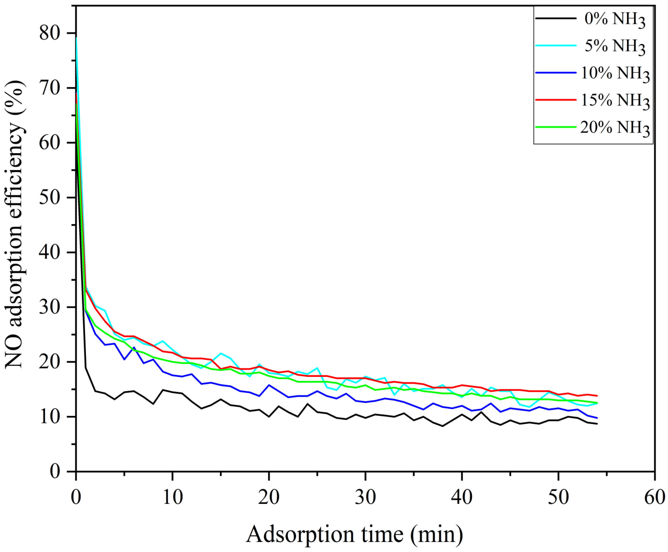


Figure 3. Effect of modified activated coke with different NH_3 concentrations on NO adsorption efficiency.

Under aerobic conditions, most NO is oxidized to NO_2. The polarity of NO_2 is stronger than that of NO, which makes it easier to adsorb on the active center of activated coke and to be reduced more easily. O_2 and NO in the gas phase react with NH_3 originally adsorbed on the surface of activated coke to generate N_2 and H_2O [36]. In addition to physical adsorption, the denitration process of activated coke has the following reactions:

$$NH_3 + \sigma \rightleftharpoons NH_3^* \tag{10}$$

$$NH_3^* + NO + O_2 \rightarrow N_2 + H_2O^* \tag{11}$$

In the denitration process of activated coke, part of NO is removed by physical adsorption, and part of it is catalytically reduced with NH_3, so as to achieve the purpose of removal. The physical adsorption of NO occupies a small part, so there is no obvious fast adsorption stage in the activated coke denitrification process. The pore structure of activated coke is only one of the factors affecting NO adsorption, whereas its surface chemical properties have a greater impact on NO adsorption.

3.1.3. SO_2/NO Adsorption Capacity per Unit Mass of Activated Coke after Modification with Different NH_3 Concentrations

Table 2 shows the adsorption capacity of SO_2 and NO per unit mass of activated coke. As can be seen, the activated coke modified with 15% NH_3 concentration has the highest SO_2 and NO adsorption capacity (14.4 and 6.58 mg/g, respectively). On the whole, the desulfurization performance of activated coke is doubled after NH_3 modification, whereas the concentration of NH_3 modification has little effect on the desulfurization performance of activated coke. NH_3 catalyzes the reduction of NO and promotes the conversion of NO into N_2, so the adsorption capacity will also increase. The values in Table 2 were also validated from recent studies. Wang et al. [33] also prepared activated coke by ammonia modification and carried out SO_2 adsorption experiments. They found that the adsorption capacity of the ammonia-modified activated coke was significantly improved compared with that of the non-ammonia-modified activated coke.

Table 2. SO_2/NO adsorption capacity per unit mass of activated coke.

Sample	SO_2 Adsorption Capacity (mg/g)	NO Adsorption Capacity (mg/g)
unmodified	7.25	4.15
5% NH_3 modified	14.2	6.21
10% NH_3 modified	13.3	5.08
15% NH_3 modified	14.4	6.58
20% NH_3 modified	14.1	6.33
3% K_2CO_3 modified	19.8	8.24
6% K_2CO_3 modified	18.8	13.2
9% K_2CO_3 modified	36.6	16.1
12% K_2CO_3 modified	68.0	18.1

3.2. Study on the Desulfurization and Denitrification Performance of K_2CO_3-Modified Activated Coke

3.2.1. Effect of Modified Activated Coke with Different K_2CO_3 Concentrations on SO_2 Adsorption Efficiency

Figure 4 shows the effect of activated coke modified with different K_2CO_3 concentrations on the SO_2 adsorption efficiency. As can be seen, the unmodified activated coke has almost no fast adsorption stage. With the increase of K_2CO_3 concentration, the fast adsorption stage of activated coke was prolonged. The SO_2 fast adsorption stage of activated coke modified with 9% and 12% K_2CO_3 concentrations lasted for 60 min, and then the SO_2 adsorption efficiency gradually decreased, indicating that its microporous pore structure is rich. The adsorption efficiency of activated coke SO_2-modified with 3% and 6% K_2CO_3 concentrations is basically maintained at about 60%. Given that K_2CO_3 solution modifies the activated coke to load K metal, which plays an important role in the adsorption of SO_2, SO_2 (adsorbed state) is oxidized and combined with H_2O to form H_2SO_4, which in turn reacts with K metal. Therefore, the higher concentration of K_2CO_3 solution will promote the SO_2 adsorption performance of modified activated coke.

