Effects of sodium modification, different reductants and SO_2 on NO reduction by Rh/Al_2O_3 catalysts at excess O_2 conditions

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Abstract

Although many catalysts of NO reduction have been developed, the presence of excess O_2 and SO_2 significantly inhibits their performance when they are used to treat the incineration flue gas. To solve such problem, this study prepared new Rh/Al_2O_3 catalysts and investigated the effects of Na modification, SO_2 and different reductants. Experimental results indicated that the average removal efficiency of NO at such high O_2 concentrations exceeded 80% when the Rh/Al_2O_3 catalysts were used. CO was a better reductant than C_3H_6 and the best concentration ratio of reductant/NO was equal to 1. Adding Na to modify Rh/Al_2O_3 catalysts significantly enhanced the removal efficiency of NO from 80 to 99% at 250–300 °C, especially at relative high SO_2 concentrations. Unfortunately, Rh–Na/Al_2O_3 catalysts do not have long-time activities for NO reduction, possibly because of the formation of $NaNO_3$. Both Rh/Al_2O_3 and Rh–Na/Al_2O_3 catalysts have good performance for NO reduction, they can feasibly be used to reduce NO in the flue gas from waste incineration.
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1. Introduction

NO is a major by-product of combustion processes and its emission from the incineration flue gas has caused public concern and regulatory scrutiny. Among the various technologies for controlling NO, the selective catalytic reduction (SCR) method using NH_3 as the reductant is the most effective. Since NH_3 in SCR processes may cause some problems of toxicity and corrosion, various reductants such as CO and C_3H_6 have been proposed to replace NH_3 [1–8].

Many catalysts have been developed for NO reduction. They can be divided into two types: noble metal catalysts and transition metal catalysts. Noble metal catalysts have higher activities than transition metal catalysts. Unlike conventional noble metal catalysts such as Pt and Pd, Rh catalysts have received considerable attentions because of their relative high activity and selectivity for NO. For example, three-way catalysts (TWCs) are usually used to control the exhaust of gasoline vehicles and Rh is one of the major active metals of TWCs. Nevertheless, Rh catalysts are rarely been applied to treat the incineration flue gas [9].

The modification of catalysts has been proposed recently to improve their activity and selectivity. By adding some additives, the surface properties as well as the adsorption and reaction activity of catalysts can be enhanced. Macleod et al. [10] found that the activity and selectivity of Rh/Al_2O_3 catalysts for $NO + C_3H_6$ reactions were excellent without O_2, and that the optimum Na content for modifying Rh/Al_2O_3 was 4–8 wt%. However, the performance of Rh/Al_2O_3 catalysts was decreased when oxygen (0.78% O_2) was present [11].

The effects of SO_2 on the NO reduction have been reported. Summers and Baron [12] indicated that Rh catalysts were more active for NO reduction in the presence of SO_2 than were other noble catalysts. Efthimiadis et al. [5,13] observed that the presence of SO_2 in the $NO + C_3H_6 + 5\%$ O_2 gas mixture increased the activity of Rh/Al_2O_3 catalysts for NO reduction because of the formation of sulfates. Although SO_2 has been verified to enhance the NO conversion over Rh/Al_2O_3 catalysts, the effects of Na addition and SO_2 on Rh–Na/Al_2O_3 catalysts in excess oxygen have not been extensively investigated.

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The flue gas from waste incineration always contains certain amounts of O_2 (6%) and SO_2 (20–200 ppm). New catalysts that can tolerate such conditions and have good activities for NO reduction must be developed. Therefore, this study prepares Rh/Al_2O_3 catalysts for NO reduction in simulated incineration flue gases that contain different concentrations of SO_2 and O_2. The effects of Na modification, reductants CO and C_3H_6, the concentration ratio of reductant/NO and SO_2 concentrations on the activity and stability of Rh/Al_2O_3 catalysts were also evaluated.

2. Experimental

2.1. Catalyst preparation

The Al_2O_3 pellets (Alfa Aesar, BET surface area: $90\,m^2\,g^{-1}$) were crushed and sieved into particles with sizes of between 350 and 420 μm to serve as the supports. The loading weight of active metal Rh was 1% and it was coated on the supports by the incipient wetness impregnation method. $Rh(NO_3)_3 \cdot 2H_2O$ and $NaNO_3$ were chosen as the precursors of active metal Rh and modifier Na, respectively. To compare the effects of Na modification on the performances of $1\%Rh/Al_2O_3$, $1\%Rh–6\%Na/Al_2O_3$ and $6\%Na/Al_2O_3$ were prepared and tested. The concentration of Na added to the catalysts was determined to be 6 wt% according to the results of previous study [10], in which the optimum Na content for $1\%Rh/Al_2O_3$ modification was in the range of 4–8 wt%. After the impregnation process, these catalysts were dried at 105 °C for 6 h and calcined at 500 °C for 6 h in air.

