

Kinetic Study of NO Reduction with Ammonia Over PAN-ACF Activated with Sulfuric Acid

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NO reduction with ammonia over PAN-ACF activated with sulfuric acid was investigated from kinetic view points to elucidate its reaction mechanism and active sites. The rate equations as for the original and activated PAN-ACF indicated the effective activation of ammonia and nitric oxide for the higher activity. Nature of adsorbed ammonia were also studied. The oxygen containing groups which were detected by ESCA and TPD are the active sites for ammonia and nitric oxide.

Introduction

The simultaneous removal of NO_x and SO_x in the dry process has been recognized as advanced technology against the flue gas to meet the future regulation. It is most desirable that the removal or reduction of NO_x can be performed efficiently at the same time of SO_x removal in the dry process which uses active coke as an adsorbent of SO_x¹. Remarkable catalytic activities of PAN-ACF activated with sulfuric acid for the reduction of nitric oxide with ammonia around 150°C have been reported^{2,3}.

In this paper the kinetics over PAN-ACF and surface characterization of the carbon surface are described to discuss the mechanism and active sites of the reaction.

Experimental

3 types of PAN-based active carbon fibers (PAN-ACF) used were supplied by Toho Beslon Co., Ltd. Their surface areas and nitrogen contents were summarized in Table 1. 5g of each sample was further activated by immersing in 200ml of sulfuric acid (0.5-1.5N) which contained prescribed amounts of H₂SO₄ (impregnation level: (pure H₂SO₄)/(ACF) by weight)⁴, agitating overnight, drying in a rotary evaporator and heat-treating under nitrogen flow at elevated temperatures between 400-600°C.

Before the reaction, the ACF was evacuated at the heat-treatment temperature for 1h in the reactor.

The reaction was pursued with a closed circulation reactor (glass made 500ml, sample 1g). The reactant gas consists of equal amount of NO and NH₃ (both 20Torr) when NO-NH₃ reaction was pursued, or NO(20Torr) when NO reduction by ACF carbon was tested.

Since nitrogen is the principal product from nitric oxide other than water or CO₂, the initial rate of N₂ formation was defined as catalytic activity or reactivity.

Adsorption of ammonia (36kPa) was observed at

423K by a constant volume vessel attached to a manometer. The amount of adsorption in the second run, which was observed after the evacuation of the carbon at 423K following the first run was defined as reversible amount, and the difference between the first and second run was irreversible amount.

The evolved substances from the PAN-ACFs while temperature rising were studied by using temperature programmed desorption (TPD) technique (carrier He 100ml/min, heating rate 10°C/min) to estimate the surface complexes produced during the activation. The desorbed gases were analyzed by a gas-chromatograph and a mass spectroscopy. The carbon surface was also analyzed with ESCA (Kokusai Denki ES200 (AlK_α, 10kV, 20mA).

Results

Catalytic activities of three types of PAN-ACF and their activated forms are summarized in Table 1 and 2. The original ACF A and B showed significant activities, whereas C did very small one. The activation with sulfuric acid enhanced the activities of all ACFs as reported previously, the degree of enhancement being very strongly dependent upon the condition of activation as well as the type of ACF. The highest activity of 63 μmol g⁻¹ min⁻¹ was obtained with ACF-B activated with 300% of sulfuric acid at 400°C.

The rate of the reaction over the original ACF-A and A-300%-400°C were described by the following equations respectively.

$$r = k P_{\text{NO}}^{1.2} P_{\text{NH}_3}^{0.3} \quad (1)$$

$$r = k P_{\text{NO}}^{0.9} P_{\text{NH}_3}^{0.7} \quad (2)$$

suggesting that importance of NH₃ and NO activation after the treatment with H₂SO₄.

The ACF adsorbed significant amount of NH₃ at the reaction temperature as shown in Table 2. Both irreversible and reversible adsorptions were enhanced very much by the activation with sulfuric acid, suggesting a reason for the activity

Table 1. Properties of PAN-ACF and Their Activities

	Surface Area (m ² /g)	Nitrogen Content (%)	N ₂ formation rate (μmol ⁻¹ min ⁻¹)	
			NO-NH ₃ reaction	NO-C reaction
ACF-A	595	6-7	19	0.54
ACF-B	710	4-6	21	1.4
ACF-C	1090	2-4	1.8	1.0

Table 2. Activities of NO-NH₃ and NO-C Reactions and Adsorption Amounts of NH₃

	N ₂ formation rate (μmol g ⁻¹ min ⁻¹)		Amount of NH ₃ adsorption (μmol g ⁻¹ min ⁻¹)	
	NO-NH ₃ reaction	NO-C reaction	rev.	irrev.
A-300%-400°C	43.6	3.8	19.0	6.1
A-300%-500°C	49	5.9	14.0	3.3
A-300%-600°C	17	2.8	10.3	3.0
B-300%-400°C	63	6.5	20.7	6.5
C-300%-400°C	32.2	1.4	19.9	7.5

enhancement.

