Infrared Characterization of Rh Surface States and Their Adsorbates during the NO-CO Reaction

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Rh surface states and their adsorbates during the NO–CO reaction have been characterized by the in situ infrared (IR) coupled with temperature-programmed reaction (TPR) technique. The TPR profiles of adsorbates and CO₂ show that Rh surface states and their adsorbates are governed by the redox reaction cycle of NO–CO. Adsorbed oxygen from dissociated NO oxidizes Rh⁰ to Rh⁺; adsorbed CO reduces Rh⁺ to Rh⁰. The extent of oxidation and reduction of Rh⁰/Rh⁺ is in part reflected in the intensity of the adsorbates residing on these sites (i.e., Rh⁺(CO)₂, Rh⁰–CO, Rh–NO⁺, and Rh⁰–NO⁻). An increasing NO/CO ratio shifts the TPR profiles of Rh⁺(CO)₂, NO conversion, and light-off to higher temperatures. The results reveal that a high NO/CO ratio or high concentration of oxidant enhances the extent of oxidation of Rh⁰ to Rh⁺, resulting in low catalyst activity for NO reduction. Keeping the Rh surface in the Rh⁰ state by a low NO/CO ratio decreases the Rh⁺(CO)₂ intensity and shifts the light-off to a lower temperature. O₂, H₂, and C₃H₈ present in simulated gas compete with NO and CO for the Rh site, lowering NO reduction activity.

Introduction

Changes in the catalyst state during reaction have long been recognized in catalysis.^{1–8} In homogeneous catalysis, the catalyst precursor transforms to the active catalyst form through ligand addition and dissociation.⁹ In heterogeneous catalysis, the catalyst surface state could undergo various forms of transformation (e.g., oxidative disruption, reductive agglomerization, redispersion, sintering, etc.), depending on the reaction environment.^{1–8,10} Despite the recognition of the possible changes in the catalyst surface state, understanding of catalyst surface states under reaction conditions has been limited. This is due to the difficulties in in situ characterization of catalyst surfaces under practical reaction conditions.

The most investigated catalysts for surface reconstruction during adsorption and reaction processes are Rh catalysts^{1,3,4,10-28} because of their important role in the automobile catalytic converter. Yang and Garland were the first to observe that adsorption of CO over Rh⁰ crystallite on SiO₂ or Al₂O₃ caused disruption of the Rh⁰ crystallites.¹ Solymosi and co-workers have found that CO adsorption on Rh led to oxidative disruption of the Rh⁰ crystallites to isolated Rh⁺ at 300 K, while CO adsorption on isolated Rh⁺ sites at temperatures above 448 K resulted in the formation of Rh⁰ crystallites.^{15,19,27} The former was termed as CO-induced oxidative disruption and the latter as CO-induced reductive agglomerization.¹⁵ The CO-induced oxidative disruption process was further shown to be involved with surface OH and was facilitated on small Rh crystallites.¹⁶ The process can be assisted by NO, which oxidizes Rh⁰ to $Rh^{+}.^{15}$

Changes in catalyst surface states undoubtedly have a great influence on the catalyst activity. Schmidt and co-workers have shown that in the pretreatment of Al_2O_3 - and SiO_2 -supported Rh catalysts (i) NO increases the Rh dispersion, (ii) H_2 causes sintering of Rh particles, and (iii) CO has no effect on the Rh

dispersion.^{10,24} They also showed that decreases in dispersion cause a decrease in catalyst activity for the NO–CO reaction.^{10,24} Hecker and Bell found that preoxidation of Rh/SiO₂ increases its activity for the NO–CO reaction, whereas prereduction of Rh/SiO₂ decreases its activity for the NO–CO reaction.¹²

Although the role of CO and NO in modifying the Rh surface state and morphology has been clearly elucidated, little is known about the effect of NO and CO partial pressures on the Rh surface states and their adsorbates/activities during the NO-CO reaction. The present study is aimed at determining the oxidation state of Rh and its adsorbates as a function of temperature and NO/CO partial pressure during the NO-CO reaction. Infrared spectroscopy (IR) coupled with temperatureprogrammed reaction (TPR) is used to determine the adsorbate structure for elucidation of the Rh surface states and product formation during the NO-CO reaction and the reaction of a gas stream simulated to automobile exhaust. To determine the role of Rh⁺ in the reaction, oxygen was added to the NO/CO stream to increase the number of Rh⁺ sites. This study is expected to contribute to a better understanding of Rh surface states during the NO-CO reaction in automobile exhaust catalysis.

