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The Topography of Rhodium in Bimetallic Rhodium–Palladium Catalysts on a Silica Support†

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Benzene and hex-1-ene hydrogenation reactions are used to obtain information about the concentration and topography of the metals on the surface of bimetallic Rh–Pd/SiO_2 catalysts.

In a previous paper,[1] the oxidation rates of CO with oxygen to produce CO_2 were compared for a series of Pd–Rh/SiO_2 catalysts prepared by different methods of impregnation. The Pd and Rh composition varied between 0% Rh–100% Pd and 100% Rh–0% Pd, maintaining a total metal load equal to 2% (w/w) with respect to the support. In brief, in the coimpregnation (CI) method the impregnation of both metals is done simultaneously, the support (Cabosil 5H) being treated with an aqueous solution of the inorganic salts of the two metals ($PdCl_2$ and $RhCl_3$). In the sequential impregnation (SI) method, the support is initially impregnated with Rh as described above and then dried and calcined at 500 °C. The Pd is then deposited in a separate second stage using an organic solution of bis(acetylacetonato)palladium in dichloromethane to avoid dissolving the deposited Rh. The CI method favours the formation of Pd and Rh alloys,[2] while the SI method should lead to a random Pd deposit on the surface of the support impregnated with Rh,[3] and should not form alloys to any significant extent.

The mixed catalysts of the same composition, but prepared by the two different methods, showed important differences in their activity towards the oxidation of CO with oxygen. In general, the CO oxidizing activity of the catalysts prepared by the CI method is lower than that of those prepared by SI. The lower activity of the former can be attributed to various factors, such as the formation of alloys superficially enriched in the less active component (Pd), the existence of very small Rh clusters that are unable to oxidize CO, and/or the presence on the surface of isolated Rh atoms on which CO is adsorbed in the *gem* form, which is a low-activity species. Although a large quantity of CO adsorbed in the *gem* form could be observed in the less active catalysts, the available experimental data did not allow a clear separation to be made of the effects of the various factors mentioned above on the CO oxidation rate.

This paper reports an attempt to obtain more information on the topography and concentration of Rh on the surface of some of these catalysts, in order to determine if, in addition to the presence of CO adsorbed in the *gem* form, the low activity of catalysts prepared by CI is due to a geometric factor (Rh cluster size on the surface) or to a superficial enrichment with Pd. To this end, hydrogenation experiments were carried out on hex-1-ene and benzene over some of the catalysts used in the oxidation of CO. According to Del Angel *et al.*,[2] the reduction of hex-1-ene can occur easily on very small Rh clusters, and this reaction is not sensitive to the metal structure. The hydrogenation of benzene, however, requires at least one Rh cluster larger than 10 Å in diameter which can accommodate the benzene molecule. A comparison of the catalyst rates in these reactions would make it possible, therefore, to obtain valuable information on the topography and composition of Rh on the surface of these bimetallic catalysts. The surface of the catalysts was also analysed by the XPS technique on a Shimadzu 750 ESCA instrument using MoKα radiation. The bond energies were referred to Si 2p adopting the value of 103.8 eV in agreement with Gallaher *et al.*[4] The atomic ratios were calculated using the Si 2p, Rh 3d and Pd 3d areas, the photoionization section given by Scofield,[5] the mean free path reported by Seah and Dench[6] and the instrument function supplied by Shimadzu.

Experimental

The hydrogenation experiments were carried out in a piston flow reactor operating under differential conditions. The reagents, hydrogen and organic compound, were fed into the reactor by bubbling the H_2 through the hex-1-ene (at 0 °C) or the benzene (at 20 °C). The amount of catalyst used was about 0.001 g for the hydrogenation of hex-1-ene, and 0.030 g for that of benzene. The catalyst had been previously activated by allowing H_2 to flow through it at 200 °C for 2 h. The temperature of the reactor was then lowered to that required for each experiment (0 °C for hex-1-ene and 80 °C for benzene hydrogenation), and the direction of the H_2 stream was reversed to make it go through the bubbler with the organic reagent. During this time the reactor remained isolated, and once the concentration of organic compound in the H_2 stream became stabilized, the flow was directed to the reactor. The reagents and products were analysed by GC, using a thermal conductivity detector and a column (6 m × 1/8 in ID) filled with 20% Carbowax on a Chromosorb support.