The ACFs reacted NO at 150°C to reduce it into N₂ as reported previously. The reactivities of ACF for this reaction are summarized in Table 2. The activation with sulfuric acid enhanced the reactivity, the enhancement depending again very much on the activation conditions in a slightly different manner from that for the NH₃-NO reaction as activation at 600°C still provided a significant reactivity against NO.

The reactivity of irreversibly adsorbed ammonia on ACF-A-300%-400°C was observed at 150°C. Its initial reactivity was comparable to the rate of the catalytic reaction suggesting that its major contribution to the catalytic reaction.

The elemental ratios to the carbon on the ACF surface obtained by ESCA are summarized in Table 3. It is clearly suggested that the activation with sulfuric acid increased the oxygen on the surface, while neither nitrogen nor sulfur increased. The amount of oxygen introduced depended on the activation conditions. The activation at 400°C introduced more oxygen than that at 600°C.

Table 3. Relative Intensities of XPS

	O _{1s} /C _{1s}	N _{1s} /C _{1s}	S _{2p} /C _{1s}
A-original	0.10	0.08	0.003
A-300%-400°C	0.29	0.08	<0.001
A-300%-600°C	0.14	0.08	0.009

Fig.1 shows the ESCA spectra of ACF-A, A-300%-400°C and A-300%-600°C. The activation at 400°C increased very much the oxygen species of its kinetic energy 950-957 eV. TPD spectra shown in Fig.2 indicated the different oxygen species on ACF surface activated differently. The activation at 400°C and 600°C increased the oxygens desorbing in CO and CO₂ at 500-700 and 700-900°C, respectively.

Discussion

The catalytic activity of ACF enhanced with

H₂SO₄ was ascribed to the activation of both NH₃ and NO on the ACF surface. The active sites for both reactants appear to be oxygen containing surface groups. The active site for ammonia may be CO₂-giving acidic sites, which decompose at rather lower temperature, whereas that for NO may be CO-giving oxidizing sites, which decompose at rather higher temperature.

References

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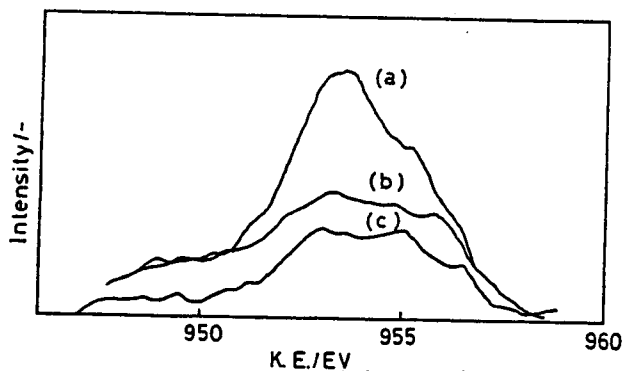


Fig. 1 XPS spectra of original and activated PAN-ACF
(a) PAN-ACF-A-300%-400°C
(b) PAN-ACF-A-300%-600°C
(c) PAN-ACF-A-original

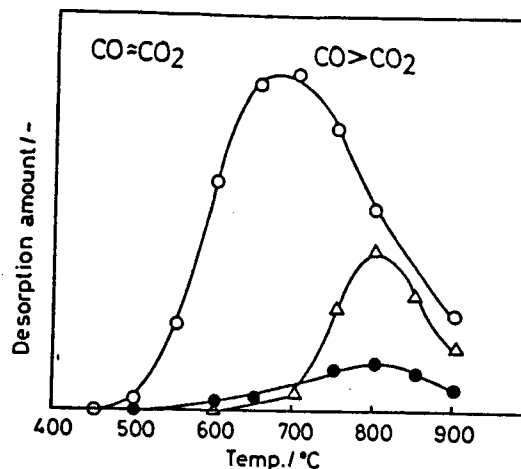


Fig. 2 TPD spectra of original and activated PAN-ACF
○ PAN-ACF-A-original
● PAN-ACF-A-300%-400°C
△ PAN-ACF-A-300%-600°C