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A Study of CO Oxidation Kinetics on Rh/Ceria

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CO oxidation kinetics, at differential conversions, have been studied on model Rh/ceria catalysts over a wide pressure and temperature range to investigate the effect of ceria support interactions with Rh on the catalytic properties. The kinetics suggest that there are two reaction mechanisms in excess CO. The first is identical to that reported for pure Rh and exhibits a reaction order of ~1 for O_2 and −1 for CO, with an activation energy between 25 and 27 kcal/mol. The second mechanism is 0.4 order in O_2 and zeroth order in CO, with a much lower activation energy, between 12 and 15 kcal/mol. This second reaction, which becomes more important for smaller Rh particle sizes, high CO pressures, and low temperatures, appears to involve reaction of oxygen from the ceria with CO from Rh. Possible implications of these results for catalytic performance are discussed.

INTRODUCTION

Supported-metal catalysts are widely used in the control of automotive exhaust emissions. In addition to alumina and precious metals, other oxides are added to the catalyst and can strongly affect the catalytic properties (1–3). In particular, ceria is usually present in significant amounts, primarily for oxygen storage (4, 6, 7), but also to enhance the activity and stability of the catalyst (4, 5). Several recent papers have shown that Rh/ceria can exhibit enhanced reaction rates for CO oxidation, along with a very different kinetic rate expression when compared to Rh or ceria individually (8, 9). Evidence that ceria can change the activation energy for CO oxidation has also been obtained by others (10, 11); however, the reasons for this enhanced activity are not known in detail.

CO oxidation over unsupported Rh is reasonably well understood from investigations on Rh single crystals (12–14). The reaction is structure insensitive, and, under reducing conditions, the Rh is saturated with CO, as shown by the fact that the reaction is inverse first order in CO and that the activation energy is equal to the heat of adsorption of CO (15). For silica- and alumina-supported Rh, the kinetics are essentially identical to those observed on bulk metals. However, for Rh/ceria, there is evidence for a second, ceria-mediated reaction under reducing conditions. Both Oh and Eickle (8) and Zafiris and Gorte (9) observed that the reaction was zeroth order in CO under some experimental conditions. It was suggested that this zeroth-order process was due to oxygen reacting indirectly from the ceria, so that the CO on the Rh is unable to suppress the rate of oxygen adsorption in this process. Confirmation of this possibility came from TPD studies, where it was shown that CO adsorbed on Rh could react with oxygen from ceria (16).

It should be noted that there were differences in the two reports of CO oxidation kinetics on Rh/ceria cited above (8, 9). Oh and Eickle observed the zeroth-order kinetics over a range of CO pressures much wider than that observed by Zafiris and Gorte. There are a number of possibilities that could account for this. Oh and Eickle worked at much lower temperatures, 469 K versus 573 K, and used a porous catalyst prepared by impregnating alumina with ceria, while Zafiris and Gorte used a model catalyst prepared by vapor deposition of Rh onto a flat ceria substrate. Therefore, the differences in the observed kinetics could be due to ceria morphology, Rh particle size, or temperature.

The goal of this present work was to investigate the kinetics more thoroughly to understand the effect of Rh particle size and temperature on the kinetics. We provide additional evidence for a second, ceria-mediated reaction involving oxygen from the ceria reacting with CO adsorbed on the Rh. We also show that the activation energy of this reaction is considerably lower than that for the rate on pure Rh, so that it dominates at low temperatures. The second reaction is enhanced for smaller Rh particle size, relative to the normal rate on Rh, further suggesting that the reaction occurs at the interface between the Rh metal and the ceria support.

