

Effect of pretreatment method of activated carbon on the catalytic reduction of NO by carbon over CuO

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Abstract

The influence of pretreatment method of activated carbon (AC) made from coconut shell, on the NO reduction by AC over CuO was studied, in which AC was used as a reducing agent and pretreated by air oxidation or wet oxidation in the HNO₃(N), H₂O₂(H), H₂SO₄(S) or H₃PO₄(P) aqueous solution. The results show that over the CuO catalyst, the reductive activity of air oxidized AC for NO increases with a rise of the air oxidation temperature of AC, and the order of the reductive activity of wet oxidized AC for NO is AC-H > AC-N > AC-S > AC-P. The surface chemical properties of these ACs were studied by XRD, TPD, Boehm titration and so on. The dispersion of CuO on AC can be improved by treating AC with the HNO₃ or H₂O₂ aqueous solution. AC treated with H₂O₂ is an effective reducing agent for the reduction of NO over CuO, and the temperature of complete reduction of NO by AC-H is 270 °C, which is 120 °C lower than that by original AC. Both the high concentration of acidic oxygen groups and moderate amount of basic sites on AC-H help to increase the conversion of NO reduced by AC-H.

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1. Introduction

One of the not yet solved problems associated with air pollution is the purification of nitrogen oxides (NO_x) in waste gases. Due to their contribution to the rain acidification, photochemical smog, global warming and depletion of the stratospheric ozone layer, it has brought to the forefront of public concern [1,2]. In the interest of eliminating the emission of NO_x, several technologies or methods have been developed, of which the selective catalytic reduction (SCR) is the most considered one [2–10]. The SCR of nitric oxide by ammonia is currently the most widespread method for the clean-up of flue-gas from stationary sources. But stoichiometric control of ammonia must be maintained to avoid the emission of unreacted ammonia. Another problem of the SCR technology is the storage and transportation of ammonia. If activated carbon is used as the reducing agent instead of ammonia to

reduce NO_x, the re-pollution of unreacted ammonia and the storage and transportation of ammonia can be avoided.

Activated carbon has a high surface area, bulk porosity and various surface chemical properties. It has been recognized as good adsorbent or support [11–16]. Using activated carbon as a catalyst for NO_x reduction with NH₃ [5], urea [6], CO [7,9] and C₃H₆ [8] as the reducing agents has drawn researchers' attention. Carbon-based catalysts offer significant advantages versus the conventional catalysts. For instance, there are various low price carbonaceous sources [17]. In the exhaust gases of stationary sources or lean-burn diesel engines there are a higher concentration of NO_x and large amounts of particulate matter that are mainly carbons and also called soot. Using the carbon particulates (soot) to reduce NO_x in the exhaust gas may be the most ideal method to remove NO_x, but the high effective catalysts must be used. In NO_x atmosphere, the catalytic removal of soot can be improved by the reaction of NO₂ and soot [18].

The adsorption capacity of AC is known to be a function of surface area, pore volume and porous structure. However, as a reducing agent, the surface chemical nature of AC plays an

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important role in the activity of carbon-based catalysts [12–16]. And the surface chemistry of AC can be changed by the interaction between the carbon surface and the reactants adsorbed, such as the treatment with oxidants (O_2 , HNO_3 , H_2O_2 , $KMnO_4$, $(NH_4)_2S_2O_8$, $HClO_4$ and so on) [19–26]. H_2O_2 treatment can affect the surface chemistry of AC moderately and produce appropriate amount of the oxygen-containing complexes and surface acid groups. However, AC treated with H_2O_2 is seldom used to reduce NO_x .

In this paper, the catalytic reduction of NO by AC has been investigated over the CuO catalyst. The effect of H_2O_2 treatment of AC on the reduction of NO catalyzed by CuO catalyst has been studied. As a comparison, the treatments of AC with air, HNO_3 , H_2SO_4 and H_3PO_4 were also carried out.

2. Experimental

2.1. Pretreatment of activated carbon

The parent activated carbon (AC) was supplied by Tangxin Activated Carbon Co. Ltd., Shanghai, and was prepared from coconut shells by carbonization under nitrogen and further activation with steam. Its BET surface area is $928\text{ m}^2/\text{g}$ with 1.79 wt% ash. AC was preoxidized in air at $300\text{ }^\circ\text{C}$, $400\text{ }^\circ\text{C}$ or $500\text{ }^\circ\text{C}$ for 6 h, which was labeled as 300AC, 400AC or 500AC. The wet oxidation of AC was carried out by impregnating AC in the aqueous solutions (2N) of HNO_3 , H_2O_2 , H_2SO_4 and H_3PO_4 for 48 h at room temperature with gentle shaking, respectively. The volume ratio of AC/solution is 1/5. Then, the samples were filtered and washed with de-ionized water to remove the remaining oxidants. The AC samples impregnated with the oxidation solution were treated in the stove at $400\text{ }^\circ\text{C}$ for 4 h. Wet oxidized carbon samples were labeled as AC-N (treated with HNO_3), AC-H (H_2O_2), AC-S (H_2SO_4) and AC-P (H_3PO_4), respectively.

