

STUDIES ON THE CATALYTIC REACTION OF NITROGEN OXIDE ON METAL MODIFIED ACTIVATED CARBON FIBERS

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1. Introduction

Nitrogen monoxide (NO) produced during the combustion processes is one of the most serious pollutants, which produces town smog and causes other serious world ecological problems. In recent years, many scientists have paid great attentions to control and remove this kind of pollutant by different techniques. Among them, catalytic technologies are attractive because of their low cost and high efficiency [1].

Nowadays, the NO is mainly treated by catalytic reduction with reducing agents such as ammonia and sulphur dioxide and so on over metal-based catalysts. The carriers of general used include active aluminum oxide, silica gel, molecular sieve, activated carbon and so on [1-5]. During the recent years, the decomposition and reduction of NO with CO over zeolite, silica gel supported catalysts also have been reported in literatures [6-7]. As we known, activated carbon fiber (ACF) is a novel catalytic carrier because it has not only nano adsorption and catalytic spaces (micro-pore with 0.5~2 nm diameter) but also good redox reaction ability. A lot of effort has been devoted to the preparation and catalytic properties of ACF supported catalysts [8-13]. Most of previous researches in literatures were focused on NO reduction with NH₃ or SO_x, as well as the catalytic oxidation of CO with air over ACF supported catalysts. However, the reduction reaction of NO with CO and the decomposition of NO over ACF carried catalysts have not yet been carefully investigated so far.

Based on our previous works, novel catalysts of metal modified ACF were produced by controlling the adsorption and redox reaction of metal ions (palladium, palladium/copper and other metals) onto ACF. The catalytic reaction of NO with CO and catalytic decomposition of NO over metal modified ACFs were carefully investigated and compared with other carriers supported catalysts in present paper. This work is significant of in the treatment of nitrogen oxide containing waste gases such as exhaust gas of mobiles and emissions from chemical plants.

2. Experimental

2.1. The preparation of catalysts

(a). One gram of ACF, GAC (granular activated carbon), CB (carbon black), graphite, zeolite-A and molecular sieve ZSM were immersed with 100 ml of 0.0056 mol/l PdCl₂ or the mixed solution of 0.0056 mol/l PdCl₂ and 0.023 mol/l CuCl₂, respectively for 24 hours. Next, they were taken out from solution and dried up at 110 °C. The loadage of metals on carriers were calculated from the weight before and after immersed. Then, the metals containing catalysts were put into a glass tube and heated at 400°C for 180 minutes in inert atmosphere. The catalysts obtained were noted as Pd/ACF, Pd/GAC, Pd/CB, Pd/G, Pd/A, Pd/ZMS, or Pd/ Cu /ACF, respectively.

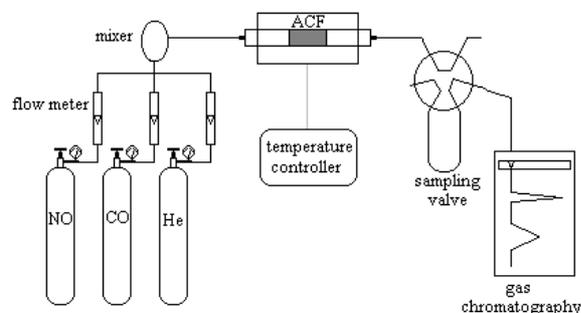
(b). 0.002 mol/l H₂PtCl₆, mixed solution of 0.002 mol/l H₂PtCl₆ and 0.023 mol/l CuCl₂ or mixed solution of 0.021 mol/l Co(NO₃)₂ and 0.023 mol/l CuCl₂ were used to immerse ACF and then operated in accordance with the procedures of (a). The catalysts obtained were noted as Pt/ACF, Pt/Cu/ACF or Co/Cu/ACF, respectively.

(b). At first, a slight activation ACF was prepared by activated with steam at activation temperature 850 °C for 30 minutes according to the procedure reported in literature [14]. 5 grams of thus produced ACF were immersed with 500 ml of 0.0094 mol/l PdCl₂ for 24 hours. Then, take them out from solution and dried up at 110 °C. The Pd-containing ACF was evenly divided into 5 parts. At last, every part of Pd-containing ACF was put into an activation furnace to be activated again with steam at 850 °C for different times. The relevant products were noted as Pd/ACF-r.

2.2. The catalytic reaction of NO

A horizontal, fixed-bed reactor made of 1cm diameter glass tube was used for the reaction measurement. The scheme of the reactor is showed in Figure 1. The feed containing NO (10000ppm) (or a mixture of NO (10000ppm) and CO (10000ppm)) in

balanced helium was fed to the reactor. The gaseous products were analyzed by a model Autosystem 9000 gas chromatograph equipped with a thermal conductivity detector.



