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Surface Study of Platinum–Tin Bimetallic Reforming Catalysts

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Adsorption measurements of hydrogen and oxygen on a series of platinum-tin catalysts with various platinum (0–0.35%) and tin (0–1.4%) contents have been effected at 450°C and 23°C using a microbalance. Adsorption of oxygen at high temperature on a prereduced catalyst shows that tin, initially in the +2 oxidation state under reduced atmosphere, is oxidized to Sn^{IV}. Moreover, electron microdiffraction shows that platinum in the presence of hydrogen is in the metallic state. On the prereduced catalyst (Pt^0–Sn^{II}/Al_2O_3), the amounts of oxygen irreversibly adsorbed at 23°C, which theoretically would be a selective measurement of the platinum surface, are linearly dependent upon the tin content. No metallic state of Sn nor Pt–Sn alloy has been found. More precisely, the amounts of oxygen adsorbed on tin-platinum/alumina catalysts are proportional to both percentage of platinum and tin on the carrier. Several hypotheses are proposed to explain these results where no reduction process of Sn^{II} is involved. A strongly preferred one is hydrogen spill-over resulting in hydrogen atoms localized on a part of the Sn^{II} sites and reacting with O_2.

INTRODUCTION

A number of bimetallic reforming catalysts have been patented, and their industrial use has appeared as a major improvement in refining technology. The most common catalysts belong to the *X*-Pt/Al_2O_3 systems, where *X* represents Sn, Pb, Re, Ir, or Ge, and Al_2O_3 is a γ-alumina support. Addition of the second metal gives to the catalyst higher selectivity and stability (*1*). Coking is decreased, and the metallic crystallites appear more resistant to aging (*2*).

The present study deals with γ-alumina-supported Pt–Sn industrial reforming catalysts (*3*), about which few theoretical investigations (*4*, *5*) have been yet published.

According to Boudart's theory (*6*) which considers the dehydrocyclization of *n*-heptane as a demanding or structure-sensitive reaction, the catalytic activity depends on the dispersion of platinum (*7*, *8*) and on its crystalline properties (*9*). Pt–Sn/Al_2O_3 catalysts exhibit a very high degree of dispersion of platinum (the crystallite size is about 20–25 Å) and a high selectivity toward aromatics during paraffin dehydrocyclization (*10*). Many explanations may be proposed. For example, Bond and Sermon (*11*) postulated an electron donation from the small metal-supported crystallites to the carrier. The aromatic selectivity is altered by promoting platinum by tin. However, the characterization of the metallic phase is difficult due to the small size of particles and to additional effects induced by the deposition of another metal.

In this paper, hydrogen and oxygen adsorptions are used to understand the bonds existing between carrier and metal

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TABLE 1

Stoichiometric Equations for the Bulk Oxidation by Oxygen at 450°C

Reactions	Weight uptake (μg/g)		
	1% Sn	0.35% Pt	0.20% Pt
(1) $Pt^0 + \frac{1}{2} O_2 \rightarrow PtO$		285	163
(2) $Pt^0 + O_2 \rightarrow PtO_2$		570	326
(3) $\underset{/\ \backslash}{Pt^{II}} + \frac{1}{2} O_2 \rightarrow \underset{/\ \backslash}{Pt^{IV}O}$		285	163
(4) $Sn^0 + O_2 \rightarrow Sn^{IV}O_2$	2700		
(5) $Sn^0 + \frac{1}{2} O_2 \rightarrow Sn^{II}O$	1350		
(6) $\underset{/\ \backslash}{Sn^{II}} + \frac{1}{2} O_2 \rightarrow \underset{/\ \backslash}{Sn^{IV}O}$	1350		

atoms, and their various implications. The activation of the Pt–Sn catalysts by hydrogen and especially the metallic influence of platinum on the tin atoms are described. To facilitate the interpretation of the results, which reveal a continuous phenomenon of bimetallic interplay, electron microdiffraction experiments have also been made.

EXPERIMENTAL

Preparation of the catalysts. The support is a high-purity γ-alumina with a BET surface area and pore volume of 188 m^2/g and 0.50 ml/g, respectively. Platinum and tin are deposited by impregnation with aqueous solutions of $SnCl_2$ and H_2PtCl_6 (*3*). Before any examination, these catalysts, referred to as $Sn–Pt/Al_2O_3$, are heated at 530°C in air for 2 hr.

