



Regeneration of hexamminecobalt(II) catalyzed by activated carbon treated with KOH solutions

Jing-yi Cheng, Lin Yang, Li Dong, Xiang-li Long*, Wei-kang Yuan

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, People's Republic of China

ARTICLE INFO

Article history:

Received 4 February 2011

Received in revised form 12 April 2011

Accepted 14 April 2011

Available online 20 April 2011

Keywords:

Activated carbon

Catalysis

Hexamminecobalt

Modification

Reduction

ABSTRACT

The combined elimination of NO and SO₂ can be realized by hexamminecobalt(II) solution which is formed by adding soluble cobalt(II) salt into the aqueous ammonia solution. Activated carbon is used as a catalyst to regenerate hexamminecobalt(II), Co(NH₃)₆²⁺, so that NO removal efficiency can be maintained at a high level for a long time. In this study, KOH solution has been explored to modify coconut activated carbon to meliorate its catalytic performance in the reduction of hexamminecobalt(III), Co(NH₃)₆³⁺. The experiments have been performed in a batch stirred cell to investigate the effects of KOH concentration, impregnation duration, activation temperature and activation duration on the performance of activated carbon. The results show that the best KOH concentration for the improvement of activated carbon is 0.5 mol l⁻¹. The optimal impregnation duration is 9 h. High temperature is favorable to ameliorating the catalytic performance of activated carbon. The optimum activation duration is 4 h.

© 2011 Elsevier B.V. All rights reserved.

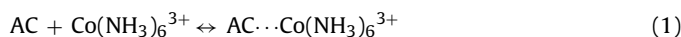
1. Introduction

NO_x and SO₂ have been widely known as typical pollutants that cause smog, acid rain and many other serious environmental problems. Therefore, it is imperative to take cogent measures to control the emission of NO and SO₂. Various wet and dry processes have been put forward. It has been agreed that using chemical additives to an aqueous scrubbing solution could have a significant impact on control strategies [1,2]. Several methods have been developed to enhance NO absorption, including the use of oxidants to oxidize NO to the more soluble NO₂ and the addition of various iron(II) chelates to bind and activate NO [3–13]. However, the method of oxidizing NO to NO₂ by H₂O₂ is very costly. The treatments with KMnO₄ and NaClO₂ are not only too expensive but also causes large amount of waste water. The method using iron(II) chelates quickly loses its scrubbing NO ability because iron(II) chelates are easily oxidized to iron(III) chelates. Therefore, so far, none of these methods have been put into commercial application.

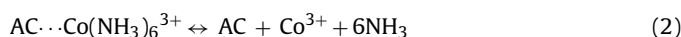
Long et al. put forward a novel technique for the simultaneous elimination of NO and SO₂ from the flue gas by adding soluble cobalt(II) salt into aqueous ammonia solution [14]. The hexamminecobalt(II) formed by ammonia binding with cobalt(II) is the active constituent of scrubbing NO from the flue gas streams. Dissolved oxygen, in equilibrium with the residual oxygen in the flue gas, is the oxidant. NO is converted into nitrate and nitrite. How-

ever, Co(NH₃)₆²⁺ may be oxidized to Co(NH₃)₆³⁺. Co(NH₃)₆³⁺ can neither activate oxygen molecules nor bind NO. The capability of removing NO with the hexamminecobalt solution will reduce as the reaction proceeds. In order to regenerate the active constituent Co(NH₃)₆²⁺ to maintain the capability of removing NO from the gas streams, coconut activated carbon has been put forward to catalyzing reduction of Co(NH₃)₆³⁺ by water [15]. The reaction scheme for the catalytic regeneration of Co(NH₃)₆³⁺ by activated carbon is illustrated as follows:

Co(NH₃)₆³⁺ may react with the acidic group on activated carbon to form a transition complex AC ···Co(NH₃)₆³⁺ (Eq. (1)).



AC ···Co(NH₃)₆³⁺ is liable to dissociate to AC, Co³⁺ and NH₃ (Eq. (2)).

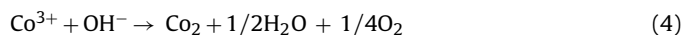


Electrochemical half-cell reduction potential of Co³⁺/Co²⁺ (1.82 v) shows that cobalt(III) is a strong oxidant and can be reduced to Co²⁺ easily.

The delocalized π electron on the surface of activated carbon can act as a Lewis base in aqueous solution [16] (Eq. (4)):



This delocalized π electron system (-Cπ) can act as a reduction center of Co³⁺. The reduction of Co³⁺ is completed as follow:



* Corresponding author. Tel.: +86 21 6425 3267; fax: +86 21 6425 3528.

E-mail address: longdragon@ecust.edu.cn (X.-l. Long).

