DOE/PC/95224--T3

TITLE: *IN SITU* INFRARED STUDY OF CATALYTIC DECOMPOSITION OF NO

REPORT TYPE: Semiannually Technical Progress Report

REPORTING PERIOD: August 1, 1996 to February 1, ~~1996~~ 1997

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ISSUED REPORT DATE: April 8, 1997

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DOE AWARD NUMBER.: DE-FG22-95PC95224

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Abstract

The growing concerns for the environment and increasingly stringent standards for NO emission have presented a major challenge to control NO emissions from electric utility plants and automobiles. Catalytic decomposition of NO is the most attractive approach for the control of NO emission for its simplicity. Successful development of an effective catalyst for NO decomposition will greatly decrease the equipment and operation cost of NO control. Due to lack of understanding of the mechanism of NO decomposition, efforts on the search of an effective catalyst have been unsuccessful.

Scientific development of an effective catalyst requires fundamental understanding of the nature of active site, the rate-limiting step, and an approach to prolong the life of the catalyst. Research is proposed to study the reactivity of adsorbates for the direct NO decomposition and to investigate the feasibility of two novel approaches for improving catalyst activity and resistance to sintering. The first approach is the use of silanation to stabilize metal crystallites and supports for Cu-ZSM-5 and promoted Pt catalysts; the second is utilization of oxygen spillover and desorption to enhance NO decomposition activity. An innovative infrared reactor system will be used to observe and determine the dynamic behavior and the reactivity of adsorbates during NO decomposition, oxygen spillover, and silanation. A series of experiment including X-ray diffraction, temperature programmed desorption, temperature programmed reaction, X-ray photoelectron spectroscopy will be used to characterize the catalysts. The information obtained from this study will provide a scientific basis for developing an effective catalyst for the NO decomposition under practical flue gas conditions.

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List of Graphical Materials

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- Figure 2 MS analysis, NO TOF, and NO conversion as a function of temperature during NO-CO-He reaction over Rh/SiO₂ catalyst: (a), (b) NO:CO:He=10:10:30 cm³/min; (c), (d) NO:CO:He=10:50:30 cm³/min; (e), (f) NO:CO:He=25:5:30 cm³/min.
- Figure 3 Absorbance intensity of SiO₂ overtone at 1860 cm⁻¹, support temperature T_s, and gas phase temperature T_g as a function of experiment time during NO-CO-He reaction over Rh/SiO₂ catalyst: (a) NO:CO:He=10:10:30 cm³/min; (b) NO:CO:He=10:50:30 cm³/min; (c) NO:CO:He=25:5:30 cm³/min.
- Figure 4 IR spectra, vibrational frequency, and integrated IR absorbance of adsorbates as a function of temperature during NO-CO-He reaction over Mn-Rh/SiO₂ catalyst: (a), (b) NO:CO:He=10:10:30 cm³/min; (c), (d) NO:CO:He=10:50:30 cm³/min; (e), (f) NO:CO:He=25:5:30 cm³/min. Heating rate = 10 K/min.
- Figure 5 MS analysis, NO TOF, and NO conversion as a function of temperature during NO-CO-He reaction over Mn-Rh/SiO₂ catalyst: (a), (b) NO:CO:He=10:10:30 cm³/min; (c), (d) NO:CO:He=10:50:30 cm³/min; (e), (f) NO:CO:He=25:5:30 cm³/min.
- Figure 6 IR spectra of adsorbates as a function of temperature during NO-CO-He (10:10:30 cm³/min) reaction over trimethylchlorosilane [(CH₃)₃SiCl] modified Rh/SiO₂ catalyst. Heating rate = 10 K/min.
- Figure 7 MS analysis during NO-CO-He (10:10:30 cm³/min) reaction over trimethylchlorosilane [(CH₃)₃SiCl] modified Rh/SiO₂ catalyst.

Executive Summary

During the third semi-annual period, two major tasks were accomplished.

- (i) A water and oxygen injection system was built to study the effect of water and oxygen on the NO decomposition catalyst. An effective catalyst for removal of NO_x from stationary sources has to work in the exhaust effluent containing oxygen and 10% steam.
- (ii) The effectiveness of silantion on the stability of the catalyst was tested. It was found that silanation slightly deactivate the catalyst and did not provide significant beneficial effect to improve the catalyst performance.