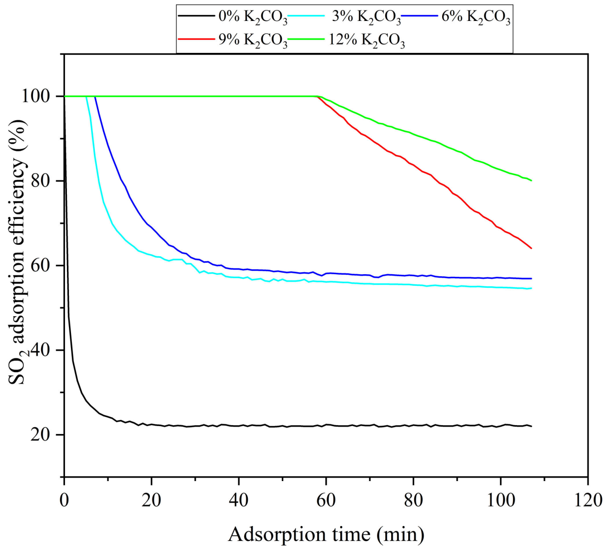


Figure 4. Effect of modified activated coke with different K_2CO_3 concentrations on SO_2 adsorption efficiency.

3.2.2. Effect of Modified Activated Coke with Different K_2CO_3 Concentrations on NO Adsorption Efficiency

Figure 5 shows that the higher the concentration of K_2CO_3 solution, the higher the denitration performance of the modified activated coke, which has a great relationship with the microporous structure and surface functional groups of the activated coke. When the modified activated coke adsorbs NO, physical adsorption and chemical adsorption exist simultaneously [37]. The role of the modifier is mainly to improve the chemical adsorption performance of the activated coke for NO by adjusting the physical and chemical properties of the activated coke surface. The adsorption efficiency of activated coke modified with 12% K_2CO_3 concentration remained at about 60% in the first 15 min. In this process, there were both physical adsorption of NO by pore structure and chemical adsorption of NO after oxidation to NO_2. The oxidized nitrogen oxides react with the metal oxides in the pore structure and are adsorbed on the surface of the activated coke. With the increase of time, the denitration performance of activated coke gradually decreased, because the activated sites of the pore structure were occupied, resulting in the gradual saturation of micropores. On the whole, the modification of K_2CO_3 solution greatly improves the denitration performance of activated coke, and the effect of 3% and 6% K_2CO_3 concentrations is more significant. With the continuous increase of K_2CO_3 concentration, this promoting effect became no longer obvious.

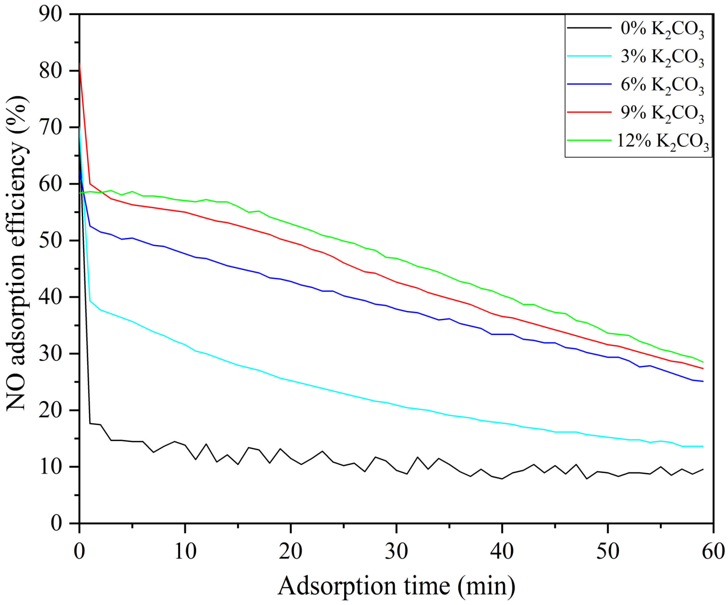


Figure 5. Effect of modified activated coke with different K_2CO_3 concentrations on NO adsorption efficiency.