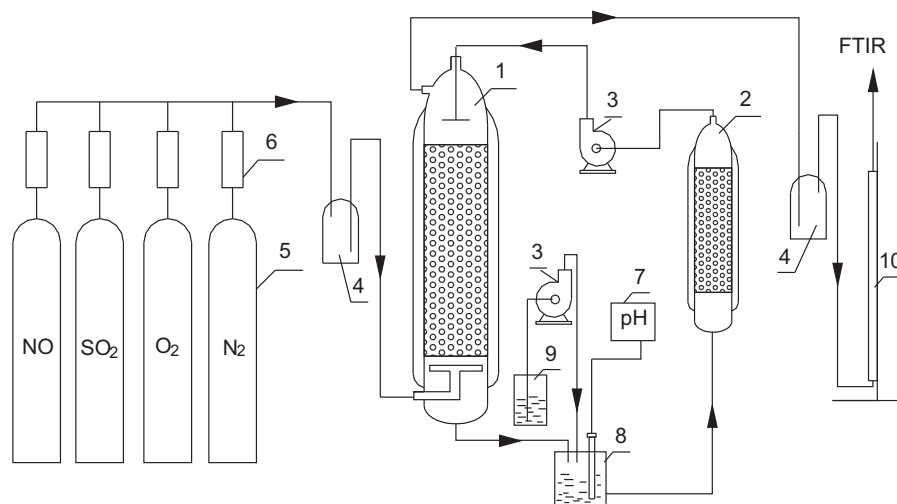
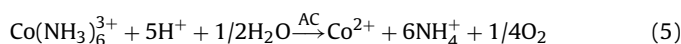


Fig. 1. Flowchart of experiments performed in a packed column: (1) packed column; (2) regeneration reactor; (3) pump; (4) buffer tank; (5) cylinder; (6) mass meter; (7) pH online control; (8) circulation tanker; (9) NaOH solution; and (10) soap-film meter.

The global reaction for the regeneration of cobalt(II) can be written as follows:



Cobalt(II) ions may combine with ammonia in the solution.



As a result, the regeneration of $\text{Co}(\text{NH}_3)_6^{2+}$ is completed.

Activated carbon (AC) with high surface area is widely used in numerous fields. The adsorption capacity as one of the most important properties is directly determined by the pore size distribution and is also strongly influenced by the surface functionality [17–19]. The catalytic capability of activated carbon is dependent on its adsorption capacity. Activated carbon modified by KOH solution may change its surface characteristics and increases its absorption capacity. Therefore, the modification by KOH solution may alter the catalytic performance of activated carbon in the catalytic reduction of $\text{Co}(\text{NH}_3)_6^{3+}$. This paper reports the study on the regeneration of $\text{Co}(\text{NH}_3)_6^{2+}$ catalyzed by coconut activated carbon treated with KOH solutions

2. Experimental

2.1. Materials

The coconut activated carbon used in the present investigation was obtained from Shanghai Activated Carbon Co., Ltd. The carbon was washed with deionized water and then dried in a vacuum drying oven before it was used in the catalytic reaction or modified with KOH solution. The activated carbon modification was completed in the following steps: (1) 1 g activated carbon was soaked in 50 ml KOH solution for a few hours at ambient temperature; (2) after being filtrated, the activated carbon was put in a vacuum drying oven at 383 K overnight; (3) the samples obtained were activated under N_2 atmosphere in a horizontal cylindrical furnace at set temperature for a few hours.

2.2. Reduction of $\text{Co}(\text{NH}_3)_6^{3+}$

Batch experiments were performed in a stirred glass flask of 500 ml to investigate the catalytic capability of the modified activated carbon in the reduction of $\text{Co}(\text{NH}_3)_6^{3+}$. A turbine impeller of diameter 3 cm was mounted on the bottom of the stirring rod. The temperature was controlled by a constant temperature bath.

400 ml $0.01 \text{ mol l}^{-1} \text{ Co}(\text{NH}_3)_6^{3+}$ solution was introduced into the glass flask. 1 g activated carbon was added into the solution as soon as the temperature reached 333 K. The stirring speed was 300 rpm. The liquid samples were withdrawn every a few minutes to determine the change of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration in the course of the experiments.

Cobalt(II) was determined spectrophotometrically at 25 °C from the absorbance at 690 nm of a solution prepared by diluting an aliquot of sample with $9 \text{ mol l}^{-1} \text{ HCl}$ solution. The influence of Co^{3+} on the detection of Co^{2+} is negligible with such analytical method. The detection was made using a 10 mm cell. The cobalt(II) calibration curve was obtained using standard cobalt acetate solutions ranged from 0.00 to 0.02 mol l^{-1} . Least-squares fits to the data yield Eq. (7) with a correlation coefficient (r^2) 0.9997.

$$C = -0.0042 + 55.001X \quad (7)$$

where X stands for absorbency and C for cobalt(II) concentration (mol l^{-1}).

