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Reducibility of Bimetallic Pd–Rh Catalysts and Its Relation with Synergism in the Oxidation Reaction of CO with O_2†

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A synergistic effect related to the greater stability of the Pd–Rh bimetallic catalysts in the reduced state in the oxidation reaction of CO is observed.

The catalysts used for the control of environmental pollution are made of combinations of the noble metals Pt, Pd and Rh. The presence of two or more metals on the surface of the catalyst may give rise to a synergistic effect in which the activity of the combined metals is greater than the sum of their separate activities. Oh and Carpenter[1] have reported the existence of a synergistic effect during the oxidation of CO by O_2 over bimetallic Pt–Rh catalysts prepared by sequential impregnation of both metals. Such an effect is not observed if the catalysts are prepared by coimpregnation of the two metals. Recently, Lakis *et al.*[2] have also found a synergistic effect for the reduction reaction of NO with CO over Pt–Rh/alumina catalysts prepared by sequential impregnation. In general, the synergistic effect has been attributed to a reaction at the Pt–Rh interface between CO adsorbed on Pt and O_2 (or NO) adsorbed on Rh.[1,2]

In the case of the oxidation of CO with O_2, the synergistic effect reported by Oh and Carpenter requires the simultaneous existence of reduced Pt over which CO is adsorbed, and oxidized Rh on whose surface the oxygen that reacts with CO adsorbed on a neighbouring Pt atom is located. It is reasonable, therefore, to assume that the existence of the synergistic effect must be closely related to the oxidation state of both metals on the surface of the catalyst. This paper discusses the possible existence of a synergistic effect of Pd–Rh catalysts supported on silica in the oxidation reaction of CO with O_2. In contrast to the Pt–Rh system, the Pd–Rh system has been rarely studied in the literature.[3–5] In particular, it is of interest to determine whether the different methods of impregnation of the two metals (coimpregnation and sequential impregnation) give rise to any differences in the stability of the reduced states of both metals on the surface of the catalyst, and to relate such differences to the existence of a synergistic effect.

Experimental

Monometallic and bimetallic catalysts were prepared with a 2% total metal load as described in ref. 6. Briefly, in the coimpregnation (CI) method the impregnation with both metals is done simultaneously, treating the silica support (Cabosil 5H) with an aqueous solution of inorganic salts of the two metals ($PdCl_2$ and $RhCl_3$). In the sequential impregnation (SI) method, in a first step impregnation is done with Rh as has been described, and this is followed by calcination at 500 °C; in a second step, Pd is deposited using an organic solution of palladium acetylacetonate in dichloromethane to avoid dissolving the Rh. Monometallic catalysts were prepared by the incipient wetness method using $RhCl_3$ and $PdCl_2$. Bimetallic catalysts having two different Pd–Rh ratios were prepared, leading to a series of six catalysts, two monometallic, which will be identified as 100Rh and 100Pd, and four bimetallic having two different Rh–Pd ratios, 70% Rh–30% Pd and 33% Rh–67% Pd, identified as 70Rh–30Pd and 33Rh–67Pd, respectively, followed by CI for those prepared by coimpregnation and SI for those prepared by sequential impregnation.

The impregnated catalysts (0.3 g) were loaded into the reactor and were subjected to a sequence of calcinations at increasing temperatures, measuring the degree of oxidation by temperature-programmed reduction experiments (TPR). The sequence of calcinations and TPR experiments is shown below:

impregnated cat. ⟶ calcin. 1 at 300°C ⟶ TPR 1
⟶ calcin. 2 at 300°C ⟶ TPR 2 ⟶ calcin. 3 at 500°C
⟶TPR 3 ⟶ calcin. 4 at 300°C ⟶ TPR 4
⟶ calcin. 5 at 700°C ⟶ TPR 5 ⟶ calcin. 6 at 300°C ⟶ TPR 6

The TPR experiments were carried out in a 20 $cm^3\ min^{-1}$ stream of 5% H_2 in Ar, with a heating rate of 10 °C min^{-1}. The H_2 consumption during the experiment was measured in the traditional way by means of a conductivity cell.