Work is currently underway to determine the mechanism of oxygen spillover and the effect of SO_2 on the catalyst activity for NO decomposition.

***In Situ* Infrared Study of Catalytic Decomposition of NO**

Rhodium is a major component in the automobile three-way catalytic converters which allow simultaneous conversion of three pollutants (i.e., NO, CO, and hydrocarbons) to CO₂ and N₂. The principal function of Rh is to catalyze the reaction of NO with CO to form N₂ and CO₂. The high cost of Rh, the narrow operating window for air/fuel ratio, and increasingly strict standards for NO_x emission have promoted extensive research to develop substitutes for the Rh-based catalyst and to improve the Rh catalyst performance. One critical technical issue related to catalyst performance is the catalyst durability (i.e., the resistance to deactivation). The major causes of deactivation of rhodium in the three-way catalytic converter are the loss of active sites by (a) Rh crystallite sinking into subsurface of γ -Al₂O₃, the major component in the washcoat, at temperatures above 873 K; (b) sintering, resulting from Rh crystallite agglomeration, (c) possible transformation of active Rh⁰ sites to less active Rh⁺ sites, and (d) poisoning.

Zirconia and α -alumina have been found to be effective in inhibiting subsurface penetration of the Rh particle. Sintering of Rh crystallites has been impeded by addition of ceria and stabilization of γ -Al₂O₃ by SiO₂, BaO, and La₂O₃. Ceria also provides a number of beneficial effects to increase the overall efficiency of the three-way catalysts, including stabilization of γ -Al₂O₃, oxygen storage, and promotion of water-gas shift reaction.

Since reduced Rh (Rh⁰) site has been found to be more active than the oxidized (Rh⁺) site for NO-CO reaction, suppression of the transformation of Rh⁰ sites to less active Rh⁺ sites allow maintenance of high activity for NO reduction. It has been suggested that removal of OH from the γ -Al₂O₃ support by alkylhalosilane may inhibit the transformation of Rh⁰ sites to Rh⁺ sites.

Poisoning of the three-way catalyst is due to irreversible adsorption of SO₂, combustion products of fuel additives, and lubricative additives. One approach to slow down poisoning is to deposit Rh at the end of the pore so that the poison species may adsorb in the outer rhodium-free shell of support which serves as a guard, thus increasing the durability of the catalyst. Species such as NiO has also been added to the catalyst to chemisorb poisons such as SO₂, thus hindering

sulfur poisoning.

While a fuel additive such as tetraethyl lead has long been known to poison the Rh catalysts, the effect of additive such as methylcyclopentadienyl manganese (MMT) on the catalytic converter has been a controversial subject. The most thermodynamic stable form of the combustion products of MMT is MnO which has been known to be the oxophilic promoter. The oxophilic promoter has been found to promote CO dissociation; it may also promote NO dissociation.

The objective of this study is to determine the effect of MnO and silanation on Rh surface states and their activity and selectivity for NO-CO reaction. 4 wt% Rh/SiO₂, Mn-Rh/SiO₂, and trimethylchlorosilane [(CH₃)₃SiCl]-treated Rh/SiO₂ were studied by *in situ* infrared spectroscopy (IR) coupled with temperature-programmed reaction (TPR). Rapid response of the product formation and adsorbates to change in reactant concentration as well as the close match between the IR spectra at the specific temperature during TPR and those during steady-state NO-CO reaction at the same temperature suggest that IR-TPR is an efficient approach to rapidly scan IR spectra of adsorbate under wide range of reaction conditions. Changes in Rh surface state with Mn and silane additives as well as temperature and reactant ratio were determined by *in situ* infrared spectroscopy (IR) of adsorbed CO and NO during reaction.

