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Evidence for a Second CO Oxidation Mechanism on Rh/Ceria

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The reaction properties of ceria-supported Rh for CO oxidation were investigated using model catalysts prepared by vapor deposition of Rh onto flat, low-surface-area ceria. Steady-state reaction rates were measured on this catalyst at 573 K for O_2 pressures between 0.1 and 8 Torr and for CO pressures between 0.1 and 600 Torr, and the rates were compared to those measured on Rh/α-Al_2O_3(0001). The rates for Rh/ceria and Rh/α-Al_2O_3(0001) are essentially identical over most of the pressure range studied, with the reaction order for CO being inverse first-order under reducing conditions. However, for higher CO pressures, the reaction becomes zeroth-order in CO on Rh/ceria. It is suggested that this is due to a second reaction mechanism involving oxygen migration from ceria to the Rh, which had previously been observed in temperature-programmed desorption measurements on the same model catalysts (Zafiris, G. S., and Gorte, R. J., *J. Catal.* **139,** 561 (1993)).

INTRODUCTION

The primary catalytic components of three-way, automotive exhaust catalysts are Group VIII metals dispersed onto a high-surface-area support, usually an alumina washcoat. Cerium oxide is usually added to the catalysts in significant quantities, since it has been shown to enhance the effectiveness of the catalyst. One of the primary roles of ceria involves oxygen storage so that the appropriate oxygen stoichiometry can be maintained in the exhaust (*1–4*), but its role is not limited to this. Ceria has been shown to improve the thermal stability of the alumina support under harsh thermal treatment conditions (*1*) and it stabilizes the dispersion of noble metals (*5*). Ceria also appears to enhance the catalytic activity of Group VIII metals. For example, Rh/ceria is reported to have a high activity for the water–gas-shift reaction, which aids in the removal of CO at low temperatures (*1, 3, 6, 7*), and some have suggested that ceria may actually alter the properties of Group VIII metals (*8–10*).

In order to better understand how Group VIII metals interact with ceria, we have been studying model catalysts prepared by deposition of Pt and Rh onto a flat, ceria substrate (*11, 12*). The primary advantage of working with model catalysts is that adsorption properties of simple reactants like CO and NO can be studied using temperature-programmed desorption (TPD) without interference from readsorption, diffusion, and dispersion effects (*13, 14*). Furthermore, it has been demonstrated that changes in the desorption kinetics of simple reactants with metal particle size manifest themselves in the steady-state reaction rates for both CO oxidation on Pt and NO reduction by CO on Rh (*15, 16*). This suggests that one should be able to relate the effect of oxide substrate on the measured TPD curves to catalytic activity.

TPD results for Rh on ceria indicated that there is a very strong support interaction for this catalyst which leads to oxygen migration from the oxide to the metal, even in ultrahigh vacuum (*11*). Following CO adsorption on an unannealed surface, we observed CO_2 desorbing from the sample in TPD at temperatures above 450 K. While the near-surface region of the ceria could be depleted of oxygen by repeated adsorption of CO, annealing to 920 K was sufficient for bringing oxygen back to the surface. TPD

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measurements of NO were also similar to what is normally observed in coadsorption of NO and oxygen, again suggesting that oxygen can migrate from ceria to the Rh surface without going through the gas phase.

To determine whether this oxygen migration can influence steady-state reaction rates, we have extended our studies of Rh/ceria to measurements of CO oxidation on the same model catalysts used in the TPD studies. For most of the conditions used in our study, the rates were found to be essentially identical to those measured on Rh/alumina. On both Rh/ceria and Rh/α-$Al_2O_3(0001)$ at 573 K in excess CO, the rates were inversely proportional to the partial pressure of CO, indicating that CO and O_2 compete for sites on the Rh surface. However, at even larger pressures of CO, we observed a shift in the rate from inverse first-order to zeroth-order in CO which we interpret as a new mechanism for CO oxidation, involving oxygen migration from the ceria. This process appears to be similar to that observed in TPD measurements of CO on these surfaces.