Experimental Section

The 2 wt % Rh/Al₂O₃ catalyst was prepared by incipient wetness impregnation of RhCl₃·2H₂O (Alfa Chemicals) onto γ -alumina support (Alfa Chemicals, 100 m²/g). The catalyst was dried overnight in air at room temperature, calcined by flowing air at 723 K for 6 h, and then reduced by flowing H₂ at 723 K for 6 h. The average Rh crystallite size was determined to be 52 Å by H₂ chemisorption.

The experimental apparatus including an in situ infrared (IR) reactor cell with CaF_2 windows has been reported in detail elsewhere.²⁹ The catalyst powder was pressed into three self-supporting disks. One (25 mg) was placed in the path of the IR beam in the center of the IR reactor cell; others (98 mg) were

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Figure 1. (a) IR spectra of adsorbates during the temperature-programmed reaction of the 0.5% NO/0.5% CO (60 cm³/min) flow at 10 K/min. (b) Adsorbate intensity vs temperature. (c) Rate of NO conversion and N_2O and CO_2 formation vs temperature.

broken into flakes and placed in the immediate vicinity of the self-supporting disk to increase NO conversion and product formation.

Flows of He, H₂, NO, CO, and simulated gas were controlled by mass flow controllers. The simulated gas consists of 0.105% NO, 0.7765% CO, 0.0865% C₃H₈, 0.2673% H₂, 0.5392% O₂, and 15.3% CO₂ balanced with He. The simulated gas composition is of the same order of magnitude as automobile exhaust composition,³⁰ except that N₂ and H₂O are not included. Prior to each TPR experiment, the catalyst was further reduced by H₂ at 673 K for 2 h and IR background spectra were collected while the catalyst was cooled in He flow from 673 to 323 K. A step switch from He to NO/CO or simulated gas flow was made at 323 K. Upon the MS intensities of gaseous species reaching a steady-state level, the temperature was increased from 323 to 673 K at 10 K/min. The background spectra were subtracted from IR spectra collected during the TPR to obtain the spectra of adsorbates.

To increase the number of Rh^+ sites, 10 cm³ of O₂ was pulsed into He flow which was further mixed with 0.5% NO/0.5% CO flow in the in situ IR cell. It is necessary to separate the O₂ pulse and the NO flow to avoid the reaction of NO with O₂ in the transportation lines at room temperature.

Results

Effects of NO and CO Concentrations on the Adsorbates and Reaction Rate. Parts a–c of Figure 1 show the IR spectra of adsorbates, variation in adsorbate intensity with temperature, and variation in the rates of NO conversion and N₂O and CO₂ formation with temperature during the TPR of 0.5% NO/0.5% CO in He at a total flow rate of 60 cm³/min. Flowing NO/CO at 323 K over the prereduced catalyst produced linear CO [Rh⁰– CO] at 2060 cm⁻¹ and bent NO [Rh⁰–NO⁻] at 1706 cm⁻¹ during the first 0.96 min. An increase in the NO/CO exposure time increased the Rh⁰–CO intensity and resulted in the emergence of *gem*-dicarbonyl [Rh⁺(CO)₂] at 2085 and 2020 cm⁻¹, nitrato species [NO₃⁻¹] on Al₂O₃ at 1617 cm⁻¹, and Rh– NCO at 2145 cm⁻¹.^{12,15} Formation of Rh⁰–NCO indicates the occurrence of N–O dissociation and combination of adsorbed N and CO as follows:

$$Rh^{0} - NO + Rh^{0} \rightarrow Rh^{0} - N + Rh^{0} - O$$
(1)

$$Rh^{0}-CO + Rh-N \rightarrow Rh^{0}-NCO + Rh^{0}$$
 (2)

Following prolonged exposure of the catalyst to 0.5% NO/0.5% CO flow at 323 K, $Rh^+(CO)_2$, Rh^0-CO , Rh^0-NO^- , Rh^0-NCO , and NO_3^- approached a steady-state level.

