Catalysis Letters 2 (1989) 235–242

REDUCTION OF NITRIC OXIDE BY CARBON MONOXIDE OVER SILICA-SUPPORTED PLATINUM-RHODIUM ALLOYS, COMPARISON WITH THE CO + O_2 REACTION

A.G. v.d. BOSCH-DRIEBERGEN, M.N.H. KIEBOOM, A. v. DREUMEL, R.M. WOLF, F.C.M.J.M. v. DELFT and B.E. NIEUWENHUYS *

Leiden University, Gorlaeus Laboratories, P.O. Box 9502, 2300 RA Leiden, The Netherlands

Received 7 January 1989; accepted 1 March 1989

The reduction of NO by CO was investigated over various silica-supported Pt-Rh alloy catalysts. Steady state catalytic activity as a function of temperature was measured over a range of gas phase compositions. The results were compared with those obtained earlier for the CO + O_2 reaction over the same catalysts. The results can be interpreted on the basis of our earlier Pt-Rh single crystal work. Important factors influencing the performance of the Pt-Rh alloy catalysts are the specific differences in intrinsic properties of Pt and Rh, the experimental conditions of the reaction and the composition of the alloy catalyst. We conclude that at the relatively high temperatures required for the CO + NO reaction the composition of the gas phase may induce large variations of the surface composition.

1. Introduction

The three-way catalyst that is utilized in automobiles for the control of pollution by exhaust emission contains both Pt and Rh as active components. This bimetallic catalyst converts simultaneously CO, hydrocarbons and nitrogen oxides into harmless CO_2, H_2O and N_2. In 1987 the automotive catalyst already accounted for more than 35% of the total Pt consumption and for 73% of the Rh consumption [1]. Despite the widespread use of the bimetallic Pt-Rh autocatalyst, little is known about the performance of Pt-Rh alloy catalysts concerning the relevant reactions [2,3]. This contrasts with the monometallic Pt and Rh catalysts about which several investigations have been reported in the literature [2–14]. Recently, we have investigated in our laboratory the properties of Pt-Rh alloys, both in the form of single crystal surfaces and SiO_2 supported catalysts [2,14–19]. A discussion of the CO + O_2 reaction over silica supported Pt-Rh alloys has been presented recently in a previous paper in this journal [2]. The present paper describes the results of a complementary investigation concerning the reduction of NO by CO over the same catalysts.

---

* To whom all correspondence should be addressed

2. Experimental

The preparation and the characterization of the alloy catalysts have been described in our previous paper [2]. The metal surface areas of the catalysts were determined by means of CO adsorption, assuming a 1 : 1 stoichiometry between noble metal surface atoms and adsorbed CO molecules. For Rh the assumption of CO/Rh surface ratio of 1 is only valid when the surface concentration of the CO dicarbonyl species is small, as is the case for our well-reduced Rh/SiO_2 catalysts [20].

The reaction rates were measured in a single-pass fixed bed flow reactor operating at atmospheric pressure. The gas stream contained 5% of the reactive gases (NO and CO), the carrier gas being argon with a total flow in the range of 25 cm^3/min. The mixture of research grade gases passed the powdered catalyst which was carried by a porous glass plate. Temperatures were measured using a calibrated chromel-alumel thermocouple attached on the porous glass plate. Analysis if the gas stream leaving the reactor was accomplished using a computer controlled quadrupole mass spectrometer which was differentially pumped by a turbomolecular pump group. Usual conditions employed 300 mg of catalyst contained in small Pyrex reactors. Rates were calculated from measurements of the total flow rate and composition of the gas stream leaving the reactor. Activities were compared as turnover frequencies, defined as molecules CO_2 formed per surface metal atom per second.

The catalyst was contacted at room temperature with the reactants stream. The catalyst temperature was increased according to a standard temperature-time program. The almost linear heating rate of 4.5 K/min was sufficiently slow to maintain steady-state reaction rate conditions at each temperature. The concentrations of the relevant gases were continuously monitored.

3. Results

To assess the effect of catalyst aging on NO reduction by CO, three series of experiments have been performed for each gas composition: the freshly reduced catalyst, the same catalyst after exposure to the reaction mixture for a period of 18 hrs. at 690 K and after subsequent cooling, a third measurement. The results of the last series of experiments were similar to the 2nd series within experimental accuracy. The freshly reduced catalyst was somewhat more active than the aged catalyst. The results presented in this paper have been obtained for the aged catalysts, but this is not relevant for the conclusions.