EXPERIMENTAL

The catalyst samples were identical to those used in previous TPD studies (*11*). The ceria film was prepared by spray pyrolysis of 0.1 *N* aqueous solution of $Ce(NO_3)_3$ (99.5% purity, Johnson–Matthey) on a 7 × 7 × 0.5-mm, α-$Al_2O_3(0001)$ substrate held between 600 and 670 K in air. The solution was sprayed onto the hot substrate using a N_2 carrier, as described elsewhere (*11, 12*). After deposition of a film ~10 μm thick, the sample was heated overnight at 500 K in air. Transmission electron microscopy (TEM), performed on a ceria film grown onto a NaCl substrate following the same procedure, showed that the film was amorphous and had significant variations in its thickness (*11*).

The reaction measurements were carried out in a system which has also been described previously (*15*). The reactor was connected to an ultrahigh vacuum chamber by an all-metal gate valve so that the sample, which was attached to a magnetically manipulated, linear-motion feedthrough, could be transferred from near-atmospheric pressures to the vacuum chamber for surface analysis. A sorption pump was used to evacuate the reactor between measurements. The UHV chamber was equipped with a quadrupole mass spectrometer, an Auger electron spectrometer (AES), an ion gun for sample cleaning, a Rh source, and a quartz-crystal film-thickness monitor for measuring the metal coverage. A known Rh coverage could be deposited onto the substrate by first measuring the metal flux from the source with the film-thickness monitor and then moving the substrate in front of the source for a fixed time, as discussed elsewhere (*17*).

The samples were heated in the reactor by passing current through a Ta foil attached to the back of samples. A chromel–alumel thermocouple, attached directly to the back side of the sample using a ceramic adhesive, was used to monitor the temperature. This configuration enabled us to heat the sample up to ~700 K under reaction conditions. The sample temperature remained uniform, even at the highest temperatures. All of the heating leads in the reactor were gold-plated in order to avoid background reactivity, and rates on the clean α-$Al_2O_3(0001)$ were not measurable under the conditions of our experiments.

The CO was research purity (99.99%) and was further purified by passing it through both an activated-carbon trap and a liquid-nitrogen trap. Following this procedure, the Rh catalyst could be exposed to 100 Torr of CO without becoming contaminated by impurities other than a monolayer of CO. The O_2 was of 99.9% purity (<0.5 ppm total hydrocarbons) and was used without any further purification. Reactions were run in a batch mode, with the pressures of each reactant having been measured with a capacitance manometer. The progress of the reaction was monitored by expanding gas samples into an evacuated sampling loop of

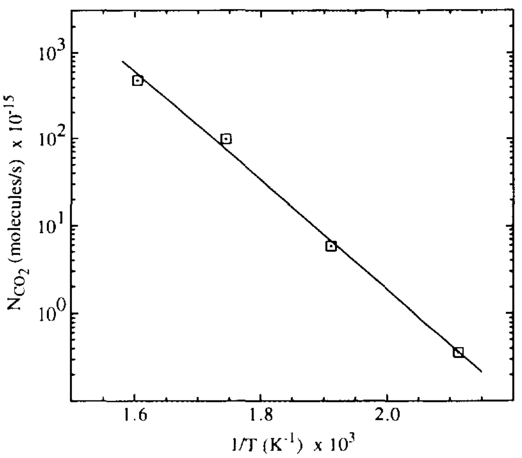

FIG. 1. CO oxidation rates on model Rh/ceria catalysts for 8 Torr each of CO and O_2.

a gas chromatograph. The reactor cell was operated as a differential batch reactor, with typical conversions less than 1%. The chromatograph was equipped with a postcolumn methanator and a flame ionization detector for detecting CO and CO_2. All of the rate measurements were performed using a metal coverage of ~5 × 10^{15} Rh/cm^2 on both ceria and α-Al_2O_3(0001). For this metal coverage, the average particle size on both substrates is greater than 10 nm, as determined from the metal dispersion calculated from CO adsorption (*11*). However, to avoid questions concerning whether adsorption properly accounts for metal surface area with ceria, the rates have not been normalized and all values in this paper are expressed as molecules of CO_2 produced per sec. For calculation of turnover frequencies and comparison to other studies, a reasonable estimate of the metal surface area in our samples would be ~0.5 cm^2.