2.3. Combined removal of NO and SO_2

Experiments for the simultaneous removal of SO_2 and NO were performed in a column absorber (18 mm i.d., 1000 mm long) packed with 2 mm glass ring. The schematic diagram of the experimental apparatus is shown in Fig. 1. The absorber temperature was controlled using a jacket through which water from a thermostatic bath was circulated. Two percent of NO in nitrogen was supplied from a cylinder, and was diluted with N_2 to the desired concentration before feeding into the absorber. SO_2 was supplied in a similar way. The $\text{Co}(\text{NH}_3)_6^{2+}$ solution was made by introducing predetermined amounts of $(\text{NH}_4)_2\text{SO}_4$, cobalt sulfate and ammonia into distilled water. The initial pH value of the $\text{Co}(\text{NH}_3)_6^{2+}$ solution was adjusted with 15 mol l^{-1} ammonia solution and detected with a pH-electrode. Then the $\text{Co}(\text{NH}_3)_6^{2+}$ aqueous ammonia solution was added into the glass circulation tank. The absorber was operated with a continuous influent gas feeding at 300 ml min^{-1} from the bottom and a continuous scrubbing solution feeding, at a superficial flow rate of $5 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$ (25 ml min^{-1}) at the top. The pH value of the scrubbing solution was maintained at about 9.0 by introducing 15 mol l^{-1} ammonia aqueous solution with a THORNTON M300 pH/ORP transmitter. The absorbent effusing from the packed column was fed into the circulation tank. When the regeneration of $\text{Co}(\text{NH}_3)_6^{2+}$ started, the absorbent in circulation tank flowed into the regeneration reactor upwardly and directly into the packed col-

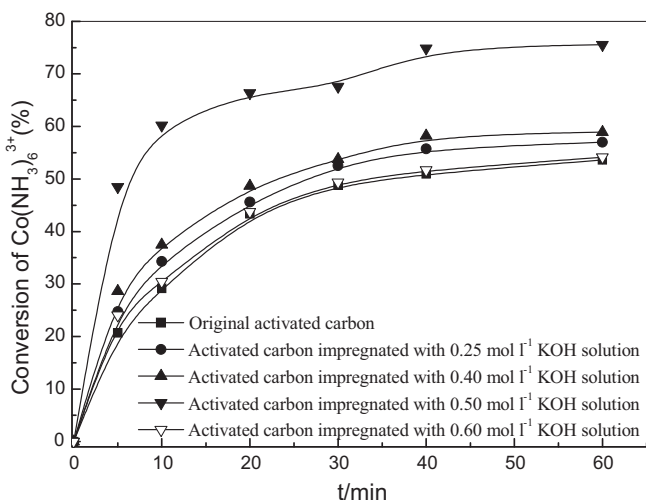


Fig. 2. Effect of KOH concentration on the catalytic performance of activated carbon (100–120 mesh activated carbon, stirred speed = 300 rpm, pH = 5.10, 60 °C).

umn to scrub NO and SO₂. The regeneration reactor was a fixed-bed with 450 mm in length and 20 mm in diameter and 40 g activated carbon was filled in it.

The experiments were carried out under atmospheric pressure. During the experiments, the quantitative analysis of gas compositions was achieved by an on-line Fourier transform infrared spectrometer (Nicolet E.S.P. 460 FT-IR) equipped with a gas cell and a quantitative package, named Quant Pad. The inlet and outlet gases were directly introduced into the gas cell of the FTIR, with pipes insulated through regulated electric coils to obtain the transient NO, NO₂, SO₂, and H₂O concentrations in both inlet and outlet gases, as well as the transient NO conversion. This set-up was conveniently operated to monitor the absorption effect of NO and SO₂.

2.4. Characterization of carbon catalysts

The concentrations of acid and basic groups on the activated carbon surface as well as their points of zero charge (pH_{pzc}) were determined by Boehm titration [20] and mass titration. The specific surface area (BET method) was determined using an ASAP2000 Surface Analyzer (Micromeritics Co. USA) using N₂ as the adsorbate.

3. Results and discussion

3.1. The effect of KOH concentration on the catalytic performance of activated carbon

Four samples of coconut activated carbon were treated with KOH solutions with concentration of 0.25 mol l⁻¹, 0.40 mol l⁻¹, 0.50 mol l⁻¹ and 0.60 mol l⁻¹, respectively, for 9 h at room temperature. And then the samples were heated under N₂ atmosphere at 973 K for 4 h. The obtained samples were used to catalyze the reduction of Co(NH₃)₆³⁺ at 60 °C. The Co(NH₃)₆³⁺ conversions obtained under the catalysis of these samples are presented in Fig. 2. It can be concluded from Fig. 2 that the catalytic capability of the activated carbon may be improved when the activated carbon is treated by KOH solution with concentration below 0.50 mol l⁻¹. For example, after one h operation, the Co(NH₃)₆³⁺ conversion reaches 75.55% under the catalysis of activated carbon treated with 0.50 mol l⁻¹ KOH solution while that is 56.96% under the catalysis of activated carbon treated with 0.25 mol l⁻¹ KOH solution. However, the Co(NH₃)₆³⁺ conversion obtained by the activated carbon treated with KOH concentration of 0.60 mol l⁻¹ is only 54.13%, which is even

