Effects of Cerium Addition on the CO–NO Reaction Kinetics over Alumina-Supported Rhodium Catalysts

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Laboratory reactor experiments have shown that the addition of cerium to a low-loaded Rh/Al₂O₃ catalyst gives rise to the following changes in the CO–NO reaction kinetics: suppression of N₂O formation, decreased apparent activation energy, and a shift to a positive-order dependence of the rate on NO partial pressure. These cerium-induced modifications of the kinetics lead to enhancement of the NO reduction activity at low temperatures. A simple kinetic analysis and temperature-programmed desorption experiments suggest that higher rates for both the NO dissociation and the low-temperature N₂ desorption steps in the presence of Ce may be responsible for the changes in the CO–NO reaction kinetics observed here. @ 1990 Academic Press, Inc.

INTRODUCTION

Cerium oxide is generally added to automotive three-way catalysts as a promoter for the water-gas shift reaction or as an "oxygen storage" component under cycled air-fuel ratio conditions (1-4). It has also been reported that cerium stabilizes the alumina support against thermally induced surface area loss and increases/stabilizes the dispersion of noble metals (4-7).

In addition to these beneficial effects, cerium can alter the kinetic behavior (and thus the performance) of automotive catalysts as a result of its interaction with supported noble metals (8-11). Our recent kinetic study of CO oxidation over cerium-containing Rh/ Al_2O_3 catalysts (10) has shown that the addition of sufficient amounts of cerium oxides $(\geq 2 \text{ wt\% Ce})$ to the low-loaded Rh/Al₂O₃ catalyst suppresses the CO inhibition effect, lowers the apparent activation energy, and decreases the sensitivity of the reaction rate to O₂ partial pressure. These cerium-induced kinetic changes and the resulting CO oxidation activity enhancement were rationalized on the basis of a mechanism involving CO₂ formation via a reaction between CO adsorbed on Rh and surface oxygen derived from the neighboring ceria particles.

The present investigation was undertaken to extend our kinetic study of the Rh/Ce/ Al₂O₃ catalyst system to the CO–NO reaction, a major reaction pathway for removal of nitrogen oxides from automobile exhaust. Previous studies of the CO-NO reaction over supported Rh catalysts (12-14) have reported the formation of N₂O as a primary nitrogen-containing reaction product at low temperatures. Cho et al. (13) and McCabe and Wong (15) have recently shown that N₂O formed during the CO-NO reaction can undergo further reaction with CO to produce N_2 . Thus, the overall reaction scheme for the CO-NO reaction over supported Rh involves the three reactions

$$CO + NO \rightarrow \frac{1}{2}N_2 + CO_2 \qquad (1)$$

$$CO + 2NO \rightarrow N_2O + CO_2$$
 (2)

$$CO + N_2 O \rightarrow N_2 + CO_2 , \qquad (3)$$

where reaction (1) represents a direct pathway for N_2 formation which is favored at high temperatures. In this paper we have examined, in laboratory feedstreams, the kinetics of the CO–NO reaction over a series of alumina-supported Rh catalysts promoted with different levels of cerium additives. The activity and selectivity of the Rh/ Ce/Al₂O₃ catalysts for the CO–NO reaction are compared and contrasted with those of the Ce-free counterpart. The observed cerium-induced modifications of the reaction kinetics are then interpreted on the basis of the adsorption characteristics of the individual reactants on the Rh surface with and without Ce.

EXPERIMENTAL

The experimental apparatus and procedures used in this study are identical to those described previously (10). Steady-state reaction rates were measured in laboratory CO–NO feedstreams (in a N_2 background) using an internal-recycle mixed flow reactor (16) equipped with continuous gas analyzers (nondispersive IR for CO and CO₂, chemiluminescence detection for NO). This stainless-steel reactor operated at atmospheric total pressure, and the gases were agitated with a magnetically driven impeller placed under the stationary catalyst basket. The internal surfaces of the reactor were coated with a thin layer of aluminum oxide to minimize the blank activity. (Even at 450°C, less than 5% NO conversion was observed from the empty reactor.) All the data reported here were obtained at an impeller speed of 1500 rpm and a space velocity of 20,600 h^{-1} (a total feedstream flow rate of 5 liters/min through 7 g of catalyst). These experimental conditions provided good gas-phase mixing within the reactor, thus allowing the reactor to be characterized as a CSTR. Prior to each experiment the catalyst samples were reduced for 15 min in 5 vol% H₂ at 450°C after a 30-min treatment in 2 vol% O₂ at the same temperature. The catalyst activity and selectivity were characterized in two ways: (1) temperature run-up- experiments (from room temperature to 450°C) with fixed composition and (2) isothermal experiments with variable composition.

