A comparison of CO oxidation on ceria-supported Pt, Pd, and Rh

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Steady-state, CO-oxidation kinetics have been studied at differential conversions on model, ceria-supported, Pt, Pd, and Rh catalysts, from 467 to 573 K, and the results compared to the alumina-supported metals. On each of the ceria-supported metals, there is a second mechanism for CO oxidation under reducing conditions which involves oxygen from ceria reacting with CO on the metals. The rates of this second process are independent of which metal is used. The process has a significantly lower activation energy (14 ± 1 kJ/mol compared to 26 ± 2 kJ/mol on alumina-supported catalysts) and different reaction orders for both CO (zeroth-order compared to -1) and O_2 (0.40 to 0.46 compared to first-order). This second process leads to significant rate enhancements over alumina-supported catalysts at low temperatures, especially for Pt. The implications of these results for automotive catalysis are discussed.

Keywords: Co oxidation kinetics; ceria-supported catalysts; Pt, Pd, Rh catalysts; automotive catalysis

1. Introduction

Ceria plays an important role in automotive emissions-control catalysts, primarily because of its ability to undergo oxidation and reduction [1–3]. While ceria itself can be catalytic for reactions like CO oxidation [4], there is significant evidence that contact with a precious metal is required in order to utilize its properties in automotive applications [5]. In particular, rate studies for CO oxidation on ceria-supported Rh have shown cooperative effects between the metal and the oxide. In excess CO, rates were found to be much higher over ceria-supported Rh compared to what would be observed over Rh and ceria separately, at least at lower temperatures [6]. It appears that there is a second mechanism, involving oxygen transfer from ceria to the metal, which results in a rate expression which is zeroth-order in CO and has an activation energy of only ~ 14 kcal/mol [7,8], compared to the inverse, first-order rate with an activation energy of 26 kcal/mol, which is observed on bulk Rh [16]. Dependence of the second mechanism on Rh particle size gave further evidence of the importance of the Rh–ceria boundary in this reaction [8]. The relative importance of the second process was significantly greater for small metal crystallites.

While there have been many studies of CO oxidation on supported precious metals, there are still important questions about the nature of the metal–ceria interface. For example, it is not known whether the second rate process involving ceria is metal specific. If the rate of oxygen transfer is limited by a kinetic barrier at the metal–ceria interface, one might expect that specific rates will be different for Pt and Pd compared to Rh. Rh is known to form compounds with rare-earth oxides [9] so that interfacial species may assist oxygen transfer between the phases. The observation that pretreatment conditions affect the observed activity of ceria-supported catalysts would suggest that these kinds of effects could well be important [10]. On the other hand, the limiting factor for oxygen transfer from ceria could simply be the barrier for oxygen abstraction from ceria itself, which would imply that the second reaction process should be independent of metal. It has recently been demonstrated that ceria structure strongly changes the oxygen transfer properties for Rh catalysts [11], so that different pretreatment conditions could simply be changing the ceria.

In the present study, we compared steady-state, CO-oxidation rates on ceria-supported Pt, Pd, and Rh catalysts over a wide range of temperatures and partial pressures. For each precious metal, a second CO-oxidation mechanism was found in excess CO, with the rates and rate expressions in this regime being virtually identical for all three metals. Large enhancements in the steady-state rates are observed on the ceria-supported catalysts over that which would be expected from the precious metals themselves, especially for Pt at lower temperatures. The results suggest that the rates are non-specific to the metal–ceria interface and that it is the ceria properties which affect the reaction in this regime.