2.2. Preparation of the catalyst

The CuO catalyst was prepared by the wet impregnation method. AC was impregnated with aqueous solution of $Cu(NO_3)_2$ at room temperature for 4 h and aged at $60\text{ }^\circ\text{C}$ for 2 h. After dried in air overnight at $110\text{ }^\circ\text{C}$, the CuO/AC samples were calcined in air at $250\text{ }^\circ\text{C}$ for 4 h. The loading of CuO was 10 wt%, which was determined by burning off the carbonaceous supports.

2.3. Characterization of activated carbon and catalyst

N_2 adsorption isotherm, BET surface area and pore size distribution curve of sample were measured at $-196\text{ }^\circ\text{C}$ on a Micromeritics ASAP 2020 Sorptometer using static adsorption procedures.

X-ray diffraction (XRD) of sample was obtained on a Rigaku D/max-II/2550/VC X-ray powder diffractometer, Cu $K\alpha$ radiation was employed and the working voltage and current were 40 kV and 100 mA, respectively.

Temperature-programmed desorption (TPD-MS) of sample was carried out in a quartz flow reactor ($\varnothing 10\text{ mm} \times 300\text{ mm}$) system coupled to a quadrupole mass spectrometer (IPC400, INFICON Co. Ltd.). 200 mg sample was used, the flow of Ar was 100 ml/min, and the heating rate was $20\text{ }^\circ\text{C}/\text{min}$ from $100\text{ }^\circ\text{C}$ up to $900\text{ }^\circ\text{C}$.

The contents of acidic and basic sites on the surface of sample were determined by the Boehm method [27]. Each 500 mg sample was placed in 30 ml vial with 0.05N aqueous solutions of NaOH, Na_2CO_3 , $NaHCO_3$ and HCl, respectively. After the vials were sealed and shaken for 24 h, the samples were filtrated and 10 ml filtrate was pipetted. Excessive NaOH or HCl were titrated with HCl and NaOH respectively. For the Na_2CO_3 and $NaHCO_3$ filtrate, 10 ml 0.05N H_2SO_4 was added and excessive H_2SO_4 was back-titrated with 0.05N NaOH after heated at $60\text{ }^\circ\text{C}$ to boil off CO_2 . The contents of acidic sites were calculated according to the assumption of the base solution, in which NaOH neutralizes the carboxylic, phenolic and lactonic or lactol groups, Na_2CO_3 neutralizes the carboxylic and lactonic or lactol groups, and $NaHCO_3$ neutralizes only carboxylic groups. The content of the surface basic sites was calculated by the amount of HCl reacted with the AC sample. After 1 g AC sample was immersed in 30 ml de-ionized water to reach equilibrium, the pH value of carbon suspension was determined by a pH meter according to the literature [20].

2.4. Testing of the catalytic reduction of NO by AC

Catalytic reduction of NO by AC was carried out at atmospheric pressure in a fixed bed microreactor ($\varnothing 10\text{ mm} \times 300\text{ mm}$), the outlet gases were analyzed by two gas chromatographs (Fuli 9790) with two thermal conductivity detectors, and a column of Poropak Q for the separation of CO_2 , N_2O , H_2O and a column of 5A zeolite for the separation of O_2 , N_2 and CO. Five hundred milligrams catalyst was used, the space velocity (GHSV) was $20,000\text{ h}^{-1}$ and the concentration of NO in Ar was 2000 ppm. The reduction reaction of NO was studied using the procedure of temperature-programmed reaction (TPR) at a heating rate of $3\text{ }^\circ\text{C}/\text{min}$ from $100\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$. In this reaction N_2 was the aim product, and N_2O was also formed but its concentration was very low and could be neglected. Therefore, the conversion of NO was calculated by the amount of nitrogen produced.