All experiments were carried out with the same series of Rh/Ce/Al₂O₃ catalysts (fixed Rh loading of 0.014 wt% and variable Ce loadings from 0 to 9 wt%) that were used in our earlier kinetic study (10). The catalysts were prepared by stepwise impregnation of

Al₂O₃ spheres (3.5 mm diameter, 112 m²/g BET surface area) to incipient wetness with aqueous solutions of Ce(NO₃)₃ and RhCl₃ (i.e., deposition of Ce followed by Rh, with a 4-h 500°C calcination step in between). The same calcination step followed the second (i.e., Rh) impregnation. Such procedures resulted in a shallow ($\leq 20 \mu$ m) Rh band near the pellets' outer edge and a uniform distribution of the Ce throughout the catalyst beads. The additional characteristics of the catalysts are given in Oh and Eickel (10).

As a limiting case of the $Rh/Ce/Al_2O_3$ system described above, a 0.014 wt% Rh catalyst supported on pure CeO₂ was prepared by pelletizing ceria powder and then impregnating the ceria pellets with an aqueous solution of RhCl₃. The ceria powder was synthesized by spray drying an aqueous solution of cerium nitrate, citric acid, and nitric acid (17), and then sintered at 800°C for 4 h in a muffle furnace before being ball milled overnight. The resulting powder was mixed with water containing 5% polyvinyl alcohol and extruded through a stainlesssteel tube to form cylindrical pellets approximately 5 mm long and 4 mm in diameter. These pellets were treated at 400°C to remove the H₂O and polyvinyl alcohol and then heated in a temperature-programmed oven at 5°C/min to 950°C. Such procedures vielded pellets with adequate mechanical strength and a stable BET area of 20 m^2/g . In view of the relatively small pore volume $(0.19 \text{ cm}^3/\text{g})$ of the support, an excess volume impregnation technique (rather than the conventional incipient wetness method) was employed for Rh deposition in order to minimize pellet-to-pellet variation in Rh concentration. After impregnation the catalyst was calcined in the usual manner (500°C, 4 h, air), and such procedures resulted in the deposition of the Rh near the periphery of the CeO_2 pellets.

Volumetric chemisorption, and temperature-programmed desorption (TPD) and infrared (IR) spectroscopies were used to characterize the H_2 , CO, and NO adsorption properties of the Rh/Al₂O₃ catalysts with and without Ce. The experimental apparatus and procedure, and the sample preparation techniques for the TPD and IR experiments have been described previously (18, 19). TPD spectra were obtained using the powder samples (~ 1 mg) scraped off the surface metal band of the Rh/Ce/Al₂O₃ catalysts used for the rate measurements. (The Rh loading in the powder sample is estimated to be ~ 0.5 wt%.) After a CO or NO dose at 0°C to the saturation coverage, the catalyst sample was heated under vacuum at a linear rate of 5°C/s while the partial pressures of desorbing gases were monitored using a mass spectrometer. IR spectra were taken at 150°C in flowing CO using 0.5 wt% Rh/Al₂O₃ and 0.5 wt% Rh/10 wt% Ce/ Al₂O₃ wafers each obtained by pressing approximately 100 mg of the impregnated powder into a 0.2-mm-thick, self-supporting disk. Note that the Rh loading in the wafers was selected to approximate the local Rh concentration in the shallow surface metal band of our 0.014 wt% Rh catalysts.

RESULTS

Effects of Ce Addition on Product Distribution

Earlier reactor studies of the CO–NO reaction over supported Rh conducted using mass spectrometry and gas chromatography (12, 13, 15) have shown that at low temperatures N₂O is the major nitrogen-containing reaction product while N₂ formation (either via an N₂O intermediate or direct recombination of N atoms) is favored at high temperatures. Thus, for the purpose of discussing the product distributions for the CO–NO reaction system, it is sufficient to consider the following two *stoichiometric* equations:

$$CO + 2NO \rightarrow N_2O + CO_2$$
$$CO + NO \rightarrow \frac{1}{2}N_2 + CO_2.$$