2.2. Activity test

Since the flue gas from waste incineration usually has complex pollutants that are harmful to the catalysts, this study aims to clarify the performance of $1\%Rh/Al_2O_3$ and $1\%Rh–6\%Na/Al_2O_3$ catalysts for NO reduction under simu-lated conditions that are similar to those of incineration flue gas. The test was performed in a fixed-bed reactor filled with 0.5 g catalyst. The feed gas mixture contained 200 ppm NO, 200–600 ppm CO/C_3H_6, 0–500 ppm SO_2, 6% O_2 and N_2. The total flow rate was 600 ml/min, and the corresponding space velocity was $70,000\,h^{-1}$. The activity test was examined over the temperature range of 150–400 °C. The concentrations of inlet and outlet gases (O_2, CO, CO_2, NO, SO_2 and C_3H_6) were continuously measured by a stack gas analyzer (HORIBA VIA-510) that was equipped with chemiluminescence (NO), electrochemistry (O_2), non-dispersive infrared (SO_2, CO and CO_2) detectors and a gas chromatographer that was equipped with a flame ionization detector (C_3H_6). Fig. 1 shows the diagram of catalytic reaction system.

2.3. Catalyst characterization

The Brunauer–Emmett–Teller (BET) surface area and pore size diameter of catalysts were determined by N_2 sorption at 77 K using a vacuum volumetric apparatus (Micromeritics Gemini V2.00). A scanning electron microscopy (SEM) was used to observe the micrographs of catalysts. The species of supports and catalysts were identified by an X-ray powder diffractometer (XRPD) (SIEMENS D5000) with a Cu-Kα radiation source at 30 kV and 20 A. The diffraction patterns were manually analyzed using the Joint Committee on Powder Diffraction Standards (JCPDS). The X-ray photoelectron spectroscopy (XPS) analyses were carried out by a VG Escalab 210 spectrometer with an Al-Kα X-ray source at 1486.6 eV.

3. Results and discussion

3.1. Characterization of catalysts

Table 1 lists the results of BET surface areas and pore size diameters of catalysts. Adding 6 wt% Na to $1\%Rh/Al_2O_3$ cata-
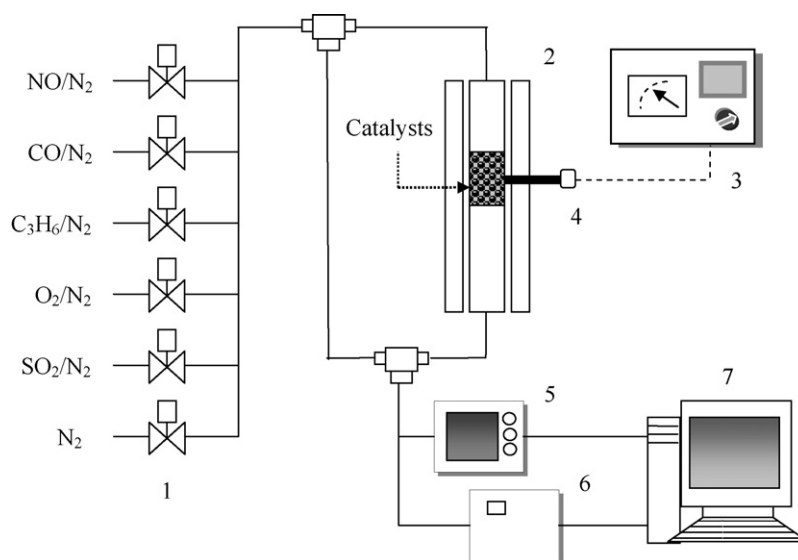

Fig. 1. Schematic of fixed-bed reaction system for activity test: (1) mass flow controller; (2) reactor; (3) temperature controller; (4) thermocouple; (5) flue gas analyzer; (6) GC-FID; (7) data output.

Table 1
Surface area and pore size diameter of fresh and reacted catalysts

Catalysts	BET surface area ($m^2 g^{-1}$)	Average pore size diameter (4 V/A by BET) (Å)
Al_2O_3 (support)	90	18.41
Rh/Al_2O_3 (fresh)	81	18.40
Rh/Al_2O_3 (0 ppm SO_2)[a]	85	18.41
Rh/Al_2O_3 (200 ppm SO_2)	85	18.40
Rh/Al_2O_3 (500 ppm SO_2)	84	18.46
$Rh–Na/Al_2O_3$ (fresh)	41	18.72
$Rh–Na/Al_2O_3$ (0 ppm SO_2)	50	18.72
$Rh–Na/Al_2O_3$ (200 ppm SO_2)	52	18.74
$Rh–Na/Al_2O_3$ (500 ppm SO_2)	40	18.74
Na/Al_2O_3 (fresh)	44	18.77
Na/Al_2O_3 (0 ppm SO_2)	37 (37)[b]	18.65 (18.65)[b]

[a] Reaction condition: [NO] = 200 ppm; [CO] = 200 ppm; $[O_2]$ = 6%, 250 °C and 120 min.
[b] Duplicate analysis.