EXPERIMENTAL

To measure differential reaction rates over a wide temperature and pressure range, without interference from

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diffusion, catalysts in which all of the Rh was present near the surface of the oxide were prepared. A thick, Al foil was first oxidized in air at 750 K to form an alumina film. A ceria film, ~10 μm thick, was then deposited onto the foil by spray pyrolysis of an aqueous solution of $Ce(NO_3)_3$ (99.5% purity, Johnson Matthey), while holding the foil between 600 and 670 K in air (17). Following the addition of ceria, the foil was annealed overnight in air at 700 K. The Rh was introduced by vapor deposition in ultrahigh vacuum, using the same methods discussed elsewhere (9, 16). A known Rh coverage could be deposited onto the substrate by exposing the substrate to the Rh source for a given length of time, with the Rh flux being measured by a quartz-crystal, film thickness monitor. The average Rh particle size could be varied by increasing the amount of metal deposited onto the substrate (18, 19). Two coverages of Rh, 5×10^{14} (0.5 monolayer [ML]) and 5×10^{15} Rh/cm^2 (5.0 ML), were examined to determine the effect of particle size.

The foil catalyst was then curled into a cylinder and placed into the reactor, which was simply a ¼-in. quartz tube. The amount of catalyst in the reactor and the total flow rate could be varied so that conversions were always differential, usually well below 1% of the limiting reagent. The total pressure in the reactor was always 1 atm, but the reactant composition could be controlled using the flow rates of air, CO, and N_2. The CO was research purity (99.99%) and was further cleaned by passing it through both an activated-carbon trap to remove carbonyls and NaOH pellets to eliminate residual CO_2. The O_2 was of 99.9% purity (<0.5 ppm total hydrocarbons) and was used without further purification. CO and CO_2 compositions leaving the reactor were measured with an on-line gas chromatograph, equipped with a methanator and an FID detector. In all cases, CO oxidation was carried out at 650 K for 1 h to pretreat the catalyst prior to measuring rates, after which reproducible rates could be obtained at all temperature and pressure conditions.

Because it was difficult to measure the metal surface areas directly, all rates in this paper are reported in terms of the external surface area of the foil. Finally, rates on the ceria substrate without Rh were at least an order of magnitude less than those measured with Rh under all conditions used in this study, so that rates on ceria itself could be neglected.

RESULTS

Reaction Orders for CO Oxidation on Rh/Ceria

To test the reactor, we first reproduced the CO pressure dependence for CO oxidation on Rh/alumina and Rh/ceria with 0.5 ML of Rh. Figure 1 shows these data for a fixed oxygen pressure of 0.3 Torr and a temperature of 573 K. On Rh/alumina, the reaction order is approximately −0.8 for the entire CO pressure range from 1.5 to 150 Torr. This is in excellent agreement with findings from the literature, which have shown inverse first order for CO : O_2 ratios greater than three (13). Under these conditions, the Rh surface is almost saturated with CO, so that the reaction is limited by the adsorption rate of O_2 and inverse first order in CO. Since CO oxidation on Rh/alumina is structure insensitive, one can estimate the surface area of the Rh by comparison of the rates to literature values. For 10 Torr CO and 0.3 Torr O_2, the specific rate of CO oxidation at 573 K is 9.6×10^{15} molecules/cm$^2 \cdot$ s on Rh(111) (14), which would imply that the Rh surface area on our sample is 0.19 cm^2 of Rh/cm^2 of foil. From the metal coverage, one can also estimate the average metal particle size to be 2.2 nm. Obviously, estimates of the absolute dispersion based on specific rates may not be precise, but comparisons of dispersion between materials should be reasonable. Also, the average particle size calculated for Rh on ceria, using rate data from Zafiris and Gorte in the inverse-first-order regime (9), is in excellent agreement with the particle size calculated from adsorption measurements for the same metal coverage (16). It is interesting to note that the dispersion for a given metal coverage in those studies was significantly lower than those found here, probably due to the fact that those samples were not exposed to air before annealing to form large metal particles.

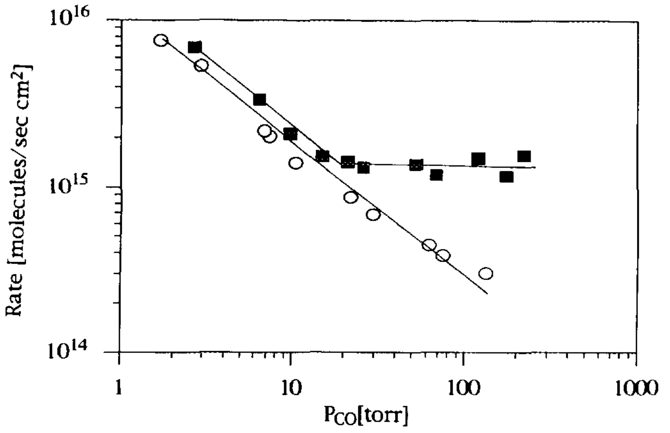

FIG. 1. CO oxidation rates on model Rh/ceria catalysts (■) and on model Rh/alumina catalysts (○) for 0.3 Torr of O_2 at 573 K.