The tin content varies from 0.0 to 1.4%, and the platinum content is 0, 0.20, or 0.35%.

Apparatus and procedures. Adsorption measurements are effected with a thermogravimetric device. A symmetrical electronic microbalance (SETARAM MTB 10) is used, with a load limit of 10 g and a sensitivity of 1 μg. The catalyst sample (2 g) on one side is equilibrated on the other side by glass microballs. The two test tubes are very carefully heated at the same temperature. Glass fittings allow the introduction of the different gases, oxygen, hydrogen, nitrogen, and helium. The vacuum system leads to pressures as low as 10^{-6} Torr, and the balance is protected from mercury vapor by a liquid nitrogen trap.

RESULTS AND DISCUSSION

Oxidation State of the Surface Pt and Sn Phases after the High-Temperature Reducing and Oxidizing Treatments

The oxidation states of the platinum and tin phases are determined by using a cycle of reduction and oxidation reactions. The catalyst, previously reduced at 510°C in a hydrogen flow at 760 Torr, is outgassed, brought to a temperature of 450°C, and then oxidized at this temperature by pure oxygen at 100 Torr. The comparison of the weight uptake recorded during this oxidation step with the theoretical one allows one to select the most probable chemical reactions and to determine the initial oxidation states of platinum and tin after reduction and evacuation.

The different chemical reactions possibly occurring during the oxidation step are listed in Table 1. For each of them is given the theoretical weight uptake, related to 1 g of a catalyst containing 1% Sn and 0.35 or 0.20% Pt.

Figure 1 shows, as a function of the tin content, the experimental amounts [q_{O_2}(irr)] of oxygen gas bound to Sn–Pt/

Al_2O_3 and Sn/Al_2O_3 after the oxidizing treatment [q_{O_2}(irr) is expressed in micrograms per gram of catalyst]. Parallel straight lines are obtained, with a slope of 1300 μg (related to 1% Sn).

Out of the two stoichiometric Eqs. (5) and (6) which account for this value, only Eq. (6) may be retained, since no metallic tin or platinum–tin alloy could be detected by electron microdiffraction; furthermore, from Mössbauer experiments (*5*), SnO_2 is the only existing phase after oxidation treatment. The fact that tin is not in the metallic state after reduction is consistent with the high chemical reactivity of SnO. It is well known indeed that this oxide is disproportionated into Sn^0 and Sn^{4+} at 370°C under low pressure, but that in air at 130°C, it is rapidly oxidized to SnO_2 (*12*). Therefore, were tin in a metallic state, according to the sequence of reactions (5) and (6), the amount of bound oxygen would be two times larger than the one which is actually measured.

TABLE 2

Amounts of Irreversibly Bound Oxygen for Tin-Free Catalysts

Catalysts	$(q_{O_2})_0$ (μg/g)
Pt(0.35%) Al_2O_3	360
Pt(0.20%) Al_2O_3	210
Al_2O_3	45

It appears then that tin, even after a reduction at 510°C by hydrogen, is tightly bonded to the alumina support and is in the +2 oxidation state. This nonmetallic state of tin is confirmed by a lack of irreversible adsorption of O_2 at room temperature on reduced Sn/Al_2O_3 catalysts.

Similarly, the oxidation of platinum may be related to the intersection of the straight lines with the y-axis in Fig. 1. In Table 2 are given in each case (0.35, 0.2, and 0.0%