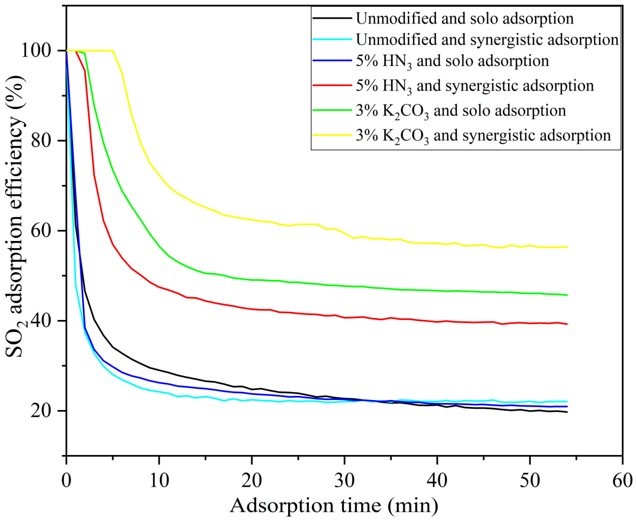
3.2.3. SO_2/NO Adsorption Capacity per Unit Mass of Activated Coke after Modification with Different K_2CO_3 Concentrations

It can be seen from Table 2 that, the SO_2 and NO adsorption of the unmodified activated coke are the smallest (7.25 and 4.15 mg/g, respectively). With the increase of modifier concentration, the adsorption capacity of SO_2 and NO in activated coke showed an upward trend, indicating that K_2CO_3 could improve the adsorption capacity of activated coke for SO_2 and NO at the same time. The desulfurization and denitration capacities per unit mass of activated coke modified with 12% K_2CO_3 concentration are 67.95 and 18.11 mg/g, respectively, which are 10 and 5 times higher than that of unmodified activated coke. In addition to physical adsorption, SO_2 in the simulated flue gas will react with O_2 to form SO_3, which will then combine with water molecules to form H_2SO_4, and H_2SO_4 will continue to react with metal oxides. NO will also react with O_2 adsorbed on the activated coke to form NO_2 (adsorbed state), and NO_2 (adsorbed state) will react with H_2O (adsorbed state) to form HNO_3 (adsorbed state) [38]. A portion of HNO_3 (adsorbed state) reacts with the metal oxides on the activated coke. After H_2SO_4 and HNO_3 react with metal oxides, more activated sites will be generated for physical and chemical adsorption of SO_2 and NO.

3.3. Study on the Solo/Synergistic Performance of Modified Activated Coke for Desulfurization and Denitrification

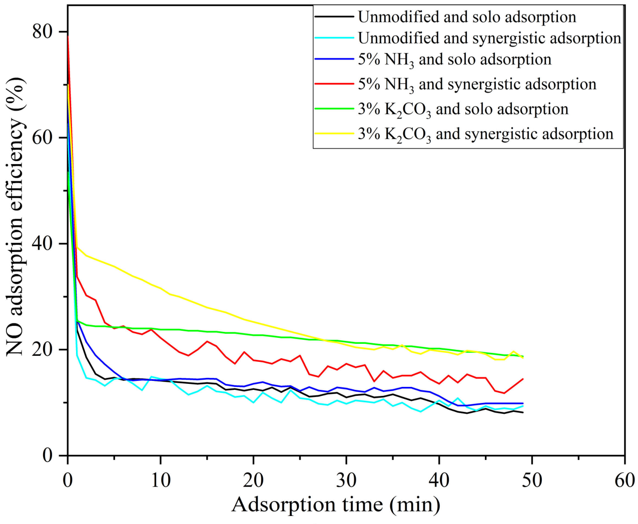
3.3.1. Solo and Synergistic Adsorption EFFICIENCIES of Activated Coke

The solo and synergistic desulfurization and denitrification efficiencies of activated coke prepared under different modification conditions are shown in Figure 6. As can be seen from the figure, when the activated coke adsorbs SO_2 solo, the adsorption efficiency of SO_2 by the activated coke modified with NH_3 is not significantly improved, which is basically the same as that of the unmodified activated coke, and the SO_2 adsorption efficiency is finally stabilized at about 22%. However, the adsorption efficiency of SO_2 by the activated coke modified with K_2CO_3 solution was significantly improved and maintained at about 50%. This is related to the pore structure and surface functional groups of activated coke. In the initial stage of SO_2 adsorption, activated coke is mainly physically adsorbed; however, the proportion of micropores of activated coke modified with K_2CO_3 solution can reach 90%, and the micropore structure is quite rich. When SO_2 adsorption was in the slow and stable adsorption stage, chemical adsorption played the main role at this time, and K_2CO_3 solution modification not only developed the microporous structure of activated coke, but also loaded K_2O in the pore structure of activated coke. K_2O reacts with SO_2, O_2, and steam to form sulfate, which also improves the adsorption efficiency of SO_2. When the activated coke was synergistically desulfurized and denitrified, the adsorption efficiency of SO_2 by the activated coke modified with K_2CO_3 solution reached 60%, which is higher than that of solo desulfurization. This indicates that synergistic desulfurization and denitrification (in the presence of NO) contribute to the adsorption of SO_2. The denitration effect of activated coke modified with K_2CO_3 is better than that of activated coke under other modified conditions, and the synergistic adsorption efficiency is higher than that of solo adsorption.