CO oxidation rates for Rh/ceria are quite different. Below ~15 Torr, the reaction order again appears to be ~−1; however, for higher CO pressures, there is a change in the reaction order. This is very reminiscent of the previous data for CO oxidation on Rh/ceria (8, 9). If one assumes that the inverse-first-order regime on Rh/ceria is due to reaction on Rh alone, one can again estimate a Rh surface area and particle size by comparing the specific rates. The average Rh particle size, ~1.6 nm, on ceria for this metal coverage is slightly smaller than alumina. At higher CO pressures, the reaction no longer appears to be poisoned by CO, as shown by the fact that the reaction order is zero. Rates measured on pure ceria under these conditions were more than an order of magnitude lower at all pressures, showing that this is not simply reaction on ceria. Since the Rh surface must remain saturated with CO, the change in the reaction order suggests the onset of a new mechanism for CO oxidation which does not require oxygen to adsorb on the Rh.

Zafiris and Gorte also reported that the O_2 pressure dependence was different for the two reaction regimes on Rh/ceria, going from 1.5 at low CO pressures to 1 at the higher CO pressures (9). In the present study, we measured CO oxidation rates as a function of O_2 pressure for two CO pressures, 8 and 170 Torr, with the data shown in Fig. 2. In agreement with the previous observations, we show a decreased pressure dependence for O_2 at the higher CO pressures, going from a reaction order of 0.9 when CO is inverse first order to 0.4 at the higher CO pressures. The approximately first-order O_2 dependence at low CO pressures provides additional evidence that the rates at the lower CO pressures simply involve reaction on the Rh surface, with no effect from ceria, since this is the usual reaction order reported for Rh in excess CO. The change in the reaction order for O_2 again suggests that a ceria-mediated rate process becomes important at higher CO pressures.

Particle-Size Dependence for CO Oxidation on Rh/Ceria

The effect of particle size on Rh/ceria was examined by comparing reaction rates as a function of CO pressure at 573 K and 0.3 Torr of O_2 for catalysts containing 0.5 and 5 ML of Rh, with the results shown in Fig. 3. The basic picture is the same for both metal coverages, with rates showing a ~−1 reaction order at lower CO pressures and a zeroth order at higher CO pressures. In the inverse-first-order regime, the rates on the 5-ML sample are a factor of ~7 higher than those on the 0.5-ML sample, indicating that the Rh surface area is seven times greater than on the 0.5-ML catalyst. Based on a comparison of rates measured on Rh(111) (13), the Rh surface areas on 5-ML and 0.5-ML Rh/ceria catalysts are 1.8 and 0.26 cm^2 of Rh/cm^2 of foil, respectively. Because the metal coverage is 10 times higher, the dispersion on the 5-ML catalyst is ~0.7 that of the 0.5-ML sample and the particle size is ~2.3 nm. The main difference between the results for the two metal coverages is that the CO pressure at which the rates deviate from a reaction order of −1 is higher on the 5-ML sample. The change in reaction order occurs at ~100 Torr of CO on the 5-ML sample, while the change occurs at ~20 Torr for 0.5 ML.

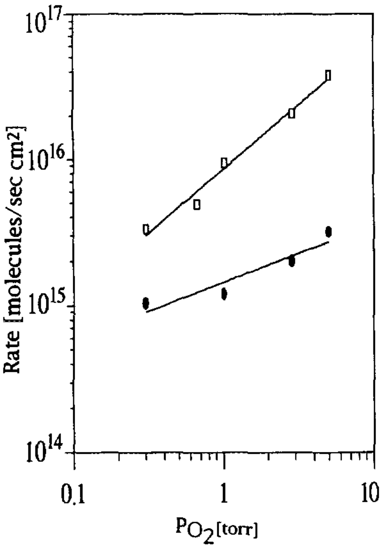

FIG. 2. CO oxidation rates on the 0.5-ML Rh/ceria catalyst as a function of O_2 partial pressures at 573 K. The rates were measured at 8 Torr (□) and 170 Torr (●) of CO.