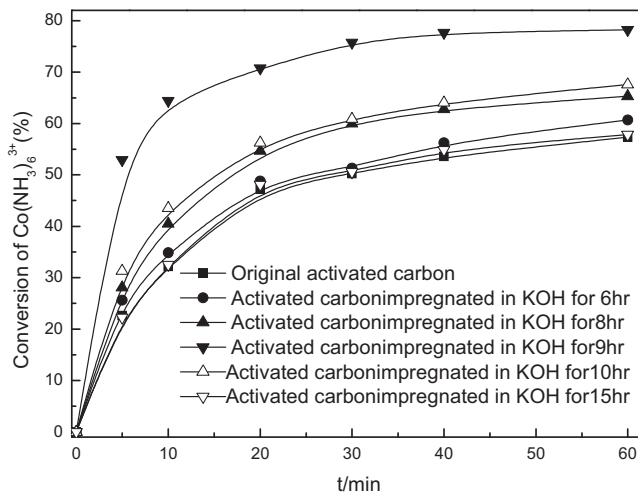


Fig. 3. Effect of impregnation time on the catalytic performance of activated carbon (100–120 mesh activated carbon, stirred speed = 300 rpm, pH = 5.05, 60 °C).

lower than that catalyzed by the activated carbon treated with KOH concentration of 0.25 mol l⁻¹. Therefore, it can be concluded that the optimal concentration for KOH solution is about 0.50 mol l⁻¹.

3.2. Effect of impregnation time on the catalytic performance of activated carbon

Five samples of coconut activated carbon were impregnated in the KOH solutions with concentration of 0.50 mol l⁻¹ at ambient temperature for 6 h, 8 h, 9 h, 10 h, and 15 h, respectively. And then they were heated under N₂ atmosphere at 973 K for 4 h. The Co(NH₃)₆³⁺ conversions obtained by the catalysis of these samples are shown in Fig. 3. It can be seen from Fig. 3 that the optimal time for carbon soaked in the KOH solution is 9 h. The catalytic capability of the carbon will decrease as the impregnation time is prolonged or shortened. For example, after 60 min run, the Co(NH₃)₆³⁺ conversion increases from 65.28% to 78.21% as the carbon impregnation time increases from 8 h to 9 h. However, the Co(NH₃)₆³⁺ conversion is only 67.59% catalyzed with the carbon soaked for 10 h, which is much lower than that catalyzed with the carbon soaked for 9 h.

3.3. Effect of activation temperature on the catalytic performance of activated carbon

To investigate the effect of activation temperature on the catalytic performance of activated carbon, the samples of carbon were soaked in the 0.50 mol l⁻¹ KOH solutions for 9 h at ambient temperature. And then they were heated under N₂ atmosphere for 4 h at 500 °C, 600 °C, 700 °C and 800 °C, respectively. The Co(NH₃)₆³⁺ conversions obtained by the catalysis of these samples are depicted in Fig. 4. It can be concluded from Fig. 4 that high activation temperature is favorable for the amelioration of the catalytic capability of carbon. After 60 min operation, the Co(NH₃)₆³⁺ conversion obtained increases from 49.3% to 72.0% when the activation temperature increases from 500 °C to 800 °C. Fig. 4 also demonstrates that the Co(NH₃)₆³⁺ reduction rate doesn't increase evidently as the activation temperature rises above 700 °C. Hence the proper activation temperature is considered to be 700 °C.

3.4. Effect of activation time on the catalytic performance of activated carbon

To examine the effect of activation time on the catalytic performance of activated carbon, four samples of carbon were soaked in

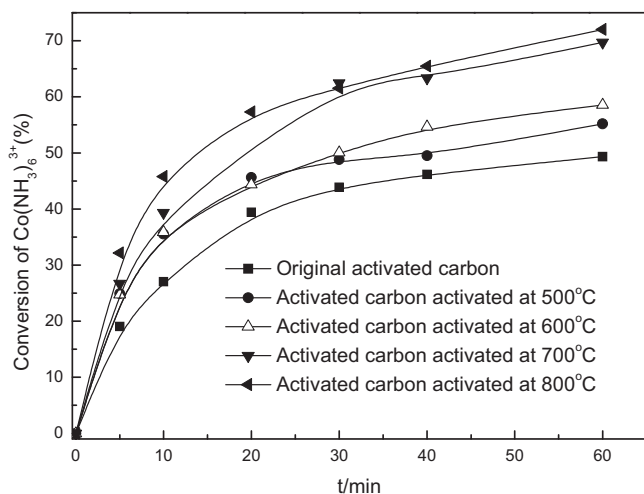


Fig. 4. Effect of activation temperature on the catalytic performance of activated carbon (100–120 mesh activated carbon, stirred speed = 300 rpm, pH = 5.15, 60 °C).

