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Influence of Carrier and Oxygen Treatment on the Catalytic Behavior of Supported Platinum–Gold Alloys

Alloys, often used in selectivity studies, have in general a surface composition different from that of the bulk, and the segregation of a component (often the component with the lower melting point) which decreases the surface energy of the surface is strongly dependent or environmental conditions (*1–3*). Also some catlaytic reactions change the surface composition of alloys (*4*). It is not surprising, therefore, that different authors obtain different results with apparently the same alloys, but nevertheless it is an unsatisfactory situation. Differences in the carriers used, or in the mode of catalyst preparation, or in the metal particle size, can be responsible for the differences observed in catalytic behavior.

Problems of this kind have been observed with Pt–Au alloys. Alloys prepared on SiO_2 by coreduction in a solution of hydrazine(chloride) revealed with hexane mainly isomerization at low Pt concentration (*5*). Alloys prepared by coimpregnation of alumina and subsequent calcination, reduction, and repeated oxidation/reduction cycles revealed mainly dehydrocyclization (*6*). Diluted Pt–Au alloys on SiO_2 isomerize hydrocarbons by a 3-ring mechanism, while alloys on Al_2O_3 do so by a 5-ring mechanism (*7*). In view of this we have now investigated the role of the carrier and of the oxygen treatment of the alloys on their catalytic behavior.

Catalysts with a composition of 4 atom% Pt and 96 atom% Au were prepared by coreduction by hydrazine (*8*) of an aqueous solution of the metal salts. Reduction can be performed with or without a carrier. In the former case metal particles are formed which rather weakly adhere to the surface of the carrier (*9*). A careful study by X-ray diffraction of supported alloys (15 wt% loading) (*9–11*) revealed that after coreduction at about 80°C alloy particles are formed with a lattice constant near to that of the solid solution. However, the composition of the particles varied with depth. When annealed at 450°C for 16 hr in hydrogen, their inhomogeneity is reduced and in the region of one-phase alloys (0–17% Pt) Au is evidently segregated at the particle surface (*11*). At 450°C two phases are at equilibrium when the Pt concentration is between 17 and 97%. Indeed, when in this concentration range a solid solution obtained by coreduction at 80°C is annealed as described, the two phases clearly separate and two lattice constants are observed (*9*) as expected according to the tabulated data on this system. This indicates that the system of Pt–Au particles on a carrier is not very far from the equilibrium state, at least as far as the surface concentration of Pt is concerned. In this paper the 4% Pt–Au alloys on SiO_2 and on Al_2O_3 were prepared with a metal loading of 15 wt% (SiO_2, < 230 mesh, Merck; γ-Al_2O_3, Woelm neutral).

After reduction in hydrogen at 450°C for 16 hr *in situ*, the catlaysts were tested in the flow apparatus described elsewhere (*5*). The activity and selectivity were defined as in our previous papers (*5, 9*)—activity by the total conversion α of hexane and selectivity S as a fraction of hexane converted into the particular products. The hexane reactions (hydrogenolysis, isomerization, and dehydrocyclization) were studied under standard conditions (1 atm H_2, 8 ml/min, 370°C) at an H_2/hexane ratio equal to 16.

In previous work from this laboratory on

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Pt–Au alloys (*5*), SiO_2 was used as a carrier, but other authors (*6*) have used Al_2O_3 which is known to stabilize small Pt particles better than SiO_2. Therefore our first task was to compare the same alloy catalyst on the two different carriers. It appeared that within the experimental error there was no difference in catalytic activity (Table 1) and starting selectivity (Fig. 1) of the same alloy (4% Pt–Au) on SiO_2 and on Al_2O_3. As can be seen from Fig. 1, however, the behavior becomes different when the catalysts are subjected to an oxidation/reduction cycle *in situ*. The Pt–Au/Al_2O_3 catalyst was subjected to two cycles. During the first, the catalyst was oxidized by pure oxygen at 1 atm pressure, 350°C, for 2 hr. Then, the catalyst was reduced by hydrogen at 350°C, for 3 hr and its catalytic activity and selectivity were redetermined (indicated as first oxidation step in Fig. 1). The second oxidation treatment was more rigorous, namely, 16 hr at 450°C, followed by reduction in hydrogen for 3 hr at 450°C (longer reduction in H_2 showed no changes), whereupon the activity and selectivity were determined again (Fig. 1, second step; Table 1). We observed a remarkable difference. While the silica-supported catalyst did not change its selectivity, Pt–Au on Al_2O_3 changed considerably. This effect was not observed when heating the sample in an inert (N_2) atmosphere. Table 1 shows another interesting effect: the oxidation/reduction treatment of the alumina catalyst leads to an *increase* in activity, while the activity of the silica catalyst decreases under the same condition. Evidently, alumina plays a role in the *increase* in activity and the change in selectivity.

