NO Reduction and Oxidation over PAN based-ACF

Je Young Kim*, Jong Gyu Lee and Ikpyo Hong

Environmental & Energy Research Center, Research Institute of Industrial Science & Technology,
P.O. Box 135 Pohang 790-600, Korea
*e-mail: *jykim@rist.re.kr.*

Abstract

Catalytic reduction and oxidation of NO over polyacrylonitrile based activated carbon fibers (PAN-ACF) under various conditions were carried out to develop removal process of NO from the flue gas. The effect of temperature, oxygen concentration and the moisture content for the reduction of NO with ammonia as a reducing agent was investigated. The reduction of NO increased with the oxygen concentration, but decreased with the increased temperature. The moisture content in the flue gas affects the reduction of NO as the inhibition of the adsorption of the other components and the reaction on the surface of ACF. For the oxidation of NO to NO_2 over PAN-ACF without using a reducing gas, it showed the temperature and the oxygen concentration of the flue gas are the important factors for the NO conversion in which the conversion increased with oxygen concentration and decreased with the temperature increase and might be the alternative option for the selective catalytic reduction process.

Keywords : *Activated carbon fiber, PAN, NOx, Reduction, Oxidation*

1. Introduction

The selective catalytic reduction (SCR) process is widely used for the flue gas de-NOx treatment technology. The typical catalysts used in this process are metal oxide and zeolite. Among the many kinds of catalysts, the catalysts containing V_2O_5 supported on TiO_2 or Al_2O_3 are thought to be the suitable catalysts for removal of NOx [1, 2].

However, to obtain high removal efficiency of NOx, the metal oxide catalysts and zeolite catalysts should be used at about 350°C (to avoid the oxidation of NH_3) and above about 180°C (to obtain good catalytic activity) [1]. Such a SCR process shows the disadvantage which sometimes requires reheating of the flue gas.

Activated carbons and cokes have been recognized as excellent adsorbents for SO_2 and catalysts for reduction of NOx with NH_3 [3], and an industrial application has been successful using active coke with high mechanical strength and moderate adsorption ability in the moving bed [3, 4]. However, activated carbon process for simultaneous removal of SO_2 and NOx required larger facility than other SCR processes.

Besides, in SCR process, ammonia cannot be fully reacted, and then the residual ammonia becomes another pollutant. If NO in oxidative atmosphere can be converted into NO_2 by catalyst, then HNO_3 can be recovered by washing the off gas and there is no additional pollutant as ammonia used as a reducing agent in SCR process. It is known that NO_2 is not released at high temperature, even though NO_2 is formed on the surface of catalyst in SCR process.

Kong and Cha [5] reported that NO with more than 5% O_2 was converted into NO_2 by char at 24°C. Mochida [6] reported pitch based activated carbon fibers had high activity for the conversion of NO to NO_2 at room temperature. These conditions are particularly suitable for the process of simultaneous removal of SO_2 and NOx in the flue gas by activated carbon.

It is well known that the pore structures (pore volume, surface area and pore size distribution) play important roles in the gas adsorption on the activated carbon.

Generally, activated carbon fibers have better pore structures than activated carbon for adsorption and desorption. However, there is few industrial application of activated carbon fibers for NOx removal so far except some research papers [6, 7].

Mochida et al. showed that PAN-ACFs have high activity for the NO reduction in the temperature range between 150°C and 350°C [6] and NO oxidation at room temperature [7]. A super activated carbon activated with KOH has been reported as having a high surface area and large micropore volume [8]. Kim and Hong have reported PAN-ACFs activated with KOH showed high efficiency for SOx removal [9].

