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Effects of Na, Cu, Ni and Co Modifications on the Activity and Characteristics of Rh/Al_2O_3 Catalysts for NO Reduction

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Abstract This study used different metals to modify Rh/Al_2O_3 catalysts for NO reduction in a simulated waste incineration flue gas containing 6% O_2. The characteristics of the modified catalysts were analyzed using BET, TEM and XRD. The results of the experiment reveal that Na addition can significantly affect the properties of Rh/Al_2O_3 catalysts on the BET surface area and Rh metal dispersion. Furthermore, Na addition was found to significantly enhance the NO conversion of Rh/Al_2O_3 at 250–350 °C. On the contrary, Cu, Ni, and Co addition was found to have slight suppression effects.

Keywords NO · Rh/Al_2O_3 · Catalyst modification · Metal

1 Introduction

In Taiwan, the selective non-catalytic reduction (SNCR) method is usually employed to control the emission of NO pollutant in municipal solid waste incinerators. This method injects ammonia or urea into the flue gas to reduce NO. Consequently, some problems regarding toxicity and corrosions are encountered. After SNCR treatment, the average concentration of NO during waste incineration is 70–120 ppm [1]; this value does not exceed the regulation limits but is quite near the threshold. Therefore, the best technology for NO removal, selective catalytic reduction (SCR), was used and studied [2–4] to treat the flue gas of waste incineration.

Compared with other de-Nox methods, SCR technology has the advantages of low reaction temperature, low fuel requirement, and no wastewater produced. The Rh-catalyst is known as one of the most active catalysts for the SCR of NO. Rhodium is widely developed and applied in three-way-catalysts (TWCs) to control the exhaust of gasoline vehicles [5]. In recent years, several studies have addressed the improvement of Rh-catalyst activity through modification of metals (e.g., Zn, Na, W, Co, Ag) [6–11], as shown in Table 1. These studies indicated that metal addition is very effective in promoting NO conversion compared with single metal catalysts. The major effects of metal addition include the changing surface chemistry of Rh and the generation of reaction intermediate. Although the modification of Rh/Al_2O_3 catalyst for NO reduction was mentioned in related studies, most of these were carried out with low or no oxygen at all. Such conditions were different from that of flue gas in waste incineration, and fewer references were focused on this point. We previously used different metals to modify the catalytic properties of the Pd/Al_2O_3 catalyst [12], and it was demonstrated that metal modification can improve the activity of the Pd/Al_2O_3 catalyst for NO reduction. However, the activity of rhodium is better than that of palladium. In addition, the optimal operation temperature for NO reduction can also be lowered down. Still, the effects of different metals on the character and activity of Rh/Al_2O_3 catalyst require further investigation.

Therefore, this study modified the Rh/Al_2O_3 catalysts with different metals (Na, Cu, Ni and Co) and investigated

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Table 1 Effect of metal addition on the NO reduction of Rh catalysts

Metal	Reductant	$[O_2]$ (%)	Effects for NO reduction	Role of metal addition	Reference
Zn	H_2	5	Enhance the catalytic activity	Improvement of surface chemistry of Rh Promotion of generation of reaction intermediate (NHx)	[6]
Na	C_3H_6	0	Enhance the catalytic activity and N_2 selectivity	Improvement of surface chemistry of Rh	[7]
	$CO + C_3H_6$	0.78	Decrease the catalytic activity and N_2 selectivity	Promotion of hydrocarbon adsorption and oxidation	[8]
W	C_3H_6	5	Enhance the catalytic activity	Improvement of surface chemistry of Rh	[9]
Co	CH_4	2	Enhance the catalytic activity	Improvement of surface chemistry of Rh	[10]
Ag	n-$C_{10}H_{22}$	10	Enhance the catalytic activity	Promotion of generation of reaction intermediate (NCO)	[11]

their performances for NO reduction with CO reductant in a simulated waste incineration flue gas containing 6% O_2. The changes in these catalysts properties were characterized through BET, TEM, and XRD analyses.