lysts significantly decreased the BET surface areas of catalysts from 81 to 41 $m^2 g^{-1}$, and increased the pore size diameter from 18.41 to 18.72 Å. As shown in Fig. 2(a) and (b), the surfaces of Rh/Al_2O_3 catalysts comprised of dense and packed particles with a diameter of 150 nm, and the surfaces of $Rh–Na/Al_2O_3$ catalysts were covered with smooth and dispersive melted particles. Since the melting point of Na is lower (97.81 °C), many melts were formed when the Rh/Al_2O_3 catalysts were coated with Na and calcined at 500 °C for 6 h. The
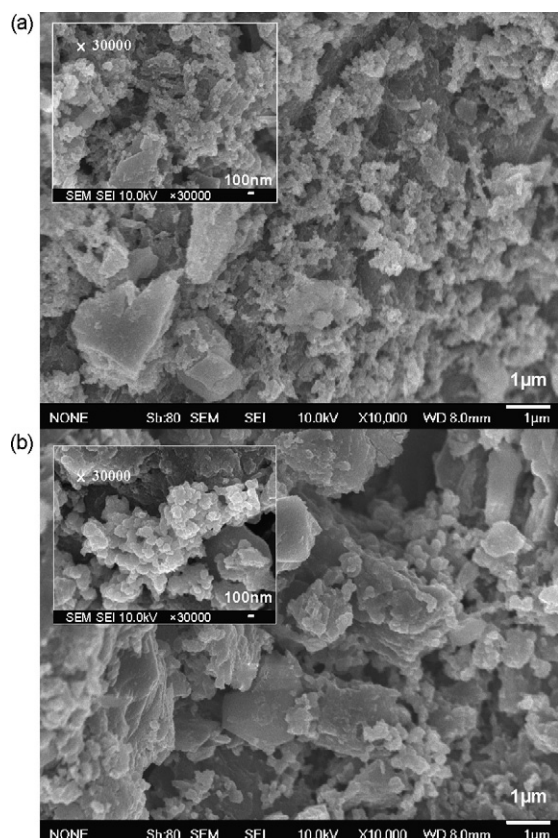

Fig. 2. SEM images (10,000× and 30,000×) of (a) Rh/Al_2O_3 and (b) $Rh–Na/Al_2O_3$ catalysts.
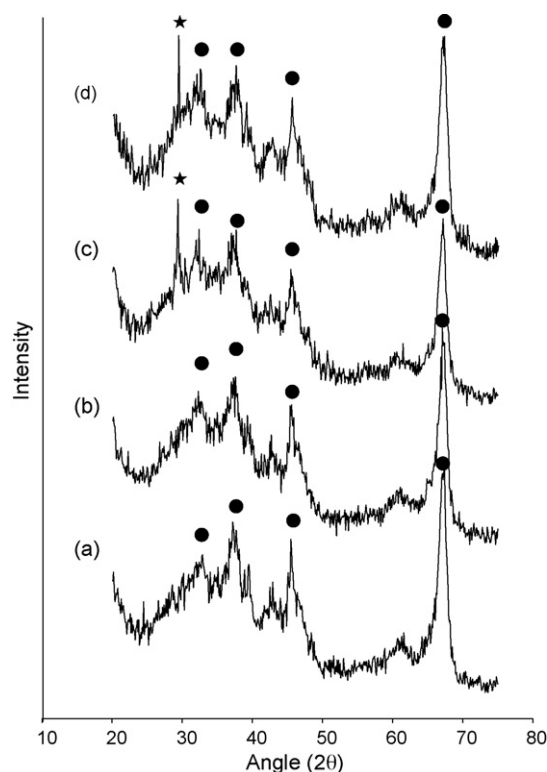
Fig. 3. XRD patterns of the catalysts: (a) Al_2O_3; (b) Rh/Al_2O_3; (c) $Rh–Na/Al_2O_3$; (d) Na/Al_2O_3. (★): Na; (●): γ-Al_2O_3.

particle sizes of $Rh–Na/Al_2O_3$ catalysts were larger than those of Rh/Al_2O_3 catalysts and their BET surface areas were lower. Table 1 also indicates that the BET surface areas of reacted Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts were slightly changed after they underwent the tests with SO_2 gas. These phenomena were attributed to the formation of some and their being adsorbed in the pore structures of catalysts during the activity tests [14].

Fig. 3 shows the XRD spectra of Rh/Al_2O_3, $Rh–Na/Al_2O_3$, Na/Al_2O_3 and Al_2O_3. The XRD patterns of every sample had peaks of γ-Al_2O_3 crystallites (2θ of 31.937, 45.765 and 66.760), and those of Na/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts had the peak of Na crystallite (2θ of 29.420). However, the XRD patterns contained no Rh crystallite peak because the concentration of Rh was lower than the XRD detection limit.

Table 2 lists the results of XPS analyses for Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts before and after activity tests. The binding energy (BE) of Al(2p) for fresh and reacted Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts were similar to that for Al_2O_3 in the literature [15]. The BE of Rh($3d_{5/2}$) was 308–309 eV for Rh_2O_3, which was attributed to Rh^{3+} [16,17]. This result reveals that the active metal Rh of Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts remained in the oxidation state, so they exhibited good activity for NO reduction even when SO_2 was present. For the catalysts after the activity tests, the BE of S(2p) at 165–168 eV and 169.4 eV were identical to those of SO_3^{2-} and SO_4^{2-}, respectively [17]. The BE of N(1s), 397–399 eV and 399–407 eV, corresponded to N^{3-} and NO^+, NO_2^-, NO_3^-, respectively [17,18]. These results demonstrated the possibility of the for-