Absence of CO_2 during the formation of various adsorbates such as $Rh^+(CO)_2$ and NO_3^- suggests that Rh^0-O produced from NO dissociation, i.e., reaction 1, provides adsorbed oxygen for oxidizing Rh^0 to Rh^+ and forming NO_3^- species.

An increase in the reaction temperature led to an increase in NO conversion and N_2O/CO_2 formation as well as variation in the intensities of Rh⁰-NCO, Rh⁺(CO)₂, Rh⁰-CO, Rh⁰-NO⁻, and NO₃⁻. To correlate adsorbate intensity and NO conversion/ product formation, variation of adsorbate intensity with temperature was plotted along with NO conversion and N₂O/CO₂ formation rates in Figure 1b,c.

Increasing the reaction temperature to 398 K decreases the Rh^0-CO intensity and increases that of $Rh^+(CO)_2$. Increases in the $Rh^+(CO)_2$ intensity reflect the increase in the number of Rh^+ sites. The light-off temperature occurs at 427 K as shown in Figure 1c, where near 50% NO conversion was achieved. Increasing the temperature above light-off causes (i) a decrease in the intensities of $Rh^+(CO)_2$ and Rh^0-NO^- , (ii) an increase in the intensities of $Rh^+(CO)_2$ and Rh^0-NO^- , (ii) an increase in the intensities of NO_3^- and carbonato (CO_3^{2-}) at 1570 cm⁻¹, (iii) an emergence of Rh^+-CO at 2087 cm⁻¹ and Rh^0-CO at 2038 cm⁻¹,^{31,32} and (iv) an increase in the NO conversion and N_2O/CO_2 formation. At 673 K, nearly complete NO conversion was achieved and Rh^+-CO at 2087 cm⁻¹ and Al-NCO at 2035 cm⁻¹ 12,15,25,32 became the dominant adsorbates on the catalyst surface.



Figure 2. (a) IR spectra of adsorbates during the temperature-programmed reaction of 5% NO/5% CO ($60 \text{ cm}^3/\text{min}$) flow at 10 K/min. (b) Adsorbate intensity vs temperature. (c) Rate of NO conversion and N₂O and CO₂ formation vs temperature.

According to the above observations, the reaction may be divided into three stages: (I) Below the light-off temperature (i.e., 427 K), low NO conversion with $Rh^+(CO)_2$ and $Rh^{0}-NO^-$ was observed. (II) Between light-off and 548 K, Al–NCO, $Rh^{0}-CO$, NO_3^- , and CO_3^{2-} were the major adsorbates. (III) Above 548 K, nearly complete NO conversion with Al–NCO and $Rh^{0}-CO$ as the main adsorbates was observed. Further increases in the temperature produced Rh^+-CO .

Parts a-c of Figure 2 show the IR spectra of adsorbates, variation in adsorbate intensity with temperature, and variation in the rates of NO conversion and N₂O/CO₂ formation with temperature during the TPR of 5% NO/5% CO in He at a total flow rate of 60 cm³/min. Comparison of the results in Figure 2 and those in Figure 1 shows that increasing the NO and CO concentrations (i) increases the light-off temperature and the Rh⁺(CO)₂ intensity, (ii) promotes the formation of Al–NCO and Rh–NO⁺ below light-off, (iii) increases the intensities of Al–NCO and Rh⁺–CO above light-off, and (iv) decreases the NO conversion.

Parts a-c of Figure 3 show the IR spectra of adsorbates, variation in adsorbate intensity with temperature, and variation in the rates of NO conversion and N₂O/CO₂ formation with temperature during the TPR of 17% NO/17% CO in He at a total flow rate of 60 cm³/min. The results in Figure 3 show that further increases in the NO and CO concentrations increase the light-off temperature as well as the intensity and wavenumber of Rh⁺(CO)₂, promote the formation of Rh⁺-CO at 2107 cm⁻¹ above light-off, and decrease the NO conversion.