2 Experimental

2.1 Preparation of Catalysts

The supports of the catalysts were prepared by crushing and sieving the Al_2O_3 pellets into particle sizes of 350–420 μm. All catalysts were prepared using the co-impregnation method. $Rh(NO_3)_3 \cdot 2H_2O$ was chosen as the precursor of the active metal rhodium, while $NaNO_3$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were the precursors of Na, Cu, Ni, and Co, respectively. Al_2O_3 supports were added to the solutions which contained the precursors of Rh and Na, Cu, Ni, and Co, then mixed with a magnetic stirrer. After the co-impregnation process, these catalysts were dried at 105 °C for 6 h and calcined at 500 °C for 6 h.

2.2 Characterization of Catalysts

The Brunauer–Emmett–Teller (BET) surface area and pore size diameter of the catalysts were determined by N_2 sorption at 77 K with a vacuum volumetric apparatus (Micromeritics Gemini V2.00). The particle size distributions of the catalysts were examined via transmission electron microscope (TEM) (JEOL JSM-1200EX) at 80 kV. An X-ray powder diffractometer (XRD) (SIEMENS D5000) was used to identify the species of catalysts with a Cu-K_α radiation source at 30 V and 20 mA. The Scherrer formula (Eq. 1) was applied to determine the crystallite size of the catalysts from the XRD spectrum:

$$D = \frac{K \times \lambda}{B \times \cos\theta} \quad (1)$$

where K is a Scherrer constant (0.89), λ is the wavelength of CuKα (0.154 nm), B is the full width at half maximum in radians, and 2θ is the angle of peak.

2.3 Activity Test

The activity tests were performed in a fixed-bed reactor, followed by placing 0.5 g catalysts into a quartz tube with an internal diameter of 8 mm. The temperature of the reactor was monitored by a thermocouple and controlled by a programmable controller. The flow rate of feed gas was precisely controlled by mass flow controllers. The feed gas was composed of 200 ppm NO, 200 ppm CO, 6% O_2, and the carrier gas N_2. The total flow rate of feed gas was 600 mL/min, and the corresponding space velocity was 70,000 h^{-1}. The activity tests were examined with temperature ranging from 150 °C to 400 °C. The concentrations of pollutants in the inlet and outlet gases were continuously measured by a stack gas analyzer (HORIBA VIA-510) with chemiluminescence (NO), electrochemistry (O_2), and non-dispersive infrared (CO) detectors. The conversions of NO and CO were calculated from the following formula (Eqs. 2, 3):

$$\text{NO conversion } (\%) = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (2)$$

$$\text{CO conversion } (\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\%. \quad (3)$$

3 Results and Discussion

3.1 Catalyst Characterization

The characterization of the catalysts is shown in Table 2. The BET data indicated adding 6 wt.% Na on the

Table 2 Properties of the catalysts

Code	Catalysts	Crystallite size D (nm)	BET surface area (m^2/g)		Average pore size (4V/A by BET) (Å)		Pore volume (cm^3/g)	
		Fresh	Fresh	Reacted	Fresh	Reacted	Fresh	Reacted
Rh/Al	1%Rh/Al_2O_3	–	96	93	12.7	12.7	0.03	0.03
Rh-Na/Al	1%Rh-6%Na/Al_2O_3	$D_{Na} = 23.2$	49	51	13.7	13.7	0.02	0.02
Rh-Cu/Al	1%Rh-6%Cu/Al_2O_3	$D_{Cu} = 12.7$	84	79	13.1	13.1	0.03	0.03
Rh-Ni/Al	1%Rh-6%Ni/Al_2O_3	$D_{Ni} = 3.3$	84	85	12.8	12.8	0.03	0.03
Rh-Co/Al	1%Rh-6%Co/Al_2O_3	$D_{Co} = 8.3$	85	86	12.7	12.7	0.03	0.03

Rh/Al_2O_3 catalysts which drastically decreased the surface areas from 96 to 49 m^2 g^{-1}. The result is illustrated from the TEM images of the catalysts as shown in Fig. 1. It is difficult to observe the appearance of Rh species on the surfaces of Al_2O_3 support because most of the surfaces were covered with melted parts due to the low melting point of Na.