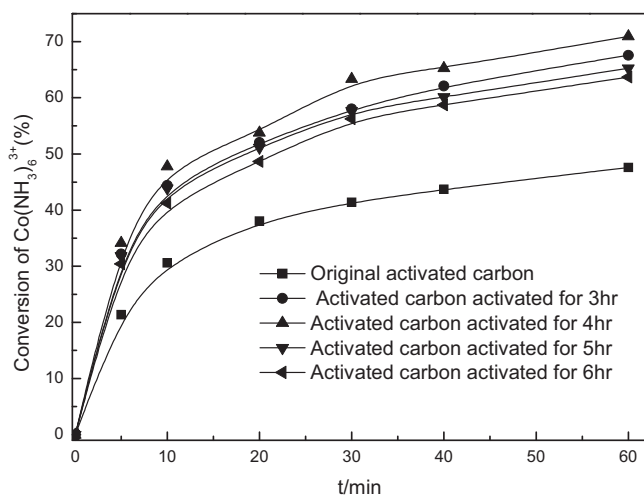


Fig. 5. Effect of activation time on the catalytic performance of activated carbon (100–120 mesh activated carbon, stirred speed = 300 rpm, pH = 5.25, 60 °C).

the KOH solution of 0.50 mol l^{-1} for 9 h at ambient temperature. And then they were heated under N_2 atmosphere at 700°C for 3 h, 4 h, 5 h and 6 h, respectively. The $\text{Co}(\text{NH}_3)_6^{3+}$ conversions obtained with the catalysis of these samples are depicted in Fig. 5. Fig. 5 manifests that 4 h may be the best time for the activation of activated carbon. The catalytic capability of the activated carbon will reduce as the activation time is longer or shorter than 4 h. For example, after 60 min operation, the $\text{Co}(\text{NH}_3)_6^{3+}$ conversions obtained under the catalysis of the carbon activated for 4 h is 70.90% while those are 67.60% and 65.28% obtained under the catalysis of the carbon activated for 3 h and 5 h, respectively.

According to the experimental results, the best condition for the treatment of coconut activated carbon is obtained as follow: KOH concentration 0.50 mol l^{-1} , soaked time 9 h, activation time 4 h, activation temperature 973 K.

3.5. Characterization of activated carbon

The modification of activated carbon alters the catalytic performance of activated carbon due to the change of the surface characteristics of the activated carbon. It is necessary to investigate the relation between the catalytic capability and the surface characteristics. Nine samples prepared for

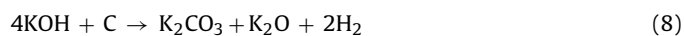
Table 1
Description of carbon samples.

Sample no.	Conditions of preparation
AC	Original coconut activated carbon
C2	Impregnation with 0.50 mol l^{-1} KOH solution for 9 h at room temperature, then heat treated for 4 h at 973 K
C3	Impregnation with 0.40 mol l^{-1} KOH solution for 9 h at room temperature, then heat treated for 4 h at 973 K
C4	Impregnation with 0.60 mol l^{-1} KOH solution for 9 h at room temperature, then heat treated for 4 h at 973 K
C5	Impregnation with 0.50 mol l^{-1} KOH solution for 15 h at room temperature, then heat treated for 4 h at 973 K
C6	Impregnation with 0.50 mol l^{-1} KOH solution for 6 h at room temperature, then heat treated for 4 h at 973 K
C7	Impregnation with 0.50 mol l^{-1} KOH solution for 9 h at room temperature, then heat treated for 4 h at 773 K
C8	Impregnation with 0.50 mol l^{-1} KOH solution for 9 h at room temperature, then heat treated for 3 h at 973 K
C9	Impregnation with 0.50 mol l^{-1} KOH solution for 9 h at room temperature, then heat treated for 6 h at 973 K

the characterization of the surface characteristics are listed in Table 1.

The concentrations of functional groups on the activated carbon surface as well as their points of zero charge (pH_{pzc}) have been determined to test whether the modification by KOH solution changes the chemistry characteristics of the activated carbon. Table 2 presents the surface functional group contents for both the modified coconut activated carbon (treated under the best modification condition) and the original coconut activated carbon. It is clear that the total basic groups on the original activated carbon are nearly equal to those on the modified activated carbon. And the change in the surface acidic functional groups after the KOH treatment can also be neglected. Thus it can be concluded that the modification by KOH solution may be almost a physical process.