RESULTS AND DISCUSSION

CO oxidation rates for 8.0 torr each of CO and O_2 are shown in Fig. 1 as a function of temperature. Assuming a Rh surface area of 0.5 cm^2 for comparison to other work, the turnover frequencies can be shown to be essentially identical to values reported for other Rh surfaces, including high-surface-area Rh/ceria and Rh/alumina catalysts and Rh single crystals at the same temperature and pressure conditions (*18–21*). The activation energy, 28.7 kcal/mole, is also very close to values reported previously. This suggests that the presence of ceria has little effect on the reaction under these conditions. At near stoichiometric ratios of CO and O_2, there is no evidence for electronic interactions between Rh and ceria. The reaction rates can be easily explained in terms of the adsorption, desorption, and surface reaction steps associated with pure Rh.

We next examined CO oxidation rates as a function of CO partial pressure at 573 K. Rates are shown in Fig. 2 for Rh/ceria at O_2 partial pressures of 8.0, 0.5, and 0.1 Torr and for Rh/α-Al_2O_3(0001) at 0.1 Torr O_2. For 8 Torr O_2, the rates on Rh/ceria are again identical to those measured previously for supported Rh catalysts and Rh single crystals over the entire range of CO pressures which were investigated (*18–21*). For O_2 : CO ratios less than ~3, the reaction is first-order in CO, but the reaction changes to inverse first-order at higher CO pres-

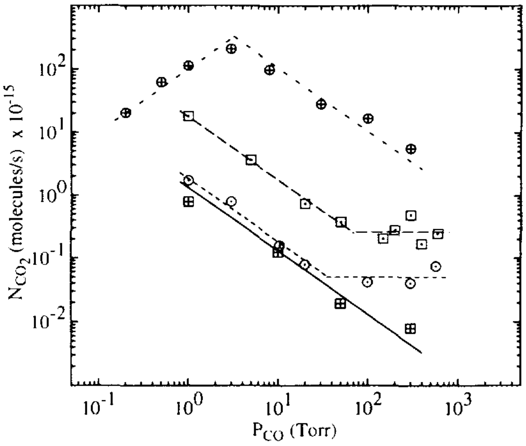

FIG. 2. CO oxidation rates on model Rh/ceria and Rh/α-Al_2O_3(0001) catalysts at 573 K. The rates were measured at O_2 pressures of 0.1 Torr on Rh/α-Al_2O_3(0001) (⊞); and 0.1 Torr (⊙), 0.5 Torr (□), and 8 Torr (⊕) on Rh/ceria.

sures. The change in the reaction order is due to a change in the predominant surface species in the two regimes. At low CO pressures, the Rh surface is covered with oxygen so that rates increase with increasing CO pressure. The inverse first-order dependence observed at higher CO pressures is a consequence of the fact that the Rh is essentially covered with CO, which in turn inhibits the adsorption of O_2 (*20*). For the above conditions, the presence of ceria does not significantly affect the order of the reaction with respect to the CO pressure.

The effect of ceria becomes apparent at the lower O_2 pressures, 0.5 and 0.1 Torr. For these O_2 pressures, we only investigated rates in excess CO, conditions which lead to a P_{CO}^{-1} dependence for the rates on Rh/alumina and Rh single crystals (*18–21*). This dependence was duplicated in our system for Rh/α-Al_2O_3(0001) at 0.1 Torr, as shown in Fig. 2. On Rh/ceria, however, the reaction exhibits a transition from an inverse first-order dependence in CO to zeroth-order at higher CO pressures. At 500 Torr CO, this change in reaction order resulted in absolute rates which were an order of magnitude higher on the Rh/ceria than on the Rh/α-Al_2O_3(0001). Furthermore, rates measured on pure ceria were also more than one order of magnitude lower than those measured on Rh/ceria in the zeroth-order regime, showing that the higher rates for Rh/ceria cannot be due to the additional reactivity of ceria. The enhanced reactivity of the Rh/ceria catalyst in excess CO is caused by interactions between Rh and ceria.