3. Results and discussion

3.1. Physicochemical properties of activated carbon

The pore structure properties of AC samples are shown in Table 1. The results show that the surface areas and total pore volumes of AC oxidized in air for 6 h increase with an increase in the oxidation temperature at $<400\text{ }^\circ\text{C}$. After being oxidized at $500\text{ }^\circ\text{C}$ for 6 h, the surface area and total pore volume of AC decrease appreciably. This may be resulted from the formation of some surface oxygen complexes at the entrance of pores. For the samples treated by the wet oxidation, the HNO_3 or H_2O_2

Table 1
Pore structure properties of the AC samples

Sample	Treatment	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	V_{mic} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)
AC	No	928	0.336	0.336	–
300AC	Air/300 °C	1044	0.421	0.397	0.024
400AC	Air/400 °C	1112	0.452	0.410	0.042
500AC	Air/500 °C	1064	0.445	0.405	0.040
AC-H	H_2O_2	1178	0.482	0.407	0.075
AC-N	HNO_3	1153	0.470	0.401	0.069
AC-S	H_2SO_4	913	0.305	0.305	–
AC-P	H_3PO_4	890	0.290	0.290	–

solution treatment increases the surface areas and total volumes of AC noticeably, especially for the AC-H sample, whose surface area reaches $1178 \text{ m}^2/\text{g}$ and is 25% larger than that of original AC. After being treated by the HNO_3 or H_2O_2 solution, the micropore and mesopore volumes of AC increase simultaneously. The reason is probably that HNO_3 and H_2O_2 acts as the etchants, and the treatment with these etchants makes AC trend toward the transformation of the super-micropores into micropores and micropores into mesopores [9], resulting in the increase in the pore size and surface area of AC. The treatment of AC with HNO_3 solution can produce more surface oxygen groups, which has been proved by the results of TPD-MS shown in Fig. 2. However, some surface oxygen groups maybe located at the entrance of pores to make the pore volume of AC decrease. At the same time, that the HNO_3 solution can dissolve some ashes in original AC leads to a collapse of some pores, so that the surface area and total pore volume of AC-N is lower than that of AC-H. Compared with the HNO_3 or H_2O_2 solution, H_2SO_4 or H_3PO_4 solution behaves the weaker oxidation property; treatment of AC with H_2SO_4 or H_3PO_4 solution leads to a little reduction of the surface area and pore volume of AC. It is possible that the sulfurous compounds or phosphorous compounds adsorbed inside the pores of AC [28], resulting in blocking some pores of treated AC.

With an increase in temperature, the surface oxygen groups on AC would react with C to form CO and CO_2 , so that the TPD technique can be used to characterize the surface oxygen groups of AC. During thermal decomposition of the surface

oxygen groups of carboxylic acid, CO_2 can be obtained at low temperature, and the decomposition of anhydrides, lactones or lactols should be at higher temperature. Carboxylic anhydrides can decompose to both CO and CO_2 , and phenols, ethers and carbonyls (and quinines) can only produce CO [29].

The TPD profiles of the AC samples before and after air oxidation are shown in Fig. 1. The main products obtained are CO_2 ($m/z = 44$) and CO ($m/z = 28$). It can be seen in the CO_2 desorption profiles that, the AC sample has two CO_2 desorption peaks at about 310 °C and 550 °C, 300AC displays three desorption peaks at about 310 °C, 550 °C and 670 °C, and 400AC and 500AC show two CO_2 peaks at about 310 °C and 670 °C. The CO_2 peak at ~ 310 °C is attributed to the carboxylic acid groups, and the CO_2 peaks at 550 °C and 670 °C may result from carboxylic anhydrides, lactones or lactols [30].

For the CO_2 desorption peak at 310 °C, it decreases obviously after AC was oxidized in air at 300–400 °C, and it can be recovered after being oxidized at 500 °C. This shows that the liable carboxylic acid groups can react with C to form CO_2 in air at 300–400 °C, and be reformed after being oxidized in air at 500 °C. For the CO_2 desorption peak at 550 °C, it consisted of two peaks according to the noticeable asymmetry, one big peak at ~ 550 °C and one small peak at ~ 670 °C. The peak at 550 °C minishes obviously and one at ~ 670 °C changes hardly, after AC is oxidized in air at 300 °C. At >300 °C of the oxidation temperature, the peak at ~ 670 °C increases with the oxidation temperature. This shows that the content of surface oxygen groups (liable lactones, carboxylic anhydrides and so on) on AC increases and its stability enhances with an increase in the oxidation temperature, which can be identified by the result of Boehm titration in Table 2.

