Improving the Activity of Rh/Al₂O₃ Catalyst for NO Reduction by Na Addition in the Presences of H₂O and O₂

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Abstract The effect of Na addition on the performance of Rh/Al₂O₃ catalyst for NO reduction with CO in the presence of H₂O and O₂ was investigated. The reacted catalysts were analyzed by the FTIR technique to identify the products for further investigation on the possible catalytic reaction mechanisms and the reasons behind the H₂O poisoning. Experimental results show that the removal efficiency of NO by Rh/Al₂O₃ catalyst was 63% at 250 °C but that decreased as the H₂O content increased. Adding Na to modify the Rh/Al₂O₃ catalyst significantly enhanced the conversion of NO to 99% at 250-300 °C even as the H₂O content was 1.6 vol%. The FTIR analyses results reveal that the abundant H₂O in the flue gas can compete with NO to adsorb on the surfaces of Rh/Al₂O₃ and Rh-Na/ Al₂O₃ catalysts and further enhance the formation of NO₃ that reacts with H. The effects of H₂O on Rh/Al₂O₃ and Rh-Na/Al₂O₃ catalysts can be eliminated by increasing the reaction temperature to higher than 300 °C. Rh-Na/Al₂O₃ is a feasible catalyst for NO reduction at such condition with relative high H₂O and O₂ contents.

 $\label{eq:keywords} \textbf{Keywords} \quad \textbf{Na} \cdot \textbf{H}_2\textbf{O} \cdot \textbf{Rh}/\textbf{Al}_2\textbf{O}_3 \cdot \textbf{NO}$

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1 Introduction

Nitrogen oxide (NO) is a pollutant produced from waste incineration processes due to the reactions of nitrogen and oxygen at high temperatures. There has been a steady growing concern over it, most especially in recent times. In Taiwan, selective non-catalytic reduction (SNCR) is a prevailing method in controlling the emission of NO. However, the injection of ammonia or urea into flue pipes may cause problems of toxicity and corrosion. Selective catalytic reduction (SCR) has been an attractive method for NO reduction because of its high control efficiency, low reaction temperature, and low energy/fuel requirement. Many studies have applied SCR for NO reduction and the feasible catalysts include transition metal catalysts (Cu, Fe, V, Co and Ni) supported by activated carbon [1, 2], noble metal catalysts (Pd-Rh) supported on alumina [3] and some combined/modified metal catalysts (Pd-Na and Rh-Na) [4-7].

Water vapor (H_2O) is usually contained in the flue gas from combustion processes. In recent years, many studies have addressed the effect of H₂O on the catalyst for NO reduction [8-16] (Table 1). The major effects of H₂O on the catalysts include: (1) competition with NO and reductant to adsorbed on the active sites of catalysts; (2) inhibit the formation of reaction intermediate; (3) promote or inhibit the adsorption of reductant, and (4) alter the chemical state of active metals. Most references have indicated that the presence of H₂O would inhibit the activity of catalysts for NO reduction. To overcome this problem, adding a second metal to the catalysts could improve the tolerances of catalysts. Kikuchi et al. [17] found that adding precious metals (Pt, Rh or Ir) to the In/H-ZSM-5 catalyst enhanced the reduction of NO with CH₄ as H_2O was present. Haneda et al. [18] doped SnO_2 on a

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Catalyst	Reductant	[O ₂] %	Effect of H ₂ O on NO conversion	Role of H ₂ O	Reference
MnO _x /Al ₂ O ₃	NH ₃	2	Inhibition	Competitive adsorption with NO and NH ₃	[8]
V ₂ O ₅ /TiO ₂	NH ₃	4	Inhibition	Competitive adsorption with NO and NH ₃	[<mark>9</mark>]
Fe/ZSM-5	iso-C ₄ H ₁₀	3	Enhancement (slightly)	Inhibits the formation of carbonaceous deposits	[10]
Pd-ZSM-5	CH_4	10	Inhibition	Inhibits the adsorption of CO	[11]
				Changes Pd active state	
Pd-Pt/SZ	CH_4	10	Inhibition	_	[12]
In ₂ O ₃ -Al ₂ O ₃	C_3H_6	10	Inhibition	Inhibits the formation of NOx	[13]
V ₂ O ₅ /AC	NH ₃	3.4	Inhibition	No competitive adsorption with NH ₃ and NO	[14]
				Promotes the adsorption of NH ₃	
La ₂ O ₂ S	CO	-	Inhibition	Competitive hydrolysis of COS	[15]
La(Co, Mn, Fe) 1-x(Cu, Pd)xO ₃	C_3H_6	1	Inhibition (slightly)	The occupation of active sites	[16]
				Competitive adsorption with NO and C_3H_6	