Effect of the NO/CO Ratio on the Adsorbates and Reaction Rate. Comparison of results of 0.1% NO/0.9% CO (Figure 4) with those of 0.5% NO/0.5% CO (Figure 1) shows that excess CO in the reactant stream decreases the light-off temperature and the intensities of Al–NCO and Rh⁺(CO)₂. No Rh⁺–CO was observed during the TPR. In contrast, comparison of results of 0.9% NO/0.1% CO (Figure 5) with those of 0.5% NO/0.5% CO (Figure 1) shows that excess NO in the reactant stream results in an increase in the light-off temperature and in the intensities of Rh⁺–CO at 2104 cm⁻¹ and Rh–NO⁺ at 1904 cm⁻¹. The Rh–NO⁺ intensity increases at the expense of Rh⁺– CO. Interestingly, Al–NCO, Rh–NCO, NO₃⁻, and CO₃²⁻ were not formed in the entire reaction process. Although NO was in great excess of CO, complete NO conversion was achieved probably due to the stoichiometric NO decomposition process (i.e., $2NO \rightarrow N_2 + 2O_{ad}$). The NO conversion began decreasing as O_{ad} accumulated on the Rh surface faster than its removal by CO to form CO₂. The NO–CO reaction eventually approached the steady-state NO conversion at 11%.

Effect of Simulated Gas on the Adsorbates and Reaction **Rate.** Parts a–c of Figure 6 show the IR spectra of adsorbates, variation in adsorbate intensity with temperature, and variation in the MS intensity with temperature of the IR cell effluent during the simulated gas TPR at a total flow rate of 60 cm³/ min. The concentration of NO in the simulated gas flow is lower than that of 0.5% NO flow, whereas the CO concentration is higher than that of 0.5% CO flow in Figure 1. Both simulated gas and NO-CO reactions produced the same type of adsorbates and products, but differed in intensity. The notable differences are that (i) the Rh⁰-CO was present in the entire temperature range during the simulated gas reaction and (ii) the NO conversion in the simulated gas reaction was considerably lower than that in the NO-CO reaction. Significant conversion of H₂, O_2 , NO, and possibly C_3H_8 as well as the formation of H_2O , CO₂, and Al-NCO began at 480 K. The highest NO conversion achieved was 30% at 560 K.

Effect of an O_2 Pulse on the Adsorbates and Reaction Rate. To determine the role of Rh⁺ in the NO–CO reaction, oxygen was added to the NO/CO stream to increase the number of Rh⁺ sites. Parts a–c of Figure 7 show the IR spectra of adsorbates, variation in adsorbate intensity with time, and variation in the MS intensity with time of the IR cell effluent while 10 cm³ of O₂ was pulsed into the 0.5% NO/0.5% CO (60 cm³/min) flow at 473 K. Argon (Ar) was added to the O₂ stream as a tracer to signify the lead–lag relationship (e.g., formation/ disappearance) between reactants, adsorbates, and products.



Figure 3. (a) IR spectra of adsorbates during the temperature-programmed reaction of 17% NO/17% CO (60 cm³/min) flow at 10 K/min. (b) Adsorbate intensity vs temperature. (c) Rate of NO conversion and N_2O and CO_2 formation vs temperature.



Figure 4. (a) IR spectra of adsorbates during the temperature-programmed reaction of 0.1% NO/0.9% CO (60 cm³/min) flow at 10 K/min. (b) Adsorbate intensity vs temperature. (c) Rate of NO conversion and N_2O and CO_2 formation vs temperature.

Flowing NO/CO over prereduced Rh/Al₂O₃ produced Al–NCO at 2253 cm⁻¹, Rh⁰–CO at 2031 cm⁻¹, and Rh⁰–NO⁻ at 1745 cm⁻¹. The difference between this spectrum and that in Figure 1 at 473 K is due to the difference in temperature history and exposure time of the catalyst to the NO/CO flow. Pulse injection of oxygen causes the following: (i) disappearance of Rh⁰–CO and Rh⁰–NO⁻, (ii) reduction in the intensity of Al–NCO, (iii) emergence of Rh–NO⁺ at 1893 cm⁻¹, and (iv) an increase in the MS intensity of NO and CO₂. The increase in the NO MS

intensity, corresponding to an increase in NO concentration, reflects a decrease in the rate of NO conversion, while the increase in the CO_2 MS intensity indicates an increase in the rate of CO_2 formation during the O_2 pulse.