The O_2 dependence can also be obtained from the data in Fig. 2. Considering the P_{CO}^{-1} regime first, most previous studies have found a first-order dependence on O_2, which can be explained by assuming that adsorption occurs through a molecular species which then dissociates rapidly (*20*). While the rates we observed on the model catalysts are very similar to those reported by others in this regime, we observe that the reaction order in oxygen is 1.5. In the P_{CO}^{0} regime, the oxygen dependence changes to first order. Using the lines to describe the data in Fig. 2, the data at 573 K fits the equation

$$r = k_1 P_{\mathrm{CO}}^{-1} P_{\mathrm{O}}^{1.5} + k_2 P_{\mathrm{O}}^{1},$$

where k_1 is ~49 × 10^{15} molecules/sec · $\mathrm{Torr}^{0.5}$ and k_2 is ~0.3 × 10^{15} molecules/sec · Torr. The change in the order of the reaction for O_2 shifts the pressure of CO at which the reaction regime changes. At 0.1 Torr O_2, the shift occurs at ~50 Torr CO; at 0.5 Torr, the shift occurs at ~120 Torr. From the kinetic expression, one can calculate that the shift in rate expression would occur at ~480 Torr of CO at 8 Torr O_2. Since this is close to the maximum pressure we could investigate, the transition to zeroth-order in CO could not be observed at this oxygen pressure.

In order to better understand the changes in the reaction rate expression on Rh/ceria, it is informative to consider our earlier TPD results for CO from Rh/ceria (*11*). Figure 3 reproduces the TPD curve for CO from Rh/

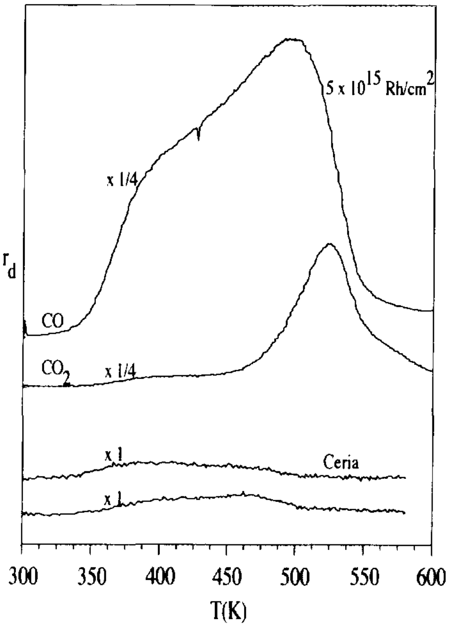

FIG. 3. TPD curves for CO from Rh/ceria and from clean ceria, taken from Ref. (*11*). Substantial quantities of CO_2 are observed during desorption of CO from Rh/ceria catalysts.

ceria at exactly the same metal coverage used in the present reaction studies, with results from clean ceria presented for comparison. This curve was obtained following adsorption of CO onto a freshly deposited Rh film and shows that substantial quantities of CO_2 desorb from the surface above 450 K. This CO_2 formation was not observed for Rh particles on either α-$Al_2O_3(0001)$ or $ZrO_2(001)$ (*22, 23*). Furthermore, since coadsorbed CO and oxygen would exhibit CO_2 formation at lower temperatures in TPD, the oxygen responsible for the CO_2 formation in the TPD curves for Rh/ceria must be due to migration of oxygen from ceria to Rh, which only occurs at higher temperatures. The possibility that CO migration onto ceria is responsible for CO_2 formation in TPD was ruled out based on TPD curves for NO which demonstrated that the entire surface of even large Rh particles was modified in a manner consistent with coadsorbed oxygen.