In present work, we studied the parameters for the NOx removal process by using PAN-ACF activated with KOH as catalyst. The investigation included (1) SCR of NOx from mixture gas in presence of oxygen 0-20 vol% and moisture content of 0-10 vol% with ammonia as a reducing agent over PAN-ACF catalyst at temperature ranging between 75°C and 150°C, (2) catalytic oxidation of NO to NO_2 over PAN-ACF
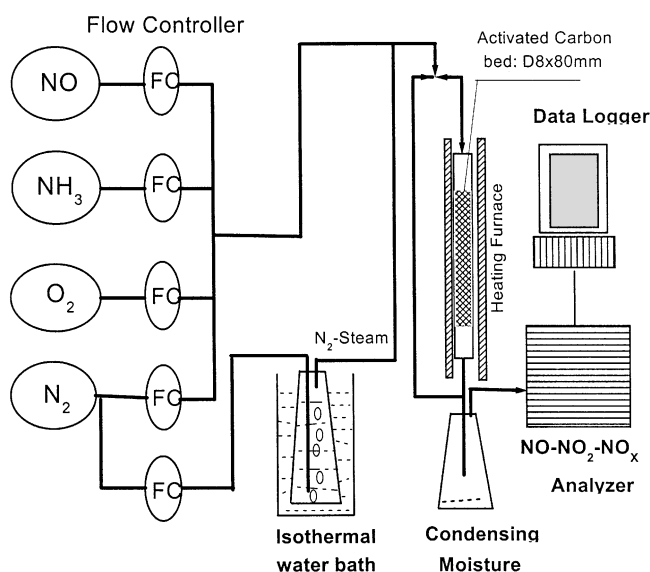
Fig. 1. Experimental apparatus.

at room temperature.

2. Experimental

The experimental apparatus consists of a fixed bed integral reactor, devices for the preparation of the gas mixtures, temperature controller and analyzer for NO, NO$_2$, NOx.

The experimental apparatus is shown in Fig. 1.

The inner diameter of quartz reactor was 8 mm and 0.4 gram of PAN-ACFs were charged in every run experiment. The length of the PAN-ACFs bed was about 80 mm. The temperature of the reactor was measured by thermocouples. Before starting an experiment, the reactor was by-passed to measure the gas composition. The gas tube consists of stainless steel tube for the pre-heating zone and Teflon tube except the heating zone.

NO, NO$_2$ and NOx were continuously measured by Chemiluminescence NO-NO$_2$-NOx analyzer.

The N$_2$, O$_2$, NO, He and water vapor were dosed as model flue gas and NH$_3$ was used as the reducing agent. The total gas flow rate was 100 ml/min (STP), i.e., the space velocity was around 15000/h. The flow rate of NO, N$_2$, O$_2$ and NH$_3$ were controlled by MKD mass-flow controller. The water vapor was controlled by the temperature of isothermal water bath and the flow rate of N$_2$. Before the mixture of gases reached to the reactor, it was pre-heated up to the reactor temperature by band heater.

PAN fibers with the composition of carbon 93%, methylacrylate 6% and itaconic acid 1% were used as the raw material for the PAN-ACF.

The received PAN fibers were immersed in 2M KOH solution for 24 hours and dried, then heat treated at 700°C for 30 min under inert atmosphere. The composition of PAN-ACFs were N: 4.44%, C: 78.72%, H: 1.56%, O: 15.28%. BET surface area was 1810 m^2/g and T-plot

Table 1. Experimental Parameters

Catalyst: PAN-ACF activated with KOH
BET surface area 1810 m^2/g
T-plot micropore volume 0.614
Catalyst bed column: Diameter 8 mm, Height 80 mm
Catalyst weight: 0.4 g
Temperature: 75-150°C for SCR
30°C for catalytic oxidation
Gas flow rate: 100 ml/min, STP
Space velocity: 1500/h
Inlet concentration of model flue gas:
Oxygen: 0-20 vol%
Water vapor: 0-10 vol%
NO: 400 ppm
NH$_3$: 400 ppm
He: 1.96 vol%
N$_2$: balance

micropore volume was 0.614.

The experiments include (1) NOx reduction without NH$_3$, (2) NOx reduction with NH$_3$, (3) NO oxidation to NO$_2$. The experimental parameters are listed in Table 1.

The NOx content was measured before the mixture of gases entered the reactor. NO was detected to be partially oxidized into NO$_2$ before it entered reactor, and its oxidation amount depended on oxygen concentration. But at high temperature or in the presence of NH$_3$ few ppm of NO$_2$ was detected at outlet of the reactor.