(**a**)

Figure 6. *Cont.*



(**b**)

Figure 6. Solo and synergistic adsorption efficiencies of activated coke with different modifications. (**a**) The adsorption efficiency of SO_2. (**b**) The adsorption efficiency of NO.

3.3.2. Capacity of Activated Coke per Unit Mass to Adsorb SO_2 and NO Solo/Synergistically

The adsorption capacities of SO_2 and NO by the activated coke prepared under different modification conditions are shown in Figure 7. As can be seen from the figure, when the unmodified activated coke adsorbs NO and SO_2 solo, the total adsorption capacity is greater than that in the synergistic adsorption, which indicates that competitive adsorption occurs when SO_2 and NO coexist. According to the adsorption theory, when the multi-component gas passes through the adsorption bed, the high boiling point will replace the low boiling point, and the high molecular weight will replace the small molecular weight. The boiling point and molecular weight of SO_2 are higher than those of NO, so SO_2 is more competitive in the adsorption process. The synergistic adsorption capacity of SO_2 and NO of activated coke modified with K_2CO_3 solution and NH_3 is higher than that of solo adsorption. This is because in the synergistic adsorption process, only the physically adsorbed NO will be replaced, whereas the chemically adsorbed NO is not easily replaced. Under the action of surface functional groups, chemically adsorbed NO reacts with adsorbed SO_2 to generate new intermediate products NO_2 (adsorbed state) and SO_3 (adsorbed state), and H_2SO_4 and HNO_3 can be generated under the action of water [39]. The presence of NO will promote the adsorption of SO_2. Therefore, the modified activated coke has higher adsorption capacity and adsorption efficiency when it is synergistically adsorbing SO_2 and NO.

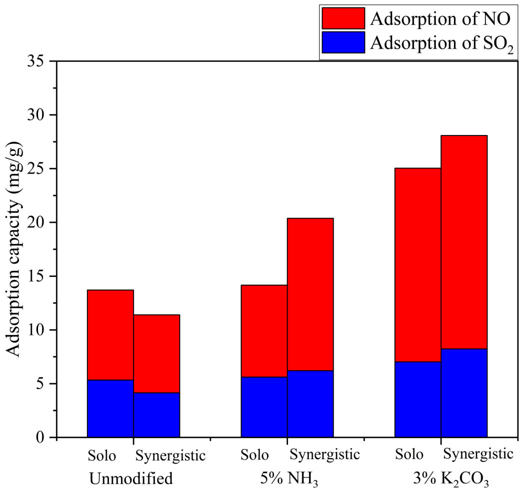


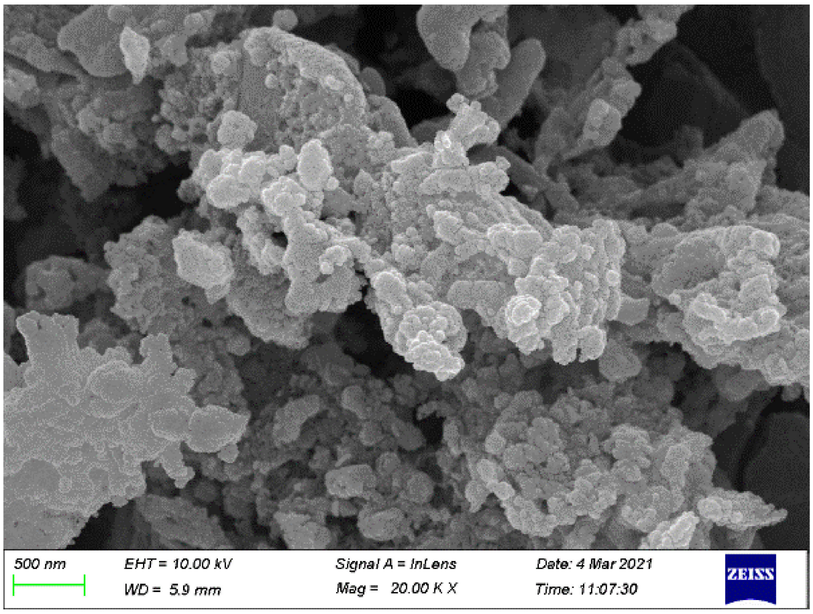
Figure 7. Sole/synergistic adsorption capacity of SO_2 and NO per unit mass of activated coke.