The results are summarized in fig. 1, which shows the temperature required to achieve a certain, fixed turnover frequency as a function of catalyst composition. The turnover frequency was calculated on the basis of the CO adsorption

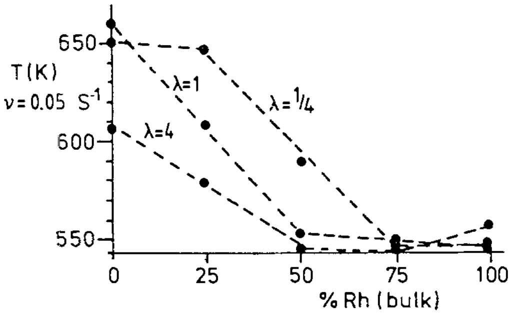

Fig. 1. Temperature for a turnover frequency of 0.05 s^{-1} for the CO+NO reaction over Pt-Rh alloys as a function of the bulk composition for three NO/CO ratios.

experiments. Five different catalysts have been used, viz. pure Pt, 25 at.% Rh, 50 at.% Rh, 75 at.% Rh and pure Rh.

The NO/CO ratio is expressed in terms of the equivalence ratio (λ), this being the ratio between the NO/CO ratio used and the NO/CO ratio at stoichiometry (NO/CO = 1). Three values of λ have been used, varying from CO rich ($\lambda = 1/4$), stoichiometry ($\lambda = 1$) to CO lean ($\lambda = 4$).

In order to compare the present results for the NO + CO reaction with those obtained earlier for the CO + O_2 reaction [2], figure 2 has been included. This figure shows the temperature required to achieve a certain, fixed turnover frequency for the CO oxidation using the same catalysts as for the NO reduction reaction.

The relevant observations in the figs. 1 and 2 may be summed up as follows:

(1) Much higher temperatures are required for achieving a certain turn-over frequency for the NO + CO reaction than for the CO + O_2 reaction.

(2) Synergetic effects like enhancement of the reaction rate for the Pt – Rh alloy catalysts compared with the pure component catalysts are absent for both reactions. In all cases the activity of the alloy catalyst is between those of the pure components.

(3) For both reactions the activities of Rh and the Rh rich alloy vary only slightly with the flow composition whereas for Pt and the Pt rich alloy the influence

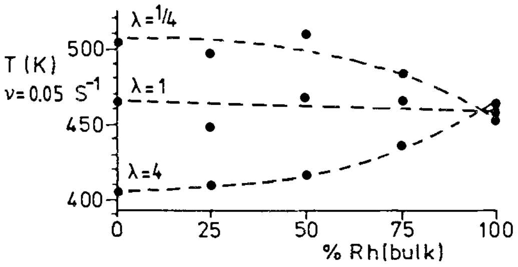

Fig. 2. Temperature for a turnover frequency of 0.05 s^{-1} for the CO+O_2 reaction over Pt-Rh alloys as a function of the bulk composition for three O_2/CO ratios (from ref. [21]).

of the flow composition is large. The effect of changing flow composition is larger for the CO + O_2 reaction than for the CO + NO reaction.

(4) Under oxidizing conditions Pt and Pt rich alloys are better catalysts for the CO + O_2 reaction than Rh and Rh rich alloys.

(5) Rh and Rh rich alloys are much better catalysts for the reduction of NO than Pt and Pt rich alloys, both under CO rich and CO lean conditions.

(6) For the CO + O_2 reaction the behavior of Pt0.75-Rh0.25 and Pt0.5-Rh0.5 is almost like that of pure Pt. The Pt0.25-Rh0.75 catalyst has an activity which is intermediate to those of Pt and Rh.

(7) For the NO + CO reaction the activity of the Pt0.25-Rh0.75 catalyst is almost equal to that of the pure Rh catalyst, independent of λ.

For stoichiometric and CO lean mixtures the Pt0.5-Rh0.5 alloy has an activity for the NO + CO reaction almost equal to that of Rh. Under reducing conditions, however, its activity is between those of Pt and Rh. The Pt0.75-Rh0.25 catalyst shows an activity equal to that of pure Pt under net-reducing conditions. Under stoichiometric and net-oxidizing conditions its activity is between those of Pt and Rh.

4. Discussion

In order to explain the results obtained for Pt-Rh alloys it is useful to discuss first briefly the behavior of the individual Pt/SiO_2 and Rh/SiO_2 catalysts and to summarize some results reported earlier for Pt-Rh alloy single crystal surfaces [14–19]. It is well established now that the main reaction pathway for CO oxidation on noble metals is a surface reaction between adsorbed O atoms and adsorbed CO molecules [6,7]. For Pt the temperature for constant turnover frequency increases with increasing CO concentration in the feed as a result of the well-known CO inhibition of the reaction rate. The Pt surface is predominantly covered with CO, leaving very little room for oxygen adsorption. For Rh the effect of CO inhibition is much smaller. Consequently, the Rh catalyst is the better catalyst under net-reducing conditions. However, under net-oxidizing conditions Pt is the most efficient catalyst, probably because of the lower metal-oxygen bond strength [6].