Results

The 4 wt% Rh/SiO₂ catalyst was prepared by incipient wetness impregnation of large pore SiO₂ (Strem, 300 m²/g) support with RhCl₃•3H₂O (Alfa Chemicals) solution. The ratio of the solution to the weight of support material used was 1 cm³ to 1 g. After impregnation, the catalyst sample was dried overnight in air at 303 K and reduced in a flow of hydrogen at 673 K for 16 h. The H₂ uptake of the catalyst was measured at 303 K by pulse adsorption method and was found to be 61 μmol/g, corresponding to a dispersion of 0.62 and a crystallite size of 15 Å based on adsorption stoichiometry of H_{ads}/Rh = 1 and a cubic shape of Rh crystallites. The Mn-Rh/SiO₂ catalyst was prepared by sequential impregnation of the unmodified Rh/SiO₂ catalyst with an aqueous solution of Mn(NO₃)₂•6H₂O (Mn/Rh=0.1). The sample was dried at 298 K overnight

and further reduced at 673 K for 16 h. The hydrogen uptake of Mn-Rh/SiO₂ was 57 $\mu\text{mol/g}$, corresponding to a dispersion of Rh metal of 0.57. The addition of Mn showed a minimal effect on hydrogen uptake. This result is consistent with the literature that the addition of Mn did not significantly influence the amount of H₂ chemisorption at room temperature.

The silane modified 4 wt% Rh/SiO₂ catalyst was prepared by preadsorbed CO and followed by injection of a known quantity (1 cm³) of trimethylchlorosilane [(CH₃)₃SiCl] vapor into the IR reactor cell in flowing Helium at 323 K. The added (CH₃)₃SiCl caused a significant decrease in the intensity of OH group at 3744 cm⁻¹, confirming the occurrence of silanization. Following the silanization, the catalyst was reduced in hydrogen at 573 K to remove methyl ligand at 2965 cm⁻¹ and Cl.

TPR-IR studies were carried out in an *in situ* infrared (IR) reactor cell with CaF₂ windows capable of operating upto 873 K and 6 MPa. The detailed description of the apparatus and experimental procedures used in this study has been reported elsewhere and is briefly described here. The reactant gases used are CO (Linde, Commercial Grade), NO, and He (Linde, UHP); the gas flows were controlled by Brooks 5850E mass flow controllers. Helium, an inert gas in the reaction, was used to keep a low concentration of the ionized species in the MS vacuum chamber for high sensitivity to reaction products. The catalyst was reduced at 673 K for 1 h prior to the TPR-IR studies. The reactant mixture with a specific NO:CO:He ratio entered the IR cell at a constant flow rate while the catalyst in the IR cell was heated at 10 K/min. The change in the concentration of adsorbates was monitored by a Nicolet 5SXC infrared spectrometer with a DTGS detector at a resolution of 4 cm⁻¹. The gaseous composition of the reactor effluents were monitored using a Balzers QMG 112 quadrupole mass spectrometer (MS). The *m/e* ratios followed by the MS were 2 for He, 28 for CO/N₂, 30 for NO, 44 for CO₂/N₂O, 46 for NO₂, and 22 for the secondary ionization of CO₂. It should be noted that N₂ and CO give the same mass-to-charge ratio (*m/e*) of 28. The absence of the secondary ionization does not allow the separation of these two species.

NO-CO Reaction over Rh/SiO₂. Figure 1(a) shows infrared spectra of adsorbates on 4 wt% Rh/SiO₂ catalyst during the TPR of NO-CO at a ratio of 1:1. The adsorbates observed for TPR are the low wavenumber Rh-NO⁻ at 1698 cm⁻¹, high wavenumber Rh-NO⁻ at 1755 cm⁻¹, cationic NO [Rh-NO⁺] at 1916 cm⁻¹, gem-dicarbonyl CO [Rh⁺(CO)₂] at 2088 and 2033 cm⁻¹, linear CO [Rh-CO] at 2055 cm⁻¹, linear CO on Rh⁺ site [Rh⁺(CO)] at 2100 cm⁻¹, isocyanate on Rh metal [Rh-NCO] at 2188 cm⁻¹, and isocyanate on SiO₂ support [Si-NCO] at 2294 cm⁻¹. The difference between the low wavenumber and the high wavenumber Rh-NO⁻ has been attributed to the different extent of electron back donation from the reduced Rh site to adsorbed NO. The mode of NO and CO adsorbates and their intensities show strong temperature dependence which can be divided into three temperature regimes: (i) the 303 K - 403 K region where the conversion of reactants is low, (ii) the 413 K - 563 K region where appreciable conversion occurred, and (iii) above 563 K, the light-off temperature. These different temperature regions give the distinct difference in both intensity and the form of adsorbates.