The conversion efficiency of mixture of NO and CO is defined as follows:

$$\text{Total conversion efficiency (\%)} = \left\{ \frac{(\text{total amount of NO and CO})_{\text{inlet}} - (\text{total amount of NO and CO})_{\text{outlet}}}{(\text{total amount of NO and CO})_{\text{inlet}}} \right\} * 100$$

The conversion rate of NO is defined as follows:

$$\text{Conversion (\%)} = \left[\frac{(\text{NO})_{\text{inlet}} - (\text{NO})_{\text{outlet}}}{(\text{NO})_{\text{inlet}}} \right] * 100$$

2.3. Catalyst characterization

The surface area and pore distribution of catalysts were obtained in an ASAP 2010M apparatus made in USA from the nitrogen adsorption isotherms at 77K.

The samples were ground to a powder and pressed into the sample holders. X-ray diffraction patterns were collected using a D/max III A X-ray diffractometer made in Japan.

3. Results and discussions

3.1. The catalytic reduction of NO with CO

Table 1 shows the catalytic reaction of NO with CO over different metal-containing ACF. It can be seen that the total conversion efficiencies of NO/CO mixture are very low over Pt/ACF, Pt/Cu/ACF and Co/Cu/ACF. Even if at 350 °C, the total conversion efficiency is only 3 to 9% over them. However, the catalytic activity for the reaction of NO/CO greatly increases over palladium-containing ACF (Table 2). The total conversion efficiency can reach 100% at 300 °C in appropriate ratio of NO/CO.

It can be seen from Table 2 that when the ratio of inlet NO/CO decreases below 1, the total conversion efficiency will decrease because the excess CO can not be oxidized to CO₂. But it should be noted that when the fed amount of NO exceeds CO, even if NO reaches 100%, the total conversion efficiency can also reach 100% over Pd/ACF and Pd/Cu/ACF at 300 °C. That is, the excess NO can be completely reacted and converted by the catalytic action of Pd/ACF and Pd/Cu/ACF. These results indicate that if the amount of NO in mixture is large than that of CO, a part of NO is reduced by CO into N₂, while the excess part may decompose into N₂ and O₂.

In thermodynamic principle, NO may decompose by into N₂ and O₂, or into N₂ and NO₂. By using of alkali solution to absorb the outlet gas before and after catalytic decomposition over Pd-containing ACF, and detecting adsorbed solution by acidic titration, it was found that the solution acidity did not changed any way even if the NO conversion rate is 100%. This means that no NO₂ is produced when NO decomposes. Therefore, we suggest that the excess NO will decompose into N₂ and O₂ by the catalysis of Pd-containing ACF over 300 °C.

Table 1. The catalytic conversion efficiency of NO/CO mixture over metal-containing ACF (%)

catalyst	Catalyst weight (g)	The conversion of NO/CO at different temperature (%)			
		100 °C	250 °C	300 °C	350 °C
Pt/ACF	0.51	/	/	2.1	9
Pt/Cu/ ACF	0.51	0	1.5	2.0	4
Co/Cu/ACF	0.51	0	2.1	3.0	3.1

*-- flow rate of CO: 21.8 mL/min; NO: 21.7 mL/min.

Table 2. The catalytic conversion rate of CO/NO mixture over Pd-containing ACF (%)

catalyst	loadage of Pd (wt%)	Conversion at different NO/CO ratio (%)						
		0/77	15/62	25/52	38/38	53/24	63/14	77/0
Pd /ACF-3	4.11	/	42	50	100	100	100	100
Pd/Cu/ACF-2	5.1	0	32	67	100	100	100	100

*--Catalytic reaction temperature: 300 °C.

3.2. The decomposition of NO over catalysts with different carriers

The comparison of different carriers in Table 3 shows that the type of carrier greatly effects on the decomposition of NO. It can be seen that porous carbons such as ACF, CB and GAC possess higher catalytic activity for NO decomposition. Catalytic conditions such as catalytic reaction temperature and

NO flow rate affect on the conversion rate of NO. With the increase of temperature, the catalytic activity of catalysts increases. However, Pd/G, Pd/ZMS and Pd/A have not any catalytic activity for NO decomposition even at 400 °C in 23 ml/min of NO flow rate though the molecular sieve ZMS and zeolite-A are also the porous carriers.