The yield of NO conversion was calculated from the inlet concentration Co=400 ppm and outlet concentration C at steady-state: NO conversion ratio=1-C/Co

3. Results and Discussion

3.1. Breakthrough curves of NOx, NO and NO$_2$ under various conditions

The typical breakthrough curves of NOx adsorption, reduction and oxidation on the PAN-ACF under various conditions are shown in Fig. 2. In Fig. 2 a) it shows that NOx was detected as NO in a few minutes after it passed to the reactor without oxygen at 30°C. The decrease of NO concentration of initial reaction was due to the adsorption of NO on the ACF. However, small amount of NO was converted to NO$_2$ in Fig. 2 b) if oxygen exists at 150°C. In the presence of NH$_3$(NH$_3$/NO=1) at 100°C as shown in Fig. 2 c), NO$_2$ was not detected at the outlet of the reactor during reaction time and NO was reduced to N$_2$ and the reduction ratio were increased with the oxygen concentration.

This shows the ammonia is the key component for the reduction of NO and oxygen concentration also affects the reduction of NO.

In Fig. 2 b), it shows that few of NO was oxidized to NO$_2$ in the presence of O$_2$ at 150°C. However, at low temperature in the presence of oxygen and long reaction time, some amount of NO was converted to NO$_2$ as shown in Fig. 2 d).

NO$_2$ was not detected during the initial 13 hrs. It indicates that the surface reaction take place between species which
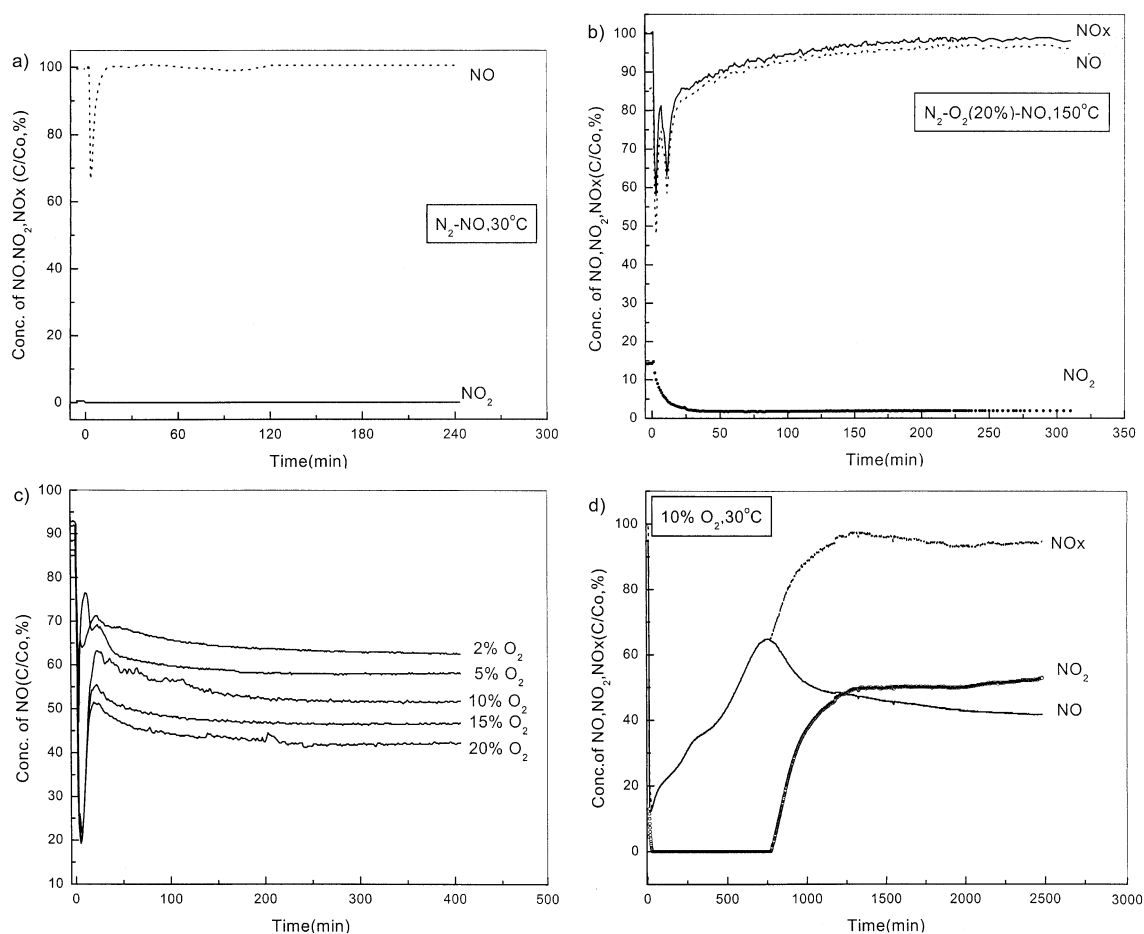
Fig. 2. Breakthrough curves of NO conversion by PAN-ACF under various conditions. (a) N_2-NO at 30°C, (b) N_2-O_2 (20 vol%)-NO at 150°C, (c) N_2-O_2-NO-NH_3 (400 ppm) NO/NH_3=1 at 100°C, (d) N_2-O_2 (10 vol%)-NO at 30°C