Table 3 lists the physical characteristics of the samples. It can be concluded that great changes have been made in the physical characteristics on the carbon surface by KOH modification. When activated carbon is treated with KOH, the following reactions may take place [21]:



The emission of carbon monoxide by the reactions between carbon and KOH, K_2O and K_2CO_3 may form micropores on the surface of the activated carbon. Therefore, modification by KOH solution increases the surface area and micropore area on the surface of the activated carbon.

It can be seen that, all of the S_{BET} , S_{mic} , and V_{mic} have the order of $\text{C2} > \text{C3} > \text{C4} > \text{AC}$, $\text{C2} > \text{C7} > \text{AC}$, $\text{C2} > \text{C5} > \text{C6} > \text{AC}$, $\text{C2} > \text{C8} > \text{C9} > \text{AC}$, which are accordance with the sequences of the $\text{Co}(\text{NH}_3)_6^{3+}$ reduction rate under the catalysis of the samples that they stand for shown in Figs. 2–5. The results show that the physical characteristics, such as surface area and micropores, are important factors determining the catalytic performance of the carbon.

C2, C3 and C4 stands for the carbons that are produced in the similar modification process except different concentrations of KOH solution. As KOH concentration increases, the reaction rates between the potassic compounds and activated carbon increases. More micropores will be produced. However, as KOH concentration increases further above 0.5 mol l^{-1} , the reactions between the potassic compounds and activated carbon becomes so violent that some micropores collapse. For example, the amount of micropores on the activated carbon treated with KOH concentration of 0.60 mol l^{-1} is lower than that on the activated carbon treated with

Table 2
Physicochemical characteristics of the carbon samples.

Carbon type	Phenolic hydroxyl (10^4 mol g^{-1})	Carboxys (10^4 mol g^{-1})	Lactonic (10^4 mol g^{-1})	Total acid groups (10^4 mol g^{-1})	Total basic groups (10^4 mol g^{-1})	pH _{pzc}
Original AC	1.70	1.29	2.91	5.90	17.27	8.72
Modified AC	1.76	1.36	2.94	6.06	17.68	9.02

Table 3
Pore structures of the carbon samples.

Sample no.	S _{BET} (m ² g ⁻¹)	S _{mic} (m ² g ⁻¹)	S _{mic} /S _{BET}	V _t (cm ³ g ⁻¹)	V _{mic} (cm ³ g ⁻¹)	V _{mec} (cm ³ g ⁻¹)	V _{mic} /V _t
AC	896	532	0.6	0.49	0.26	0.22	0.55
C2	1136	878	0.77	0.53	0.36	0.11	0.68
C3	952	601	0.63	0.53	0.29	0.23	0.55
C4	932	560	0.60	0.54	0.27	0.25	0.5
C5	1127	643	0.57	0.53	0.30	0.19	0.57
C6	945	628	0.66	0.51	0.28	0.23	0.59
C7	1055	691	0.65	0.52	0.33	0.12	0.63
C8	1039	763	0.73	0.51	0.32	0.16	0.63
C9	956	692	0.72	0.52	0.28	0.24	0.54

KOH concentration of 0.50 mol l⁻¹. Therefore, the catalytic capability of the carbon decreases.

C2, C5 and C6 stands for the carbons that are produced in the similar modification process except different impregnation duration. Long duration benefit the diffusion of KOH to the carbonaceous materials, which is favorable for the reactions between the potassic compounds and carbon. Therefore, the surface area and micropores increase with the impregnation duration. However, as the duration increases beyond 9 h, too much carbon reacts with the potassic compounds and some micropores collapse. Hence the catalytic capability of the carbon begins to decrease because of the decreases of surface area and micropores.

C2 and C7 stands for the carbons that are produced in the similar modification process except different activation temperature. Dynamically, the reaction rates between potassic compounds and carbon increase with temperature. The micropores and surface area produced increase with the activation temperature. Therefore, the catalytic capability of the carbons is improved greatly.

C2, C8 and C9 stands for the carbons that are produced in the similar modification process except different activation duration. The modification increases the micropores on the carbon so that the adsorption ability of the carbon increases. However, as the activated time increases over 4 h, the micropores on the carbon will reduce because some micropores collapse due to the long reaction time between potassic compounds and carbon. Meanwhile pyrogenation under long activation duration may also result in the loss of micropores. Therefore, the catalytic ability decreases with the activation time.

As discussed previously, modification by KOH solution increases the surface area and micropores on the surface of the activated carbon due to the reactions between the potassic compounds and carbon. The impregnation and activation conditions may determine the surface characteristics of modified carbon. The catalytic capability of the carbon samples is dependent on their physical characteristics.

