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MnOx/Sewage Sludge Char를 이용한 저온 NH_3 SCR의 반응 메커니즘

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Reaction Mechanism of Low Temperature NH_3 SCR over MnOx/Sewage Sludge Char

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하수슬러지 촤에 MnOx를 담지한 촉매를 사용하여 NH_3를 환원제로 하는 선택적 촉매 환원반응의 반응 메커니즘 분석을 수행하였다. XRD 분석 결과 활성 Mn phase는 Mn_3O_4인 것으로 여겨졌다. 또한 150℃ 이하에서는 흡착반응이 주요한 질소산화물 저감 메커니즘으로 작동하였으나, 100～150℃에서는 환원반응도 질소산화물 저감에 관여하는 것으로 보여졌다. 실험결과에 기초하여 활성 촤와 여기에 MnOx를 담지한 촤에서의 반응속도상수를 비교하였다. MnOx 담지 촤는 높은 충돌계수와 낮은 활성화 에너지에 기인하여 높은 반응속도 상수와 높은 NOx 제거 효율을 나타내었다. 두 가지 촤 모두 본 실험 조건하에서 활성화 에너지는 상대적으로 낮았다(10～12 kJ/mol).

The reaction mechanism of selective catalytic reduction of NOx over sewage sludge char impregnated with MnOx using NH_3 as the reducing agent was investigated. The active Mn phase was shown to be Mn_3O_4 from the XRD analysis. Adsorption was the dominant NOx removal mechanism at low temperatures below 150 ℃ although reduction reaction also contributed partly to the NOx removal at 100～150 ℃. The reaction rate constants of NOx removal over non-impregnated and MnOx-impregnated active chars were compared based on experimental results. The MnOx-impregnated char was shown to have a higher reaction rate constant and a higher NOx removal efficiency due to a higher collision coefficient and a lower activation energy. The activation energy for both chars was shown to be relatively low (10～12 kJ/mol) under the experimental conditions of this study.

Keywords: *NOx, sewage sludge char, reaction mechanism, Mn*

1. Introduction

Nitrogen oxide (NOx) is a group of reactive gaseous species that irritates respiratory system of humans and animals. It causes not only acid rain but also photochemical smog and ozone via photochemical reactions. A variety of researches have been conducted to reduce NOx emissions. The most widely used NOx-reducing method over the world is the selective catalytic reduction (SCR). In particular, investigations on various catalysts for application to SCR processes have been carried out[1,2]. It is V_2O_5/TiO_2 (anatase) catalyst blended with WO_3 and MoO_3 that is used most widely in stationary NOx emission sources such as incineration plants and thermal power plants. While V_2O_5 catalysts have high NOx reduction efficiencies and are resistant to SO_2, their temperature window is relatively narrow (300～400 ℃). Within this temperature range, exhaust gas usually contains particulate matter, which causes inactivation and poisoning of catalysts, and other pollutants including SO_2 and As. Therefore, efforts have been made to develop low-temperature SCR catalysts that are active below 300 ℃[3].

Sewage sludge produced during the waste water treatment had been disposed mainly via landfill and ocean dumping in Korea until the amendment of Enforcement Regulation for Waste Management Law in 2001 that banned the landfill of sewage sludge. Since the amendment, most sewage sludge has been disposed by ocean dumping. As the 1996 Protocol to the London Convention took effect, however, regulation for ocean dumping of waste including sewage sludge was tightened to a large extent so that the ocean dumping of sewage sludge exceeding the standards 1 and 2 is banned from February 2008 and from February 2011, respectively, which urgently calls methods for in-land treatment of sewage sludge. Incineration, a representative in-land treatment process in which sewage sludge is burned and then the residues are

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landfilled, can reduce the volume landfilled by 80～90%. However, incineration exhaust contains secondary pollutants including dioxins, sulfur oxides, nitrogen oxides, and hydrogen chloride. In addition, the heavy metal concentration in incineration residues is high causing potential soil pollution. An alternative way of sewage sludge treatment is thermal treatment including pyrolysis and gasification. Thermal treatment is advantageous over incineration in that it can treat sewage sludge stably and by-products can be used as energy resources. Solid product obtained from thermal treatments is called char. Because of its merits of waste recycling and low cost, investigations are under way to reuse the char as fertilizer, adsorbent, and solid fuel[4]. Reuse of sewage sludge char is drawing a large attention in terms of reuse of a by-product as well as reduction of the amount of sludge to treat[5].