Parts b and c of Figure 7 show that the appearance of the gaseous NO profile lagged behind changes in the Rh $-NO^-$ and Rh $-NO^+$ profiles, indicating the transfer of Rh $-NO^-$ to Rh $-NO^+$ prior to desorption as gaseous NO. The significant increase in the CO₂ formation rate during the O₂ pulse can be understood



Figure 5. (a) IR spectra of adsorbates during the temperature-programmed reaction of 0.9% NO/0.1% CO (60 cm³/min) flow at 10 K/min. (b) Adsorbate intensity vs temperature. (c) Rate of NO conversion and N_2O and CO_2 formation vs temperature.



Figure 6. (a) IR spectra of adsorbates during the temperature-programmed reaction of simulated gas ($60 \text{ cm}^3/\text{min}$) flow at 10 K/min. (b) Adsorbate intensity vs temperature. (c) MS intensity vs temperature.

by the high O_2 concentration, i.e., 50 000 ppm, at the maximum point of the pulse, which is 1 order of magnitude greater than that of NO and CO. High O_2 concentration appeared to cause rapid CO oxidation, depleting Rh⁰–CO for NO reduction.

shown by the significant difference in the IR spectra before and after the O_2 pulse.

As the O_2 pulse left the IR reactor cell, CO began to reduce the Rh⁺ site to Rh⁰ as evidenced by gradual reappearance of Rh⁰-CO. In the absence of O_2 , the reduction process of Rh⁺ to Rh⁰ is significantly faster than the oxidation process. As a result, the catalyst surface did not return to its initial state, as Since the first O_2 pulse resulted in an increase of the steadystate NO conversion (i.e., lowered the NO MS intensity) and CO_2 formation (i.e., intensified the CO_2 MS intensity) as well as modified the catalyst surface, the second O_2 pulse was carried out to further examine the effects of O_2 .

Comparison of the results of the first pulse (Figure 7) and second pulse (Figure 8) shows that they differed in the rates of



Figure 7. (a) IR spectra of adsorbates during the first O_2 pulse (10 cm³) into the 0.5% NO/0.5% CO (60 cm³/min) flow at 473 K. (b) Adsorbate intensity vs time. (c) MS intensity vs time.



Figure 8. (a) IR spectra of adsorbates during the second O_2 pulse (10 cm³) into the 0.5% NO/0.5% CO (60 cm³/min) flow at 473 K. (b) Adsorbate intensity vs time.

disappearance and formation of adsorbates and gaseous products. The second O_2 pulse results in (i) a short lead–lag relationship among reactants, adsorbates, and products, (ii) a slow rate of disappearance for Rh⁰–CO and Al–NCO, and (iii) formation of NO₂. An initial high rate of NO₂ formation during the second O_2 pulse suggests that the reduced Rh⁰ site plays a significant role in the NO₂ formation. The low rate of NO₂ formation during the trailing portion of O₂ could be due to oxidation of Rh⁰ to

 Rh^+ by O_2 . In contrast to the first O_2 pulse, all the reaction rates returned to the same steady level prior to the second O_2 pulse 150 s after the pulse.

Discussion

The generally accepted mechanism for the NO–CO reaction is listed in Table 1.^{12,33} This mechanism may describe the reaction process on the Rh single-crystal surfaces which contain

 TABLE 1: General Proposed NO-CO Reaction

 Mechanism^a

$S + NO_{(g)}$	\Leftrightarrow	S-NO
$S + CO_{(g)}$	\Leftrightarrow	S-CO
S−NO + S	\rightarrow	S-N+S-O
S-CO+S-O	\rightarrow	$2S + CO_{2(g)}$
S-NO + S-N	\rightarrow	$2S + N_2O_{(g)}$
S-N+S-N	\rightarrow	$2S + N_{2(g)}$
		(0)

 a S = active site.