3.6. Simultaneous removal of NO and SO₂

The variation of NO removal efficiency with time coupled with the regeneration of hexamminecobalt(II) catalyzed by original coconut activated carbon and the coconut activated carbon modified by KOH is shown in Fig. 6. The modified coconut activated carbon was obtained under the best condition described previously. The experiment is carried out at 50 °C with 5.0% oxygen,

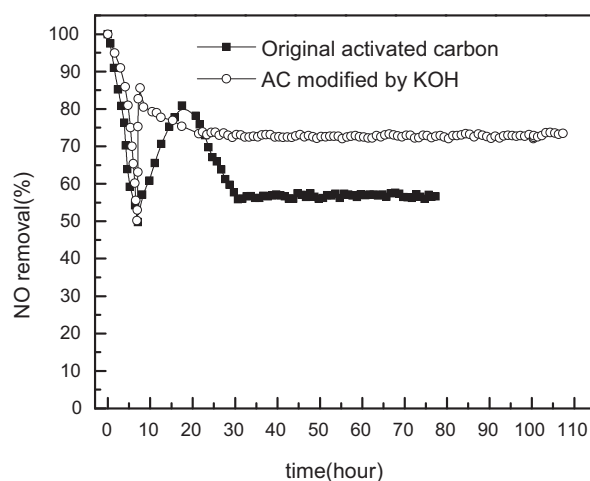


Fig. 6. NO removal efficiency with time coupled with the regeneration catalyzed by AC and AC modified by KOH (50 °C, NO = 600 ppm, SO₂ = 1500 ppm, O₂ = 5%).

an initial hexamminecobalt(II) concentration of 0.04 mol l⁻¹, and inlet NO and SO₂ concentrations of 600 and 1500 ppm, respectively. The flow rate of scrubbing solution feeding into the regeneration column is 25 ml min⁻¹. The regeneration temperature is 90 °C. During the whole operation, no SO₂ is detected in the outlet gas stream by FTIR. At the first 7 h, these two operations have nearly the same NO removal efficiencies. The system has an initial NO removal efficiency of 100%, which declines to about 50% after 7 h. After activating the regeneration system, the NO removal efficiencies rise quickly. Thirteen h later after the Co(NH₃)₆²⁺ regeneration catalyzed by the original activated carbon, the NO removal rises to 78.17%. Then the NO removal efficiency drops to about 57%. However, a rapid increasing of NO removal is observed for Co(NH₃)₆²⁺ regeneration catalyzed by the modified activated carbon. NO removal efficiency goes up to 85.57% only 0.6 h later after the catalytic regeneration by the modified activated carbon. And then the NO removal efficiency is maintained at a level of 73% during all the experiment time. This test demonstrates that the modified activated carbon can obtain a much higher NO removal efficiency than the original activated carbon. The modification by KOH is an efficient measure to improve the catalytic performance of coconut activated carbon in the simultaneous removal of SO₂ and NO with Co(NH₃)₆²⁺ ammonia solution.

4. Conclusions

The coconut activated carbon is modified with KOH solution. The following specific conclusions can be drawn from the experimental results.

- (1) The catalytic performance of the coconut activated carbon may be improved when the activated carbon is treated by KOH solutions. The optimal concentration for KOH solution may be 0.50 mol l^{-1} .
- (2) The catalytic capability of the carbon increases with the impregnation time. The optimal time for carbon soaked in the KOH solutions is 9 h.
- (3) High activation temperature is favorable for the improvement of the catalytic capability of carbon. The proper activation temperature is considered to be 700°C .
- (4) 4 h may be the best time for the activation of activated carbon. The catalytic capability of the carbon will decrease as the activation time is prolonged or shortened.
- (5) Modification by KOH solution increases the surface area and micropore on the surface of the activated carbon due to the reactions between the potassic compounds and carbon. The physical characteristics, especially the micropore and the surface area, are important factors determining the catalytic performance of the carbon.
- (6) The modified coconut activated carbon can obtain a much higher NO removal efficiency than the original coconut activated carbon. The modification by KOH can improve the catalytic performance of coconut activated carbon in the simultaneous removal of SO_2 and NO with $\text{Co}(\text{NH}_3)_6^{2+}$ ammonia solution.
- (7) There are some metal cations and other oxidants in the flue gases. The influences of these metal cations and oxidants on the catalytic regeneration of hexamminecobalt(II) are planned to be investigated. A pilot experiment to testify this technology using the actual flue gases will also be carried out in the future.

Acknowledgements

The present work is supported by the Ministry of Science and Technology of China (No. 2006AA05Z307) and the state key laboratory of chemical engineering (SKL-ChE-08C05).