The present results illustrate again that Rh is a much better catalyst for the NO reduction by CO than Pt, an observation that is consistent with literature data [4–6]. The most likely mechanism of the NO + CO reaction is NO dissociation followed by reaction of adsorbed CO molecules and O adatoms and by combination of N adatoms to molecular nitrogen [4,6,10–13]. The dissociation step of NO is usually considered as one of the slowest steps in the reaction sequence. The NO dissociation is more difficult on Pt than on Rh [6]. Hence, the relatively low activity of Pt for the NO + CO reaction is consistent with this mechanism. Under our experimental conditions the effect of change of the feed composition was very small for Rh. This observation is consistent with the literature data that show that the reaction rate on Rh/Al_2O_3, Rh(111) and Rh(100) varies only slightly with the CO partial pressure [11,13]. For Pt our results point to a significant CO inhibition although much smaller than for the $CO + O_2$ reaction. This result may indicate that adsorbed CO does not only inhibit the dissociative adsorption of oxygen but also the dissociation of NO on Pt. The NO dissociation may require an ensemble of more than one vacant platinum atom.

In earlier studies we have shown that the surface composition of Pt-Rh alloys varies strongly with the experimental conditions such as the equilibration temperature used and the gas composition [14–19]. For clean surfaces, Pt surface enrichment was observed following annealing above 1000 K. Low temperature annealing results in a surface composition close to the bulk composition. The surface composition is extremely sensitive to the composition of the gas phase or to impurities present in the sample. For example, small amounts of sulfur induce a Rh surface segregation [21]. CO does not influence the surface composition [15]. However, oxygen and NO in the gas phase induce a Rh surface segregation because of the high Rh-O bond strength relative to that of Pt-O [15]. Hence, an initial surface composition, which has been achieved by equilibration at a chosen temperature, can easily be altered. This makes the discussion of the present results more complicated.

As we have discussed in our previous paper [2] the almost equal activity of the Pt, Pt0.75-Rh0.25 and Pt0.5-Rh0.5 catalysts for the $CO + O_2$ reaction suggests that all the surfaces of these catalysts are Pt rich, after reduction with hydrogen and subsequent exposure to the reaction mixture up to 550 K. A similar behavior has been found for a Pt-Rh(410) single crystal surface [15]. The Pt0.25-Rh0.75 catalyst shows for that reaction an activity between those of Pt and Rh. Hence, it is reasonable to visualize the surface of the Pt0.25-Rh0.75 catalyst as being composed of both Pt and Rh. For the $CO + O_2$ reaction the thermodynamically more favorable Rh surface segregation under net-oxidizing conditions does not occur under our experimental conditions. This may be caused by the relatively low reaction temperatures since complete CO conversion is already reached at temperatures far below 575 K. For Pt-Rh alloy single crystals we found O induced Rh surface segregation at temperatures above 600 K [15]. At lower temperatures O induced Rh surface segregation is kinetically hampered.

A comparison of the figs. 1 and 2 reveals some interesting differences in the behavior of the Pt-Rh alloy catalysts for the $CO + O_2$ and for the $CO + NO$ reactions. For the $NO + CO$ reaction the Pt0.5-Rh0.5 alloy catalyst behaves like pure Rh under stoichiometric and net-oxidizing conditions whereas under net-reducing conditions its activity is between those of Pt and Rh. This suggests that the surface composition varies with the experimental conditions, from almost pure Rh under stoichiometric and net-oxidizing conditions to a, perhaps bulk-like surface composition under net-reducing conditions. This effect of O (from O_2 or NO) induced Rh surface segregation was indeed observed on well-defined Pt-Rh alloy surfaces at temperatures above 600 K [15]. The Pt0.75-Rh0.25 alloy behaves almost like pure Pt under net-reducing conditions whereas its activity is between those of Pt and Rh under stoichiometric and oxidizing conditions. Again, it suggests that the surface composition changes with the feed composition using the relatively high temperatures required for this reaction. The composition changes from Pt rich at $\lambda = 1/4$ to Rh rich at $\lambda = 4$.