Table 1 Effect of H₂O on the SCR of NO with reductant over various catalysts

Ga₂O₃-Al₂O₃ catalyst for NO reduction with C₃H₆ and found that SnO₂ can accelerate the reaction of NOx and C₃H₆ as H₂O was present. Quincoces et al. [19] reported that adding Co to the Pd/SZ catalyst increased its tolerance for H₂O and catalytic activity for NO reduction. They also mentioned that adding Co could improve the chemical stability of Pd during catalysis process. Mulla et al. [20] indicated that adding K to Pt/Al₂O₃ catalyst can increase its catalytic activity, but this promotion effect was decreased when H₂O introduced into the reaction because the active sites were blocked by H₂O. From the above reference reviews, the H₂O tolerances of different catalysts promoted by adding a second metal are not clear. It is necessary to develop an amended catalyst with higher H₂O tolerance and investigate the possible reaction mechanisms for NO reduction in such oxygen positive conditions.

Rhodium receives considerable attentions due to its high activity and selectivity for NO reduction. Rhodium was widely used in the three-way-catalysts (TWCs) to control the exhaust of gasoline vehicles. The applications of Rhcatalysts for NO reduction with different reductants were carried out recently [21-27]. Furthermore, the effects of SO₂ on the Rh-catalysts for NO reduction with different reductants [5, 28-30] and the improvements of Rh-catalysts by adding Co, Na, W, Ag, Zn, and Au [31-37] have been studied. Among the modification of metal addition, Na receives considerable attentions because it's high promotion on the activity of the catalysts for NO removal [4-7, 32, 33, 38–42]. However, most of them were performed at no oxygen or at the reaction condition different from that in the flue gas of waste incineration. The effects of H₂O on Rh-catalysts and modified Rh-catalysts in oxygen positive conditions similar to the incineration flue gas have not yet investigated. Our group has previously studied the performance of the Rh/Al₂O₃ catalyst on NO reduction and its modification by adding Na [5, 6]. The characterization of Rh/Al₂O₃ and Rh-Na/Al₂O₃ catalysts before and after the reaction have been carried out, including the dispersion of Rh and Na, BET surface area, the oxidation state of Rh, etc. Furthermore, the results also demonstrated that Na modification could improve the activity of the Rh/Al₂O₃ catalyst for NO reduction at relatively high SO₂ and O₂ concentrations. Based on previous experiences, this study further investigated the effects of different H₂O contents on the Rh/Al₂O₃ and Rh-Na/Al₂O₃ catalysts for NO reduction similar to the flue gas of waste incinerator. Fourier Transform-Infrared (FTIR) analysis was used to identify the products on the surface of the catalyst and investigate the possible reaction mechanisms at different operation conditions.

2 Experimental

2.1 Catalyst Preparation

Commercial Al₂O₃ pellets (Alfa Aesar, 90 m² g⁻¹) were crushed and sieved into particle sizes between 350 and 420 µm to serve as the supports. The precursors of the active metal Rh and the additive Na were Rh(NO₃)₃ · 2H₂O and NaNO₃, respectively. The 1%Rh/Al₂O₃ and 1%Rh-6%Na/Al₂O₃ catalysts were prepared by impregnation method. The Al₂O₃ supports were added with the solutions containing the precursors of Rh and Na, and completely mixed by a magnetic stirrer. After impregnation for 8 h, these catalysts were dried at 105 °C for 6 h and calcined at 500 °C for 6 h in air.

2.2 Reaction System

Figure 1 depicts the schematic diagram of the reaction system for the catalyst tests. The activity test was measured

using a fixed-bed reactor filled with 0.5 g catalysts. The inlet gas contained 200 ppm NO, 200 ppm CO, 6% O₂ and varying amounts of H₂O balanced with N₂. The total flow rate of the feed gas was 600 ml/min, and the corresponding space velocity was 70,000 h⁻¹. The activity test was performed at the temperature range of 150–400 °C. The H₂O vapor was generated by passing N₂ through a gas-wash bottle containing deionized water, and the H₂O content was measured by a hygrometer (Lutron HT-315). The H₂O content was controlled at 0.5, 1.6, 2.6, and 3.6 vol%. The concentrations of the inlet and outlet gases were continuously measured by a stack gas analyzer (HORIBA VIA-510) with chemiluminescence (NO), non-dispersive infrared (CO), electrochemistry (O₂) detectors.

