Desulfurization Activity of Cobalt-Blended into Activated Carbon by One-step Activation Method

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Activated carbon was prepared from walnut shell and blended with Co_2O_3 powder by one-step activation method. Better development of texture properties on activated carbon was observed by scanning electron microscopy. N_2 adsorption-desorption confirmed that the surface area and micro pores volume increased 45 % and 34.2 % after cobalt addition, respectively, compared to blank samples. The results of Fourier-transform infrared spectra indicated that cobalt oxide improved the formation of basic functional groups ($\text{C}=\text{O}$) which would considerably affect the adsorption capability. The surface chemical properties of the activation samples were characterized by energy dispersive spectrum, X-ray diffraction and X-ray photoelectron spectra. Results showed that Co and CoO co-existed on activated carbon after activation. The desulfurization capacity of activated carbon-Co5 was 191.7 mg/g and 49.4 % higher than activated carbon.

Keywords: Activated carbon, Cobalt, Blend, Physicochemical properties, Desulfurization activity.

INTRODUCTION

Sulfur dioxide emitted from the combustion of fossil fuels has been regulated strictly due to its connection with the formation of acid rain, urban smog and health hazards. Recently, a variety of flue gas desulfurization (FGD) technologies have been developed to control the emission of SO_2 . Among which adsorption desulfurization attract worldwide interest because of its simple process and higher desulfurization efficiency. Many adsorbents have been studied for flue gas desulfurization, such as activated coke¹⁻⁴, metal supported porous materials⁵, activated carbon fiber (ACF)⁶⁻⁸, activated carbon^{9,10} and zeolite¹¹. Activated carbon has been demonstrated to be one of the most effective adsorbents because of its extensive surface area, multi-pore structure and various surface chemical groups. Nevertheless, the cost can be very expensive when activated carbon is used for flue gas desulfurization, due to the low sulfur capacity of normal activated carbon. Therefore, proper modification for activated carbon is needed to improve its affinity with SO_2 .

Desulfurization capacity of activated carbon depends on its porosity, surface chemistry and inorganic composition. These factors can be regulated by adding transition metals to improve the desulfurization activity of activated carbon, such as Fe ¹², Ni ¹³, Mn ^{14,15}, Co ^{16,17}, Cu ⁵ and V ⁴. The enhancement of adsorption capacity on SO_2 is related with kind of metals and its chemical forms and position in carbon. Some investigators have pointed out that cobalt as a catalyst for activated carbon

modification is quite effective and shows the best activity for removal of SO_2 ^{18,19}. The location of metals in carbon depends on the loading methods. Both impregnation and blending method are commonly used for loading metal onto activated carbon. The metal oxides are always located on the surface of activated carbon by impregnation method, but by blending method, the metal oxides are distributed throughout the activated carbon matrix¹⁹. It is well known that the reaction between metal oxides and carbon during activation process helps the development of texture structure. Therefore, with blending method, it is possible that the evenly distribution of metal oxides in activated carbon is conducive to the production of porosity and improve the desulfurization activity of activated carbon. In this study, walnut shell was carbonized firstly to prepare char, which were then blended with Co_2O_3 powder and formed column mixture by extrusion molding. This mixture was consequently activated at 1148 K. Co_2O_3 could be self-assembled on the formed column activated carbon by the one-step direct pyrolysis method to form the cobalt oxide/carbon.

The aim of this paper is to find out the effect of the one-step activation method on the physicochemical properties of activated carbon and to study the role of Co_2O_3 in activated carbon or the sulfur dioxide adsorption performance. The surface physical and chemical properties of modified activated carbon were characterized and analyzed. The sulfur dioxide adsorption capacity of the sample was investigated. Furthermore, the possible SO_2 adsorption mechanism was also discussed.

EXPERIMENTAL

Preparation of activated carbon samples: Walnut shell, from Sichuan province, P.R. China, was used as the raw material. Elemental analysis showed that the walnut shell mainly consisted of C 48.99 wt. %, H 5.74 wt. %, and N 0.24 wt. %.