Compared with the spectra of TPD- CO_2 , the formation of CO is mainly at high temperature, which may be attributed to the fact that the CO-desorbing functional groups, such as hydroxyl, carbonyl and quinone groups, are more thermally stable than the CO_2 -desorbing groups. In the TPD-CO profile of 500AC, there is one CO-desorbing peak at 700 °C. For original AC, 300AC and 400AC, in addition to the large peak at 700 °C, there is a small badly resolved peak at about 830 °C. With a decrease in the oxidation temperature, the area of desorption

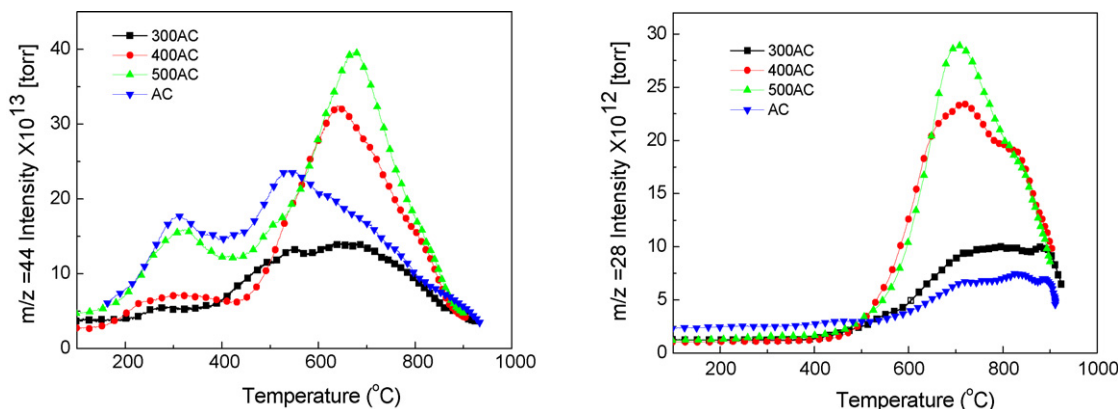


Fig. 1. TPD profiles of CO ($m/z = 28$) and CO_2 (44) on carbons pretreated in air at 300–500 °C for 6 h.

Table 2
The concentration of acidic and basic sites on carbons obtained by Boehm titration

Sample	Acidic sites (mmol/g)				Basic sites (mmol/g)	pH
	Lactonic	Carboxylic	Phenolic	Total		
AC	0.381	0.115	0.012	0.508	1.676	9.34
300AC	0.410	0.095	0.239	0.744	1.335	6.02
400AC	0.592	0.118	0.338	1.048	0.529	5.08
500AC	0.606	0.142	0.340	1.088	0.470	4.74
AC-H	0.713	0.296	0.257	1.366	0.553	4.51
AC-N	0.784	0.409	0.443	1.636	0.246	3.97
AC-S	0.538	0.090	0.252	0.880	0.475	5.64
AC-P	0.556	0.076	0.272	0.904	0.430	5.35

peak of CO decreases noticeably, and the original AC has a smallest peak area of CO desorption. The desorption peak of CO at 700 °C can be assigned to phenolic and carbonyl groups, and the small peak at about 830 °C is attributed to stable oxides like semiquinones, quinones or the same complexes at different environments [29].

The TPD spectra of AC samples pretreated with different wet oxidation methods are shown in Fig. 2. Like 400AC, the CO₂- and CO-desorbing peaks increase greatly after AC is treated by wet oxidation. AC-N has the largest peak areas of CO and CO₂, and AC-S has the lowest peak areas of CO and CO₂. AC-N has only one CO-desorbing peak at 700 °C, and AC-H, AC-P and AC-S has a small CO-desorbing peak at about 830 °C except for the main peak at 700 °C. Compared with the TPD profiles of 400AC, the intensities and areas of the desorption peaks of CO and CO₂ of ACs oxidized wetly with different solutions are varied somewhat, which means using different oxidation solutions can vary effectively the amount of the surface oxygen groups on AC. AC-N and AC-H give out much more amounts of CO₂ and CO than that of 400AC, and AC treated with H₃PO₄ or H₂SO₄ has the similar TPD profiles to that of 400AC. That is to say, HNO₃ and H₂O₂ are more effective oxidants than H₃PO₄ and H₂SO₄ for the pretreatment of AC.

The small desorption peak of CO at about 830 °C may be attributed to semiquinones or quinines that are weak basic complexes. This is because that AC-H, AC-P and AC-S have higher amount of basic sites than AC-N (Table 2). The total amount of the oxygen-containing surface groups on AC treated with the wet oxidation decreases in the order of AC-N > AC-

H > AC-P > AC-S. The results above show that the amount of the surface oxygen groups on AC can be modified easily by the different wet oxidation methods.

The concentration distributions of the acidic and basic sites on AC obtained by Boehm titration are shown in Table 2. The results show that the amounts of lactonic groups are much more than that of carboxylic groups and phenolic groups in all the samples. After being treated with the oxidants (air or acid), the amount of surface acidic oxygen groups on AC increase noticeably, which is consistent with the results obtained by CO- and CO₂-TPD.