3 Results and Discussion

3.1 Effect of H₂O on Rh/Al₂O₃ Catalyst

Figure 2 shows the effect of varying H_2O content on the Rh/Al₂O₃ catalysts for 200 ppm NO reduction with 200 ppm CO and 6% O₂. The reaction temperatures were maintained in the range of 150–400 °C. When the H₂O content was 0.5 vol%, the maximum NO conversion and CO conversion were 63% at 250 °C and 99% at 150–400 °C, respectively. As the H₂O content increased to 1.6–3.6 vol%, the NO conversion significantly decreased at 250 °C. Since H₂O was adsorbed on the active sites of the catalysts, the reaction occurrence of pollutants with the catalysts decreased [3, 9, 43]. Figure 2 also shows that the inhibition of H₂O on the Rh/Al₂O₃ catalyst decreased

Fig. 1 Schematic of reaction system for activity test: (1) mass flow controller; (2) gas-wash bottle; (3) gas mixed bottle; (4) hydrometer; (5) fixed-bed reactor; (6) thermocouple; (7) temperature controller; (8) flue gas analyzer; (9) data output when the reaction temperature was higher than 300 °C. This result coincides with the work of Papawfthimiou et al. [44]. Moreover, the CO conversions via the Rh/Al₂O₃ catalyst were not significantly influenced by the varying H₂O content and all approached 100% at 150–400 °C. Our previous study [5] demonstrated that the Rh/Al₂O₃ catalyst offered optimal CO oxidation efficiency. Therefore, H₂O exhibited an inhibitory effect on the Rh/Al₂O₃ catalyst for NO conversions at 1.6–3.6 vol% at a temperature of 250 °C. It did not, however, have any effect on CO conversions.

3.2 Effect of H₂O on Rh-Na/Al₂O₃ Catalyst

Figure 3 shows the effect of H₂O on the Rh-Na/Al₂O₃ catalyst for NO reduction with CO as a function of reaction temperature. When the H₂O content was controlled at 0.5 vol%, adding Na to the Rh/Al₂O₃ catalyst significantly promoted the catalytic activity for NO conversion at 250-350 °C. This result is attributed to the Na-induced promotions of NO adsorption and dissociation on the surface of the catalysts [32]. When the H₂O content was lower than 1.6 vol%, the NO conversions of the Rh-Na/Al₂O₃ catalyst maintained 99% at 250 °C. The NO conversions remained at 74 and 67% even when the H₂O content increased to 2.6 and 3.6 vol%, respectively. The decreased NO conversions could be attributed to the active sites of the catalyst being occupied by huge amounts of H_2O [3, 43]. The conversion of CO by Rh-Na/Al₂O₃ catalysts under varying H₂O content is also shown in Fig. 3. The CO conversions of Rh-Na/ Al₂O₃ catalysts were near 90% at 250 °C when the H₂O content was 1.6 vol%. However, it decreased to 70% at 2.6-3.6 vol%H₂O. Therefore, the role of H₂O on the SCR





Fig. 2 Effect of H_2O content on the activity of Rh/Al_2O_3 catalysts as a function of temperature. Conditions: [NO] = 200 ppm; [CO] = 200 ppm; $[O_2] = 6\%$; $[H_2O] = 0.5-3.6$ vol%; catalyst weight = 0.5 g

reaction of the Rh-Na/Al₂O₃ catalyst was inhibiting the NO and CO conversions at 2.6–3.6 vol% at 250 °C. Furthermore, when the reaction temperature was higher than 300 °C, the inhibitory effect of H₂O on the Rh-Na/Al₂O₃ catalyst for NO and CO conversions were removed. The H₂O content in the incineration flue gas is usually at 2.6 vol%. Adding Na to the Rh/Al₂O₃ catalysts can significantly improve the removal efficiency of NO at 250–300 °C and especially at relative high H₂O and excess O₂. Thus, the Rh-Na/Al₂O₃ catalyst is more feasible and suggested to be used at such conditions in the incineration flue gas.