Oxygen migration from ceria can also explain the change in reaction order on Rh/ceria at higher CO pressures. The P_{CO}^{-1} dependence on the reaction rate is due to competitive adsorption between CO and oxygen. In excess CO, the surface is essentially saturated with CO, which causes the adsorption rate of O_2 to decrease inversely with CO pressure. For CO pressures below 100 Torr in our study, this mechanism dominates on Rh/ceria; however, at higher CO pressures, oxygen migration from ceria, which is not hindered by the saturation coverage of CO, becomes faster than the adsorption rate of O_2 on CO-covered Rh. Under steady-state reaction conditions, it is likely that Rh sites near the ceria interface are most important for catalyzing the reaction. Since the surface is essentially saturated with CO under these conditions, the reaction is not affected by further increases in the CO pressure.

It is also interesting to compare the rates of CO_2 formation at the peak temperature in TPD to the steady-state rates of CO oxidation. Since the signal in TPD is proportional to the desorption rate, one can estimate the reaction frequency from Fig. 3 to be on the order of 10^{-2}/sec at the peak maximum of 525 K. Assuming a Rh surface area of 0.5 cm^2 on our sample and 10^{15} sites/cm^2, the reaction frequency at steady state for 0.1 Torr O_2 and 573 K is $\sim 10^{-1}$/sec in the zeroth-order regime. Transient and steady-state rates are not directly comparable, since steady-state conditions would require reoxidation of ceria. However, the fact that the rates are of a similar magnitude does point out that it is reasonable to consider the migration process observed in TPD to be operative in the steady-state measurements.

Others have also observed evidence for oxygen migration from ceria to Rh in reaction measurements. Harrison *et al.* reported that Rh caused the reduction of surface ceria to occur at significantly lower temperatures in temperature-programmed reduction experiments (*1*), and Schlatter and Mitchell observed enhancements in CO oxidation on Rh/ceria under transient conditions (*6*). Oh and Eickel examined CO oxidation on Rh/ceria/alumina and observed a change in the reaction order for CO with increasing CO pressures, similar to what we show in Fig. 2 (*18*). In their work, the transition to zeroth-order occurred at lower CO pressures, ~5 Torr at an O_2 pressure of ~4 Torr. While they were working at lower temperatures than we used in our study, 469 versus 573 K, we believe the major difference between our results and theirs is the Rh particle size and catalyst structure. The average particle size in our samples was very large, ~15 nm, and the oxide was relatively flat compared to what would be expected for alumina-supported ceria. It is entirely reasonable that oxygen migration would occur much more easily on the samples used by Oh and Eickel, so that P_{CO}^{0} regime would be observed at lower CO pressures. The relative importance of this second mechanism should depend on the catalyst morphology.

It does not appear likely that the properties of the metallic Rh itself are being substantially modified by the presence of ceria.

While there have been reports for strong support interactions with metals on ceria, this appears to occur only after high-temperature reduction (*9*). While the second reaction mechanism for CO oxidation was only observed under reducing conditions, this occurred at relatively low temperatures and we did not observe changes in the rate with time. Also, the rates at lower CO pressures were essentially identical on Rh/ceria and Rh/α-Al_2O_3(0001), which implies that the adsorption and reaction properties of the Rh are not significantly modified by the presence of ceria.

The importance of the second CO-oxidation mechanism to automotive catalysis is not known. The primary function of Rh is to catalyze NO_x removal, and how strongly interactions with ceria affect this reaction is not yet clear. Also, ceria plays other important roles in automotive catalysis which were not considered in our study. However, depending on the reactant pressures, our results suggest that rate enhancements due to interactions between Rh and ceria of several orders of magnitude are possible. Also, it is certainly interesting that a metal and its support can interact in a manner which leads to the kind of enhancements in the reaction rate which were observed in this study. Whether these enhancements can be observed with other metals, such as Pt (*12*), and other reactions will be the topic of future studies.

SUMMARY

We have observed a second mechanism for CO oxidation on Rh/ceria catalysts which involves the migration of oxygen from the ceria to the Rh. This mechanism causes the reaction to shift from inverse first-order in CO to zeroth-order at high CO pressures and can lead to significant rate enhancements.

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