TABLE 2: Proposed Mechanism for the NO-CO Reaction^a

I. Adsorption				
step 1	$Rh^0 + CO_{(g)}$	$\overrightarrow{}$ Rh ⁰ -CO (linear CO)		
step 2	$2Rh^0 + CO_{(g)}$	\rightleftharpoons (Rh ⁰) ₂ -CO (bridged CO)		
step 3	$Rh^+ + 2CO_{(g)}$	\rightleftharpoons Rh ⁺ (CO) ₂ (gem-dicarbonyl)		
step 4	$Rh^0 + NO_{(g)}$	\rightleftharpoons Rh ⁰ -NO ⁻ (bent NO)		
step 5	$Rh^+ + CO_{(g)}$	\rightleftharpoons Rh ⁺ -CO (linear CO)		
step 6	$Rh^+ + NO_{(g)}$	\rightleftharpoons Rh–NO ⁺ (cationic NO)		
step 7	Rh^0 -CO + NO _(g)	$\approx Rh^0 - NO^- + CO_{(g)}$		
step 8	$Rh^+(CO)_2 + NO_{(g)}$	\rightleftharpoons Rh-NO ⁺ + 2CO _(g)		
II. Oxidation				
step 9	$Rh^0-NO^- + Rh^0$	\rightleftharpoons Rh ⁰ -N + Rh ⁰ -O		
step 10	Rh^0-O+Rh^0	\rightleftharpoons (Rh ⁺) ₂ O ²⁻		
III. Reduction				
step 11	$2Rh^{+}(CO)_{2} + O^{2-}$	$\approx 2Rh^0 - CO + CO_{2(g)} + CO_{(g)}$		
step 12	$Rh^0-CO + Rh^0-O$	$\approx 2Rh^0 + CO_{2(g)}$		
step 13	$(Rh^+)_2O^{2-} + Rh^0 - CO$	\Rightarrow 3Rh ⁰ + CO _{2(g)}		
IV. Formation of N_2 , N_2O , and $-NCO$				
step 14	$Rh-NO + Rh^0-N$	$\rightleftharpoons 2Rh^0 + N_2O_{(9)}$		
step 15	Rh^0-N+Rh^0-N	$\approx 2Rh^0 + N_{2(q)}$		
step 16	Rh^0-N+CO	\rightleftharpoons Rh ⁰ -NCÕ ^s		
step 17	$Rh^0-NCO + Al$	\rightleftharpoons Al-NCO + Rh ⁰		
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^{*a*} Rh⁰-NO⁻ as a whole should be considered a neutral species.

only the reduced Rh sites. For supported Rh catalyst containing both Rh⁰ and Rh⁺ sites, a more comprehensive mechanism is needed to explain the formation and disappearance of adsorbates and reactants/products. Table 2 lists both observed adsorbates and postulated steps involved in the NO–CO reaction on Rh⁰ and Rh⁺ sites of supported Rh catalysts.³⁴

Adsorption of NO and CO and Surface Redox Reaction. Rh⁰ chemisorbs CO as linear CO [Rh⁰–CO] (step 1) and bridged CO [(Rh⁰)₂–CO] (step 2) and NO as bent NO [Rh⁰-NO⁻] (step 3); Rh⁺ chemisorbs CO as *gem*-dicarbonyl [Rh⁺(CO)₂] (step 4) and linear CO [Rh⁺–CO] (step 5) and NO as cationic NO [Rh–NO⁺] (step 6).^{1,3,4,11,12,15–17,23,25,27} Competitive adsorption studies at 300 and 373 K²⁵ show that NO competes over CO for Rh⁰ sites (step 7); NO can replace Rh⁺(CO)₂ to form Rh– NO⁺, and CO can replace Rh–NO⁺ to produce Rh⁺(CO)₂ (step 8), depending on NO and CO partial pressures. Adsorbates on Rh⁺ sites shift from Rh⁺(CO)₂ to Rh⁺–CO and then to Rh– NO⁺ as the NO/CO ratio increases from 1/9 to 9/1 (Figures 1–5).

Since the formation of these adsorbates is governed by the availability of Rh^0 and Rh^+ sites, the formation of these adsorbates may be explained by redox of Rh^0/Rh^+ . The reduced Rh^0 site can be oxidized to a Rh^+ site via adsorbed oxygen (i.e., Rh^0-O) from NO dissociation (step 9). Conversion of adsorbed oxygen into an oxygen anion in the metal oxides (step 10) generally takes place at high temperature and prolonged O_2 exposure. Nevertheless, Rh appears to have a propensity to be oxidized at low temperature due to oxidative disruption of Rh crystallites brought about by both NO and CO. Rh⁺ can be reduced to Rh⁰ via either the reaction of adsorbed oxygen with Rh⁺(CO)₂ (step 11) or the reaction of O²⁻ with Rh⁰–CO (step 13).^{27,34}