3.3 Results of FTIR Analyses

Figures 4 and 5 show the FTIR spectra of the reacted Rh/ Al₂O₃ and Rh-Na/Al₂O₃ catalysts, respectively. Based on above experimental results, the Rh/Al₂O₃ catalysts tested at 200–300 °C with 0.5–1.6 vol%H₂O and the Rh-Na/Al₂O₃ catalysts tested at 200–300 °C with 0.5–2.6 vol%H₂O were chosen to perform the FTIR analysis. The FTIR results clearly point out the effects of H₂O on the catalysts for NO and CO conversions. In the FTIR spectra of the Rh/Al₂O₃ catalysts, the major adsorption regions were observed at 1,550–1,300, 2,000–1,600, and 3,700–3,500 cm⁻¹. The first region at 1,550–1,300 cm⁻¹ assigned to nitrate species



■ 0.5 vol% ■ 1.6 vol% ■ 2.6 vol% ■ 3.6 vol%

Fig. 3 Effect of H_2O content on the activity of Rh-Na/Al₂O₃ catalysts as a function of temperature. Conditions: [NO] = 200 ppm; [CO] = 200 ppm; [O₂] = 6%; [H₂O] = 0.5–3.6 vol%; catalyst weight = 0.5 g

such as NO₃ and NO₂ [36]. The second region at 2,000- $1,600 \text{ cm}^{-1}$ attributed to the adsorption of NO on the active sites of Rh [36, 45-48]. The third region at 3,700- $3,500 \text{ cm}^{-1}$ assigned to the OH decomposed from H₂O [36, 49]. On the other hand, no significant adsorption bands at 2,210 cm⁻¹ assigned to CO [45, 46] was observed in the FTIR spectra of Rh/Al₂O₃ catalysts. The mechanism of NO reduction with CO by Rh/Al₂O₃ catalyst to form N₂ at absent O₂ conditions is proposed as follows: First, NO is adsorbed on the active sites of Rh/Al₂O₃ catalysts to form N(a) and O(a) (Eq. 1). Second, the reductant CO is adsorbed on the active sites (Eq. 2) and reacted with N(a) to form NCO(a) (Eq. 3). Finally, NCO(a) reacts with NO(a) to form N_2 and CO_2 (Eq. 4). This observed mechanism also coincides with certain studies [47, 48, 50, 51]. The bands at 2,180–2,210 cm^{-1} assigned to NCO species [45] were not observed in Fig. 4. At O₂ positive conditions, the presence of high concentration O₂ promoted the oxidation reaction of NO to form NO₂ over Rh-catalysts. The mechanisms were illustrated in Eqs. 5 and 6. The results also consistent with the works of Flores-Moreno et al. [52] and Mendioroz et al. [25]. When H_2O introduced into the reactor and its content increased to 1.6 vol%, the peak intensity at 3,700–3,500 cm⁻¹ assigned to OH species [36,



Fig. 4 Effect of H₂O on the FTIR spectra of Rh/Al₂O₃ catalyst for NO + CO + O₂ reaction: (*a*) 0.5 vol%H₂O-200 °C, (*b*) 0.5 vol%H₂O-250 °C, (*c*) 0.5 vol%H₂O-300 °C, (*d*) 1.6 vol%H₂O-200 °C, (*e*) 1.6 vol%H₂O-250 °C, and (*f*) 1.6 vol%H₂O-300 °C

49] significantly increased. The H₂O vapors in the flue gas can be adsorbed on the active sites of the catalysts and produce H and OH (Eq. 7) [3, 43]. However, the peak intensity at 1,500–1,300 cm⁻¹ assigned to NO₃ and NO₂ species was increased (Fig. 4e, f). This result indicated that the formation of nitrate species (NO₃ and NO₂) was increased and they were produced from H reacting with NO₂ or OH reacting with NO.

$$Rh * +NO(g) \rightarrow Rh - NO \rightarrow Rh - N + Rh - O$$
 (1)

$$Rh^* + CO(g) \rightarrow Rh - CO + Rh - O \rightarrow CO_2 + 2Rh^*$$
(2)

$$Rh - N + Rh - CO \rightarrow Rh - NCO$$
 (3)

$$Rh - NCO + Rh - NO \rightarrow N_2 + CO_2 + 2Rh^*$$
 (4)

$$\begin{array}{l} Rh-NO+Rh-O\rightarrow Rh-NO_{2}+Rh-O\\ \rightarrow Rh-NO_{3} \end{array} \tag{5}$$

$$\begin{aligned} \operatorname{Rh}-\operatorname{NO}_3 + \operatorname{Rh}-\operatorname{CO} &\to \operatorname{Rh}-\operatorname{NO}_2 + \operatorname{Rh}-\operatorname{CO}_2 \\ &\to 2\operatorname{Rh}^* + \operatorname{NO}_2 + \operatorname{CO}_2 \end{aligned} \tag{6}$$

$$Rh^* + H_2O(g) \rightarrow Rh - H_2O \rightarrow Rh - H + Rh - OH$$
 (7)