The oxidation of AC with air is influenced markedly by the oxidation temperature, and the oxidation at gradually increasing temperature can increase the total acidic sites on AC at the expense of their basic sites. On the surface of AC treated with air, there are mainly lactonic and phenolic groups, and the concentration of carboxylic group is lower. This may be due to the pyrogenation of the carboxylic groups at high temperature, resulting in a reduction of its concentration [31], and also due to the partial condensation of the carboxylic and phenolic groups to form lactonic groups during an oxidation.

Compared with the oxidation of air, the wet oxidation can vary more efficiently the amount of the surface acidic oxygen groups of AC. Among the wet oxidation methods used, the treatment with HNO₃ make AC have the maximum amount of the acidic sites and minimum amount of the basic sites. Treatment with H₂O₂ can increase obviously the acidic sites and somewhat basic sites on AC, as compared with the oxidation with air at 400 °C. As a gentle oxidizing agent, H₂O₂

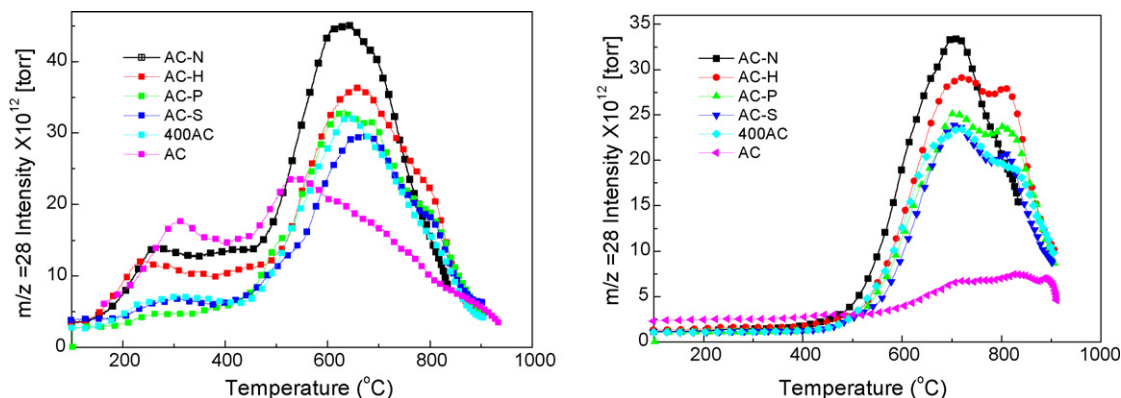


Fig. 2. TPD profiles of CO ($m/z = 28$) and CO₂ (44) on carbons pretreated with different wet oxidation.

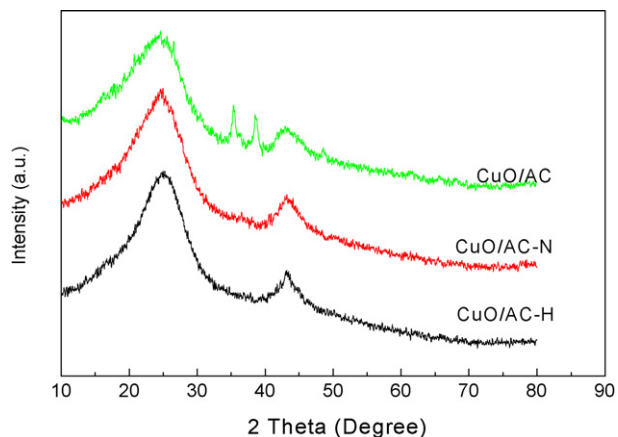


Fig. 3. XRD patterns of CuO supported on AC.

can also oxidize the surface of AC to form some basic groups such as quinones, chromenes or pyrenes. For AC treated with H_3PO_4 and H_2SO_4 solution, the total acidic sites increase slightly, but the basic sites decrease greatly. Because the H_3PO_4 or H_2SO_4 aqueous solution has a lower oxidizability and strong acidic properties, and they can dissolve some ashes in AC, resulting in the decrease of the surface area of AC. The change of the surface chemistry of treated AC is mainly caused by the calcination in air after being impregnated.

The pH values of AC suspension in de-ionized water are also shown in Table 2. For the original AC, its suspension solution is basic (pH = 9.34), and for all the treated AC samples, their pH values are lower than 7. Especially for the suspension solution of AC-N, its pH value is only 3.97. The pH value of AC suspension solution is corresponding to the total amount of acidic sites on AC and has a good agreement with the amount of the surface oxygen groups on AC.