Sewage sludge char has been used in various applications either as it is or after activation through physical and/or chemical methods. In particular, it was reported that sewage sludge char can replace activated carbon used in the de-NOx process. According to the results reported in Park *et al.*[6,7], the catalyst prepared by impregnating sewage sludge char with Mn exerted high activity for NOx removal at low temperature. Park *et al.*[6,7] investigated the influences of various operating conditions such as temperature and activation method on removal of NOx. They obtained the highest NOx removal efficiency with the char catalyst that was produced through chemical activation using KOH and impregnated with Mn. Reaction kinetics of sewage sludge char, however, was hardly analyzed in their study. Therefore, in this study, the kinetics of NOx removing reactions by the sewage sludge char impregnated with Mn (Mn/Sewage sludge char) is investigated.

2. Experimental

2.1. Catalyst

In this study, the same catalysts as had been used in our previous study were used. Refer to[6,7] for detailed data for catalyst characteristics and abbreviations. X-ray diffraction was used to analyze the crystal structure of the MnOx impregnated on char under the conditions of Cu Kα radiation and 2θ = 10～90°.

2.2. De-NOx Reaction

De-NOx experiments were performed following the method described in detail in the previous paper[6,7]. An SUS tubular fixed-bed reactor, with an inner diameter of 130 mm and a height of 1500 mm, was fabricated to measure the NO_x removal efficiency of the produced chars. The composition of the inlet gas was maintained at 1000 ppm of NO, 1000 ppm of NH_3, and 5 vol% of O_2. The W/F (char sample weight/feed flow) ratio was 5.0 g·min/L (SV ≒ 6000 h^{-1}). The NO concentrations of inlet and outlet streams were measured by a NO_x analyzer (42C, ThermoIns.). After 1 h reaction time, the NO_x removal efficiency was calculated by the following equation :

$$NO_\chi \ Removal\ Efficiency\ (\%) = 100 \times \left(\frac{C_{NO}^{i} - C_{NO}}{C_{NO}^{i}} \right)$$

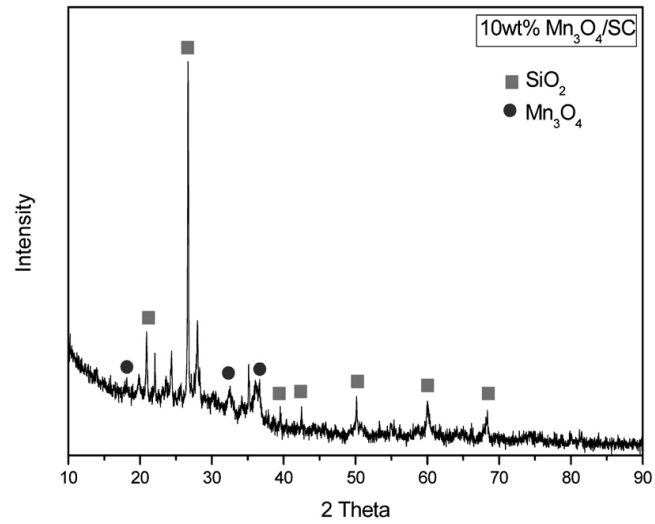

Figure. 1. XRD patterns of MnOx over sludge char.

C_{NO}^{i} : inlet NO concentration (ppm)

C_{NO} : outlet NO concentration (ppm)

3. Results and Discussion

3.1. MnOx Active Species

XRD measurement was carried out to analyze the crystal structure of MnOx impregnated on sludge char (Figure 1). As is shown in Figure 1, the MnOx impregnated on sludge char turned out to be Mn_3O_4. The previous study[6,7] showed that impregnation of char with MnOx enhanced the NOx removal efficiency. At temperatures above 150 ℃, at which reduction reaction of NH_3 and NO is the main mechanism, Mn_3O_4 functioned as the active site. At lower temperatures (≤ 150 ℃), the improved NOx removal efficiency by impregnation of Mn_3O_4 was explained by Marban *et al.*[8] as follows. Mn_3O_4 is composed of octahedral Mn_2O_3 phase and tetrahedral MnO phase. NO can be adsorbed on the oxygen vacancies of octahedral Mn_2O_3 as is shown in Eq. (1). It may be even reduced into N_2 by the reaction shown in Eq. (2). The mechanism shown in Eqs. (1) and (2) explains how the NOx removal efficiency could be improved by impregnation of MnOx at low temperature as well.

$$\{O{=}Mn\text{-}\square\text{-}Mn{=}O\}^{O} + NO \leftrightarrow \{O{=}Mn\text{-}[NO]\text{-}Mn{=}O\}^{O} \quad (1)$$

$$2\{O{=}Mn\text{-}[NO]\text{-}Mn{=}O\}^{O} \rightarrow 2\{O{=}Mn\text{-}O\text{-}Mn{=}O\}^{O} + N_2 \quad (2)$$