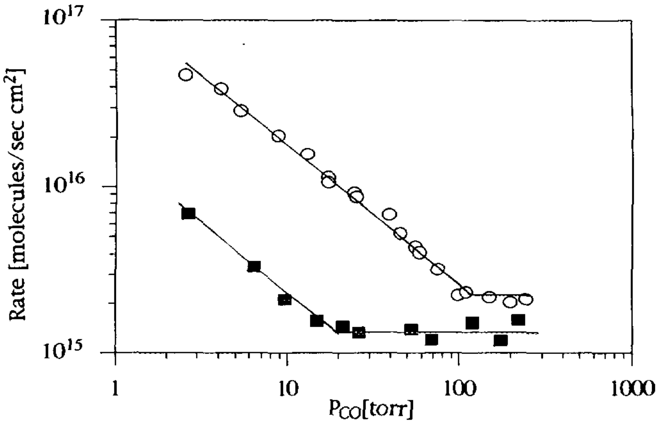

FIG. 3. CO oxidation rates on 5-ML (○) and 0.5-ML (■) Rh/ceria catalysts for 0.3 Torr of O_2. The rates were measured at 573 K.

The difference in the transition can be understood by assuming that the reaction at high CO pressures is dominated by a second process at the interfacial sites, similar to what has been assumed previously by others (8, 9). Assuming that the specific rates for both processes are independent of particle size, the total reaction rate for a hemispherical particle with diameter D is given by

$$R_t = (\pi/2)D^2 \times r_{Rh}\{1 + 2/D \times (r_i)/(r_{Rh})\}, \qquad [1]$$

where R_t is the total reaction rate on the particle, r_{Rh} is the specific rate on pure Rh, and r_i is the specific rate at the interfacial sites. According to the rate expression, the importance of the interfacial reaction should vary inversely with particle size. However, the data indicate that the in-

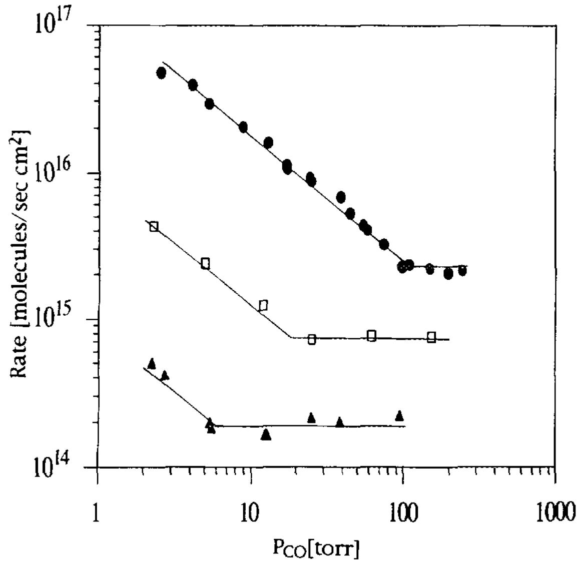

FIG. 4. CO oxidation rates on Rh/ceria for 0.3 Torr of O_2. The rates were measured at 573 K (○); 515 K (□), and 467 K (▲).

terfacial reaction decreases even more rapidly than $1/D$. Since the O_2 and CO pressure dependences for r_i/r_{Rh} has also been shown to vary as $P_{CO}P_{O_2}^{-0.5}$, the interfacial reaction will also be most important at high CO pressures and low O_2 pressures.

Temperature Effects on Rh/Ceria

Finally, we examined the effect of temperature on CO oxidation kinetics over Rh/ceria, again looking at the CO pressure dependence at a fixed O_2 pressure of 0.3 Torr. In Fig. 4, rate data are shown for three different temperatures, 467, 515, and 573 K, on the 5-ML Rh/ceria catalyst. Clearly, the transition from the inverse-first-order rate occurs at lower CO pressures at the lower temperatures. If one again assumes that the two reaction regimes are caused by different sites, the activation energies of these two processes must be quite different.