2. Experimental techniques

Because of the difficulties in measuring rates over a wide range of temperatures and partial pressures while avoiding diffusional effects, the measurements were made using model catalysts, as described in a previous publication [8]. The alumina support was prepared by oxidizing an Al foil in air at 750 K. The ceria support was prepared by spray pyrolysis of a $Ce(NO_3)_3$ solution onto the alumina film, to give a ceria film 10 μm thick. The ceria was calcined in air at 700 K overnight before introducing the precious metals. (Because the pretreatment temperature for ceria can strongly affect the results, care was taken to ensure that the treatment conditions for each catalyst were identical [11]. For the preparation conditions in this paper, line broadening of the X-ray diffraction pattern indicated that the average crystallite size of the ceria was 80 to 120 Å.) Each metal was introduced by vapor deposition in a vacuum chamber equipped with a quartz-crystal, film-thickness monitor. This technique deposits the metals near the external surface of the oxide support, so that diffusional difficulties can be minimized, even though the oxide itself may be porous. A coverage of 5×10^{15} atoms/cm^2 was used in each of the catalysts.

Reaction rates were measured by placing the foil catalysts in a 1/4 inch, quartz tube. While the total pressure in the reactor was always 1 atm, the flow rates of CO, air, and N_2 could be varied to control the partial pressures. The CO was cleaned by passing it through an activated-carbon trap to remove carbonyls and through a packed bed of NaOH pellets to remove residual CO_2. CO and CO_2 compositions leaving the reactor were measured with an on-line gas chromatograph, equipped with a methanator and an FID detector. Conversions of the limiting reagent were maintained well below 1% in most experiments, so that differential conditions were achieved. All the rates in this work have been normalized to the external surface area of foil.

Test reactions on the empty reactor showed no reaction at all. Rates were observed on ceria which were positive order in CO, but these were always at least one order of magnitude lower than rates observed in the presence of metal. Because the ceria films were porous, no attempt was made to try to calculate rates in the absence of metal, except to show that the ceria itself did not contribute in a significant manner.

3. Results and discussion

3.1. CO oxidation on alumina-supported catalysts

To provide a comparison between the different metals, we first examined CO oxidation rates on alumina-supported Pt, Pd, and Rh. The rates were measured in excess CO because this maintains the metals in the reduced state and because the rate expression is well established and understood [15–17]. The rates are shown as a function of CO pressure in fig. 1 for a temperature of 573 K and an O_2 pressure of 2.2 Torr; the parameters which best fit the rate data are given in table 1. The rates are approximately inverse, first-order in CO, in agreement with rates measured on the bulk metals and conventional, alumina-supported catalysts [12,13]. The reaction order of -1 arises from the fact that the precious metals are saturated with CO at these temperatures and pressures, so that the rate is limited by adsorption of O_2. In agreement with this, the activation energy is equal to the heat of adsorption of CO [14]. As observed in other studies, the rates are approximately first order in O_2 on each metal, probably indicating that adsorption into a molecular, undissociated species limits the rates [15]. (Note: The rates were initially measured at 0.3 Torr of O_2 in order to make a direct comparison with previous studies of CO oxidation over Rh/ceria [8]; however, the rates were so low on Pt/alumina at higher CO pressures as to make the measurements difficult with the amount of catalyst we used. Except for decreasing the rates by the amount expected for a rate which is approximately first order in O_2, all observations at 0.3 Torr O_2 were identical.)

Since CO oxidation is relatively insensitive to structure on Pt, Pd, and Rh, except for very small crystallites of Pt [14], the metal surface area, and therefore the aver-

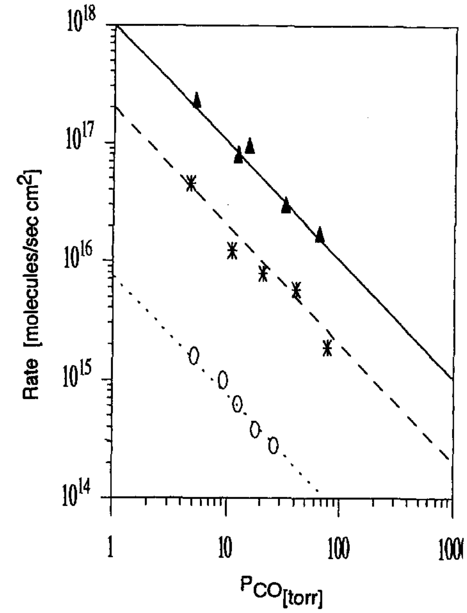

Fig. 1. Differential reaction rates for CO oxidation on Rh/alumina (▲), Pd/alumina (∗), and Pt/alumina (○) at 573 K as a function of CO pressure. The O_2 pressure was fixed at 2.2 Torr.