3.2. Low-temperature Adsorption Mechanism

It has been reported in the literature that reduction of NOx emission below 150 ℃ is achieved by adsorption[6,7]. Based on NH_3 step response experiments under NO-NH_3-O_2 condition, however, Zhu et al. [9] suggested a different pathway. They reported that when an inlet gas containing 610 ppm of NO, 700 ppm of NH_3, and 3.5 vol% of O_2 was provided into activated coke reactor at 30 ℃, NO concentration at reactor exit was measured to be 240 ppm, which is translated to the NOx removal efficiency of 60.7%. After ensuring that NO concentration

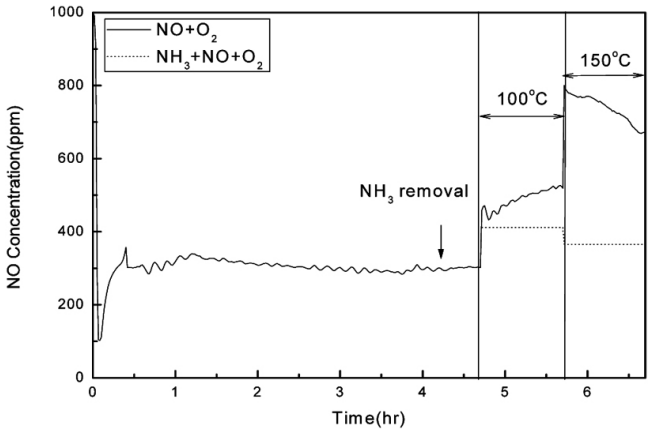

Figure 2. NOx removal below 150 ℃ over SCK-2.0-600.

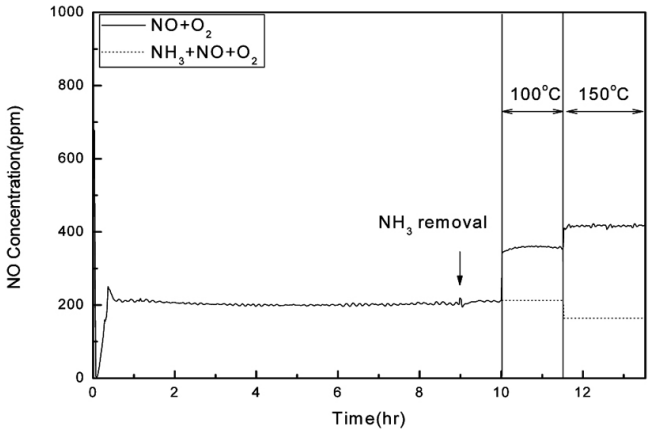

Figure 3. NOx removal below 150 ℃ over 3 wt% MnOx/SCK- 2.0-600.

is maintained constant at the above-mentioned reaction condition, NH_3 supply was ceased to investigate its effect on NOx removal. The NO concentration at the reactor exit was observed to increase to 470 ppm first and then decrease back to 320 ppm. The authors argued that the reduction of NO concentration without supply of NH_3 can be ascribed to oxidation of NO by O_2 followed by adsorption on the surface of activated carbon. In their experiments, the adsorption efficiency of NO via reaction between NO and O_2 was 47.6%, which is lower by about 13% than the NOx removal efficiency of 60.7% obtained with NH_3 supply. Based on this result, the authors suggested that the NOx removal over carbon catalyst at low temperature is achieved by both oxidation followed by adsorption and reduction reaction with NH_3.

To investigate further the NOx removal mechanism at low temperature (below 150 ℃), similar experiments to those of Zhu *et al.*[9] were carried out in this study. Figures 2 and 3 show the results obtained using SCK-2.0-600 and 3 wt% MnOx/SCK-2.0-600, respectively. At 50 ℃, NO concentration was shown to be independent of NH_3 supply in both experiments, indicating that NOx removal at 50 ℃ is solely due to adsorption. At 100 ℃, however NO concentration increased significantly when NH_3 supply was ceased. This trend was even more pronounced at 150 ℃. These results suggest that both adsorption and reduction reaction contribute to removal of NOx at 100 ℃ and at 150 ℃

Table 1. Removal Rate Constants (k) for NO Reduction with NH_3 over SCK-2.0-600 and 3 wt% MnOx/SCK-2.0-600

Sample	k (cm^3/g · s)		
	150 ℃	200 ℃	250 ℃
SCK-2.0-600	36.38	51.80	66.78
3 wt% MnOx/SCK (SCK-2.0-600)	65.43	93.74	112.23

and that the relative contribution of adsorption decreases with increasing temperature. Nevertheless, the NOx removal due to adsorption is generally more important than that through the reduction reaction below 150 ℃.