3.4. Changes of Surface Microstructure before and after Adsorption of Modified Activated Coke

Scanning electron microscopy and infrared spectroscopy were performed on the activated coke before and after adsorption to understand the surface morphology and functional group changes of the activated coke adsorbing SO_2 and NO. This section takes 5% NH_3- and 3% K_2CO_3-modified activated coke as an example.

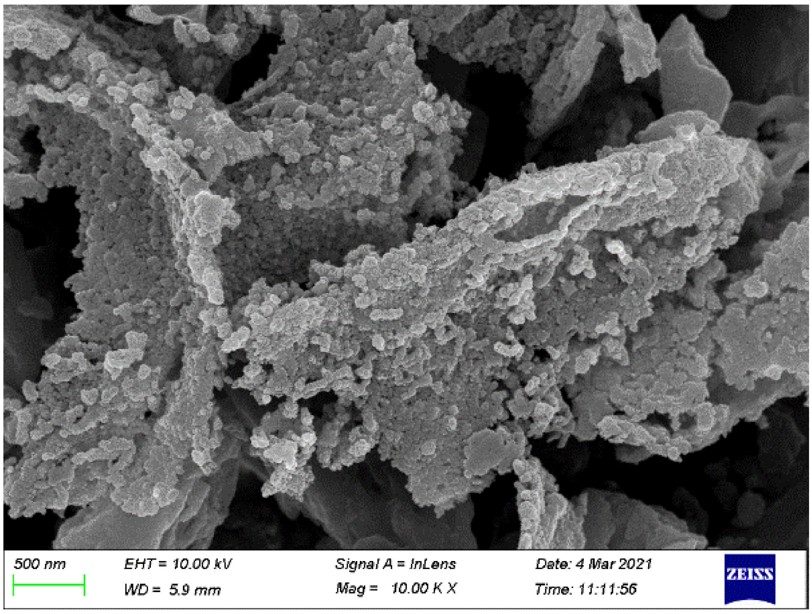
3.4.1. Study on the Microstructure Change of Activated Coke Modified with 5% NH_3

Figure 8a shows that the pore structure of the NH_3-modified activated coke is relatively developed, exists in a layered structure, and has a large number of slits and pores. After the adsorption of SO_2 and NO, the surface becomes more disordered, the pore structure of the activated coke does not change much, and the layered structure still exists; however, a large number of crystalline particles are scattered on the surface of the activated coke. This is because the SO_2 and NO adsorbed by the activated coke react with it and exist in the form of crystals on its surface. In order to further verify the adsorption forms of SO_2 and NO by activated coke, infrared spectroscopy analysis was performed on activated coke before and after adsorption. Figure 9 shows that the activated coke mainly shows strong absorption peaks at 3400–3700, 1400, and 1100 cm^{-1} and weaker absorption peaks at 2800 and 2400 cm^{-1}. The peak at 3430 cm^{-1} is due to OH stretching vibrations generated by hydroxyl functional groups and adsorbed moisture [40–42]. The peak at 1400 cm^{-1} is formed by C-H bending vibration, which proves the existence of aliphatic structure. Comparing the infrared spectra before and after adsorption, the types of surface functional groups of activated coke have not changed, but an obvious absorption peak appears around 3680 cm^{-1}, indicating the existence of a trace amount of NH_4^+. The peak at 1100 cm^{-1} also increases significantly, indicating that SO_4^{2-} appears after the activated coke adsorbs SO_2 [33]. Therefore, after the activated coke adsorbs SO_2 and NO at the same time, SO_2 mainly exists on the surface of the activated coke in the form of H_2SO_4 and $(NH_4)_2SO_4$. The peaks around 870 cm^{-1} are mainly related to the presence of C-H groups at the edge of the aromatic ring. The peak around 650 cm^{-1}, the out-of-plane bending vibration peak of hydroxy −OH is located when hydrogen bond association occurs.



(**a**)

Figure 8. *Cont.*



(**b**)

Figure 8. SEM images of 5% NH_3-modified activated coke before and after adsorption of SO_2 and NO. (**a**) Before adsorption, (**b**) After adsorption.