Table 2
Results of XPS analyses for the catalysts

| Catalysts	Binding energy (eV)				
	Al(2p)	Rh($3d_{5/2}$)	Na(1s)	N(1s)	S(2p)
Rh/Al$_2$O$_3$ (fresh)	74.8	308.6	–	–	–
Rh/Al$_2$O$_3$ (C$_3$H$_6$ + 0 ppm SO$_2$)	74.8	308.6	–	399.2	–
Rh/Al$_2$O$_3$ (C$_3$H$_6$ + 100 ppm SO$_2$)	74.4	308.8	–	401.4	167.2
Rh/Al$_2$O$_3$ (CO + 0 ppm SO$_2$)	74.6	308.4	–	399.4	–
Rh/Al$_2$O$_3$ (CO + 200 ppm SO$_2$)	74.4	308.4	–	401.6	165.8
Rh/Al$_2$O$_3$ (CO + 500 ppm SO$_2$)	74.4	308.2	–	400.0	169.4
Rh–Na/Al$_2$O$_3$ (fresh)	74.2	308.4	1069.8	–	–
Rh–Na/Al$_2$O$_3$ (C$_3$H$_6$ + 0 ppm SO$_2$)	74.2	309.2	1070.2	399.4	–
Rh–Na/Al$_2$O$_3$ (CO + 0 ppm SO$_2$)	74.6	309.0	1070.4	397.6	–
Rh–Na/Al$_2$O$_3$ (CO + 200 ppm SO$_2$)	74.2	308.6	1069.6	406.8	168.0
Rh–Na/Al$_2$O$_3$ (CO + 500 ppm SO$_2$)	74.0	308.8	1070.0	401.0	166.2
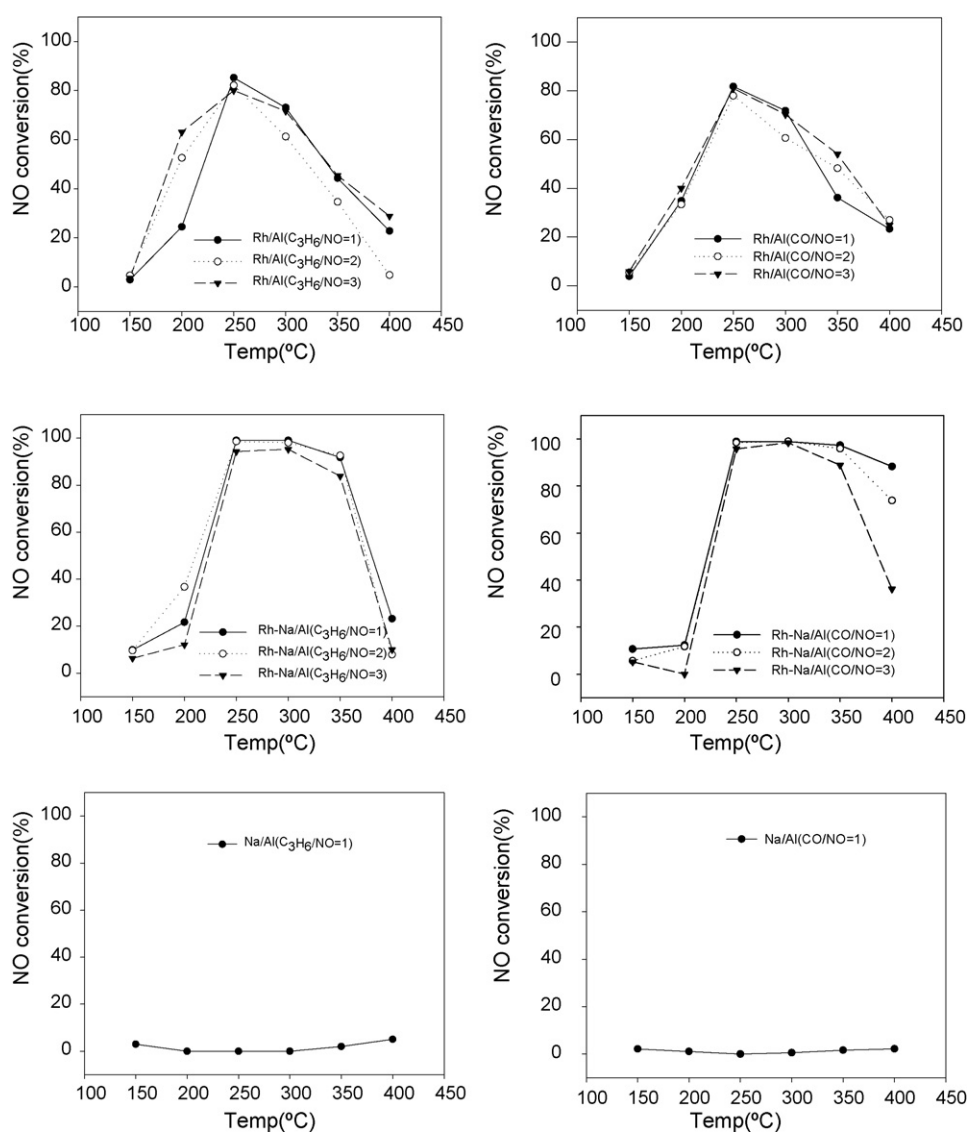
Fig. 4. Effects of reductant concentrations on NO conversion as a function of temperature. Reaction condition: [NO] = 200 ppm; [C$_3$H$_6$] = [CO] = 200–600 ppm; [O$_2$] = 6%; catalyst weight = 0.5 g.

mation of $NaNO_3$, Na_2SO_4 and $Al_2(SO_4)_3$ during the catalytic reactions.