TABLE 1

Conversion of *n*-Hexane at 370°C over Supported Pt–Au Catalysts

	Conversion (%/g catalyst)	
	Before oxidation	After second oxidation step[a]
Pt–Au/Al_2O_3	2.9	6.0
Pt–Au/SiO_2	2.6	2.0

[a] See Fig. 1.

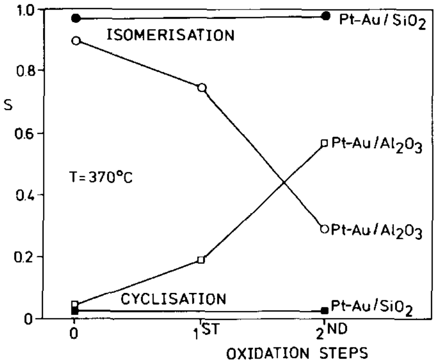

FIG. 1. Changes in selectivity *S* of two Pt–Au catalysts (on Al_2O_3 and on SiO_2) as a result of oxygen treatment.

For comparison the following experiments were performed. A pure-Pt catalyst was prepared with 1 wt% Pt on SiO_2 and on Al_2O_3 (the same amount of Pt on the carrier as was present in the alloys). Both were subjected to the two-stage oxidation/reduction cycles and the results are shown in Table 2 where the selectivity is shown before oxygen treatment and after the second oxidation/reduction step. If activation of the Al_2O_3 carrier or stabilization of Pt ions in Al_2O_3 were responsible for the behavior in Fig. 1, one would expect to find the same behavior also with pure Pt on Al_2O_3. However, as can be seen this is not the case and another explanation should be sought.

Looking at Fig. 1 we can observe that the Pt–Au/Al_2O_3 catalyst changed its selectivity after the two oxidation/reduction cycles toward the behavior of the pure-Pt catalysts. Therefore, a 0.2% Pt/SiO_2 catalyst was prepared and it appeared (see Table 3) that this catalyst showed a striking resemblance to the Pt–Au/Al_2O_3 catalyst after the oygen treatment. With these reuslts in mind it was tempting to attribute the changes in behavior of the Pt–Au/Al_2O_3 catalyst to a segregation of Pt from the alloy particle. From the results it was obvious

TABLE 2

Selectivity of Supported Pt Catalyst

Selectivity for isomerization	Before oxidation	After second oxidation step
Pt/Al_2O_3	0.60	0.54
Pt/SiO_2	0.58	0.60

that the oxygen atmosphere and the Al_2O_3 carrier were essential in the mechanism of this segregation. The following tentative explanation is now suggested and schematically shown in Fig. 2.

The oxygen atmosphere induces the segregation of Pt to the surface of the alloy particle (gas-induced segregation was observed with Pt–Au alloys by Bouwman and Sachtler (*1*)) and the Pt oxidizes to a Pt oxide. This Pt oxide is able to "wet" the surface of the Al_2O_3 carrier (*12, 13*) (but not the SiO_2 carrier) and migrates easily at elevated temperatures. In the reduction step that follows, the PtO_x (now spread all over the alumina surface) is reduced to small Pt particles, at a certain distance from the alloy particles (after segregation now mainly Au particles) which slows down the reverse alloying process. This results in an increase in activity and a change in selectivity with a pattern resembling the selectivity pattern of a 0.2 wt% Pt/SiO_2 (small Pt particles) catlayst. In the case of the SiO_2-supported Pt–Au alloy the Pt oxide accumulates on the surface of the alloy particle or in the close neighborhood and upon reduction again forms a Pt–Au alloy.

TABLE 3

Selectivities of Supported Pt–Au and Supported Pt

Selectivity[a]	Pt–Au/Al_2O_3 after second oxidation step	0.2% Pt/SiO_2
S_{cr}	0.14	0.13
S_{iso}	0.30	0.32
S_{cycl}	0.56	0.55

[a] cr, hydrogenolysis (cracking); iso, isomerization; cycl, dehydrocyclization.

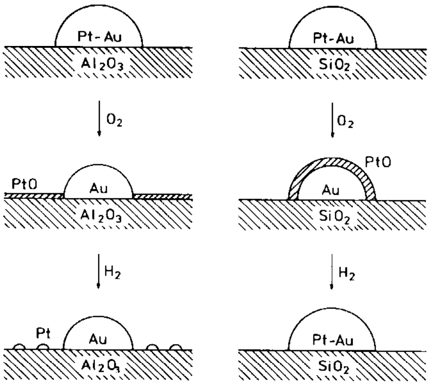

FIG. 2. Schematic representation of the behavior of Pt–Au alloy particles on Al_2O_3 and on SiO_2 during oxidation and subsequent reduction.

Even though the explanation of the results is a tentative one, the observed phenomena are undoubtedly due to the combination of catalyst treatment and Al_2O_3 used as a support. In this case it is demonstrated that for various Pt–Au alloy catalysts the differences in catalytic behavior can sometimes be understood and it is clear that in general oxygen treatment of Pt alloys on Al_2O_3 can bring about unwanted changes in the composition of the catalyst.

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