Table 3. The decomposition of NO over the Pd-containing catalysts with different carriers

catalyst	loadage of Pd (wt%)	Catalyst weight (g)	Conversion % at 300°C with 23 ml/min of NO	Conversion % at 300°C with 77 ml/min of NO	Conversion % at 400°C with 23 ml/min of NO
Pd/ACF	14.14	0.5907	100	100	100
Pd/CB	16.63	0.5132	100	86.1	100
Pd/GAC	12.28	0.7843	63.2	24.4	/
Pd/G	20.97	0.4177	0	0	0
Pd/ZMS	17.49	0.5002	0	0	0
Pd/A	16.45	0.5792	0	0	0

Figure 2 shows the effects of NO flow rate on decomposition of NO over Pd/ACF, Pd/CB and Pd/GAC. For the catalysis of ACF-Pd, the conversion rate of NO keeps to 100 % until the NO flow rate reaches 150 ml/min, and then drops down to 77% when NO flow rate arrives 200 ml/min. But for Pd/CB, the conversion rate begins to decrease when the NO flow rate rises to 50 ml/min. While, for Pd/GAC, the conversion rate of NO greatly decreases even in low flow rate.

Based on the comparison above, it can be concluded that ACF is the best catalytic carrier for NO decomposition. The high catalytic activity of Pd/ACF may be explained by two reasons. The first reason is that ACF possesses suitable porous structure and high surface area. It was known from experimental results

that ACF has abundant micro pore with narrow diameter distribution and large surface area, which is advantageous to the dispersion of palladium. The micro pore volume, median pore diameter and BET surface area of ACF used are 0.462 ml/g, 0.551nm and 1016 m²/g, respectively. After loaded palladium, the micro pore volume and BET surface area of ACF decrease to 0.371 ml/g and 635 m²/g, respectively, and the median pore diameter slightly increase to 0.554 nm. The observation of SEM indicated that few palladium particles could be seen on the surface of ACF. These indicate that most of palladium is adsorbed in the micro pores of ACF. So we propose the structure of Pd/ACF as the scheme of Figure 3. It is believed that the

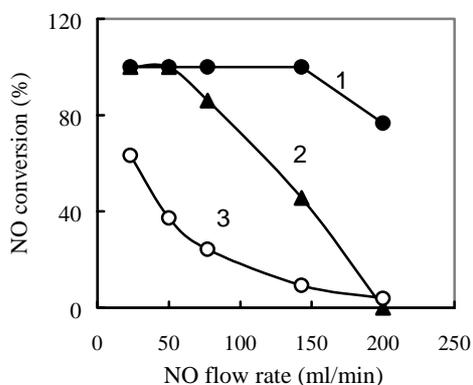
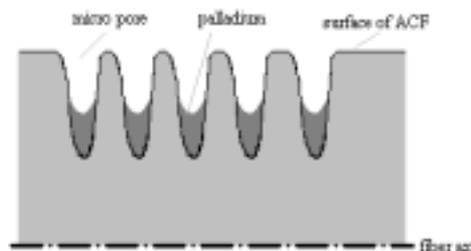


Fig. 2. Effect of NO flow rate on NO decomposition

1.ACF-Pd; 2.CB-Pd; 3.GAC-Pd



appropriate filling of Pd (or Pd and other metals) into the micro pore of ACF can produce a kind of high active catalyst which consists of nano catalytic metals and nano reaction spaces just like showing in Figure 3. Table 4 shows the surface area of different catalysts.

Table 4. The surface area of different catalysts

catalyst	Pd/ACF	Pd/CB	Pd/GAC	Pd/G	Pd/ZMS	Pd/Z
Surface area (m ² /g)	635	447	605	5	230	59

The second reason is that ACF have reduction ability [14,15] and so is advantageous to transform palladium ion into active elemental palladium. The previous works have also proved that ACF can act as an active carrier for the reduction of NO with NH₃ [8-10]. Similarly, porous carbon black and granular activated carbon possess reduction ability to a certain extent so they also present catalytic ability for NO decomposition. Graphite, molecular sieve ZMS and zeolite-A have not chemical action with palladium, so the relevant catalysts present not any catalytic activity for NO decomposition even at 400 °C. Though the decomposition of NO over Cu-ZSM-5 has been reported, the catalytic reaction is usually carried out

over 500 °C [6-7]

3.3. The effect of Pd loadage on catalytic activity

The loadage of palladium directly determines the number of active site of catalyst so must affect the decomposition ability of NO. Table 5 shows the catalytic properties of the Pd/ACF with different Pd loadage. Along with the decrease of Pd loadage, the active site decreases so that the decomposition speed of NO slows down. However, increase of catalytic reaction temperature can make up the decrease of Pd loadage to some extent.