3.2. Effect of concentration ratio of reductant/NO

Fig. 4 shows the conversion of NO by Rh/Al_2O_3, $Rh–Na/Al_2O_3$ and Na/Al_2O_3 catalysts with different concentration ratios of reductant/NO. The composition of the feeding gas mixture was 200 ppm NO, 200–600 ppm CO, 200–600 ppm C_3H_6, 6% O_2 and balanced as carrier gas N_2. As the concentration ratio of reductant/NO increased from 1 to 3, the curves of NO conversions versus operating temperature exhibited similar trends. The maximum NO conversions of Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts were both achieved at the concentration ratios of C_3H_6/NO and CO/NO equal to 1. Under the same conditions, Na/Al_2O_3 had relative lower NO conversion.
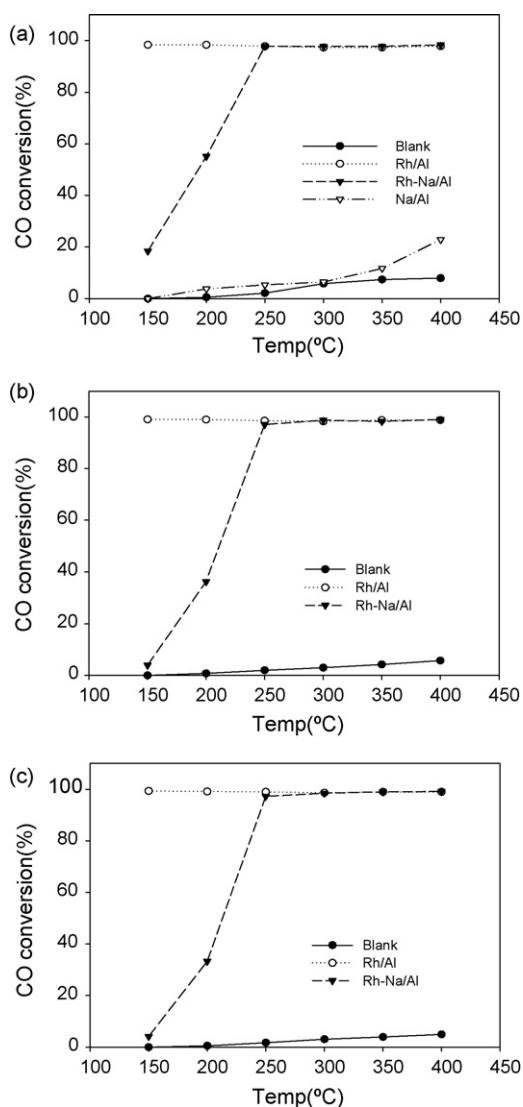

Fig. 5. Effects of reductant concentrations on CO conversion as a function of temperature: (a) CO/NO = 1; (b) CO/NO = 2; (c) CO/NO = 3. Reaction condition: [NO] = 200 ppm; [CO] = 200, 400 and 600 ppm; [O_2] = 6%; catalyst weight = 0.5 g.

Some tests were carried out with only one reductant (CO) and different CO/NO concentration ratios to understand the oxidation efficiency of reductants (Fig. 5(a)–(c)). The results indicate that Rh/Al_2O_3 catalysts offered very good CO oxidation efficiency even as the CO concentration was increased from 200 to 600 ppm. No residual CO remained in the flue gas. The reaction temperature for $Rh–Na/Al_2O_3$ catalysts must be higher than 250 °C to ensure CO conversion. The curves of CO conversion versus operating temperature were similar at different concentration ratios of reductant/NO. As expected, Na/Al_2O_3 did not have oxidation activity on CO conversion, even when the concentration ratio of CO/NO equal to 1 (Fig. 5(a)).

3.3. Effect of Na modification

The effects of Na modification and different reaction temperatures on the NO conversion are shown in Fig. 4. The operating temperatures were controlled in the range of 150–400 °C. The maximum NO conversions of Rh/Al_2O_3 catalysts with C_3H_6 or CO reductant were near 80% at 250 °C. This result reveals that Rh/Al_2O_3 catalysts had good reduction ability at lower temperatures and relative high oxygen conditions. Na/Al_2O_3 did not exhibit any activity on the NO conversion even when the reaction temperature was increased to 400 °C. When Na was added to modify the Rh/Al_2O_3 catalysts, the NO conversion increased to near 100% at 250–300 °C and the reaction window was widened to 300 °C. The Na-induced increase of NO conversion is ascribed to the enhancements of NO adsorption and dissociation on the surfaces of catalysts [10]. However, the NO conversion of Rh/Al_2O_3 catalysts was slightly suppressed by Na modification at a lower reaction temperature of 200 °C. The possible reason is the active sites of catalysts being blocked by Na compounds [10]. Fig. 5 also indicates that the CO conversions by $Rh–Na/Al_2O_3$ catalysts were decreased as the operating temperatures were lower than 250 °C. On the contrary, the CO conversions by Rh/Al_2O_3 catalysts approached 100% and remained stable at 150–400 °C.