Effects of Temperature on the Surface State and Reaction Rate. Variation of Rh⁺(CO)₂ intensity with temperature can be attributed to the dependence of the redox reaction cycle of NO– CO on temperature (i.e., activation energy for reduction and oxidation steps). Figures 1–4 show that the Rh⁺(CO)₂ intensity increased with temperature at low NO conversion. An increase in the Rh⁺(CO)₂ intensity suggests that the oxidation rate (step 10) increases faster with temperature than the reduction rate (step 11). As temperature approaches the point where appreciable NO conversion occurs, further increasing the temperature leads to a decrease in the Rh⁺(CO)₂ intensity with increasing CO₂ formation. Formation of CO₂ (steps 11–13) is a result of removal of both Rh⁰–O and (Rh⁺)₂O^{2–}. In other words, part of the CO₂ formation is a result of reduction of Rh⁺ to Rh⁰.

Effects of the NO/CO Concentration and Ratio on the Surface State and Reaction Rate. Absence of CO_2 formation and a gradual increase in the $Rh^+(CO)_2$ intensity at 323 K in Figure 1 suggest that oxygen from dissociated NO oxidized Rh^0 to Rh^+ instead of reaction with CO to form CO_2 . The extent and rate of oxidation increased with the partial pressure of NO and CO (i.e., concentration). An increase in the intensities of $Rh^+(CO)_2$ and $Rh-NO^+$ indicates an increase in their number and sites for adsorption.

In the absence of gaseous product, the number of adsorbates and corresponding sites may be related to the adsorbate intensities by their extinction coefficient. Extinction coefficients have been determined to be 10.8 cm/ μ mol for Rh⁺(CO)₂ and 9.9 cm/ μ mol for Rh⁰–NO⁻.³⁵ The Rh–NO⁺ extinction coefficient has not yet been determined. Thus, the relative abundance of Rh⁺ and Rh⁰ sites may be estimated by the intensity of the adsorbates residing on them.

A shift in the TPR curves of NO conversion, CO₂ formation, and Rh⁺(CO)₂ to low temperatures at NO/CO = 1/9 (Figure 4) suggests that excess CO accelerates the rate of the reduction step. In contrast, a high NO/CO ratio (Figure 5) shifts the TPR curves of NO conversion and CO₂ formation to high temperatures and slows the reduction step. The NO/CO ratio affects not only the surface state but also the activation energy of the redox steps. The dependence of the activation energy of the redox steps on the NO/CO ratio is reflected by the slope of the Rh⁺(CO)₂ and CO₂ formation curves. The sharper change in these curves indicates the greater difference in activation energy between the reduction and oxidation steps.

Effects of Oxygen on the Surface State and Reaction Rate. Disappearance of Rh⁰–CO and emergence of Rh–NO⁺ in Figures 7 and 8 indicate that adsorbed oxygen from the oxygen molecule depletes Rh⁰–CO and oxidizes Rh⁰ to Rh⁺. The spectra of adsorbates during oxygen addition resemble that of NO/CO = 9/1 at 473 K, indicating that O₂ and NO play similar roles in the redox cycle of the Rh catalyst surface. The presence of oxygen in the reactant stream oxidizes the Rh surface and slows the NO–CO reaction.

The most obvious effect of the oxygen pulse is to increase the NO conversion and CO_2 formation. The enhancement of the catalyst activity brought about by the oxygen pulse is consistent with the observation that preoxidation increases the activity for the NO–CO reaction over Rh/SiO₂.¹² The observed increase in the intensities of Rh⁰–CO and (Rh⁰)₂–CO and decrease in the Rh–NO⁺ intensity suggest that the oxygen pulse modifies the Rh surface, increasing the number of reduced Rh⁰ sites and promoting the NO dissociation.

An interesting observation during the first and second oxygen pulses is the lack of correlation between the recovery of the NO conversion/CO₂ formation rates and that of Rh⁰–CO IR intensity. For example, at 240 s in both Figures 7a,c and 8a,c, NO conversion and CO₂ formation rates reached the steady state, whereas the intensities of Rh^0 –CO and Rh^+ –CO continued to change with time. Accordingly, the reaction step, which consumed the IR-observable adsorbates, is not the rate-determining step.