The XRD patterns of CuO supported on AC are shown in Fig. 3. There are two broad diffraction peaks of the graphitic structure, which indicates that AC used is of a low graphitization degree. The peaks at $2\theta = 35.5^\circ$, 38.6° , 48.6° are the diffraction peaks of CuO. Among the three samples, CuO/AC has the obvious diffraction peaks of CuO, and there is no any diffraction signal of CuO or other Cu-containing species for the CuO/AC-N and CuO/AC-H samples. This suggests that

CuO located on AC-N and AC-H is highly dispersed and the treatment of AC with HNO_3 and H_2O_2 aqueous solution can improve the dispersion of CuO on the AC surface. This is because of the interaction of the metal precursor molecules with carbonaceous supports by means of the surface oxygen complexes, leading to a high dispersion. Zhu et al. [32] also reported that acidic treatments of carbons may improve nickel distributions on the carbon support by making more nickel ions diffused into the inner pores of carbons. So an increase in the surface oxygen groups on AC-N and AC-H favors the dispersion of CuO on AC, and treatments of AC with HNO_3 and H_2O_2 may make more copper ions diffused into the inner pores of AC.

3.2. Catalytic reduction of NO_x by activated carbon over CuO

Fig. 4(a) shows the catalytic activities of CuO for the reduction of NO by AC pretreated with air at different temperatures. It can be seen that the reductive activity of AC is improved evidently by the treatment of air oxidation and influenced substantially by the oxidization temperature. NO can be completely reduced at 390°C by AC over CuO/AC; over CuO/300AC, the complete conversion temperature ($T_{100\%}$) of NO is 380°C ; over CuO/400AC or CuO/500AC, $T_{100\%}$ is only 325°C .

The reduction of NO by wetly oxidized AC is shown in Fig. 4(b). The results show that the treatment of wet oxidation can improve significantly the activity of AC to reduce NO. $T_{100\%}$ are 285°C , 270°C , 320°C and 310°C over CuO/AC-N, CuO/AC-H, CuO/AC-P and CuO/AC-S respectively, which are lower about 100°C than $T_{100\%}$ over CuO/AC.

It is obvious that the oxidation treatment can lead to an increase of surface oxygen-containing groups on the surface of AC and also improve the rate of AC reducing NO over CuO. The results in Fig. 4 show that, for the reduction of NO by AC, the activity of AC treated by HNO_3 or H_2O_2 is much higher than that of AC oxidized in air, which is indeed consistent with the amount of surface oxygen groups shown in the results of TPD and with the total acidic sites shown in the result of Boehm titration. That is to say, the activity of AC reducing NO can be

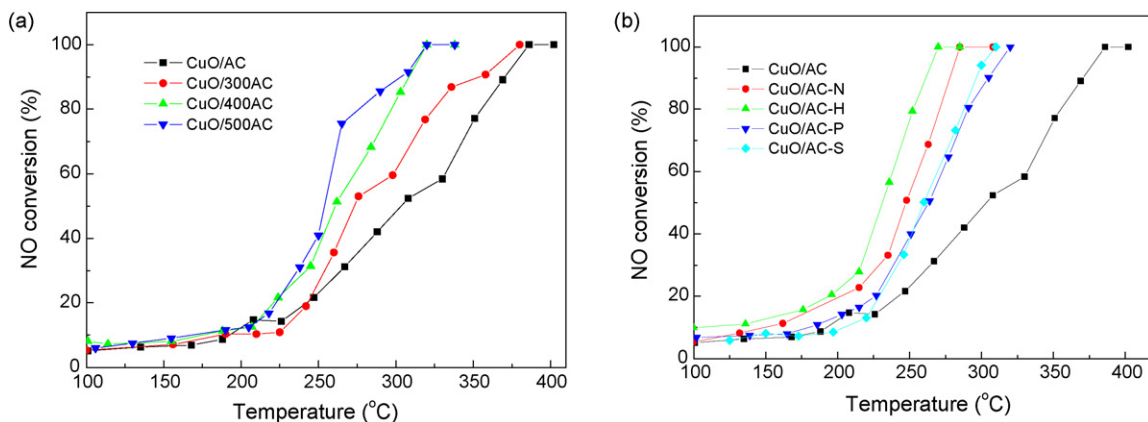


Fig. 4. Effect of the reaction temperature on the NO conversion.