At the end of the sequence of calcinations the activity of the different catalysts in the oxidation reaction of CO with O_2 was determined. After the last TPR experiment (TPR 6), H_2 was desorbed for 1 h at 300 °C in a 100 $cm^3\ min^{-1}$ stream of pure Ar. The temperature was then decreased to 60 °C and the catalyst dispersion, which will be used later in the calculation of the TOF, was measured as described below. The catalyst was calcined in a 20 $cm^3\ min^{-1}$ stream of pure O_2 (1 h at 300 °C) with the purpose of oxidizing the Rh. The temperature was then reduced to room temperature under O_2, and a CO and He stream was connected, adjusting the CO and O_2 flows to 5 $cm^3\ min^{-1}$ and 30 $cm^3\ min^{-1}$, respectively, and the total flow was adjusted to 100 $cm^3\ min^{-1}$ with He. The reactor temperature was increased slowly, and samples of the stream at the reactor outlet were taken after the required temperature had remained constant for 15 min. The samples were analysed by gas chromatography to determine the CO_2 concentration. The reactor was of the piston flow type, and was operated under differential conditions (less than 10% conversion). The thickness of the catalytic bed was approximately 0.4 cm.

The catalyst dispersion was determined by H_2 chemisorption at 60 °C to avoid the formation of hydrides,[7] using the traditional dynamic method, *i.e.* measuring the adsorption of H_2 pulses sent into the feed stream of the reactor (40 $cm^3\ min^{-1}$ of Ar).

Results and Discussion

H_2 consumption by the catalysts following the calcinations described above are shown in Fig. 1, expressed as % of H_2 consumed relative to the total theoretical consumption needed to produce the reduction of the completely oxidized catalyst. Considering that the reduction of Pd and Rh is complete at temperatures below 200 °C, the H_2 consumption during the TPR experiments represents the degree of oxidation reached by the catalyst after each calcination experiment. Fig. 1a shows the results obtained with the monometallic catalysts 100Rh and 100Pd. It is seen that in the calcinations at temperatures up to 500 °C the Pd catalyst is easier to oxidize than the Rh catalyst, and this is reflected in the higher H_2 consumption shown by the former. In later calcinations both catalysts show similar degrees of oxidation. The behaviour of the bimetallic catalysts with a high Rh content, 70Rh–30Pd, is shown in Fig. 1b. The catalysts prepared by the two methods of impregnation (CI and SI) behave very similarly. What is most interesting is that these bimetallic catalysts show greater stability in the reduced state than that shown by the separate metals in the monometallic catalysts. Fig. 1c shows

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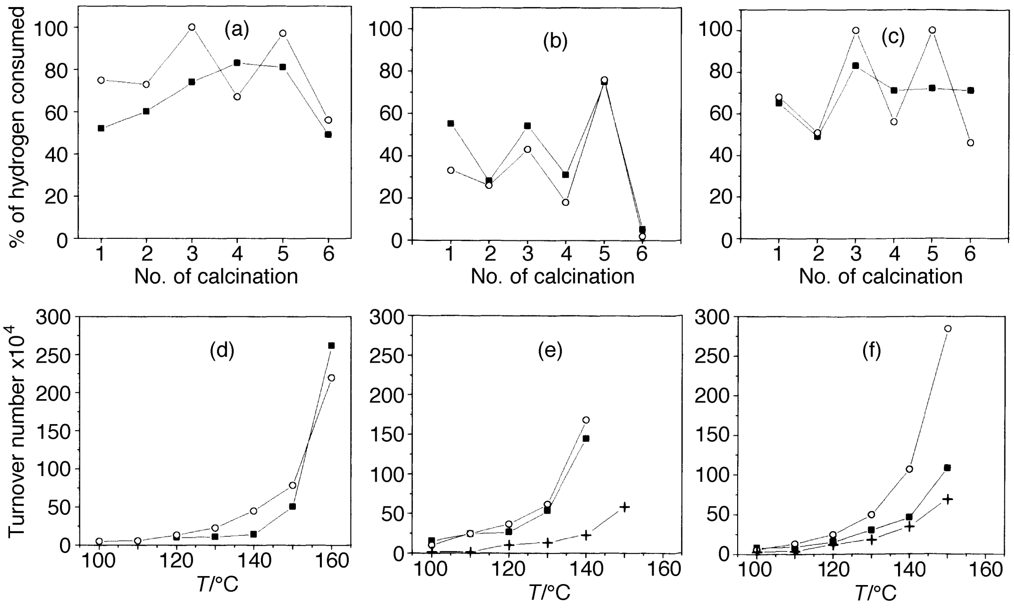