Table 1
Summary of rates for CO oxidation on alumina-supported catalysts

	Particle size (um)	Activation energy [a] (kcal/mol)	O_2 order [b]	CO order [c]
Pt/alumina	7.3	29 ± 1	0.85	−0.85
Pd/alumina	6.3	32 ± 1	1	~ −1
Rh/alumina	3.0	–	–	–

[a] Determined using a temperature range from 467 to 624 K.
[b] Measured at 573 K using P_{CO} of 24 Torr for Pt/alumina and 6 Torr for Pd/alumina.
[c] Measured at 573 K using P_{O_2} of 2.2 Torr on Pt/alumina and 0.3 Torr on Pd/alumina.

age particle size, can be estimated by comparing the rates in fig. 1 to specific rates from the literature [16,17]. Rates of CO oxidation on Rh(111), Pd(110) and Pt(100) were used for comparison. (Note: Since the calculated particle size will scale linearly with the measured rate, the turnover frequencies used in the calculation are critical.) The average particle sizes for Pt and Pd calculated in this manner, 7.3 nm for Pt and 6.3 nm for Pd, are somewhat smaller than that determined for films containing the same metal coverages on an α-Al_2O_3(0001) support in previous studies, 14 nm for 5 ML of Pt and 8.8 nm for 3.5 ML of Pd [18,19]. It is entirely reasonable given that the rough, alumina films in the present study could well have helped maintain dispersion. The average particle size calculated for Rh, 3.0 nm, differs more from the α-Al_2O_3(0001)-supported analog [20], but is again reasonable.

Overall, the data for the alumina-supported catalysts are in excellent agreement with published rate data. While data with much higher [14] and lower [17] activation energies have been reported for alumina and silica supported catalysts, especially for Pt at low temperatures, that data can be understood as resulting from structure sensitivity caused by the CO desorption properties [14,17]. The data also demonstrate previous observations that Rh is more active than Pd, which in turn is more active than Pt, as reported previously for Rh, Pd, and Pt wires [13].

3.2. Ceria-supported catalysts

Fig. 2 shows CO oxidation rates on Rh/ceria, Pd/ceria and Pt/ceria, again for metal coverages of $5 \times 10^{15}/cm^2$, at 573, 515 and 467 K as a function of CO pressure, for a fixed O_2 pressure of 0.3 Torr. The data are summarized in table 2. As stated earlier, the ceria sup-