In the 303 - 403 K region, the low wavenumber (LW) Rh-NO⁻ species at 1698 cm⁻¹ is the predominant adsorbate. Increase in temperature increased the intensity of LW Rh-NO⁻ with a red shift (decrease in the wavenumber). The variation of intensity and wavenumber of the species are plotted in Fig 1 (b). The corresponding MS analysis (Fig. 2 (a)) of the NO and NO TOF (Fig. 2 (b)) show that NO conversion is below .

In the 403 - 563 K region, the product formation and NO conversion increased, as shown in Figs. 2 (a) and (b). The increase in NO conversion and products formation were accompanied with the change in mode of adsorbates and their intensities. The concomitant disappearance of HW Rh-NO⁻ and the increase in intensities of Rh⁺(CO)₂ and Rh-NO⁺ suggests that oxygen resulted from the dissociation of HW Rh-NO⁻ converted Rh⁰ to Rh⁺ (i.e., oxidative disruption), which have also been observed during pulse NO-CO reaction studies over Rh/SiO₂ and Rh/Al₂O₃ catalysts. The absorbance intensity of Rh⁺(CO)₂ as a function of temperature, plotted in Figure 1 (b) shows that Rh⁺(CO)₂ intensity increased to its maximum at 473 K and decreased. The absence of significant variation of LW Rh-NO⁻ suggest that the reduced Rh site for the adsorbates remains

nearly constant below the lightoff temperature. The appearance of Rh-NCO and the increase in Si-NCO intensity with temperature reveals that NCO is migrated from Rh site to SiO₂ site.

A major change in adsorbate intensity is observed at 563 - 573 K where lightoff occurred. All the NO and CO adsorbates show a dramatic decrease to near zero coverage while gaseous CO₂ bands at 2361 and 2330 cm⁻¹ and Si-NCO increased to a constant density. The MS analysis shown in Fig. 2 (a) reveals that the lightoff took place at 573 K where 50% NO conversion is achieved. The sharp increase in product formation and NO conversion appears to be due to the heat effect on the rate of NO-CO reaction. The catalyst support temperature measured by intensity of SiO₂ overtone is 637 K while the temperature of gaseous reactant measured by thermocouple is 573 K. The significant temperature difference between catalyst support (T_s) and gas phase (T_g) as shown in Fig. 3 (a) reveals that heat released from reaction caused a rapid temperature rise, resulting a sharp increase in reaction rate. Assuming the activation energy did not vary before and after lightoff, extrapolation the TOF for NO conversion to higher temperature show the nonisothermal effectiveness factor is 5 at the light-off and 1.2 above the lightoff at 673 K.

NO-CO TPR experiment under various NO/CO ratios was also conducted to determine the effect of partial pressure of reactants on the structure adsorbates and catalyst surface state. The reactant ratio NO to CO = 1:5 in Fig. 1 (c) resemble the CO/NO ratio in the typical exhaust of an automobile engine. Figs. 1 (a), (c) and (e) show that LW Rh-NO⁻, Rh⁺(CO)₂, and Rh⁺(CO) were the major adsorbates observed below light-off temperatures and were completely disappeared above light-off temperatures.

Comparison of Figs. 1 (c) and (d) with (a) and (b) reveals that increasing in CO partial pressure caused (i) increase in linear CO [Rh-CO] at 2055 cm⁻¹ in 303 - 413 K range, (ii) decrease in HW Rh-NO⁻ and LW Rh-NO⁻ in the 413 - 563 K region, and (iii) lowering Rh⁺(CO)₂ intensity shifting its maximum intensity to 523 K. Above light-off temperature, incising in CO partial caused significant increase in both Rh-NCO and Si-NCO intensity and the formation of linear CO on the reduced Rh. The formation of Rh-CO is resulted from the reductive agglomeration of Rh⁺ to Rh⁰.