3.4. Effect of reductant

Figs. 6 and 7 show the NO conversion with reductants C_3H_6 and CO, respectively, over Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts. The reaction temperature was controlled at 250 °C for Rh/Al_2O_3 catalysts and 250 and 300 °C for $Rh–Na/Al_2O_3$ catalysts. The reaction time was continued for 120 min to evaluate the long-time performance and stability of each catalyst. With C_3H_6 reductant, the NO conversions of Rh/Al_2O_3 catalysts at 250 °C could reach 80% and keep stable (Fig. 6). The possible mechanism for the $C_3H_6 + O_2 + NO$ reaction is as follows. The reaction gas NO is adsorbed on the active sites of Rh/Al_2O_3 catalysts, forming N(a) and O(a) (Eq. (1)) [6]. The reductant C_3H_6 firstly reacts with O_2 to form CO which is then adsorbed on the active sites (Eqs. (2) and (3)), before reacting with N(a) to form NCO(a) (Eq. (4)) [5]. Finally NCO(a) reacts with NO(a) to form N_2 and CO_2 (Eq. (5)) [5,6].
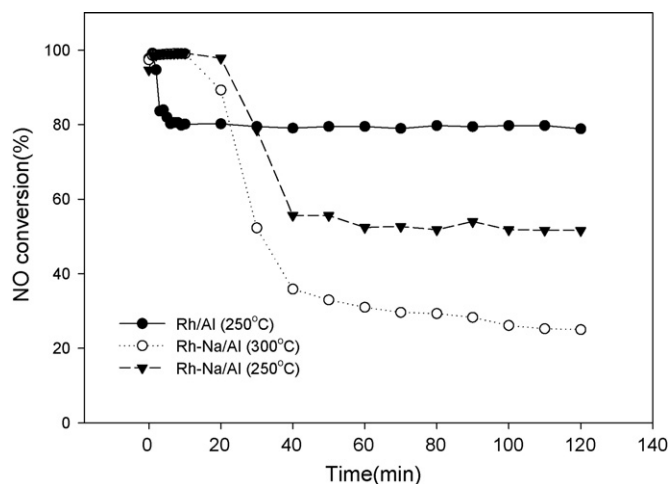
$$NO \rightarrow NO(a) \rightarrow N(a) + O(a) \tag{1}$$
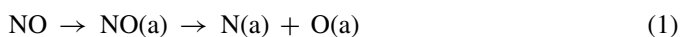
Fig. 6. Effects of C_3H_6 reductant on the conversions of NO over Rh/Al_2O_3 and Rh–Na/Al_2O_3 catalysts. Reaction condition: [NO] = 200 ppm; [C_3H_6] = 200 ppm; [O_2] = 6%; catalyst weight = 0.5 g.

$$C_3H_6 + O_2 \rightarrow [C_xH_yO_z] \rightarrow CO_x(CO + CO_2) + H_2O \quad (2)$$

$$CO \rightarrow CO(a) \quad (3)$$

$$N(a) + CO(a) \rightarrow NCO(a) \quad (4)$$
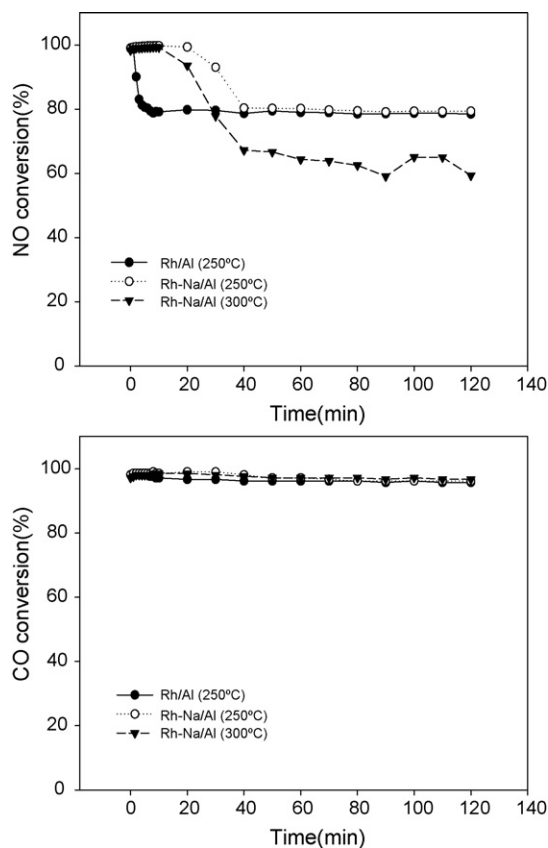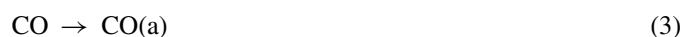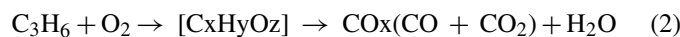
$$NCO(a) + NO(a) \rightarrow N_2 + CO_2 \quad (5)$$

Fig. 7. Effects of CO reductant on the conversions of NO and CO over Rh/Al_2O_3 catalysts. Reaction condition: [NO] = 200 ppm; [CO] = 200 ppm; [O_2] = 6%; catalyst weight = 0.5 g.