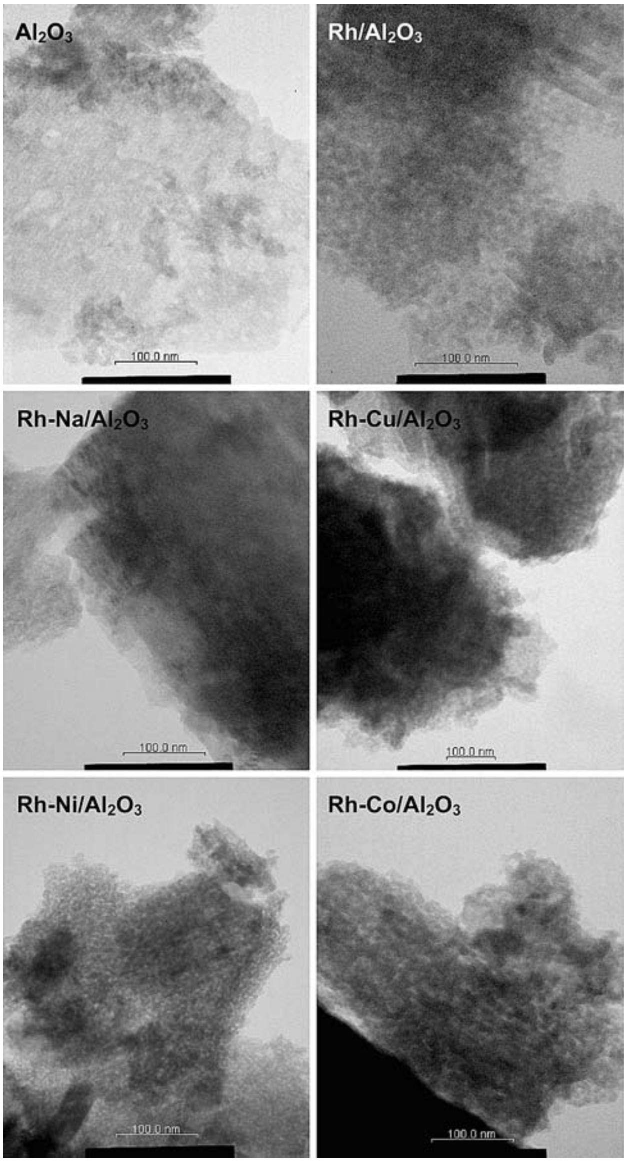

Fig. 1 TEM images of the catalysts

Figure 2 shows the XRD patterns, and all catalysts had peaks of γ-Al_2O_3 crystallites at 2θ of 66.761, 45.764, and 31.937. However, no Rh crystallite peak can be observed since the concentration is lower than the detection limit of XRD analysis. Na crystallite (2θ of 29.420) is obtained in Rh-Na/Al_2O_3 catalysts (Fig. 2b). Adding Cu, Ni and Co metals to Rh/Al_2O_3 catalysts produced the crystallite compounds of CuO (2θ of 35.538, 38.730, 38.940), NiO