Results and Discussion

Bimetallic catalysts containing 0.66% Rh and 1.34% Pd were chosen for this work. The catalyst prepared by the CI method showed a CO oxidizing activity markedly lower than that of the catalyst prepared by SI. The oxidation rates of CO at 100 °C with these catalysts expressed as TOF Turn Over Frequency), *i.e.* in mol of CO_2 produced per mol of exposed metal (Pd + Rh) on the surface per second, are shown in Table 1, which also shows the reduction rates of hex-1-ene and benzene found in this study. It is important to note that the activity of Rh in all the reactions considered was far greater than that of Pd, so it can be assumed that the changes in the activity of the catalyst may be attributed to the supported Rh phase. It is seen that, in the oxidation of CO and reduction of benzene reactions, the activity of the catalyst prepared by the CI method is considerably lower than that of the catalyst prepared by SI. However, in the hydrogenation of hex-1-ene both catalysts have similar activities. Table 2 shows the relationship between the activities of the two catalysts in the various reactions considered in this study. It can be seen

Table 1 Activities of catalysts for the various reactions

	TOF (s^{-1})		
Catalyst	CO oxidation[a]	Hex-1-ene hydrogenation	Benzene hydrogenation
CI	0.300×10^{-3}	7.83	0.035
SI	1.337×10^{-3}	7.97	0.051
Monometallic (0.66% Rh)	—	25.61	0.302

[a]From ref. 1.

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Table 2 Relation between the activities of CI and SI catalysts

Reaction	Ratio TOF(CI)/TOF(SI)
CO oxidation	0.22
Hex-1-ene hydrogenation	0.98
Benzene hydrogenation	0.70

Table 3 XPS characterization and chemisorption results of catalysts

	XPS (atomic ratio)		Gas adsorbed (mol/mol metal)[a]	
Catalyst	Rh/Si	Pd/Si	H/metal	CO/metal
CI	0.0020	0.0040	0.37	0.46
SI	0.0023	0.0042	0.30	0.27
Monometallic (0.66% Rh)	—	—	0.42	—

[a]From Ref. 1.

that the ratio of the activities is almost unity for the hydrogenation of hex-1-ene. If it is accepted that the reaction is not sensitive to structure, this result suggests that the quantity of Rh on the surface of both catalysts is the same. Table 1 also reports the activity for the hydrogenation of hex-1-ene of a monometallic Rh catalyst with the same Rh content as the bimetallic catalysts (0.66% Rh). This catalyst was prepared by the wetness impregnation method using a $RhCl_3$ solution as described in reference 1. If the TOFs of the bimetallic catalysts prepared using the CI and SI methods are calculated by the number of Rh atoms on the surface, considering the bulk composition, TOFs equal to 23.73 and 24.15 s^{-1} are obtained for the CI and SI catalysts, respectively, in excellent agreement with the TOF of the monometallic catalyst, thus confirming the assumption that the surface composition is the same as the bulk composition, for both bimetallic catalysts. This conclusion is also supported by the results of the XPS characterization given in Table 3, which shows that the surface composition of both catalysts is almost the same, and it also similar to that of the bulk. Therefore, it is reasonable to suppose that the differences in the activities of these catalysts in the oxidation of CO and the reduction of benzene cannot be attributed to differences in their surface composition.

In the reduction of benzene, the lower activity of the catalyst prepared by CI as compared to that prepared by SI would be due to the existence of a greater number of Rh atoms forming a small-size cluster (smaller than 10 Å) on which the hydrogenation of benzene is hindered.[2]

In conclusion, it can be said that the low activity of the catalyst prepared by CI in the oxidation of CO is essentially due to the topography of Rh on the surface of the bimetallic catalyst, and not to a decrease in the concentration of this metal on the surface.

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