It follows from material balance considerations that

$$\Delta N_2 O = \Delta N O - \Delta C O, \qquad (4)$$



FIG. 1. The CO–NO reaction stoichiometry as a function of temperature over $0.014 \text{ wt}\% \text{ Rh}/\text{Al}_2\text{O}_3$ with and without Ce in a feedstream containing 1 vol% CO and 0.1 vol% NO.

where Δ refers to the amounts of reactants (product) consumed (produced) during the reaction. The relationship given by Eq. (4) has been experimentally verified for Rh/ Al₂O₃ (13). Equation (4) can be rearranged to give

$$\frac{\Delta N_2 O}{\Delta NO} = 1 - \frac{\Delta CO}{\Delta NO} , \qquad (5)$$

which states that the selectivity to N_2O is directly related to the CO-NO reaction stoichiometry characterized by the ratio between ΔCO and ΔNO . Since our reactor system is not equipped to directly measure N₂O formation, we chose to use the ratio $\Delta NO/$ ΔCO as a convenient way to monitor the selectivity for forming N₂O versus N₂. Note that $\Delta NO/\Delta CO = 1$ corresponds to no N₂O formation, while $\Delta NO/\Delta CO = 2$ to 100% N₂O selectivity. Figure 1 shows plots of $\Delta NO/\Delta CO$ versus temperature for 0.014 wt% Rh/Al₂O₃ (solid circles) and 0.014 wt% Rh/9 wt% Ce/Al₂O₃ (open circles). The data of Fig. 1 were generated during temperature run-up experiments in a feedstream containing 1 vol% CO and 0.1 vol% NO. In accordance with results previously reported for supported Rh without Ce (12, 13), the CO-NO reaction over the Rh/Al₂O₃ catalyst is characterized by high selectivities to N₂O (i.e., $\Delta NO/\Delta CO$ approaching 2) at low temperatures and by high selectivities to N₂ at



FIG. 2. The CO–NO reaction stoichiometry as a function of temperature over $0.014 \text{ wt\% Rh/Al}_2O_3$ with and without Ce in a feedstream containing 0.1 vol% CO and 0.5 vol% NO.

high temperatures (i.e., $\Delta NO/\Delta CO \approx 1$; $T > 300^{\circ}$ C). For the Ce-containing Rh/Al₂O₃ catalyst, on the other hand, $\Delta NO/\Delta CO \simeq 1$ was observed over the entire temperature range investigated here. (Reliable measurements of $\Delta NO/\Delta CO$ were not feasible at temperatures below 250°C because the NO conversion was too low.) This indicates that the addition of cerium to the Rh/Al₂O₃ catalyst suppresses the formation of N₂O in the reducing feedstream containing 1 vol% CO and 0.1 vol% NO. When the feedstream contains a large excess of NO over CO, however, the product selectivity changes little upon Ce addition and is dominated by N₂O formation over a wide range of temperatures (see Fig. 2).

Effects of Ce Addition on Kinetics

The apparent activation energy for the CO–NO reaction kinetics over supported Rh has been reported to change with temperature (12). An Arrhenius plot of our rate data for the 0.014 wt% Rh/Al₂O₃ catalyst (Fig. 3) shows the same trend; that is, the apparent activation energy changes from 28 kcal/mol at $T < 280^{\circ}$ C to 38 kcal/mol at $T > 280^{\circ}$ C. Generally, such an increase in activation energy with temperature indicates a shift in the rate-controlling step to an alternate or parallel path (20). (This change in activations because, contrary to our obser-



FIG. 3. Arrhenius plot for CO_2 production rate over 0.014 wt% Rh/Al₂O₃ in a reactant mixture containing 1 vol% CO and 0.5 vol% NO.

vation, they would cause the activation energy to decrease with increasing temperature.) As will be discussed later, the change in the activation energy depicted in Fig. 3 is likely to reflect a shift in the rate-controlling step from the low-temperature N_2O/N_2 formation path (involving reactions between NO_a and N_a) to the high-temperature N_2 formation path (involving recombination of N_a) as the catalyst temperature is increased. In contrast, the CO–NO reaction over the Rh/ Al_2O_3 catalyst containing 9 wt% Ce is characterized by a constant apparent activation energy of ~18 kcal/mol throughout the temperature range investigated (see Fig. 4).

The results discussed above certainly at-



FIG. 4. Arrhenius plot for CO_2 production rate over 0.014 wt% Rh/9 wt% Ce/Al₂O₃ in a reactant mixture containing 1 vol% CO and 0.5 vol% NO.