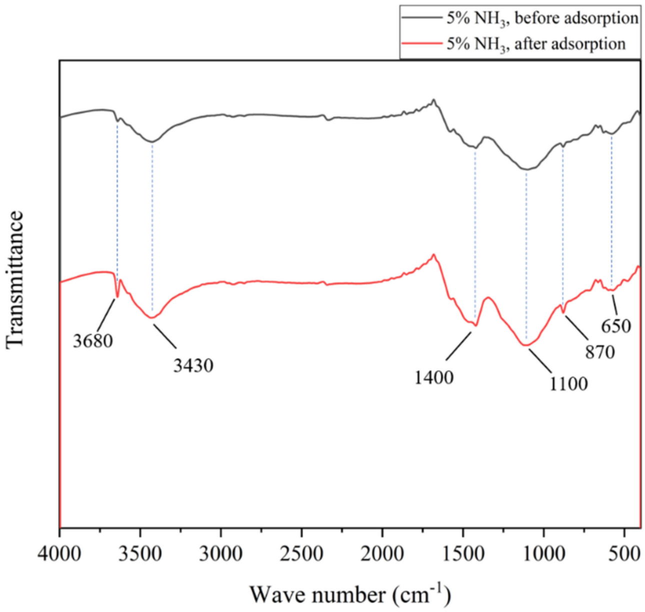


Figure 9. FTIR spectra of 5% NH_3-modified activated coke before and after adsorption of SO_2 and NO.

3.4.2. Study on the Microstructure Change of Activated Coke Modified with 3% K_2CO_3

Part of the pore structure of the activated coke modified with K_2CO_3 solution merges and collapses to form super-large pores, and the originally occluded pore structure will be activated and opened to generate cracks and pore structures. Comparing the SEM images of the activated coke before and after adsorption of SO_2 and NO, the surface of the activated coke in Figure 10a is relatively smooth, and there are a large number of small block structures. The activated coke in Figure 10b also has a large number of small block structures, and small particles appear on the surface, because SO_2 and NO exist in the form of crystals on the surface of the activated coke after being adsorbed. Chemisorption involves two factors: one is the surface functional group, and the other is the metal oxide supported on the surface of the activated coke. Figure 11 shows the FTIR spectra of the activated coke before and after adsorption of SO_2 and NO. As can be seen, the types of functional groups on the surface of the activated coke do not change between the wavenumbers of 4000 and 400 cm^{-1}, but the content of some functional groups increases. There is a strong peak at 3430 cm^{-1}, which is formed by the stretching vibration of the O-H bond in carboxylic acid, and there are a large number of hydroxyl functional groups in the adsorbed activated coke. The peak at 1127 cm^{-1} is also significantly increased, indicating that SO_4^{2-} appears after the activated coke adsorbs SO_2. The peak at 1427 cm^{-1} is caused by NO_3^- stretching vibration, indicating the presence of KNO_3, and it also corresponds to the pyridine functional group [43,44]. K_2CO_3 modification does not change the chemical surface functional groups, but loads K_2O in the microporous structure, which provides activated sites for SO_2 and NO adsorption, thereby playing a role in promoting desulfurization and denitrification.