3.3. Catalytic Reduction Reaction Rate of NOx

Muniz *et al.*[10] investigated the effects of the concentrations of NH_3 and NO on the efficiency of NO removal over activated carbon fiber. They reported that the NO removal reaction is 1st order and 0th order with respect to NO and NH_3 concentrations, respectively. Garc´ıa-Bordejé *et al.*[11] also reported experimental results supporting the NO removal rate that is 1st order and 0th order with respect to NO and NH_3 concentrations, respectively. Based on their results, they suggested the following reaction rate equation.

$$r_{NO} = k[NO] \tag{3}$$

Garc´ıa-Bordejé *et al.* and Boyano *et al.*[11,12] confirmed that the external diffusion limitations are not considerable in SCR reactions and inferred the following relation between the reaction constant k and NO removal efficiency X under that condition.

$$k = -\frac{F_0}{[NO]_0 W}\ln(1-X) \tag{4}$$

F_0 : molar NO feed rate (mol/s)
$[NO]_0$: molar NO concentration at the inlet (mol/cm^3)
W : catalyst weight (g)

Table 1 summarizes the reaction rate constants over activated sludge char and MnOx-impregnated char calculated using Eq. (4). Only the results obtained at high temperatures (150∼250 ℃) are shown here to account for the reduction reaction of NO with NH_3 because NO removal below 150 ℃ was dominated by adsorption. It is shown in this Table that the reaction constant is higher for the Mn-impregnated catalyst that has higher NOx removal efficiency.

The reaction rate constant scales with temperature and the relation is given by the following Arrhenius equation :

$$k = A\exp(-\frac{E_a}{RT}) \tag{5}$$

where k is the reaction rate constant, A the collision coefficient or the pre-exponential factor, E_a the activation energy (J/mol), R the gas constant (8.314 J/mol · K), and T the absolute temperature (K). Applying

Table 2. Kinetic Parameters for NO Reduction with NH_3 over SCK-2.0-600 and 3 wt% MnOx/SCK-2.0-600

Sample	Collision coefficient, A ($cm^3/g \cdot s$)	Activation energy, E_a (kJ/mol)	Coefficient of determination, R^2
SCK-2.0-600	881.83	11.19	0.98
3 wt% MnOx/SCK (SCK-2.0-600)	1144.82	10.00	0.97

the reaction constant k to Eq. (5), the activation energy and the collision coefficient for each char can be estimated[13]. Since a linear relationship exists between natural logarithm of the reaction rate constant, ln(k), and the reciprocal of temperature, 1/T, one can obtain the collision coefficient and the activation energy from the y-intercept and the gradient, respectively, by plotting ln(k) as a function of 1/T.

Table 2 shows the values for the collision coefficient and the activation energy obtained in this way. Mn-impregnated SCK catalyst was shown to have a lower activation energy and a higher collision coefficient than the non-impregnated catalyst, resulting in a higher reaction rate constant.

Marbon *et al.*[14] and Kapteijn *et al.*[15] argued that the low activation energy of about 15 kJ/mol in low-temperature SCR can be attributed to the characteristics of Langmuir-Hinshelwood (LH) mechanism. In LH mechanism, when NO and NH_3 are adsorbed, lattice oxygens at active sites receive hydrogen atoms from NH_3 to reduce the active sites. Then, the adsorbed $-NH_2$ and $-NO_2$ reacts with each other to produce N_2 and H_2O and the reduced active sites are oxidized by gas-phase O_2. The heat released by adsorption and oxidation reaction in LH mechanism is the reason of low activation energy[11]. Based on this explanation, it may be suggested that the reduction of NO with NH_3 over sludge char is dictated by Langmuir-Hinshelwood mechanism. However, it should be noted that this is a hypothesis which has not been assessed thoroughly and additional investigations are required to verify it.

4. Conclusions

NOx removal over char catalysts at temperatures below 150 ℃ took place mostly by adsorption. At 100 ℃ and 150 ℃, however, reduction reaction also contributed partly to NOx removal. The relative contribution of adsorption decreased with increasing temperature below 150 ℃.

The reaction rate constants of NOx removal over activated char and MnOx-impregnated char were obtained from experimental results. The MnOx-impregnated char was shown to have a higher NOx removal efficiency and a higher reaction rate constant than non-impregnated char. The collision coefficient and the activation energy were calculated by applying the reaction rate constants obtained at different temperatures to Arrhenius equation. The MnOx-impregnated char was shown to have a higher collision efficiency and a lower activation energy. The activation energy was shown to be 10～12 kJ/mol under the experimental conditions used in this study.

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