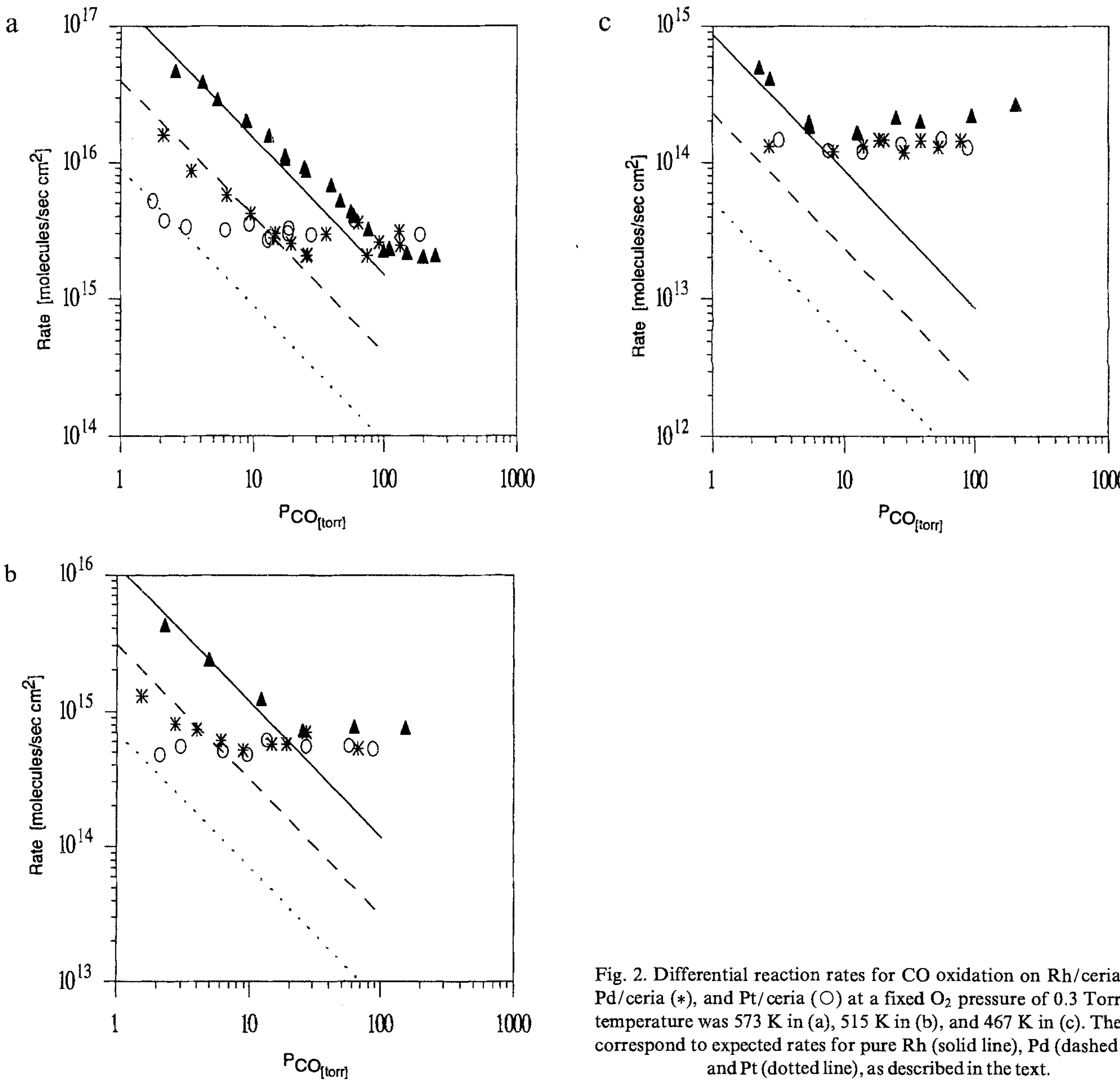

Fig. 2. Differential reaction rates for CO oxidation on Rh/ceria (▲), Pd/ceria (∗), and Pt/ceria (○) at a fixed O_2 pressure of 0.3 Torr. The temperature was 573 K in (a), 515 K in (b), and 467 K in (c). The lines correspond to expected rates for pure Rh (solid line), Pd (dashed line), and Pt (dotted line), as described in the text.

Table 2
Summary of rates for CO oxidation on ceria-supported catalysts

	Particle size (um)	Activation energy [a] (kcal/mol)	O_2 order [b]	
			(when $r \propto P_{CO}^{-1}$)	(when $r \propto P_{CO}^{0}$)
Pt/ceria	2.7	13 ± 1	–	0.46
Pd/ceria	4.2	13 ± 1	0.9	0.44
Rh/ceria	2.3	12 ± 1	0.9	0.40

[a] Determined using a temperature range from 467 to 624 K, in the zeroth-order regime.

[b] Measured at 573 K. CO pressures chosen to determine O_2 dependence when $r \propto P_{CO}^{-1}$ and when $r \propto P_{CO}^{0}$ are 6 and 46 Torr for Pd/ceria and 8 and 170 Torr for Rh/ceria. For Pt/ceria, O_2 dependence was determined at P_{CO} 24 Torr.

port, without precious metal, exhibited rates that were at least an order of magnitude lower than any reported in the figure, so that all rates are either due to the precious metals or ceria in contact with the precious metals.