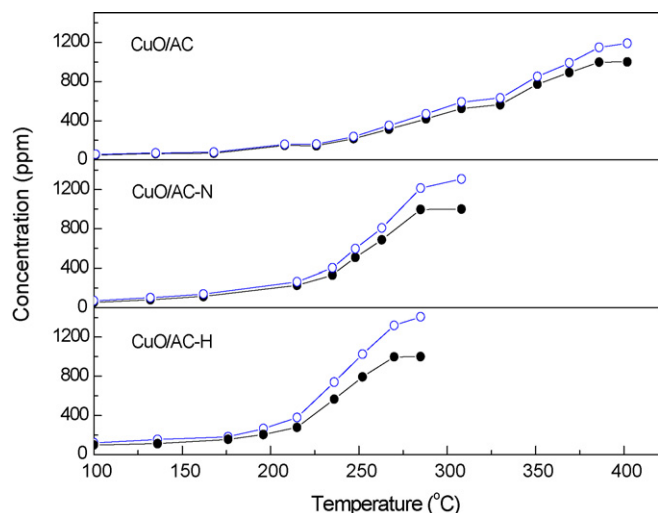


Fig. 5. Products concentrations vs. the reaction temperature in the reduction of NO by AC over CuO (●, N₂; ○, CO₂).

improved by increasing the content of the acidic surface oxygen groups on AC.

Fig. 5 shows the change of the products (N₂ and CO₂) concentrations in the reduction of NO by AC over the CuO catalyst. No CO or N₂O was detected in the range of reaction temperature. For the reaction of $2\text{NO} + \text{C} \rightarrow \text{N}_2 + \text{CO}_2$, the number of N₂ mole produced should equal to that of CO₂ formed in the products if no oxygen is added or adsorbed on the catalyst surface. The results in Fig. 5 show that, increasing the reaction temperature, the evolutions of N₂ and CO₂ increase obviously, but the concentration of CO₂ is always higher than that of N₂. This means that except for NO, the surface oxygen-containing groups also react with AC, which may promote the reduction of NO. The results also show that the CO₂ concentration using AC oxidized by HNO₃ or H₂O₂ as a reducing agent is higher than that of CO₂ using original carbon as a reducing agent, which results from the more surface oxygen groups on AC-N or AC-H.

Fig. 6 shows the effect of the reaction time on the NO conversion, at the reaction condition of 500 mg CuO/AC-H, the space velocity (GHSV) of 20,000 h⁻¹, 2000 ppm NO/Ar and 265 °C. The results show that the more than 90% NO conversion can be sustained when the reaction time is <38 h, and the conversion of NO decreases dramatically after the reaction time is >38 h, which shows carbon on the deactivated catalyst is almost depleted completely. That is to say, as a reducing agent carbon has been damaged through its oxidization to CO₂ by NO, and serious damage of carbon causes the decrease of the NO conversion.

3.3. Discussion about the catalytic reduction mechanism of NO_x by activated carbon

In the catalytic reduction of NO_x by AC, NO_x is firstly dissociatively chemisorbed on the Cu sites, the adsorbed oxygen on the Cu sites transfers to the carbon to form the carbon–oxygen complexes, then the carbon–oxygen complexes

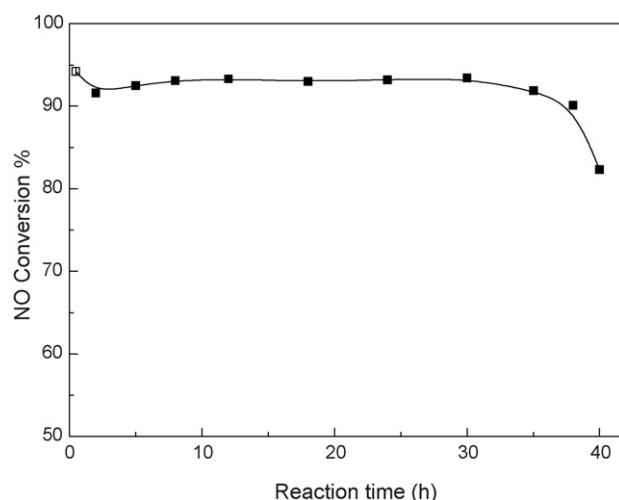


Fig. 6. Effect of the reaction time on the NO conversion over CuO/AC-H (reaction conditions: 2000 ppm NO/Ar, GHSV of 20000 h⁻¹, 500 mg CuO/AC-H, at 265 °C).

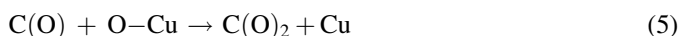
decompose to form CO₂, which may slow down or even stop if the oxygen cannot transfer from the Cu sites to the carbon active sites and then release timely [33–35]. So that quick oxygen transfer and release can promote the overall reaction. This situation is similar to that reported by Almusaiteer et al. [36], that is, NO decomposes on Rh/C to N₂ and decomposed oxygen reacts with carbon to form CO₂.