Firstly, walnut shells presented as particles ranging in 0.14–0.28 mm by crushed and sieved. Then they were carbonized in an electric furnace (SX2-8-10P, Chengdu, China) at 773 K for 1 h at the heating rate of 5 °C/min under nitrogen atmosphere. Subsequently, the char powder sieved with 200-mesh screen was mixed with Co_2O_3 by blending for 0.5 h. The mixture was stirred thoroughly with binder in kneading machine and molded under 4 MPa in a vacuum extruder to form a column with diameter of 3 mm. Finally, the mixture was activated in the furnace at 1148 K for 2 h under CO_2 atmosphere (1000 mL/min). The prepared activated carbons were named as AC and the sample containing Co_2O_3 was labeled as AC-Cox (x = 2, 5, 7 and 10 %).

Characterization of the activated carbon: Iodine value was measured by China National Standards (GB/T12496.10-1999) to assess the adsorption capability of the prepared activated carbons. Thermographies of the samples was obtained with scanning electron microscopy (SEM) using JSM7500F scanning electron microscopy (JEOL). The main element contents were carried out using energy dispersive spectrometer (EDS) with X-Max 51-XXM0019 instrument (Oxford Instruments) and scanning electron microscopy. BET surface and pore volume were measured on Quadrasorb 2 SI-MP-20 (UK Malvern Instruments Co. Ltd.) using nitrogen adsorption at 77 K. The surface chemical properties of the samples was analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS). Detailed analysis was described as follows: XRD patterns were obtained with an X-Pert PRO MPD diffractometer at 30 kV and 20 mA employing CuK_α radiation and step-scanning over 2θ range 10–80°. XPS analysis was applied to determine the surface chemical composition and functional groups, using a XSAM 800 spectrometer (KRATOS). Functional groups were discussed by Fourier transforms infrared spectroscopy (FTIR that Bruker Tensor27 spectrometer in the range of 4000–500 cm^{-1} on sample pellets).

Desulfurization experiment: Desulfurization experiments were carried out in a fixed-bed reactor system. 2000 ppm SO_2 mixed with 9 vol. % O_2 , 10 vol. % water vapor and balance N_2 flow through the columnar reactor ($\varnothing 18 \text{ mm} \times 300 \text{ mm}$) which was filled with 15 g of samples at 600 h^{-1} , 353 K. The SO_2 concentration was monitored by Gas analyzer (Gasboard-3000). The test was stopped at the breakthrough concentration of 1500 ppm. Use the curves of sulfur capacity and of SO_2 concentration to calculate the capability of SO_2 adsorption.

RESULTS AND DISCUSSION

Optimization of preparation condition: The different amount of Co_2O_3 was added to prepare activated carbons to evaluate the performance of samples. The iodine value and yield were chosen as the indicators and the results are showed in Fig. 1. The iodine value curve appears a hump-shape. With the increase of Co_2O_3 loading amount, the iodine value increase firstly and then decrease due to the pores blockage caused by

Fig. 1. Effect of loading amount of Co_2O_3 on the iodine value and yield of carbon adsorbents

the excess Co_2O_3 addition. The highest iodine value is 773.22 mg/g when the loading amount is 5 %. Meanwhile, with the increase of loading amount, the yield of activated carbon increases continually. In view of the iodine value and the yield, 5 wt. % loading amount of Co_2O_3 was selected for modified activated carbon in the following studies.

Characterization of prepared samples

Physical properties: SEM technique was employed to observe the surface morphology of Co_2O_3 /carbon before and after activation. The results are presented in Fig. 2. The carbon has rough areas with irregular macro pore before activation. After activation, the surface of AC-Co5 has more folds and well pore structure. There are noticeable scattering of cobalt compounds particles on the surface of Co_2O_3 /carbon and some are trapped into the pores, indicating that the cobalt oxide particles are well assimilated in the carbon samples.