The data for Rh/ceria have been discussed previously [8]. The reaction can be described as being the sum of two rate expressions, an inverse-first-order rate at the lower CO pressures, followed by a zeroth-order regime at the higher pressures. The pressure at which the break from inverse-first-order to zeroth-order occurs decreases at lower temperatures, indicating that the activation energy of the zeroth-order process is lower, 12–15 kcal/mol compared 26 kcal/mol. The O_2 pressure dependence also changes, from approximately first order to 0.40. Given that the activation energy in the inverse-first-order regime, as well as the reaction orders for CO and O_2, are identical to that for bulk Rh, it would appear that ceria does not affect the rates in this regime. One can again estimate the Rh particle size, 2.3 nm, as discussed for Rh/alumina. The solid lines in the figs. 2a, 2b and 2c are the rates to be expected from Rh alone and the rates at the lower CO pressures on Rh/ceria are identical to the pure Rh data.

The results and conclusions for Pd/ceria are virtually identical to that for Rh/ceria. At the lower CO pressures and higher temperatures, one again observes an inverse-first-order rate. If one calculates a dispersion for the Pd from these rates, the particle size can be estimated to be a reasonable 4.2 nm. Using an activation energy of 26 kcal/mol, rate data for Pd in the absence of ceria would fall along the dashed lines in fig. 2. Of particular interest is the fact that the rates become zeroth order at almost the same rate at which the break occurs on Rh/ceria. Due to the lower intrinsic activity of Pd, the break to zeroth order occurs at lower CO pressures and is not even observable at 467 K. In the zeroth-order regime, the reaction order for O_2 is 0.44 and the activation energy 13 ± 1 kcal/mol, virtually the same as found for Rh/ceria.

For Pt/ceria, the rates were zeroth order in CO at all temperatures and virtually identical to the zeroth-order rates for Rh/ceria and Pd/ceria. The activation energy and reaction order in O_2 were also identical at 13 ± 1 kcal/mol and 0.46, respectively. In order to make a comparison for the rates one would observe for pure Pt, we assumed a very high dispersion, corresponding to a particle size of 2.7 nm, to calculate the rates shown in the dotted line of fig. 2. Because it is unlikely that the Pt dispersion could be much higher than this, the dotted line actually represents an upper limit for the rates one would observe on pure Pt. It is therefore immediately obvious that the rates for Pt/ceria are much higher than that which would be expected for Pt/alumina, particularly at the lower temperatures.

The most reasonable explanation for the rate data in fig. 2 is that a similar mechanism is responsible for the zeroth-order regime on each of the metals. This regime obviously involves both the precious metals and the ceria. For Rh/ceria, it has previously been proposed that the ceria-mediated reaction involves CO from the metal reacting with oxygen from the ceria. This could occur via migration of the oxygen to the metal or from reaction at the interface between the metal and oxide phases. In either case, the rate will depend on metal particle size, as has been observed for Rh/ceria [8]. Since the metal is saturated with CO under reducing conditions, the rate is independent of CO pressure. The ceria is not covered with CO, so that O_2 adsorption is not inhibited [24]. The reaction approaches half order in O_2, as expected for dissociative adsorption, because there is no molecular adsorption state similar to that found on the precious metals.

The most interesting aspect of the data is that the rates are virtually identical for each of the metals. The scatter in the rates for the various metals can easily be accounted for by either differences in the particle sizes of each metal or variations in the ceria substrate. (While we tried to use identical preparation procedures for each ceria film, the rates in the zeroth-order regime are very sensitive to ceria structure [11].) The identical rates for each metal imply that there is no metal-dependent barrier preventing reaction at the interface. The fact that the rates under these conditions are strongly dependent on ceria structure would suggest the reactivity of lattice oxygen in ceria limits the rate [21].