FIG. 5. Arrhenius plots for CO_2 production rates over 0.014 wt% Rh/Al₂O₃ containing variable levels of Ce in a reactant mixture containing 1 vol% CO and 0.5 vol% NO.

test to the modifications of the catalytic properties of the Rh/Al₂O₃ catalysts in the presence of 9 wt% Ce. In order to investigate how the kinetic behavior of the Rh/Ce/ Al₂O₃ catalysts changes with Ce loading, we conducted additional temperature runup experiments with 0.014 wt% Rh/Al₂O₃ catalysts containing 0.5 and 2 wt% Ce. The results of such experiments are presented in Fig. 5 in Arrhenius plots of the reaction rates measured in the reactant stream containing 1 vol% CO and 0.5 vol% NO. For direct comparison, the rate data for the cases of 0 and 9 wt% Ce are also reproduced in the same figure. It can be seen from Fig. 5 that the reaction rate (as well as the apparent activation energy) over the Rh/Al₂O₃ catalyst is not significantly altered by the addition of 0.5 wt% Ce. Note, however, that the Ce additive at a 2 wt% level is nearly as effective as that at a 9 wt% level in modifying the kinetic behavior of the Rh/Al₂O₃ catalyst; that is, the rate data for the Rh/Al_3O_3 catalysts containing both 2 and 9 wt% Ce are clustered closely and are characterized by substantially higher reaction rates (more than five times for $T < 250^{\circ}$ C) and lower apparent activation energies than the Cefree counterpart. Table 1 shows the activation energy values determined from the rate data of Fig. 5. Two values are listed for each of the samples containing 0 or 0.5 wt% Ce—the first for temperatures below 270°C and the second for temperatures between 285 and 300°C.

Furthermore, the addition of cerium to the Rh/Al₂O₃ catalyst alters the dependence of the reaction rate on the partial pressures of the individual reactants. Table 2 compares the exponents of the power-law rate expressions for the CO-NO reaction over Rh/Al₂O₃, Rh/Al₂O₃ containing 9 wt% Ce, and Rh/CeO₂. The parameter values listed in Table 2 were obtained from the reaction rates measured under isothermal conditions (260°C for Rh/Al₂O₃ and Rh/Ce/Al₂O₃; 275°C for Rh/CeO₂) while varying the CO concentration between 1 and 5 vol% and the NO concentration between 0.1 and 0.8 vol%. In accord with Hecker and Bell (12), the Rh/Al₂O₃ catalyst exhibits a weak positive-order dependence (+0.11) on the partial pressure of CO and a weak negativeorder dependence (-0.05 for CO consumption rate and -0.14 for NO consumption rate) on the partial pressure of NO. Upon addition of 9 wt% Ce to the Rh/Al₂O₃ catalyst, the reaction rate becomes negative order in CO and positive order in NO. It is interesting to note that the small negativeorder dependence on $P_{\rm CO}$ and the moderate positive-order dependence on $P_{\rm NO}$ observed for Rh/Ce/Al₂O₃ carry over to the ceria-supported Rh catalyst (i.e., 100% Ce).

Effects of Ce Addition on Adsorption Characteristics

In order to obtain a mechanistic understanding of the Ce-induced changes in activ-

TABLE	1
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Apparent	Activation	Energy	as	a	Function
	of Ce	Loading			

Ce loading (wt%)	Activation energy (kcal/mol)
0	28, 38
0.5	29, 38
2	19
9	18

TABLE	2
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Power-Law Parameters for the CO-NO Reaction

	CO consum	CO consumption rate ^a		NO consumption rate ^a		
	m	n	m	п		
Rh/Al_2O_3 $Rh/Ce/Al_QO_3$	$+0.11 \pm 0.01$ -0.09 ± 0.03	-0.05 ± 0.01 +0.40 ± 0.07	$+0.11 \pm 0.02$ -0.19 ± 0.03	-0.14 ± 0.02 +0.30 ± 0.08		
Rh/CeO_2	-0.12 ± 0.03	$+0.53 \pm 0.01$	-0.18 ± 0.05	$+0.50 \pm 0.03$ $+0.54 \pm 0.02$		

^{*a*} Rate $\alpha P_{\rm CO}^m P_{\rm NO}^n$.

ity and selectivity we have described thus far, it would be instructive to examine the adsorption characteristics of the individual reactants on the catalyst surface with and without Ce. In this section we discuss the adsorptive properties of CO, NO, and H₂ characterized by volumetric chemisorption, TPD, and IR.