References

- [1] C. Mackell, B.K. Hodnett, G. Papparatto, Testing of the $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst-sorbent in extended operation for the simultaneous removal of NO_x and SO_2 from flue gases, *Ind. Eng. Chem. Res.* 39 (2000) 3868–3874.
- [2] J.J. KACZUR, Oxidation chemistry of chloric acid in NO_x/SO_2 and air toxic metal removal from gas streams, *Environ. Proc.* 15 (4) (1996) 245–253.
- [3] H. Chu, T.W. Chien, S.Y. Li, Simultaneous absorption of SO_2 and NO from flue gas with $\text{KMnO}_4/\text{NaOH}$ solutions, *Sci. Total Environ.* 275 (2001) 127–135.
- [4] T.W. Chien, H. Chu, H.T. Hsueh, Kinetic study on absorption of SO_2 and NO_x with acidic NaClO_2 solutions using the spraying column, *J. Environ. Eng.* 129 (2003) 967–974.
- [5] E.B. Myers, T.J. Overcamp, Hydrogen peroxide scrubber for the control of nitrogen oxides, *Environ. Eng. Sci.* 19 (2002) 321–327.
- [6] E.K. Pham, S.G. Chang, Removal of NO from flue gases by absorption to an iron(II) thiocholate complex and subsequent reduction to ammonia, *Nature* 36 (1994) 139–141.
- [7] Y. Shi, D. Littlejohn, S.G. Chang, Kinetics of NO absorption in aqueous iron(II) bis (2,3-dimercapto-1-propanesulfonate) solutions using a stirred reactor, *Ind. Eng. Chem. Res.* 35 (1996) 1668–1772.
- [8] A. Wanat, T. Schneppenseper, A. Karocki, G. Stochel, R. van Eldik, Thermodynamics and kinetics of Ru(III)(EDTA) as an efficient scavenger for nitric oxide in aqueous solution, *J. Chem. Soc., Dalton Trans.* 6 (2002) 941–950.
- [9] T.T. Suchecki, B. Mathews, H. Kumazawa, Kinetic study of ambient temperature reduction of Fe(III)EDTA by $\text{Na}_2\text{S}_2\text{O}_4$, *Ind. Eng. Chem. Res.* 44 (2005) 4249–4253.
- [10] R. Dilmore, R.D. Neufeld, R.W. Hammack, Laboratory-scale iron EDTA-based NO_x scrubbing process with biological treatment and regeneration of spent scrubber water, *Environ. Eng. Sci.* 23 (2006) 788–802.
- [11] W. Li, C.Z. Wu, Y. Shi, Metal chelate absorption coupled with microbial reduction for the removal of NO_x from flue gas, *J. Chem. Technol. Biotechnol.* 81 (2006) 306–311.
- [12] W. Li, C.-Z. Wu, S.-H. Zhang, K. Shao, Y. Shi, Evaluation of microbial reduction of Fe(III)EDTA in a chemical absorption-biological reduction integrated NO_x removal system, *Environ. Sci. Technol.* 41 (2007) 639–644.
- [13] S.-H. Zhang, X.-H. Mi, L.-L. Cai, J.-L. Jiang, W. Li, Evaluation of complexed NO reduction mechanism in a chemical absorption-biological reduction integrated NO_x removal system, *Appl. Microbiol. Biotechnol.* 79 (2008) 537–544.
- [14] X.-L. Long, W.D. Xiao, W.K. Yuan, Removal of nitric oxide and sulfur dioxide from flue gas using a hexamminecobalt(II)/iodide solution, *Ind. Eng. Chem. Res.* 43 (2004) 4048–4053.
- [15] X.-L. Long, Z.-L. Xin, H.-X. Wang, W.D. Xiao, W.K. Yuan, Simultaneous removal of NO and SO_2 with hexamminecobalt(II) solution coupled with the hexamminecobalt(II) regeneration catalyzed by activated carbon, *Appl. Catal. B: Environ.* 54 (2004) 25–32.
- [16] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Utrilla, Carbon materials as adsorbents in aqueous solutions, *Chem. Phys. Carbon* 27 (2001) 227–405.
- [17] A. Celzard, A. Perrin, A. Albinia, E. Broniek, J.F. Mareche, The effect of wetting on pore texture and methane storage ability of NaOH activated anthracite, *Fuel* 86 (1-2) (2007) 287–293.
- [18] P. Chingombe, B. Saha, R.J. Wakeman, Surface modification and characterization of a coal-based activated carbon, *Carbon* 43 (2005) 3132–3143.
- [19] B.C. Jiang, Y.C. Zhang, J.X. Zhou, K. Zhang, S.Y. Chen, Effects of chemical modification of petroleum cokes on the properties of the resulting activated carbon, *Fuel* 87 (2008) 1844–1848.
- [20] H.P. Boehm, Some aspects of the surface chemistry of carbon blacks and others carbons, *Carbon* 53 (5) (1994) 759–768.
- [21] B.K. Pradhan, N.K. Sandle, Effect of different oxidizing agent treatments on the surface properties of activated carbons, *Carbon* 37 (1999) 1323–1332.