For Rh–Na/Al_2O_3 catalysts, the NO conversion increased to near 100% and kept stable for 10 min at 250 and 300 °C. When the reaction time exceeded 20 min, the NO conversion decayed to 51 and 25% at 250 and 300 °C, respectively. Although Na modification has been proposed to enhance the performances of Rh/Al_2O_3 catalysts on NO reduction in the absence of oxygen, the results were quite different as oxygen (6%) was present. The decrease of NO reduction by Na modification may be related to the formation of $NaNO_3$. Since NO may react with O_2 to form NO_2 or NO_3 on the active sites [19,20], the adsorbed NO_3 can react with Na to form $NaNO_3$. The adsorbed NO_3 cannot react with other materials on the surfaces of catalysts, so the performance of Na modified Rh/Al_2O_3 catalysts becomes worse. Additionally, C_3H_6 prefers to react with oxygen rather than NO at high temperature and under high oxygen conditions, the NO conversion is therefore decreased.

For CO reductant, the NO conversions of Rh/Al_2O_3 catalysts and Rh–Na/Al_2O_3 catalysts have similar trends with C_3H_6 reductant (Fig. 7). The Rh/Al_2O_3 catalysts have 80% NO conversion and 100% CO conversion. The possible reaction pathway is similar to that given by above Eqs. (1) and (3)–(5). The initial conversion of NO by Rh–Na/Al_2O_3 catalysts was 99% but this value remained stable for only 20 min. It had decreased from 99 to 80% after 20 min due to the formation of $NaNO_3$. After 40 min, the NO conversions were near 80 and 60% at 250 and 300 °C, respectively. Comparing the NO conversions with different reductants, the use of CO not only had higher NO conversion but also had better stability at 250 or 300 °C than C_3H_6. The possible reason for this difference is that CO reductant can react with NO immediately while C_3H_6 reductant needs to transform to CO before NO reduction can proceed.

3.5. Effect of SO_2

The effects of different SO_2 concentrations on Rh/Al_2O_3 catalysts are shown in Figs. 8 and 9. With C_3H_6 reductant, the NO conversion did not change significantly when 100 ppm SO_2 was contained in the feed gas (Fig. 8). The results also indicate that the SO_2 conversion reached 100% and kept stable for 120 min.
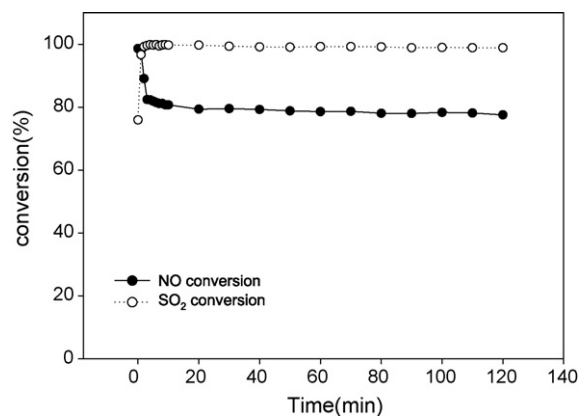

Fig. 8. Effects of SO_2 on the conversions of NO and SO_2 over Rh/Al_2O_3 catalysts. Reaction condition: [NO] = 200 ppm; [C_3H_6] = 200 ppm; [SO_2] = 100 ppm; [O_2] = 6%; catalyst weight = 0.5 g.
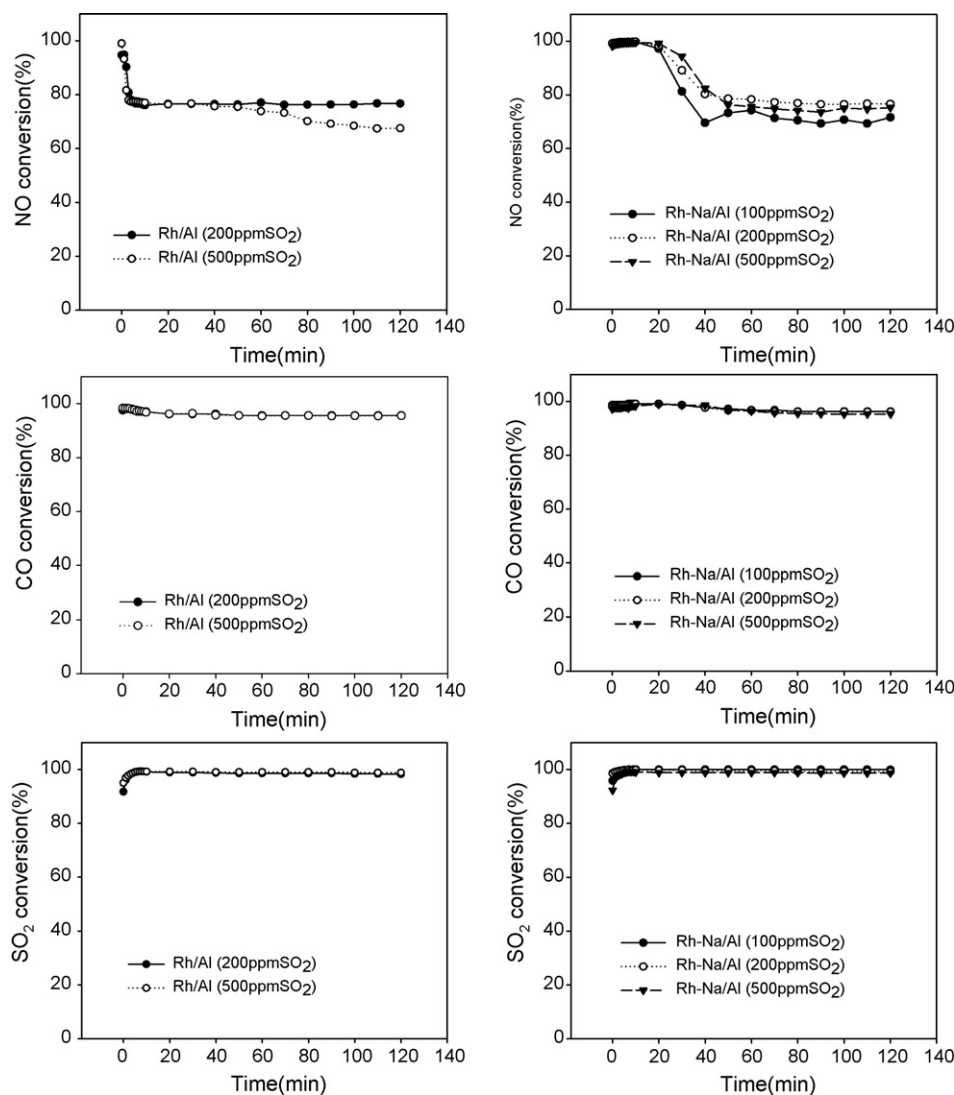
Fig. 9. Effects of different concentrations of SO_2 on the conversions of NO, CO and SO_2 over Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts. Reaction condition: [NO] = 200 ppm; [CO] = 200 ppm; [SO_2] = 100, 200 and 500 ppm; [O_2] = 6%; catalyst weight = 0.5 g.