The catalysts' capacities for adsorbing H₂ and CO were measured at 35°C as a function of Ce loading using a constant-volume chemisorption apparatus (Micromeritics ChemiSorb 2800). The standard pretreatment given all samples included flowing O₂ for 1 h, flowing H₂ for 1 h, and evacuation for 2 h (all at 450°C) followed by cooling to 35°C under vacuum. Catalysts with a nominal Rh loading of 0.5 wt% (actual loading = 0.495 wt%) were used for more reliable chemisorption measurements. The uptake values reported in Table 3, obtained by extrapolating to zero pressure the linear isotherms measured over the range from 10 to 27 kPa, represent the amounts of the individ-

ual adsorbates irreversibly adsorbed onto the catalyst. H₂ uptake is virtually independent of the Ce loading and corresponds to ~60% Rh dispersion when 1:1 chemisorption stoichiometry is assumed between surface Rh atoms and adsorbed hydrogen atoms. CO uptake is little affected by the presence of 2 wt% Ce; however, a moderate decrease in CO uptake (by \sim 13%) was observed when 9 wt% Ce was added to the Rh/ Al₂O₃ catalyst. The observation of CO/Rh atomic ratios in excess of unity indicates that at least part of the Rh exists as isolated atoms or ions, forming a dicarbonyl species (i.e., two CO molecules on one Rh site) during CO chemisorption.

The presence of a dicarbonyl species on the catalyst surface was confirmed by IR spectroscopy of CO adsorption on the 0.5 wt% Rh/Al₂O₃ catalysts with and without Ce. As shown in Fig. 6, both the Rh/Al_2O_3 and the Rh/10 wt% Ce/Al₂O₃ catalysts exhibit essentially the same spectral features: a combination of the linear-CO band (at

Effect of Ce Loading on H_2 and CO Adsorption						
Metal content (wt%)	H ₂		СО			
	Uptake (µmol/g)	H/Rh	Uptake (µmol/g)	CO/Rh		
0.5 Rh/0 Ce/Al ₂ O ₃	14.7	0.61	77.3	1.59		
0.5 Rh/2 Ce/Al ₂ O ₃	15.1	0.62	75.2	1.55		
$0.5 \text{ Rh/9 Ce/Al}_2O_3$	14.3	0.59	67.9	1.40		

TABLE 3



FIG. 6. IR spectra (displaced vertically for clarity) of CO adsorbed on 0.5 wt% Rh/Al_2O_3 with and without Ce. The spectra were taken at 150°C in flowing CO.

 \sim 2060 cm⁻¹, associated with reduced, contiguous Rh surfaces) and the dicarbonyl bands (at 2085 and 2020 cm⁻¹, associated with isolated Rh sites). Although not shown in Fig. 6, the intensity of the bridged-CO band near 1850 cm⁻¹ was low. It is interesting to note that the frequencies for both the dicarbonyl and the linear-CO species remain virtually unchanged upon Ce addition to the Rh/Al₂O₃ catalyst. This suggests the absence of appreciable electronic effects caused by the Ce additive. Close similarities in IR spectra of CO adsorbed at room temperature on Rh/SiO2 with and without Ce have also been reported by Solymosi et al. (21).

The adsorptive properties of CO and NO on Rh/Al₂O₃ with and without Ce were also characterized by temperature-programmed desorption (TPD) spectroscopy. Figure 7 compares the TPD spectra of CO obtained using the powder samples scraped off the surface band of the 0.014 wt% Rh/Al₂O₃ catalysts containing 0, 2, and 9 wt% Ce. Each of the spectra in Fig. 7, collected after a CO dose to the saturation coverage, exhibits two distinct CO desorption peaks: one around 50°C (associated with CO weakly adsorbed onto the blank alumina support) and the other around 230°C (associated with CO adsorbed on Rh). Considering the rather broad and poorly resolved nature of the spectra, the small shift in the position of the high-temperature peak (± 5 about 230°C) from one spectrum to another is probably insignificant. Thus, in accord with the IR results described above, the CO adsorption characteristics on supported Rh do not appear to be significantly altered by the presence of cerium.