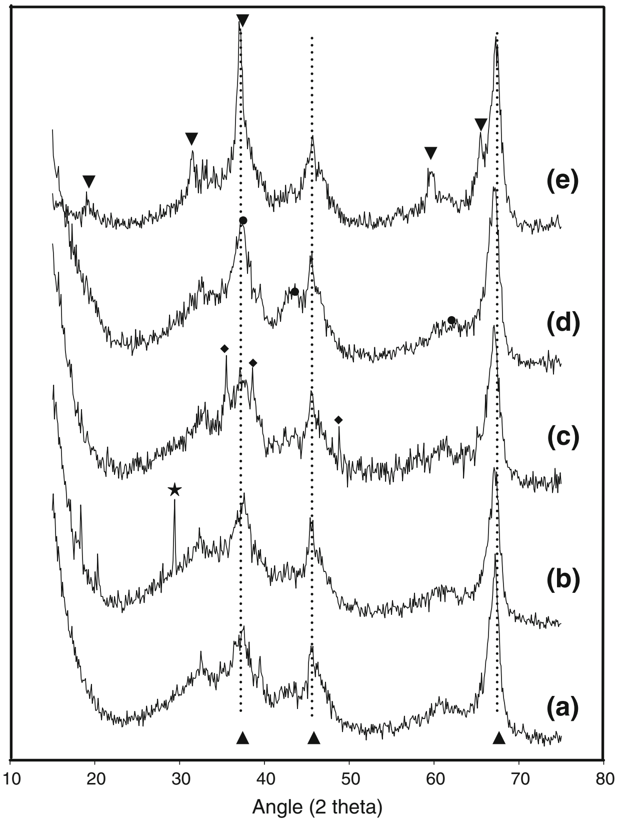

Fig. 2 XRD patterns of the catalysts: (a) Rh/Al_2O_3; (b) Rh-Na/Al_2O_3; (c) Rh-Cu/Al_2O_3; (d) Rh-Ni/Al_2O_3; (e) Rh-Co/Al_2O_3 (▲: γ-Al_2O_3; ★: Na; ◆: CuO; ●: NiO; ▼: Co_3O_4)

(2θ of 43.295, 37.278, 62.913) and Co_3O_4 (2θ of 36.936, 65.408, 31.346), respectively. As the catalysts were calcined under air condition, the chemical species of Cu, Ni and Co were transferred to the oxidation state. The species are identified by JCPDS including γ-Al_2O_3, Aluminum oxide (JCPDS#29-1486); Na, Sodium (JCPDS#22-0948); CuO, copper oxide (JCPDS#41-0254); NiO, Nickel oxide (JCPDS#4-0835); and Co_3O_4, Cobalt oxide (JCPDS#74-1657). Table 2 reports the crystallite size as determined from the results of the XRD spectrum. The crystallite size of metal on the Rh/Al_2O_3 catalysts follows the sequence of Na > Cu > Co > Ni, so the addition of Na can decrease the BET surface area of the Rh/Al_2O_3 catalysts.

3.2 Performances of Different Modified Rh/Al_2O_3 Catalysts

The NO and CO conversions of Rh/Al_2O_3 and Rh-M/Al_2O_3 (M = Na, Cu, Ni, Co) catalysts as a function of reaction temperature are shown in Fig. 3a–b. The maximum NO conversions of Rh/Al_2O_3 catalysts were near 72% at 250 °C. The CO conversions of Rh/Al_2O_3 catalysts remained 100% at 150–400 °C. This result reveals that the Rh/Al_2O_3 catalysts had reduction and oxidation ability at relative high oxygen conditions.