Fig. 2. SEM photographs of AC-Co5 (1) before activation and (2) after activation

The nitrogen adsorption and desorption isotherm for sample AC-Co5 is exhibited in Fig. 3. The adsorption and desorption branches are increased with the increase of relative pressure at first and then became horizontal and parallel to each other over a wide range of relative pressure. This represents type 1 isotherm, which is characteristic of microporous materials. Furthermore, the surface area and micropore volume of activated carbon-Co5 increase 45 % and 34.2 %, respectively, compared to activated carbon. This is caused by the reaction of metal oxides and carbon substrate during carbon gasification process. It is known that larger surface area and

Sample	AC	AC-Co5
BET surface area (m ² /g)	464.044	672.856
HK micropore volume (cc/g)	0.149	0.200
HK micropore width (nm)	0.553	0.558

Fig. 3. The nitrogen adsorption and desorption isotherms of activated carbon-Co5 (above) and structure parameters of activated carbon and activated carbon-Co5 adsorbent (below)

pore volume, especially micro pore volume, are beneficial for removal of SO₂. The former favors the dispersion of active ingredient and the latter helps the diffusion of reactive molecules. Therefore, it is reasonable to deduce that activated carbon-Co5 would perform well in desulfurization experiment due to their better development in texture properties.

Chemical properties: Energy dispersive spectra of AC-Co5 before and after activation are shown in Fig. 4. As seen the spectra showed the presence of cobalt, oxygen and carbon. The characteristic K α and K β peaks of cobalt are obtained at 6.93 and 7.65 keV, respectively¹⁶. The carbon content is slight decrease after activation but it is still over 85 %. The meanwhile, the O content is decreased and Co content is increased obviously after the activation with Co₂O₃. This occurred because of the reaction between Co₂O₃ and carbon during activation process, which led to the consumption of C and O in the form CO or CO₂. It is speculated that the cobalt oxide plays an important role to accelerate the chemical changes in the material.

The chemical constitution of the AC-Co5 was examined by XRD and XPS. The results are showed in Figs. 5 and 6. Broad peaks which presented at $2\theta = 24^\circ$ and 44° prove the existence of amorphous carbon structure (Fig. 5(1)). Peaks at $2\theta = 26.6^\circ$ and 50.1° are sharp and minor, corresponding to SiO₂^{16,17}. And peaks of metallic Co are observed at 44.8° , 51.7° and 76.3° , indicating that Co₂O₃ have been reduced during carbon activation. According to XPS spectrum (Fig. 6(1)), the Co 2p_{3/2} region consists of only one peak at 780.7 eV is observed²⁰ due to Co²⁺, reported to have BE values between 779 and 781 eV. XPS only detect the depth of surface at 2 nm, explaining the absence of Co metal species in form of metallic. Trace amounts and highly dispersed Co metal oxides which covered the surface of the sample caused the Co metal in form

Fig. 4. EDS spectra of AC-Co5 (1) before activation and (2) after activation

Fig. 5. XRD patterns of AC-Co5 after activation (1) before desulfurization and (2) after desulfurization

Fig. 6. XPS metal spectra of AC-Co5 (1) after activation (before desulfurization) and (2) after desulfurization

of metallic over the limit of XPS test so that it is unexposed and undetectable. Based on the result obtained from these two analytical methods, it can be concluded that the chemical valence of Co_2O_3 is reduced to CoO and Co after activation. This occurred during activation process when high temperature 1148 K was employed, in which condition added metal oxides decomposed and then may be reduced by reaction with carbon substrate to a lower and more stable oxidation states²¹.

The FTIR of AC-Co5 before and after activation are shown in Fig. 7(1) and 7(2). These carbons show similar FTIR spectra, suggesting that they have similar functional groups on the surface. Their intensities and slightly shift indicates slight differences in wavenumbers, inspecting small difference in the surface chemistry²². The broad band at 3400 cm^{-1} are observed which is attributed to the presence of O-H stretching vibration. Hydrogen bonding made it become the mode of hydroxyl functional groups²³. C=O stretching vibration which presented as the band at 1630 cm^{-1} belonging to different functional groups, including quinones, lactones, aldehydes and ketones²⁴. Between 1300 and 900 cm^{-1} can be identified as the C-O vibration. The intense band at around 1150 , 1100 and 1050 cm^{-1} is probably assigned to C-O vibrations in the structure of ether, the primary and secondary C-OH, respectively²⁰. After activation, the band at 3400 cm^{-1} is much less pronounced, corresponding to gasification of H_2O when 1148 K was employed during activation process. Enhancement of C=O (1630 cm^{-1}) is a symbol of carbonyl carbon, indicating alkaline oxygen-containing function groups increased and more alkaline delocalized π electrons formed. This is caused by the reaction between cobalt oxides and the carbons. C=O is conducive to the adsorption of SO_2 ^{25,26}. However, the slight increment of C-O, which could be attributed to the transformation of inorganic compounds, is unfavorable for adsorption of SO_2 ²⁷. Furthermore, the aromatic hydrogen (band at 700 and 900 cm^{-1}) observed for carbon sample before activation disappeared after reaction with CO_2 under high temperature during activation process.