have been adsorbed in large amount. However, it is not clarified the difference of the breakthrough time of NO and NO_2 on the PAN-ACF in this paper.

3.2. Effect of Temperature on NO reduction

At the temperature range between 75°C and 150°C, the relationship of the steady-state NO conversion and temperature in the presence of NH_3 is shown in Fig. 3. In the presence of high concentration of oxygen (10%, 15%, 20% by volume), NO conversion decreases with the increased temperature. It can be explained as favored adsorption of reactants in the micropores of the PAN-ACF, enhancing the reaction rate by increased local concentration NO, NH_3 and O_2 at low temperature.

However, in the presence of low concentration of oxygen (2% and 5% by volume), NO conversion does not decrease with the increased temperature, but nearly independent of temperature. The reason is not clear still. But it may be related with the formation of NO dimmer on the surface of PAN-ACF as reported by Kong and Cha [5] that NO dimmer (or NO_2) have great effects on SCR.

The formation of NO_2 is markedly influenced by the oxygen concentration and temperature, which will be discussed later.
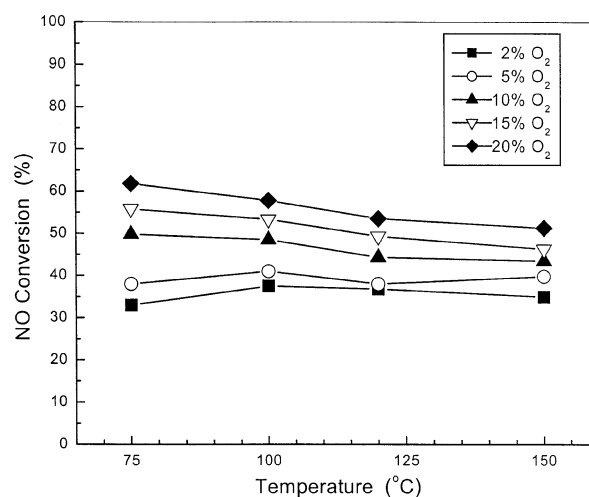

Fig. 3. Effect of temperature and O_2 concentration on NO conversion by NH_3 over PAN-ACF [N_2-O_2-NO (400 ppm)-NH_3 (400 ppm)].

3.3. The Effect of Oxygen on NO Reduction

Generally, NO conversion increased with the concentrations of oxygen, NO and NH_3.
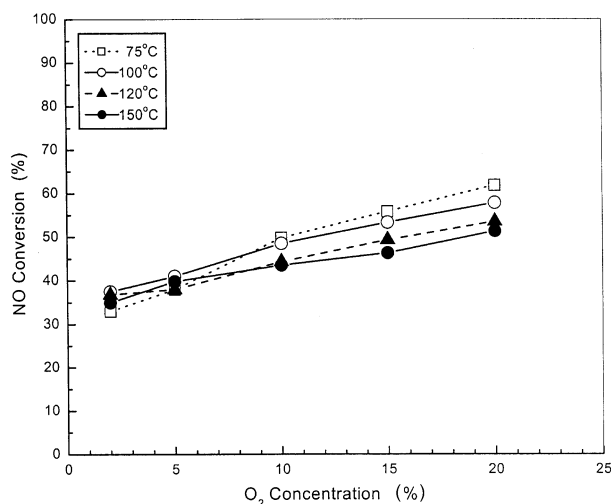
The simple form of reaction rate of SCR for NOx from

Fig. 4. Effect on O_2 concentration and temperature on NO conversion by NH_3 over PAN-ACF [N_2-O_2-NO (400 ppm)-NH_3 (400 ppm)].