Fig. 1 (e) shows that high NO partial pressure resulted in: (i) formation of a neutral NO [Rh-NO⁰] at 1855 cm⁻¹ in the low conversion region between 303 and 413 K, (ii) formation and growth of two bands at 1761 and 1822 cm⁻¹ starting at 373 and 463 K, respectively, in the 413 - 563 K region. The bands are having the same intensity at 493 K and are unequivocally assigned to HW Rh-NO⁻ and neutral Rh-NO, respectively. The vibrational frequencies also coincide with the IR spectra of gem-dinitrosyl [Rh⁺(NO)₂] which was observed on Rh⁺ site on Rh/Al₂O₃ and Rh-Y zeolite [15,16]. The intensities of Rh-NO⁺, Rh-NO, and HW Rh-NO⁻ bands decreased above 493 K. The intensity of LW Rh-NO⁻, remaining largely unchanged below 493 K, increased and completely disappeared above 583 K. Above 563 K, linear CO was not observed. In addition, isocyanate species were not observed both in the 413 - 563 K region and above 563 K, indicating that excess NO probably inhibited NCO formation.

NO-CO Reaction over MnO Modified Rh/SiO₂. TPR results obtained for the NO-CO reaction over MnO modified Rh/SiO₂ under various NO/CO ratios are presented in Figs. 4 and 5. In the 303 - 413 K region, Fig. 4 (a) shows two shoulder bands at 1615 and 1731 cm⁻¹ which were not observed under the same condition (NO/CO = 1) on Rh/SiO₂ (Fig. 1 (a)). The bands are remained to be assigned. In the 413 - 563 K region, the formation of Rh⁺(CO) and Rh⁺(CO)₂ on the Mn-Rh/SiO₂ begins at 453 K which is at a higher temperature compared to that on the Rh/SiO₂ at 413 K under the same condition.

Fig. 4 (c) shows the formation of Rh-CO at 2060 cm⁻¹ at NO/CO = 0.2, indicating higher ratio of CO to NO kept the catalyst surface at a reduced state in the 303 - 413 K region. Fig. 4 (c) also shows that LW Rh-NO⁻ is the only adsorbed NO which is in contrast to the case on Rh/SiO₂ that Rh-NO⁰ and HW Rh-NO⁻ are also observed in the 413 - 563 K region. The absence of HW Rh-NO⁻ together with the low intensities of Rh⁺(CO)₂, and with LW Rh-NO⁻ as the predominant adsorbed NO on Mn-Rh/SiO₂ at all NO/CO ratios, suggest that adding Mn to Rh/SiO₂ resulted in forming large Rh crystallite. In contrast to Rh/SiO₂, the disappearance of Rh⁺(CO)₂ did not accompany the formation of Rh-CO on Mn-Rh/SiO₂ above the light-off temperature.

NO-CO Reaction over Silane Modified Rh/SiO₂. Figs. 6 and 7 shows the IR spectra and MS analysis obtained during the NO-CO (1:1) TPR study on silane modified Rh/SiO₂ catalyst. Careful comparison of Figs. 1 (a), 4 (a), 6 and 7 concludes that silanization of surface OH group did not inhibit the oxidative disruption of Rh⁰ to Rh⁺, as evidenced by the formation of Rh⁺(CO)₂ and the absence of linear and bridged CO. The intensities of Rh⁺(CO)₂ are the lowest on silane modified Rh surface compared to those on unmodified and MnO modified Rh/SiO₂. The adsorbed oxygen resulted from the NO dissociation of HW Rh-NO⁻ at 1755 cm⁻¹ oxidized Rh⁰ to Rh⁺ which chemisorbed CO as Rh⁺(CO)₂. The absence of light-off characteristic during the TPR study suggests that the catalyst might be poisoned by (CH₃)₃SiCl.

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Fig 7

M97054072

Report Number (14) DOE/PC/95224--T3

Publ. Date (11) 1997 04 08

Sponsor Code (18) DOE/EE, XF

JC Category (19) UC-101, DOE/ER

DOE