Figure 5 shows the FTIR spectra of Rh-Na/Al₂O₃ catalyst reacted at different conditions. At 0.5 vol%H2O, 200 °C, and 1.6 vol%H₂O, 200 °C, the spectrum peaks were weak. That was attributed to the low activity of Rh-Na/Al₂O₃ for NO and CO conversions at such conditions. When the reaction temperature increased to 250-300 °C, the NO conversions increased to near 100% and those peaks intensity became stronger. Some studies [32, 53] addressed that the addition of Na can promote the adsorption and dissociation of NO on the surface of Rh/ Al₂O₃ catalysts (Eq. 1). The selectivity of N₂ over Rh/ Al_2O_3 catalyst can be promoted by Na addition (Eq. 8). Furthermore, the spectra at 2,264–2,267 cm^{-1} assigned to the formation of HNCO [45] were observed at when the flue gas contained 0.5 vol%H₂O and the reaction temperatures were 250 and 300 °C (Fig. 6). The results indicated that some H₂O dissolved to H and reacted with NCO to form HNCO (Eq. 9).

$$Rh - N + Rh - N \rightarrow Rh - N_2 \rightarrow N_2(g)$$
 (8)

$$Rh - H + Rh - NCO \rightarrow HNCO(g) + 2Rh^*$$
 (9)

When the H_2O content increased from 0.5 to 1.6 vol%H₂O, the intensity of each peak was similar at the reaction temperature of 250 and 300 °C. This phenomenon is consistent with the results in Fig. 3 that near 100% NO conversion obtained. Therefore, adding Na to modify Rh/Al₂O₃ catalyst could maintain its activity for NO conversion even as the H₂O content increased to 1.6 vol%. From the FTIR results, the peak intensities of NO₃, NO and OH at 250 °C increased when the H₂O content changed to 2.6 vol% (Fig. 5). The peaks at 2,264-2,267 cm⁻¹ assigned to HNCO species did not observed when the water content increased to 2.6 vol% (Fig. 6). Since the abundant adsorbed H and OH occupied the Rh active sites and modifier Na, the conversions of NO and CO thus decreased at 250 °C. This phenomenon indicated that increased in the formation of nitrate species (NO₃ and NO₂) obtained from H reacted with NO₂ or OH reacted with NO. Na may react with NO₃ to form NaNO₃ [5, 7]. Moreover, the performance of the Rh-Na/Al₂O₃ catalyst at 300 °C did not decrease even though the content of H₂O increased to 3.6 vol%. The inhibition effect of H₂O on the catalysts can be eliminated by increasing the reaction temperature.

Fig. 5 Effect of H_2O on the FTIR spectra of Rh-Na/Al₂O₃ catalyst for NO + CO + O₂ reaction



4 Conclusion

The effects of different H_2O content on the activity of Rh/ Al₂O₃ and Rh-Na/Al₂O₃ catalysts for NO reduction with CO at positive oxygen conditions were investigated. Based on the results, the following conclusions were obtained:

- (1) Increasing the H_2O content (1.6–3.6 vol%) significantly decreases the catalytic activity of Rh/Al₂O₃ for NO reduction at 250 °C. However, the CO conversions at 150–400 °C did not affected by the increase of H_2O content.
- (2) The addition of Na on Rh/Al₂O₃ can significantly improve the removal efficiency of NO to 99% at





250–350 °C with 0.5–1.6 vol%H₂O. As the H₂O content increases to 2.6–3.6 vol%, the NO conversion rate decreased but was still higher than that by Rh/ Al_2O_3 catalyst.

- (3) The FTIR results illustrated that H₂O can compete with NO to adsorb on the active sites of catalysts and enhance the formation of NO₃ to react with H in the catalytic reactions of Rh-Na/Al₂O₃, NO, CO, and O₂.
- (4) The effect of H₂O on the activity of Rh/Al₂O₃ and Rh-Na/Al₂O₃ for NO reduction can be eliminated by increasing the reaction temperature to 300 °C.

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