The observations in fig. 2 also have practical implications. First, ceria greatly enhances CO oxidation rates on the precious metals at low temperatures, in agreement with the decreased light-off temperatures observed for ceria-supported catalysts [10]. Second, ceria enhances rates of CO oxidation significantly more for Pt than for Rh. This may help explain why interactions between Pt and ceria are more critical than between Rh and ceria in some catalyst formulations [22].

Furthermore, since the enhancements are not specific to the metal, it would appear that it is the oxide properties, and not specific interactions between the precious metal and ceria, which are the limiting factor in producing better catalysts. Contact between the two phases is obviously still necessary, and the structure sensitivity of oxygen abstraction from ceria makes the phenomenon complex. However, there is the implication that future advances in catalyst design will come from a better understanding of the oxide properties themselves. These complex materials provide a very fertile area for future work [23].

4. Summary

Rate measurements for CO oxidation on ceria-supported Pt, Pd and Rh indicate that a second, ceria-mediated process occurs on each of the materials. The process involves reaction of lattice oxygen with CO adsorbed on the precious metal and its rate is independent of metal. This process dominates at low temperatures and high CO pressures.

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References

[1] J.C. Summers and S.A. Ausen, J. Catal. 58 (1979) 131.
[2] H.C. Yao and Y.F. Yu Yao, J. Catal. 89 (1984) 254.
[3] E.C. Su, C.N. Montreuil and W.G. Rothschild, Appl. Catal. 17 (1985) 75.
[4] A. Tschope, W. Liu, M. Flytzani-Stephanopoulos and J.Y. Ying, J. Catal. 157 (1995) 42.
[5] J.G. Nunan, H.J. Robota, M.J. Cohn and S.A. Bradley, J. Catal. 133 (1992) 309.
[6] S.H. Oh and C.C. Eickle, J. Catal. 112 (1988) 543.
[7] G.S. Zafiris and R.J. Gorte, J. Catal. 143 (1993) 88.
[8] T. Bunluesin, H. Cordatos and R.J. Gorte, J. Catal. 157 (1995) 222.
[9] L.G. Tejuca, J.L.G. Fierro and J.M.D. Tascon, Adv. Catal. 36 (1989) 237.
[10] C. Serre, F. Garin, G. Belot and G. Maire, J. Catal. 141 (1993) 9.
[11] H. Cordatos, T. Bunluesin, J. Stubenrauch, J.M. Vohs and R.J. Gorte, J. Phys. Chem. 100 (1996) 785.
[12] Y.F. Yu Yao and J.T. Kummer, J. Catal. 106 (1985) 307.
[13] Y.F. Yu Yao, J. Catal. 87 (1984) 152.
[14] G.S. Zafiris and R.J. Gorte, J. Catal. 140 (1993) 418.
[15] J.A. Rodriguez and D.W. Goodman, Surf. Sci. Rep. 14 (1991) 27
[16] C.H.F. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher and S.H. Oh, J. Phys. Chem. 92 (1988) 1563.
[17] P. J. Berlowitz, C.H.F. Peden and D.W. Goodman, J. Phys. Chem. 92 (1988) 5213.
[18] E.I. Altman and R.J. Gorte, J. Catal. 110 (1988) 191.
[19] H. Cordatos, T. Bunluesin and R.J. Gorte, Surf. Sci. 323 (1995) 219.
[20] E.I. Altman and R.J. Gorte, J. Catal. 113 (1988) 185.
[21] E.S. Putna, J.M. Vohs and R.J. Gorte, submitted.
[22] R.W. Joyner, Zirconium in catalysis: a review of current scientific literature, prepared for Magnesium Elektron Ltd.
[23] P. Fornasiero, R. Di Monte, G. Ranga Rao, J. Kaspar, S. Meriani, A. Trovarelli and M. Graziani, J. Catal. 151 (1995) 168.
[24] G.S. Zafiris and R.J. Gorte, J. Catal. 139 (1993) 561.