Fig. 7. Fourier-transform infrared spectra of AC-Co5 (1) before activation, (2) after activation and (3) after desulfurization

Adsorption performance of SO_2 : The breakthrough curves of AC and AC-Co5 are presented in Fig. 8. AC-Co5

exhibits better performance in SO_2 adsorption experiment since it has kept 100 % of SO_2 removal efficiency for longer time than that of AC. AC-Co5 kept 100 % of SO_2 removal for more than 20 h, while only 10.5 h for AC. The breakthrough capacity of AC-Co5 is 191.7 mg/g , which is 49.4 % higher than that of AC (128.3 mg/g). The breakthrough time of AC-Co5 is 41.5 h, which is 17 h longer than AC (24.5 h).

Fig. 8. The breakthrough curves of AC and AC-Co5

The remarkable desulfurization activity enhancement of AC-Co5 is due to its extensive surface area, multi-pore structure, various surface functional groups and the catalytic activity of metal specie on the carbon surface. As mentioned before, activated carbon developed better texture properties after 5 wt. % Co_2O_3 addition. This has positive effect on SO_2 removal by activated carbon, since higher surface area favors the dispersion of the active ingredient and larger micro pore volume is related to the diffusion of reactive molecules. On the other hand, the basic oxygenate functional groups formed on the activated carbon surface after activation is also beneficial for the desulfurization process. Furthermore, the catalytic activities of metal species contributed to the better desulfurization performance presented by Co_2O_3 modified activated carbon. The oxidation state of Co_2O_3 was reduced to Co^0 and Co^{2+} during carbon activation (Fig. 5(1) and 6(1)). With the participation of O_2 during desulfurization process, Co metal species with reduced state or intermediate state would be gradually oxidized to active Co_2O_3 which have much higher catalytic activity than normal Co_2O_3 . Sulfur dioxide then oxidized to SO_3 while active Co_2O_3 involved during desulfurization system. At the same time, active Co_2O_3 converted reduced into intermediate state (Co^{2+}). This process was followed by H_2SO_4 generation with H_2O . Cobalt metal species with intermediate state (Co^{2+}) would be oxidized by O_2 in desulfurization system and form active Co_2O_3 again²⁸. This catalytic activity of modified activated carbon is reported to be the dominate factor that govern its sulfur capacity. Enhancement of C=O (1630 cm^{-1}) is conducive to the adsorption of SO_2 (Fig. 7(2)).

Surface chemistry changes after desulfurization: In order to explore some surface chemical changes in the desulfurization process, AC-Co5 after desulfurization was characterized

by XRD, XPS and FTIR. In Fig. 6(2), after reacted with SO₂, the binding energies for Co 2p_{3/2} is found at 783.3 eV and 787.8 eV, which corresponding to cobalt(II) and cobalt(II) satellite ions^{29,30}. According to Klinik and Grzybek³¹, the higher binding energy of Co 2p_{3/2} after removal of SO₂ may indicates that the active material is present as CoSO₄. This result is also presented by XRD pattern (Fig. 5(2)).

In Fig. 7(3), the peak intensity at 1065 cm⁻¹ is obviously enhanced due to the formation of C-O structures after SO₂ adsorption, indicating the catalysis activity of cobalt³². The possible desulfurization mechanism could be described as following formula. Moreover, after SO₂ adsorption, the peak of 3430 cm⁻¹ was much less pronounced, suggesting the reaction between OH groups and sulfur oxide.

Based on the above analysis, some surface chemical reaction actually took place in the desulfurization process, which is one of the factors of the degradation of desulfurization performance.

Conclusion

The cobalt oxide/carbon is prepared by using walnut shells as precursor and cobalt oxide as activating agent. The cobalt oxide plays an important role on the formation of porous structure and functional groups. Chemical states of Co on activated carbon were reduced during activation process and presented as Co⁰ and Co²⁺. The desulfurization activity enhancement of cobalt oxide/carbon adsorbents is mainly because of the existence of Co active species.

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