In the catalytic reduction of NO by AC, the carbon active sites play a key role [33], although these carbon active sites may be transient species with a very short half-life. By those carbon active sites, it is in favor of the release of dissociated oxygen (O_{ad}) from the Cu sites and its adsorption on AC, while two N_{ad} decomposed from NO combine to N₂. The acidic surface oxygen groups on AC can react easily with carbon to form CO₂ and CO. After CO₂ and CO desorb, a large number of free active sites on the carbon surface would form [37], and these “nascent” sites have a higher affinity toward NO. After AC is treated with the HNO₃ or H₂O₂ solution, more acidic surface oxygen groups on the surface of AC can be formed. Therefore, the treatment of AC with the HNO₃ or H₂O₂ solution can produce the more carbon active sites on AC, to accelerate the reduction of NO by AC at the beginning of the reaction. During the reduction of NO by AC, the decomposition of carbon–oxygen complexes would produce the carbon active sites to sustain the reduction of NO by AC.

The treatment of AC with HNO₃ can increase more acidic surface oxygen groups than that with H₂O₂, but CuO/AC-H has a higher activity than CuO/AC-N, which means that the acidic surface oxygen groups are only one of the factors that affect the reductive activity of AC. The results in Table 2 show that, by the moderate oxidation of H₂O₂ the acidic surface oxygen groups of AC-H increase obviously and its basic sites can also be preserved a lot. It is well known, that the basic sites have an affinity towards weakly acidic molecules like NO. Therefore, the presence of the surface basic sites helps to the adsorption of NO and then adsorbed NO is dissociated to O_{ad} and N_{ad} on Cu sites, O_{ad} is accepted by the carbon active sites and then

released [33], and $2N_{ad}$ combines to N_2 . If the concentration of the surface basic sites is too high, the acidic sites on AC would decrease correspondingly, resulting in inhibiting the release of O_{ad} from carbon active sites timely, that is, the reduction of NO by AC would be inhibited. So that the acidic surface oxygen groups with high concentration and moderate basic ones on the surface of AC-H are responsible for the increase of reductive activity of AC to NO over the CuO catalyst.

On the basis of our results and discussions above, the possible mechanism for the NO reduction by oxidized carbons over CuO is suggested as follows:



where CO_x is a surface oxygen-containing group, C_f is a carbon active site, Cu is a catalytic active site, O–Cu and N–Cu are oxygen (O_{ad}) and nitrogen (N_{ad}) adsorbed on the catalytic active sites and C(O) and $C(O)_2$ are the carbon–oxygen surface complexes. Eq. (1) shows a formation of carbon active sites which can accelerate greatly the transfer and release of O_{ad} decomposed from NO; Eqs. (2) and (3) represent the dissociative chemisorptions of NO and formation of N_2 on the catalytic active site; Eqs. (4) and (5) represent the transfer of oxygen from a catalyst to the edge carbon active sites to form carbon–oxygen surface complexes; Eqs. (6) and (7) show the formation of CO_2 from the carbon–oxygen surface complexes and the recovery of C_f on AC.

In the reaction steps above, Eq. (1) may be essential at the beginning of NO reduction by AC and determines the formation of C_f on AC. During the reduction of NO by AC, the release of the carbon–oxygen surface complexes of C(O) and $C(O)_2$ can activate the adjoining carbon to form C_f , so the catalytic reduction of NO by AC can sustain for a long time till the complete consumption of AC. It can be seen that dissociative chemisorption of NO and transfer and release of O_{ad} over CuO are important for a good catalyst used in the NO reduction by carbons. Moderate amount of basic sites on the surface of AC-H would be helpful to the dissociative chemisorption of NO and a large amount of surface oxygen groups would produce many carbon active sites (C_f) for the transfer and release of oxygen adsorbed, so that CuO/AC-H should be an effective catalyst for the NO reduction by carbons.

4. Conclusions

CuO is an excellent catalyst for the reduction of NO by AC. The surface chemistry of AC can be modified by air

oxidation or wet oxidation with the HNO_3 , H_2O_2 , H_2SO_4 and H_3PO_4 aqueous solution, which would affect the catalytic reduction of NO by AC. The oxidation treatment can increase effectively the surface oxygen acidic groups on AC. Increasing the oxidation temperature of AC in air can improve the reactivity of AC. The different wet oxidation methods of treating AC can influence obviously the reduction of NO by AC. The dispersion of CuO on AC can be improved by treatments of AC with HNO_3 and H_2O_2 . AC treated with H_2O_2 is the best reducing agent for the reduction of NO over CuO, and the temperature of complete reduction of NO by AC-H is 270 °C, which is 120 °C lower than that by original AC. This may be attributed to the high amount of surface acidic groups and relatively moderate amount of basic sites on the surface of AC-H.

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