Table 5. NO decomposition over the Pd/ACF with different Pd loadage

NO flow rate (ml/min)	NO conversion %			
	Pd loadage 9.57% Temperature 300°C	Pd loadage 11.14% Temperature 300°C	Pd loadage 14.14% Temperature 300°C	Pd loadage 14.14% Temperature 400°C
23	65.70	100	100	100
50	34.51	92.72	100	100
77	16.17	60.35	100	100
143	/	28.31	100	100
200	/	21.69	66.61	100

3.4. The effect of second time activation on catalytic activity

In order to study the action of micro pore on catalytic reduction of NO, a series of Pd-based ACF catalysts were designed by first loading palladium on ACF and following by second time activation with steam. The catalytic activities of produced Pd/ACF-r were showed in Table 6. When the activation time increases, the micro pore and surface area of fibers are sure to increase (for example, the surface area of Pd/ACF-r0 is 650 m²/g, while that of Pd/ACF-r30 is

1191 m²/g), but their catalytic activities for NO decomposition decrease obviously. This indicates that the new increasing micro pores are helpless for catalysis because there is not active palladium in them.

On the other hand, the amorphous elemental palladium generally presents higher catalytic activity than crystal one. Therefore, when the Pa-containing ACF was activated for second time at 850 °C, the original amorphous elemental palladium will translate into perfect crystalline and so reduce its catalytic activity.

Table 6. The catalytic decomposition of NO over Pd/ACF-r

catalyst	Activation time (min)	NO conversion (%)				
		Flow rate 23 ml/min	Flow rate 50 ml/min	Flow rate 77 ml/min	Flow rate 143 ml/min	Flow rate 200 ml/min
Pd/ACF-r-0	0	77.4	44.0	31.5	18.5	14.0
Pd/ACF-r-5	5	50.4	13.9	8.9	4.2	0
Pd/ACF-r-10	10	25.4	10.5	9.9	5.8	0
Pd/ACF-r-20	20	18.4	3.4	4.6	7.6	0
Pd/ACF-r-30	30	6.9	0	0	0	0

*--The Pd loadage is 9.6% before second time activation. Activation temperature 850 °C

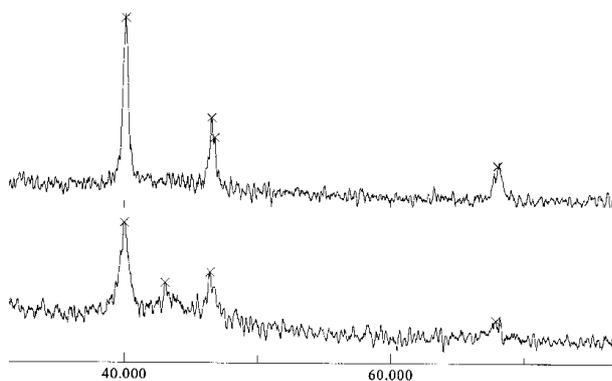
3.5. The effect of Cu on catalytic

In order to modify the structure of palladium on ACF, increase the catalytic decomposition activity for NO and decrease of usage of palladium, a mixed solution of Pd and Cu was used to impregnate ACF. The catalyst thus produced is proved to be more active than single component Pd/ACF catalyst by the

comparison of Table 7 with Table 5. It can be found that the catalytic activity of Pd/Cu/ACF with 5.1% Pd/Cu has exceeded that of Pd/ACF with loadage of 14.14 %. The results of X-ray diffraction (Figure 4) shows that Pd/Cu/ACF presents wider Pd peaks than Pd/ACF. This indicates that the crystalline of palladium is more unperfect on Pd/Cu/ACF than on Pd/ACF.

Table 7. NO decomposition over the Pd/Cu/ACF with different loadage at 300 °C

loadage %	Catalyst weight (g)	NO conversion %				
		Flow rate 23 ml/min	Flow rate 50 ml/min	Flow rate 75 ml/min	Flow rate 143 ml/min	Flow rate 200 ml/min
2.8	0.502	100	77	71	35	
5.1	0.514	/	100	100	100	90
7.8	0.557	/	100	100	100	100
9.9	0.502	/	100	100	100	100



4. Conclusions

Pd/ACF and Pd/Cu/ACF have high catalytic activity for the reaction of NO/CO. The total conversion rate of NO/CO can reach 100% in appropriate condition. But Pt/ACF, Pt/Cu/ACF and Co/Cu/ACF have low catalytic activity in similar circumstance. Pd-modified ACF possesses high catalytic decomposition of NO at 300 °C. Pd/CB and Pd/GAC present good catalytic decomposition ability for NO only at low flow rate. While Pd/G, Pd/ZMS and Pd/A have not any catalytic activity for NO decomposition even at 400 °C. It is believed that the appropriate filling of Pd and Pd/Cu into the micro pore of ACF can produce a kind of high active catalyst that consists of nano catalytic metals and nano reaction spaces. When catalytic reaction temperature and

loadage of Pd increase or NO flow rate decreases, NO decomposition rate increases. The new increasing micro pores, which are produced by second time activation and in which there is not any palladium, are helpless for catalytic decomposition of NO. The Cu mixed impregnation with Pd can lead the crystalline of palladium to more unperfect on Pd/Cu/ACF so that increase the catalytic activity.

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