The properties of the Pt0.25-Rh0.75 alloy are notable. For the $CO + O_2$ reaction its behavior was intermediate of those of Pt and Rh, suggesting a surface with both Pt and Rh present in large concentrations. For the NO + CO reaction its behavior is like that of Rh under stoichiometric and oxidizing conditions as expected on the basis of our previous discussion. However, for the NO + CO reaction this alloy also behaves like pure Rh under reducing conditions ($\lambda = 1/4$). It might be that, under the conditions of the NO + CO reaction with $\lambda = 1/4$, the surface of this catalyst contains many Rh and Pt atoms as should be expected. The relatively high activity of this catalyst (Rh like) might then be caused by the beneficial effect of the presence of both Pt and Rh: the easy dissociation of NO on Rh sites, the low CO inhibition on Rh sites and a beneficial effect of Pt, for example, on the amount of N on the surface. On Rh(111) the surface is populated by a high concentration of adsorbed N under reaction conditions [13]. These N adatoms may act as a reaction inhibitor since sites are occupied that cannot be used for the reaction. On Pt surfaces the N surface concentration is much smaller than on Rh surfaces [14,15].

Summarizing, in this paper novel results have been presented concerning the NO reduction over Pt-Rh alloy catalysts. It appears that the catalytic properties of supported Pt-Rh alloys can be understood on the basis of our single crystal work using the surface composition and the specific properties of Pt and Rh.

Acknowledgement

The authors acknowledge the Johnson Matthey Technology Centre (Reading, U.K.) for the loan of the Pt and Rh salts. This research was supported in part by NATO via grant = 86.352.

References

[1] *Platinum 1988* (Johnson Matthey Public Limited Company, London) p. 29 and p. 59.

[2] A.G. van den Bosch-Driebergen, M.N.H. Kieboom, A. v. Dreumel, R.M. Wolf and B.E. Nieuwenhuys, Catal. Letters 2 (1989) 73.

[3] S.H. Oh and J.E. Carpenter, J. Catal. 98 (1986) 178.

[4] K.C. Taylor, *Automotive Catalytic Converters* (Springer/Berlin, 1984).

[5] K.C. Taylor, in: *Catalysis and Automotive Pollution Control*, Vol. 30 of Stud. Surf. Sci. and Catal., eds. A. Crucq and A. Frennet (Elsevier, Amsterdam, 1987) p. 97.

[6] B.E. Nieuwenhuys, Surf. Sci. 126 (1983) 307 and refs. therein.
[7] T. Engel and G. Ertl, Adv. Catal. 28 (1979) 1.
[8] W.F. Egelhoff, *Chem. Phys., Solid Surfaces and Heterog. Catalysis*, eds. D.A. King and D.P. Woodruff, Vol. 4 (Elsevier, Amsterdam, 1982).
[9] D'Arcy Lorimer and A.T. Bell, J. Catal. 59 (1979) 223.
[10] W.C. Hecker and A.T. Bell, J. Catal. 92 (1985) 247.
[11] S.H. Oh, G.B. Fisher, J.E. Carpenter and D.W. Goodman, J. Catal. 100 (1986) 360.
[12] H.A.C.M. Hendrickx, A.M.E. Winkelman and B.E. Nieuwenhuys, Appl. Surf. Sci. 27 (1987) 458.
[13] S.B. Schwartz, G.B. Fisher and L.D. Schmidt, J. Phys. Chem. 92 (1988) 389.
[14] F.C.M.J.M. van Delft, G.H. Vurens, M.C. Angevaare-Gruter and B.E. Nieuwenhuys, in: *Catalysis and Automotive Pollution Control*, Vol. 30 of Stud. Surf. and Catal., eds. A. Crucq and A. Frennet (Elsevier/ Amsterdam, 1987) p. 229.
[15] F.C.M.J.M. van Delft, J. Siera and B.E. Nieuwenhuys, Surf. Sci., submitted.
[16] F.C.M.J.M. van Delft and B.E. Nieuwenhuys, Surf. Sci. 162 (1985) 538.
[17] R.M. Wolf, M.J. Dees and B.E. Nieuwenhuys, J. Physique C7 47 (1986) 419.
[18] F.C.M.J.M. van Delft, A.D. van Langeveld and B.E. Nieuwenhuys, Surf. Sci. 189/190 (1987) 1129.
[19] F.C.M.J.M. van Delft, J. Siera, R.J. Vreeburg, M.J. Koster van Groos, A.D. van Langeveld and B.E. Nieuwenhuys, Proc. 9th Int. Congr. on Catal. Calgary, Vol. 3 (1988) p. 1124.
[20] Y.E. Li and R.D. Gonzalez, Phys. Chem. 92 (1988) 1589.
[21] T.T. Tsong, Surf. Sci. Rep. 8 (1988) 198.