In contrast, substantial changes in NO TPD spectra were observed when cerium was added to the Rh/Al₂O₃ catalyst. Figure 8 shows the TPD curves obtained after saturation coverage of NO for the 0.014 wt% Rh/Al₂O₃ catalysts containing 0, 2, and 9 wt% Ce. For all three catalysts studied, both molecular NO and N₂O desorb in a single, broad peak centered near 150°C. The major difference in the NO TPD spectra of Fig. 8 lies in the N₂ desorption features shown by the dashed curves. For Rh/Al₂O₃ itself (spectrum a), most N₂ desorbs in a peak centered at 430°C, with a small amount desorbing at lower temperatures (<200°C). A similar N₂ desorption spectrum has been observed during a recent TPD study of NO on small (~25 Å) Rh particles supported on α -Al₂O₃ (22). The addition of 2 wt% Ce (spectrum b) increases substantially the amount of N₂ desorbed at low temperatures, forming a desorption peak near 140°C. When 9 wt% Ce was added to the Rh/Al₂O₃ catalyst



FIG. 7. TPD spectra (displaced vertically for clarity) of CO from 0.014 wt% Rh/Al_2O_3 with and without Ce. The samples were initially saturated with CO at 0°C.



FIG. 8. TPD spectra of NO from 0.014 wt% Rh/ Al_2O_3 with and without Ce. The samples were initially saturated with NO at 0°C.

(spectrum c), the intensity of this low-temperature N₂ desorption peak increased further (without significantly changing its position) and became even stronger than that of the high-temperature peak. Thus, the major effect of Ce addition on NO TPD features is the enhancement of the low-temperature $(\sim 140^{\circ}C)$ N₂ desorption peak. Separate TPD experiments with 9 wt% Ce/Al₂O₃ (but containing no Rh) showed no appreciable desorption of nitrogen-containing species, indicating little adsorption of NO on Ce/ Al_2O_3 . This suggests that the Ce-induced changes in the N₂ desorption spectra described above are not due to additional desorption features derived from the Ce by itself, but to interactions between Rh and Ce on the catalyst surface.

The low-temperature N₂ peak observed for the Ce-containing Rh/Al₂O₃ catalysts is perhaps best attributed to the reaction of atomic nitrogen with molecularly adsorbed NO (i.e., NO_a + N_a \rightarrow N₂ + O_a + S). This interpretation is supported by the spectra shown in Fig. 8; the fact that the low-temperature N₂ peak is observed only under conditions where NO desorption occurs concurrently suggests that N₂ is formed at low temperatures via a reaction involving molecularly absorbed NO (23). Since the N_2O peak also appears at about the same temperature as the NO peak, it is reasonable to assume that N_2O is formed by the reaction $NO_a + N_a \rightarrow N_2O + 2S (12, 13, 23)$. The high-temperature N₂ peak centered at 430°C is ascribed to the recombination of adsorbed nitrogen atoms (23, 24), because previous spectroscopic studies have shown that all adsorbed NO has either desorbed or dissociated by the time the catalyst surface reaches that temperature (25, 26). The peak temperature of 430°C observed here is similar to the temperature of the high-temperature N_2 peak on Rh(100) (27).

DISCUSSION

The discussion presented in the preceding section on the interactions of NO and CO with Rh surfaces suggests that the mechanism of the CO–NO reaction over supported Rh can be represented by the following set of elementary processes:

$$CO + S \rightleftharpoons CO_a$$
 (6)

$$NO + S \rightleftharpoons NO_a$$
 (7)

$$NO_a + S \rightarrow N_a + O_a$$
 (8)

$$NO_a + N_a \rightarrow N_2O + 2S$$
 (9)

$$NO_a + N_a \rightarrow N_2 + O_a + S \qquad (10)$$

$$N_a + N_a \rightarrow N_2 + 2S \tag{11}$$

$$CO_a + O_a \rightarrow CO_2 + 2S.$$
 (12)

The underlying assumption in the interpretation of our data is that the basic reaction mechanism described above remains unchanged upon Ce addition, but the rates of the individual elementary reaction steps can be affected by the presence of Ce. Previous studies (13, 15) have shown that N₂O can dissociatively adsorb and undergo further reaction with CO on supported Rh surfaces; however, due to very weak adsorption of N₂O molecules and their slow dissociation on the surface, the rate of the N₂O-CO reaction was found to be negligibly low in the temperature range of our kinetic experiments ($<300^{\circ}$ C). Consequently, steps involving readsorption and surface reaction of N₂O have not been incorporated into the mechanism proposed above.