For the inverse-first-order regime, the activation energy obtained from the lines through the data at 467, 515, and 573 K is 25 ± 1 kcal/mol on the 5-ML Rh/ceria catalyst. The inverse-first-order regime is only observed at the two higher temperatures on the 0.5-ML sample, with a calculated activation energy of 27 kcal/mol. This is in good agreement with the activation energy determined on Rh single crystals (12–14), providing further evidence, along with the O_2 and CO pressure dependences, that the reaction under these conditions is unaffected by the presence of ceria. The activation energy of the ceria-mediated reaction is 12 ± 1 kcal/mol on the 5-ML sample and 15 ± 1 kcal/mol on the 0.5-ML sample.

DISCUSSION

The CO oxidation rates measured in this article provide further evidence for a second, ceria-mediated reaction on ceria-supported Rh. At the higher temperatures and intermediate CO pressures, the rate expression is identical to that observed on pure Rh. The rate is approximately inverse first order in CO and first order in O_2 and has an activation energy of 25 to 27 kcal/mol. For lower temperatures and higher CO pressures, the second reaction dominates. The pressure dependences for both CO (zeroth order) and O_2 (0.4 order) and the activation energy (12 to 15 kcal/mol) for this mechanism are very different.

It is difficult to deduce a detailed picture of the second mechanism from the kinetics, but a few features are apparent. Clearly, the reaction is not poisoned by CO, which implies that it occurs at sites on the periphery of the Rh particles, which must remain saturated with CO. The zeroth-order dependence for CO can be explained using the model of Zafiris and Gorte, which involves reaction of CO from the Rh with oxygen from the ceria (9). Since ceria could provide a reservoir of oxygen for the reaction, the decreased dependence of the rate on the oxygen pressure is also consistent.

The apparent, strong dependence of the relative importance of the interfacial reaction with particle size is interesting. We offer two possible explanations. First, Stubenrauch and Vohs have recently shown that Rh particles on a $CeO_2(111)$ crystal behave very differently from Rh on polycrystalline ceria which was annealed to only 870 K (20). For CO on $Rh/CeO_2(111)$, almost all of the CO desorbed intact, with little CO_2 formation in TPD. This appears to indicate that the structure of the ceria surface can have a significant effect on the adsorption and reaction properties of the catalyst. While care was taken to use the same catalyst preparation procedures in each case, differences in the structure of the ceria, unintentionally introduced, could shift the transition. The second explanation comes from a recent study by Lambert and co-workers, who have suggested that ceria in the vicinity of a noble metal can become catalytically active for CO oxidation (21). If this is true, the dependence of the reaction on particle size could be complex.

Independent of the details of the second mechanism, all of the differences between the results of Oh and Eickel (8) and Zafiris and Gorte (9) can be accounted for by the temperature dependences of the two mechanistic steps. This is significant because the structures of the catalysts in these two studies were very different. Oh and Eickel used an alumina support, impregnated with ceria, while the support in the study of Zafiris and Gorte was bulk ceria. This implies that bulk ceria is not necessary for observing the ceria-mediated reaction.

The ceria-mediated reaction on Rh/ceria is potentially very significant. Because of the lower activation energy of this step, Rh/ceria should exhibit enhanced activity at the lower temperatures during catalyst light-off due to this mechanism. There is evidence that strong interactions between Rh and ceria can cause deactivation, making it questionable whether or not one can take advantage of the high activity at low temperatures in automotive applications, at least for Rh (22); however, oxidation reactions involving both the catalytic metal and the support may well find importance in other applications and reactions.

SUMMARY

Kinetic studies of CO oxidation on Rh/ceria indicate that a second process can dominate the rates for small Rh particles, at low temperatures, high P_{CO}, and low P_{O_2}. The second mechanism involves reaction of oxygen from ceria with CO from Rh, which gives rise to both the particle-size and rate expression dependences.

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