Fig. 5. Effect of moisture on NO conversion by NH_3 over PAN-ACF [N_2-O_2 (15 vol%)-NO (400 ppm)-NH_3 (400 ppm)-H_2O], temperature 100°C.

dry flue gas is expressed as the following power rate law [11]:

$$r_{NO} = kP_{NO}^{\alpha}P_{NH_3}^{\beta}P_{O_2}^{\gamma}$$

The value of the apparent reaction orders α is about 0.8 [11], and γ is in the range of 0.25 to 0.5 [1, 11, 12]. The order γ relates to the kind of catalyst. But it was reported that the value of γ was obtained in low concentration of oxygen. In high concentration of oxygen in the present work shown in Fig. 4, NO conversion linearly increases with the oxygen concentration between 2% and 20%. Also it was found that no NO conversion to N_2 was taken place in the absence of oxygen under the condition of NH_3 presence.

Therefore, the presence of oxygen is necessary for SCR of NO by NH_3 over PAN-ACF, in agreement with Richter et al. [3].

A much higher NO conversion is achieved in the presence of higher oxygen concentration.

3.4. The Effect of Moisture on NO reduction

The effect of moisture on NO reduction is known as complex. Some researchers reported it has no obvious effect or even positive effect on NO reduction under some conditions [3, 5, 13]. They considers the moisture may absorb some NO_2 on the surface of carbon. However, the adsorption of moisture is taken place faster than other species, then inhibit the adsorption of other component and reaction [14, 15].

The present work also showed that moisture inhibited the activity of PAN-ACF for SCR of NO as shown in Fig. 5. Generally, there exists about 5-10% of moisture in the flue gas. The moisture exists as the vapor state at 100°C and condensed in the micropore after adsorption.

Therefore, it is necessary to remove moisture from the flue gas before the operation of SCR of NO by ammonia in using PAN-ACF as catalyst.

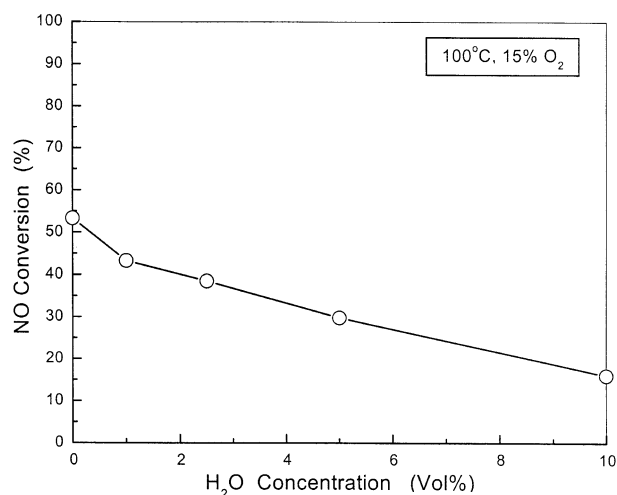### 3.5. The Catalytic Oxidation of NO to NO₂

As shown in Fig. 2 d), about 55% of NO was oxidized to NO_2 catalytically at steady state and 5% of NO was reduced to N_2 over the PAN-ACF in the presence 10% of O_2 and in absence of ammonia at temperature 30°C. The dependence of NO oxidation to NO_2 on oxygen concentration is shown in Fig. 6. The conversion of NO to NO_2 increased with the oxygen concentration.