The rate of NO consumption during the CO-NO reaction, \tilde{R}_{NO} , is given by

$$\hat{R}_{\rm NO} = 2r_{\rm N_2} + 2 r_{\rm N_2O}, \qquad (13)$$

where r_{N_2} and r_{N_2O} denote the rates of N₂ and N₂O formation, respectively. From reactions 9 through 11, r_{N_2} and r_{N_2O} can be expressed, in terms of the surface coverages θ values, as

$$r_{\mathrm{N}_2} = k_{\mathrm{N}_{2,\mathrm{L}}} \theta_{\mathrm{NO}} \theta_{\mathrm{N}} + k_{\mathrm{N}_{2,\mathrm{H}}} \theta_{\mathrm{N}^2} \qquad (14)$$

$$r_{\rm N_2O} = k_{\rm N_2O} \theta_{\rm NO} \theta_{\rm N}, \tag{15}$$

where $k_{N_{2,L}}$, $k_{N_{2,H}}$, and $k_{N_{2}O}$ are the rate constants for reactions (10), (11), and (9), respectively. Substitution of Eqs. (14) and (15) into Eq. (13) yields

$$\vec{R}_{\rm NO} = 2 \left[(k_{\rm N_{2,L}} + k_{\rm N_{2}O}) \theta_{\rm NO} \theta_{\rm N} + k_{\rm N_{2,H}} \theta_{\rm N}^2 \right].$$
(16)

The first term on the right-hand side of Eq. (16) is associated with the formation of N_2 and N₂O at low temperatures, while the second term is associated with the high-temperature N₂ formation step involving recombination of adsorbed N atoms. In the temperature range of our rate measurements (<300°C), the overall reaction rate over Cecontaining Rh/Al₂O₃ would be dominated by the first term of Eq. (16), with little contribution from the second term which has a much higher activation energy (estimated to be ~40 kcal/mol from Fig. 8). For Rh/Al_2O_3 , however, the low-temperature processes represented by the first term are strongly suppressed (as evidenced by their low intensities in the TPD spectra of Fig. 8a) and thus cannot dominate the CO-NO reaction kinetics throughout the temperature range of interest here. Consequently, as illustrated in Fig. 3, the rate data for Rh/Al_2O_3 are characterized by two distinct apparent activation energies—one corresponding to the low-temperature processes (reactions (9) and (10)) and the other to the high-temperature process (reaction (11)).

A kinetic analysis of the CO-NO reaction by Hecker and Bell (12) indicates that when the dissociation of NO (reaction (8)) is the rate-limiting step, the catalyst surface would be predominantly covered with molecularly adsorbed NO and thus a negative first-order dependence on NO partial pressure (i.e., strong NO inhibition effect) is expected for the overall reaction rate. However, our rate data in Table 2 show drastically different dependencies on NO partial pressure: -0.05 or -0.14 for Rh/Al₂O₃ and +0.40 or +0.30 for Rh/Ce/Al₂O₃. Such weak negative or moderate positive reaction orders in NO suggest that the NO dissociation rate over the Ce-free and Ce-containing Rh/ Al₂O₃ catalysts is fast enough not to be ratelimiting under the conditions of our experiments. Our earlier kinetic modeling study of the CO-NO reaction over Rh (28) has shown that when the NO dissociation rate is reasonably rapid, the catalyst surface is largely covered with both adsorbed nitrogen atoms and molecularly adsorbed NO, and the surface coverages by CO_a, O_a and vacant sites are very small. (The low surface coverage of CO is a direct consequence of the increased CO desorption rate resulting from strong N_a-CO_a repulsive interactions on the surface (28).) Thus,

$$\theta_{\rm NO} + \theta_{\rm N} \approx 1.$$
 (17)

At 260°C, where the isothermal data of Table 2 were obtained for Rh/Al_2O_3 and $Rh/Ce/Al_2O_3$, the NO consumption rate given by Eq. (16) can be approximated by

$$\tilde{R}_{\rm NO} \approx 2(k_{\rm N_{2,L}} + k_{\rm N_{2}O})\theta_{\rm NO}\theta_{\rm N}.$$
 (18)

Upon substitution of Eq. (17), Eq. (18) becomes

$$\tilde{R}_{\rm NO} \approx 2(k_{\rm N_{2,L}} + k_{\rm N_{2}O})\theta_{\rm NO}(1 - \theta_{\rm NO}).$$
 (19)