Effects of Simulated Gas on the Oxidation State and Reaction Rate. The species in the simulated gas can be grouped into reductant (i.e., CO, H₂, C₃H₈) and oxidant (i.e., NO, O₂). The Rh surface state is expected to be influenced by the relative rate of the reduction and oxidation with reductant/oxidant. It is interesting to note that the surface state of Rh in the simulated gas environment (Figure 6) resembles that of Rh in the NO/ CO = 1/9 (Figure 4) environment as evidenced by similarity in the Rh⁰-CO and Rh⁺(CO)₂ intensities. The decrease in the $Rh^+(CO)_2$ intensity accompanied with the increase in NO conversion and CO₂ formation in Figures 1-5 was also observed for the simulated gas reaction in Figure 6. However, the catalyst in the simulated gas environment exhibits a significantly lower activity for the NO-CO reaction than that in the NO/CO = 1/9 environment. Low NO conversion could be due to competition of reductants for the same Rh⁰ sites since all the reactions between the oxidant and reductant have the same light-off temperature. Results of this study will serve as an excellent basis to estimate the potential loss in catalyst activity as the conditions move from the ideal NO-CO setting to the simulated gas reaction environment.

Reaction of Al–NCO. The decrease in the Al–NCO intensity during the O_2 pulse and simulated gas reaction could be due to the reaction of adsorbed oxygen with Al–NCO to produce N_2 and CO_2 as follows:

$$2\text{Al}-\text{NCO} + 2\text{O}_{ad} \rightarrow \text{N}_2 + 2\text{CO}_2 \tag{3}$$

Reaction 3 requires either (i) migration of adsorbed oxygen from the Rh site to the Al₂O₃ site for reaction with Al–NCO or (ii) migration of adsorbed Al–NCO from Al₂O₃ to Rh to react with adsorbed oxygen on Rh sites. The latter appears to be more likely than the former because of facile migration of Al–NCO.

Conclusions

In situ IR coupled with TPR studies allow observation of various forms of NO and CO adsorbates as a function of temperature and reactant partial pressures. Below light-off, Rh⁺-(CO)₂, Rh–NO⁺, Rh⁰–CO, and Rh⁰–NO⁻ are the major adsorbates; above light-off, Rh⁺–CO, Rh⁰–CO, and Al–NCO are the major adsorbates. Al–NCO formation is enhanced and Rh–NO⁺ is suppressed in the reducing (i.e., low NO/CO ratio) environment and vice versa in the oxidizing environment (i.e., high NO/CO ratio or in the presence of O₂).

Variation in the intensities of NO and CO adsorbates with temperature and reactant partial pressures indicates the dependence of the redox reaction cycle on temperature and reactant partial pressures. The oxidation rate increases faster with temperature than the reduction rate below light-off and vice versa above light-off. The extent and rate of oxidation increase with the partial pressure of NO and CO. The shift in the TPR curves of NO conversion, CO₂ formation, and Rh⁺(CO)₂ to low temperatures at NO/CO = 1/9 suggests that excess CO accelerates the rate of the reduction step. In contrast, a high NO/CO ratio shifts the TPR curves of NO conversion and CO₂ formation to high temperatures and slows the reduction step. The presence of oxygen in the reactant stream oxidizes the Rh surface and slows the NO–CO reaction. Adsorbed oxygen from the oxygen molecule depletes adsorbed CO and oxidizes Rh⁰ to Rh⁺.

Although the surface state of Rh in the simulated gas environment resembles that of Rh in the NO/CO = 1/9 (i.e., reducing) environment, the NO reduction activity under the simulated gas environment is significantly lower than under the NO/CO = 1/9 environment. Low NO conversion under simulated gas reaction conditions can be attributed to competition of reductants for the same Rh⁰ sites. The significant difference in the NO reduction rate between the NO–CO reaction and simulated gas reaction points to (i) the importance of studying the NO–CO reaction under practical conditions and (ii) the need to keep Rh in the reduced state and to ensure the proper balance of competitive adsorption for NO, CO, and C₃H₈.

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