Another dominant factor for the conversion of NO to NO_2 is the reaction temperature as shown in Fig. 7. The conversion of NO to NO_2 markedly decreased with the increased reaction temperature. But the conversion temperature of NO to NO_2 increased with the oxygen concentration. The conversion of NO to NO_2 at the conditions of 5% oxygen ceased at 75°C. But at the higher concentration of oxygen (15%), the conversion ceased at 100°C. At the reaction temperature of 75°C with 15% of oxygen, the NO was converted to NO_2 about 20%. This result shows low temperature and high con-
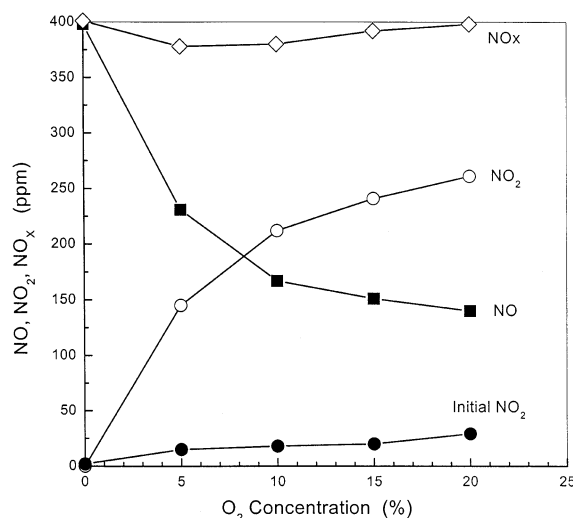

Fig. 6. Effect of O_2 on NO conversion over PAN-ACF without NH_3 [N_2-O_2-NO (400 ppm)], temperature 30°C.
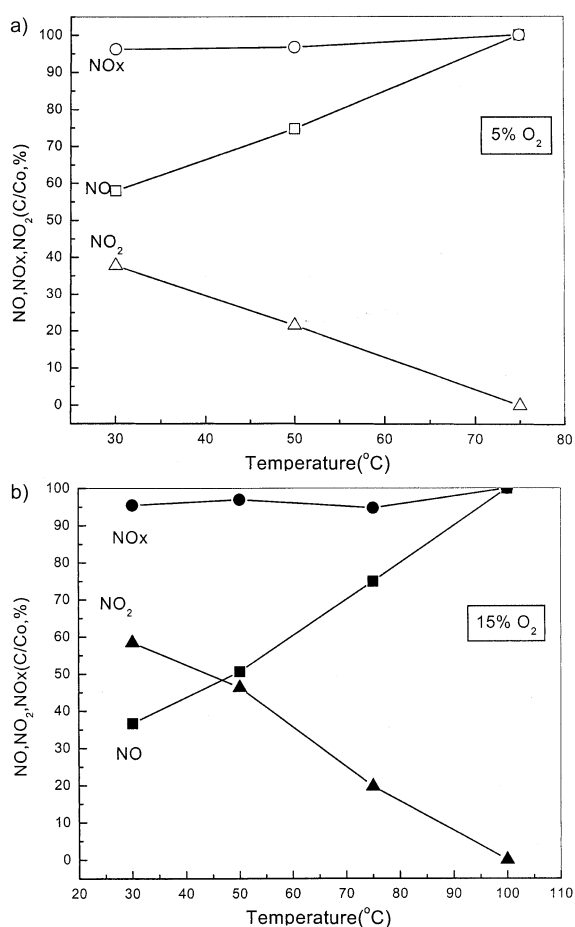
Fig. 7. Effect of temperature on NO conversion over PAN-ACF without NH_3 [N_2-O_2-NO (400 ppm)]. (a) O_2: 5 vol%, (b) O_2: 15 vol%

centration of oxygen are favorable conditions for the catalytic oxidation of NO.

The catalytic oxidation of NO to NO_2 in this experiment showed some possibilities of NO removal by oxidation with high conversion of NO without NH_3 as SCR.

4. Conclusion

The investigation of the catalytic reduction and oxidation of NO over PAN-ACF has led to the following conclusions:

1) The selective catalytic reduction of NO by ammonia with PAN-ACF increases with the oxygen concentration and decreases with the temperature. However, there is little temperature dependence on NO reduction if the oxygen concen-

tration is less than 5 vol.% in the model flue gas.

2) The conversion of NO in the range from 45% to 62% at steady state can be obtained at the temperature range between 75°C and 150°C and 10-20 vol% of oxygen in the dry model flue gas.

3) It is necessary to have higher than 10 vol% of oxygen and low reaction temperature to get high conversion of NO. The higher oxygen concentration in the micropores of PAN-ACF enhances the formation of NO-dimmer.

4) Moisture inhibits the catalytic activity of PAN-ACF due to the inhibition of the adsorption of NO on the surface of ACF.

5) NO can be oxidized to NO_2 by O_2 over the PAN-ACF at room temperature in dry conditions. The overall NO conversion ratio by catalytic oxidation at room temperature is higher than that by SCR.

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