Equation (19) indicates that the rate of the CO-NO reaction at low temperatures would

exhibit a positive-order dependence on NO partial pressure at low surface coverages of NO and a negative-order dependence at high θ_{NO} . This implies that under the conditions of our isothermal experiments at 260°C, the surface of the Rh/Al₂O₃ catalyst is covered with a relatively high concentration of adsorbed NO molecules ($\theta_{NO} > 0.5$) while the surface coverage of NO for the Ce-containing Rh/Al₂O₃ catalyst is low. This difference in the surface coverage of NO under reaction conditions strongly suggests that the NO dissociation rate is substantially higher on Rh/Ce/Al₂O₃ than it is on its Ce-free counterpart.

Regarding the mechanism by which ceria promotion of Rh/Al₂O₃ might enhance the dissociation of NO, it is conceivable that near the perimeter of ceria islands, NO can adsorb in such a fashion that the nitrogen end of the molecule is attached to the Rh and the oxygen end to an oxygen-deficient cerium species. This concurrent interaction of both ends of the NO molecule with the catalyst surface should weaken the N-O bond and thereby facilitate NO dissociation. A similar mechanism has been proposed to explain the effects of metal oxide promoters on the dissociation of CO (29-32). Further spectroscopic work aimed at directly monitoring NO dissociation would be required to clarify and verify our mechanistic hypothesis on the role of ceria additives in facilitating the dissociation of NO on supported Rh surfaces.

The underlying reasons for the weak lowtemperature N_2 desorption peak observed for Rh/Al₂O₃ in Fig. 8 are uncertain. In principle, the suppression of the low-temperature N_2 desorption feature (which involves a reaction between adsorbed NO and N) can occur as a result of low surface concentrations of N atoms encountered when the NO dissociation step is slow enough to be ratelimiting. However, this possibility can be ruled out on the basis of the NO partial pressure dependencies presented in Table 2, which suggest that the NO dissociation step on Rh/Al₂O₃, although slower than that on Rh/Ce/Al₂O₃, is reasonably fast. Our argument is further supported by the results of a recent NO TPD study by Altman and Gorte (22). Thus, the difference in the low-temperature N₂ desorption rates between Rh/Al₂O₃ and Rh/Ce/Al₂O₃ shown in Fig. 8 is likely to reflect changes in the intrinsic rate of N atom removal from the surface, rather than changes in surface concentrations caused by different NO dissociation kinetics.

Equation (16) indicates that the selectivity of Rh for forming N₂ versus N₂O at low temperatures is determined by the relative magnitudes of the rate constants, $k_{N_{21}}$ and $k_{\rm N,O}$. The low intensities of the low-temperature N_2 and N_2O peaks in the TPD spectra for Rh/Al₂O₃ shown in Fig. 8a make it difficult to draw a definite conclusion about their relative magnitudes. However, it is clear from Figs. 8b and 8c that an increase in the Ce loading increases the intensity of the lowtemperature N_2 peak relative to that of the N_2O peak. This observation is consistent with the results of our reactor experiments, which show the suppression of N₂O formation in the presence of cerium (see Fig. 1).

CONCLUSIONS

Our laboratory reactor experiments have shown that the addition of cerium to a lowloaded Rh/Al₂O₃ catalyst results in modifications of the kinetics of the CO-NO reaction. The Ce-induced changes in the kinetics include suppression of N₂O formation, decreased apparent activation energy, and a shift to a positive-order dependence of the rate on NO partial pressure. Results of IR and TPD studies show that the CO adsorption characteristics on Rh/Al₂O₃ are not significantly altered by the presence of Ce. However, substantial differences were observed in the N₂ desorption features during NO TPD from Rh/Al₂O₃ and Rh/Ce/Al₂O₃. The major difference is in the amount of N₂ desorbing in the low-temperature peak centered around 140°C, which is assigned to a reaction between adsorbed NO and N atoms; the intensity of the low-temperature N₂ desorption peak increases substantially as cerium is added to the Rh/Al₂O₃ catalyst. Also, the simple kinetic analysis presented here suggests that the surface coverage of NO under reaction conditions is higher on Rh/Al₂O₃ than it is on Rh/Ce/Al₂O₃, presumably as a result of a higher NO dissociation rate in the presence of Ce. This enhancement of the NO dissociation rate and the low-temperature N₂ desorption rate appears to be responsible for the observed Ceinduced modifications of the CO–NO reaction kinetics.

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