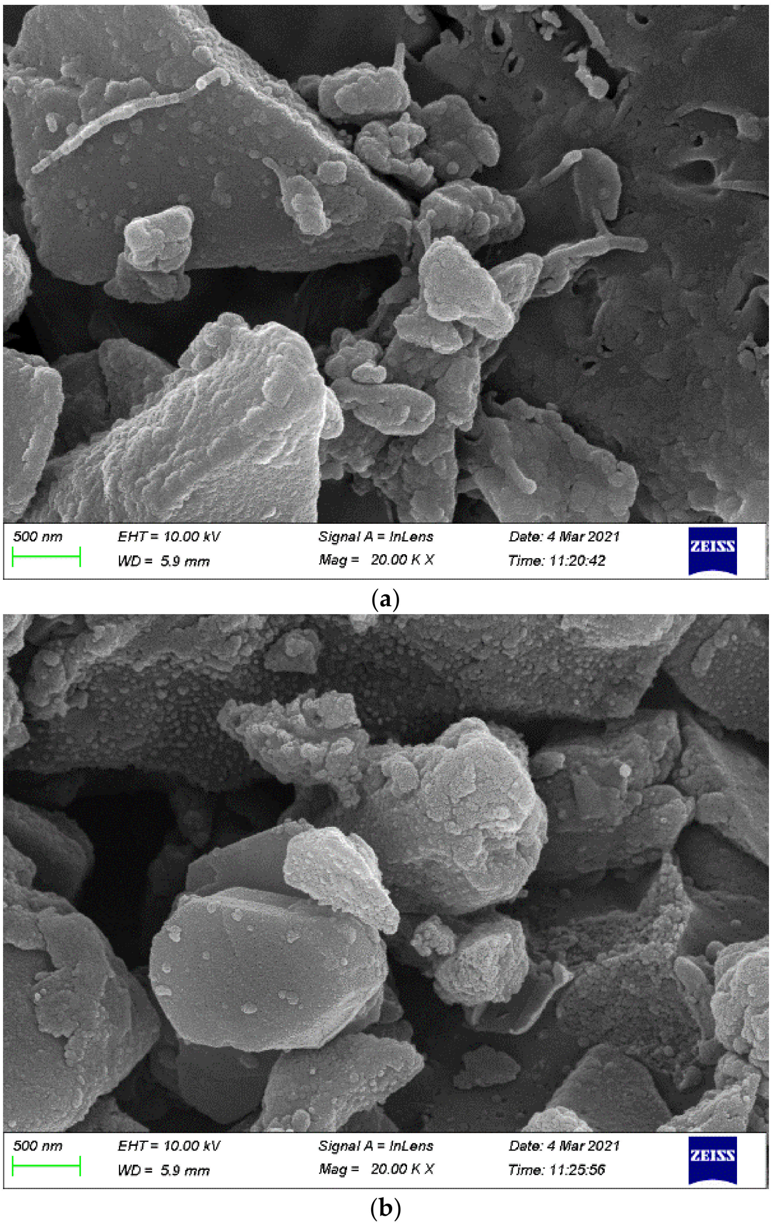


Figure 10. SEM images of 3% K_2CO_3-modified activated coke before and after adsorption of SO_2 and NO. (**a**) Before adsorption, (**b**) After adsorption.

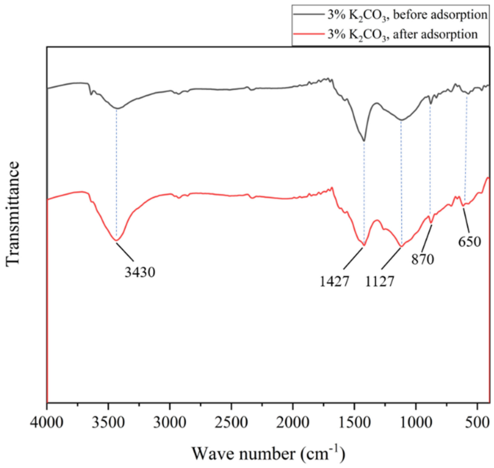
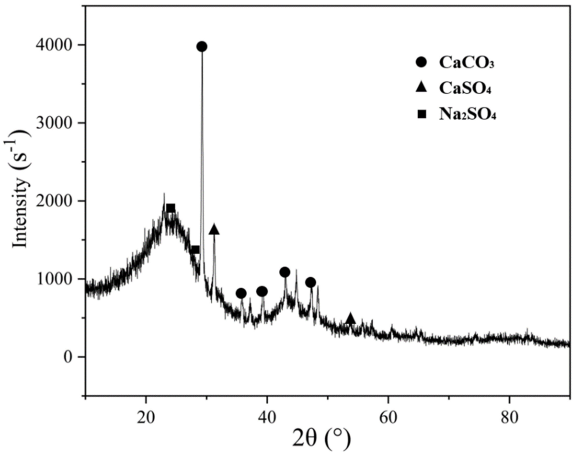


Figure 11. FTIR spectra of 3% K_2CO_3-modified activated coke before and after adsorption of SO_2 and NO.

3.5. Phase Analysis of Activated Coke after Adsorption

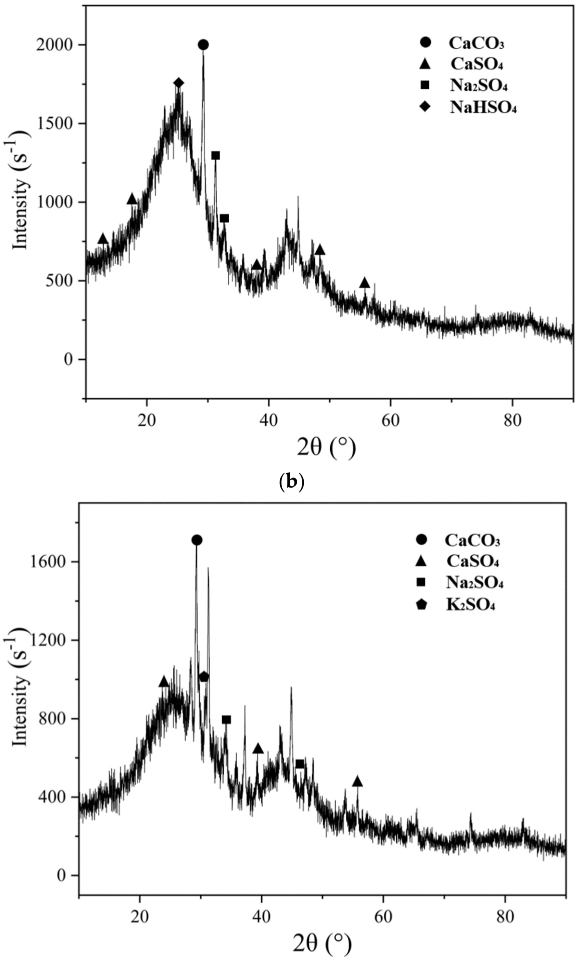
This section takes unmodified activated coke, 5% NH_3-modified activated coke, and 3% K_2CO_3-modified activated coke as examples. Infrared spectroscopy and X-ray diffraction analysis were performed on the activated coke after synergistic adsorption of SO_2 and NO to determine the changes in the surface functional groups and crystallite structure of the activated coke.