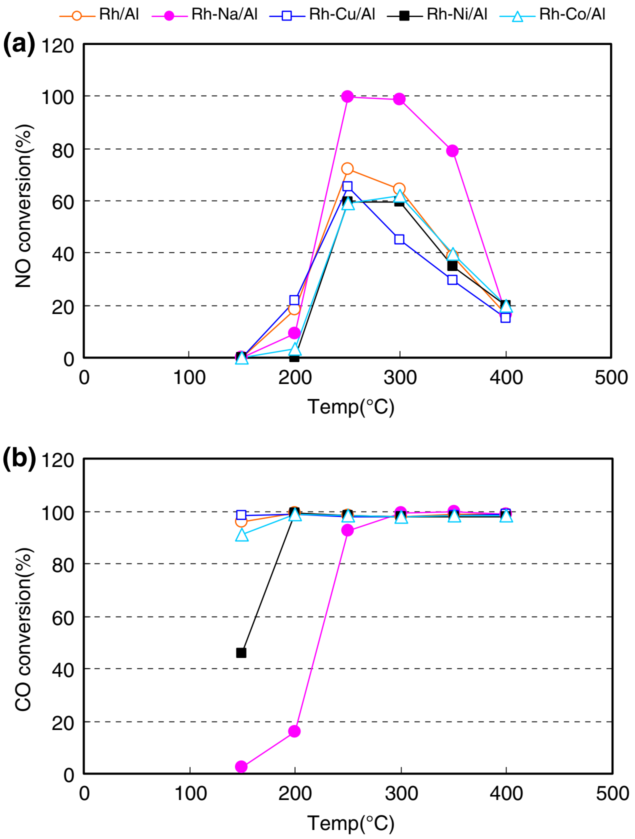

Fig. 3 Effect of metal modified Rh/Al_2O_3 catalyst in the SCR of NO by CO: (**a**) NO conversion; (**b**) CO conversion. Reaction condition: NO = CO = 200 ppm, O_2 = 6%, catalyst weight = 0.5 g and total flow rate = 600 mL/min

When Na was added to modify the Rh/Al_2O_3 catalysts, the NO conversion increased to nearly 100% at 250–300 °C. This result is attributed to the Na-induced enhancements of NO adsorption and dissociation on the surfaces of the catalysts [7]. The NO conversion of Rh/Al_2O_3 catalysts was slightly suppressed by Cu modification, but the CO conversion was not. Ni and Co addition also slightly suppressed the NO conversions of the Rh/Al_2O_3 catalysts. In particular, the CO conversion of the Rh/Al_2O_3 catalysts was suppressed by Ni addition from 100% to 46% at 150 °C. The results are evident from the XRD results of the catalysts. The predominant species of the Rh-M/Al_2O_3 catalysts were CuO, NiO, and Co_3O_4, so the metal oxides suppressed the catalytic reduction of NO with the reductant CO by the Rh/Al_2O_3 catalysts. This finding is supported by some studies [13, 14], which indicated that the catalysts containing metal aluminates had higher activity for NO reduction than metal oxides at low temperatures. As a result, adding Na to modify the Rh/Al_2O_3 catalysts can significantly improve the efficiency of NO removal in the simulated flue gas which contains 6% O_2.

4 Conclusions

The influence of metal addition on the activity of Rh/Al_2O_3 catalysts for NO reduction by CO was investigated at excess oxygen condition. The Rh/Al_2O_3 catalysts were modified by adding different metals (Na, Cu, Ni, and Co) via the co-impregnation method. Their properties were characterized using BET, TEM, and XRD analyses. The experimental results indicated that Na addition can significantly affect the properties of Rh/Al_2O_3 catalysts especially on the surface area as well as Rh metal dispersion. Moreover, Na addition also promoted the NO conversion of Rh/Al_2O_3 catalysts at 250–350 °C. On the contrary, Cu, Ni, and Co addition revealed slight suppression effects.

References

1. Kuo JH, Tseng HH, Rao PS, Wey MY (2008) Appl Therm Eng (in press)
2. Tseng HH, Wey MY, Liang YS, Chen KH (2003) Carbon 41:1079
3. Chen JC, Wey MY, Yeh CL, Liang YS (2004) Appl Catal B 48:25
4. Lu CY, Wey MY (2007) Fuel Process Technol 88:557
5. Iliopoulou EF, Efthimiadis EA, Vasalos IA, Barth JO, Lercher JA (2004) Appl Catal B 47:165
6. Hasegawa Y, Haneda M, Kintaichi Y, Hamada H (2005) Appl Catal B 60:41

7. Macleod N, Isaac J, Lambert RM (2000) J Catal 193:115
8. Macleod N, Isaac J, Lambert RM (2001) Appl Catal B 33:335
9. Halkides TI, Kondarides DI, Verykios XE (2003) Appl Catal B 41:415
10. Quincoces CE, Incollá M, De Ambrosio A, González MG (2000) Stud Surf Sci Catal 143:925
11. Sato K, Yoshinari T, Kintaichi Y, Haneda M, Hamada H (2003) Catal Commun 4:315
12. Chen JC, Chang FY, Wey MY (2008) Catal Commun 9:1106
13. He C, Paulus M, Chu W, Find J, Nickl JA, Köhler K (2008) Catal Today 131:305
14. Hamada H, Kintaichi Y, Sasaki M, Ito I (1991) Appl Catal 75:L1