Fig. 1 % H_2 consumed after the calcinations described in Experimental (a, b and c), and activity (d, e and f) of the different catalysts: (a) catalyst 100Rh (■) and 100Pd (○); (b) catalyst 70Rh–30Pd CI (■), catalyst 70Rh–30Pd SI (○); (c) catalyst 33Rh–67Pd CI (■), catalyst 33Rh–67Pd SI (○); (d) catalyst 100Rh (■) and 100Pd (○); (e) catalyst 70Rh–30Pd CI (■), catalyst 70Rh–30Pd SI (○), theoretical catalyst (+); (f) catalyst 33Rh–67Pd CI (■), catalyst 33Rh–67Pd SI (○), theoretical catalyst (+)

the behaviour of the bimetallic catalysts with a lower Rh content, 33Rh–67Pd. It can be seen that the stability of the metals in the reduced state is lower than that of the 70Rh–30Pd catalysts, and that their behaviour is similar to that of the pure Pd catalyst (100Pd).

The activity of the different catalysts, expressed as TOF{[(moles of CO_2 produced)/[(moles of exposed metal) × s]}, is shown in Fig. 1e, f. Fig. 1d shows the results of the monometallic catalysts 100Rh and 100Pd. It can be seen that the activities of both catalysts are similar and remain low at temperatures below 150 °C. Above that temperature the activity increases considerably, leading to ignition of the catalysts at temperatures around 170 °C. The activity of the bimetallic catalysts 70Rh–30Pd is shown in Fig. 1e, which also shows the activity of a theoretical catalyst having the same composition assuming that the activity of both metals in the bimetallic catalyst is the same as that of the monometallic catalysts of Fig. 1d. It is seen that both bimetallic catalysts have greater activity than the sum of the monometallic ones, thereby showing clearly a synergistic effect. In contrast to what Oh and Carpenter observed, the catalyst prepared by the CI method also shows a synergistic effect. Fig. 1f shows the activity of the 33Rh–67Pd catalysts. It is seen that while the CI catalyst has an activity that is very similar to that of the theoretical catalyst, the activity of the SI catalyst is significantly higher than the sum of the activities of the monometallic catalysts.

The activity results show the existence of a synergistic effect for the 70Rh–30Pd bimetallic catalysts prepared by both CI and SI. On the other hand, in the catalysts with a lower Rh content, 33Rh–67Pd, only those prepared by the SI method show a synergistic effect. Although it is not possible to discard the existence of a synergistic mechanism similar to that proposed by Oh and Carpenter for the Pt–Rh catalysts, an alternative explanation can be proposed for the synergistic effect of our catalysts. In fact, it is well known that the activities of the metals Pd and Rh is much greater in the reduced than in the oxidized state. When the degree of oxidation of the monometallic catalysts 100Rh and 100Pd after the last calcination at 300 °C (calcin. 6) is compared to that of the bimetallic catalysts 70Rh–30Pd prepared by either the CI or SI method, it can be concluded that in the reduced state both bimetallic catalysts have a greater stability than the monometallic catalysts. In the case of the 33Rh–67Pd catalysts, in the reduced state the SI catalyst has a greater stability than the CI catalyst, in agreement with the higher activity shown by the catalyst prepared by sequential impregnation.

Table 1 Chemisorption of hydrogen results

Catalyst	moles of H/moles of metal
100Rh	0.34
70Rh–30Pd CI	0.45
70Rh–30Pd SI	0.58
33Rh–67Pd CI	0.62
33Rh–67Pd SI	0.40
100Pd	0.51

Conclusions

The results of the activity of the different catalysts make it possible to conclude that there is a synergistic effect which may be related to the greater stability of the bimetallic catalysts in the reduced state. However, it is not possible to reject the existence of a synergistic mechanism similar to that reported in the literature for Pt–Rh catalysts. It is quite possible that the synergistic effect may be due to a combination of both phenomena.

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