Since the SO_2 is adsorbed on the catalysts and oxidized to SO_3, the SO_3 reacts with the supports to form aluminum sulfate [5]. Rh is active for not only the reduction of NO but also the oxidation of SO_2. Fig. 9 displays the conversions of NO, CO and SO_2 as functions of reaction time for Rh/Al_2O_3 catalysts with CO reductant. The concentrations of SO_2 were controlled at 200 and 500 ppm and the reaction temperature was 250 °C. The conversions of NO did not change with 200 ppm SO_2, but decreased to 68% after 80 min with 500 ppm SO_2. From the results of XPS analyses, some SO_4^{2-} species were found on the surface of Rh/Al_2O_3 catalysts as the feed gas contained excess oxygen and 500 ppm SO_2. The abundant SO_2 were adsorbed on the catalysts and reacted to form SO_3^{2-}. Since the active sits of catalysts were occupied by the adsorbed SO_3^{2-}, the NO conversion was thus decreased. This inference is supported by the work of Efthimiadis et al. [5], who found that more SO_2 than NO was absorbed on the active sites of catalysts. However, the conversion of SO_2 was very high (near 100%) and remained stable for 120 min even though the concentration of SO_2 in the feed gas was increased

to 500 ppm. The CO conversion was also high and stable at different concentrations of SO_2.

Fig. 9 shows the effects of SO_2 concentrations (100, 200 and 500 ppm) on $Rh–Na/Al_2O_3$ catalysts as functions of reaction time. The addition of Na in Rh/Al_2O_3 catalysts still promoted the initial conversion of NO (99%) with CO reductant at different SO_2 concentrations. When the reaction time was increased to 120 min, the NO conversions decreased slightly from 80 to 70, 76 and 75% at 100, 200 and 500 ppm SO_2, respectively. According to the results of XPS analyses (Table 2), NO_3^- and SO_3^{2-} were identified on the surfaces of $Rh–Na/Al_2O_3$ catalysts. These species may react with Na to form $NaNO_3$ and Na_2SO_4 and cause the NO conversions decreased. On the other hand, the conversions of CO and SO_2 over $Rh–Na/Al_2O_3$ catalysts were high and stable. Similar to the results of Rh/Al_2O_3 catalysts, different concentrations of SO_2 did not have significant effect on the conversions of CO and SO_2.

Totally speaking, Rh/Al_2O_3 catalysts have good ability for NO reduction with CO reductant in the presences of SO_2

and excess O_2. The NO conversion was high and stable at 0–200 ppm SO_2 but decreased at 500 ppm SO_2. Fortunately, the concentration of SO_2 in the flue gas from waste incineration is usually lower than 200 ppm. Rh/Al_2O_3 catalysts are effective for NO reduction under such flue gas conditions. Adding Na to Rh/Al_2O_3 catalysts can significantly improve the removal efficiency of NO at 250–300 °C and especially at relative high SO_2 concentrations. The $Rh–Na/Al_2O_3$ catalysts are also suggested to use under such flue gas conditions.

4. Conclusion

The catalytic reduction of NO with CO and C_3H_6 were carried out by Rh/Al_2O_3 and $Rh–Na/Al_2O_3$ catalysts in the simulated flue gas containing excess oxygen and different concentrations of SO_2. Rh/Al_2O_3 catalysts had good performances for NO reduction with CO reductant in the presences of SO_2 and excess oxygen. Adding Na to modify Rh/Al_2O_3 catalysts can increase the NO conversion and widen the reaction temperature windows and improved the performances at high SO_2 conditions. However, $Rh–Na/Al_2O_3$ catalysts do not have long-time activities for NO reduction due to the formations of $NaNO_3$ and Na_2SO_4.

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