Figure 12 shows that there are many high-intensity graphite characteristic diffraction peaks in the standard graphite X-ray diffraction spectrum. The appearance of characteristic peaks can represent the degree of graphitization. The more diffraction peaks in the spectrum, the higher the degree of graphitization and the better the order of carbon materials. On the whole, the characteristic peaks of the three activated cokes are similar, and there are four characteristic peaks at about 23°, 44°, 65° and 82°of 2θ, which correspond to the (002), (100), (110) and (006). The intensities of the diffraction peaks decrease in turn, indicating that the graphitization intensity of the activated coke decreases, and the crystallinity decreases, which promotes the development of the pore structure. Figure 12a shows that when 2θ is about 29°, there is an obvious diffraction peak, indicating that the activated coke contains $CaCO_3$ crystals, and the diffraction peak at about 31° indicates that there are $CaSO_4$ and Na_2SO_4 crystals. Figure 12b shows that besides $CaCO_3$, $CaSO_4$, and Na_2SO_4 crystals, there are also a large number of $NaHSO_4$ crystals. Figure 12c shows that there is a large amount of K_2SO_4 in the 2θ range of 20–40°. XRD analysis found that SO_2 is adsorbed and combined with the substances in the activated coke in the form of $SO_4{}^{2-}$ to form sulfate minerals.



(**a**)

Figure 12. *Cont.*



(**b**)

(**c**)

Figure 12. XRD pattern of activated coke after adsorption. (**a**) Unmodified. (**b**) 5% NH_3 modified. (**c**) 3% K_2CO_3 modified.

4. Conclusions

The desulfurization and denitrification performance of the activated coke prepared by different modification methods was analyzed through solo and synergistic desulfurization and denitrification experiments of activated coke. The active coke before and after adsorption was characterized and analyzed. The specific conclusions are as follows:

1. NH_3 modification has a promoting effect on the adsorption of SO_2 and NO in activated coke. With the continuous increase of NH_3 concentration, the promoting effect is continuously enhanced, but the increase is not large. The presence of NH_3 causes NO to undergo a reduction reaction to generate N_2. A large number of crystalline particles appeared in the adsorbed activated coke. Combined with the FTIR spectrum after adsorption, SO_2 was oxidized and combined with steam to form sulfate, which existed on the surface of activated coke in the form of crystals.
2. K_2CO_3 solution modification greatly improves the desulfurization performance of activated coke. The fast adsorption stage of activated coke modified with 9% and 12% K_2CO_3 solutions was as long as 60 min, and the adsorption efficiency decreased slowly. The desulfurization efficiency of activated coke modified with 3% and 6% K_2CO_3 concentrations is approximately the same, and both are stable at about 60%. SO_2 and NO are oxidized and combined with steam to form H_2SO_4 (adsorbed state) and HNO_3 (adsorbed state), which regenerate activated sites. Through FTIR analysis, KNO_3 was formed on the surface of the adsorbed activated coke.

3. The K_2CO_3 solution modification did not change the surface functional groups of the activated coke, but the developed microporous structure and the loading of metal oxides enhanced the SO_2 and NO adsorption capacity of the activated coke. When the unmodified activated coke synergistically adsorbs SO_2 and NO, there is a competitive adsorption between NO and SO_2; however, when the activated coke treated with K_2CO_3 solution and NH_3 synergistically adsorbs SO_2 and NO, both have a promoting effect. The vibration of different bonds will lead to the generation of absorption peaks in the same wavenumber range. With the adsorption of SO_2 and NO on the activated coke, the functional groups on the surface of the activated coke will be reacted to generate $SO_4{}^{2-}$ and $NO_3{}^{-}$. The XRD patterns showed that the intensity of the diffraction peaks of the three decreased in turn, and the degree of graphitization decreased, indicating that the microporous structure was more developed. $CaSO_4$ and Na_2SO_4 crystals appeared after the adsorption of NH_3-modified activated coke, and K_2SO_4 existed after the adsorption of K_2CO_3 solution-modified activated coke. After SO_2 is adsorbed, it combines with the substances in the activated coke in the form of $SO_4{}^{2-}$ to form sulfate minerals.

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