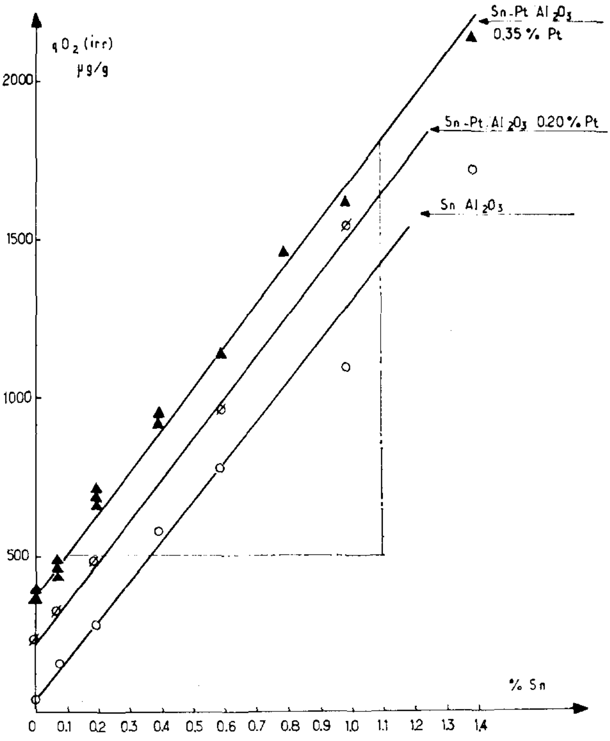


FIG. 1. Variation of the amounts of adsorbed oxygen at 450°C as a function of tin content.

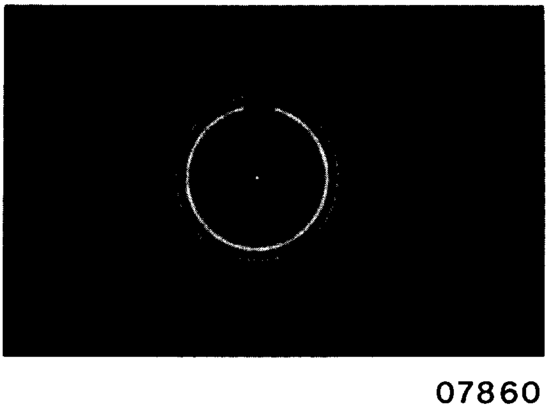
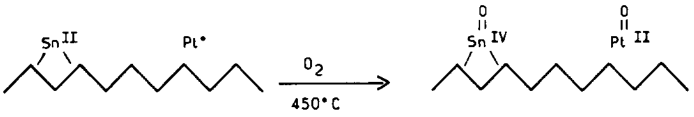


FIG. 2. Electron diffraction pattern of platinum in a reduced catalyst.

Pt, respectively) the amounts $(q_{O_2})_0$ of irreversibly bound oxygen for a tin-free catalyst. The differences, 315 (= 360 − 45) and 165 μg/g (= 210 − 45) between the observed values are very close to the stoichiometric ones corresponding to Eq. (1) or (3) in Table 1. Since the electron microdiffraction patterns (Fig. 2) show that platinum on the catalyst reduced in hydrogen at 510°C is in a metallic state, Eq. (1) and not Eq. (3) should be selected and we may safely assume that after the oxidation step, platinum is in the +2 oxidation state.

In conclusion, the following scheme illustrates the transition from the reduced to the oxidized state of the Pt–Sn reforming catalysts:



Micrographs of platinum crystallites presented in Fig. 3 show that their size exhibits a unimodal distribution at about 20–25 Å.

Irreversible Adsorption of O_2 and H_2 at Room Temperature

Adsorption of oxygen and hydrogen is followed at room temperature under a pressure of 100 Torr. Before any adsorption, the catalysts are previously reduced at 510°C in a hydrogen flow, evacuated, and cooled to room temperature. The weight measurements during the consecutive adsorptions and evacuations, summarized in Table 3, allow one to determine the quantities of gases reversibly and irreversibly adsorbed (q-rev. and q-irr.).

It must be remembered that the reduced Sn/Al_2O_3 catalysts and the carrier do not adsorb oxygen irreversibly at room temperature. On the contrary, the amounts of irreversibly adsorbed oxygen [q_{O_2}(irr)] by $Pt\text{–}Sn/Al_2O_3$ catalysts depend on the tin content.

Moreover, a second adsorption cycle at room temperature (evacuation, H_2 adsorption, evacuation, and O_2 adsorption) leads to the same quantity, q_{O_2}-irr. This phenomenon is observed again after three or four cycles, and then the irreversible adsorption capacity decreases, probably due to an excessive consumption of hydrophilic centers of the carrier in the vicinity of the metallic sites, thus preventing further migration of water molecules.

According to Table 3, Fig. 4 presents the variations of q_{O_2}-irr. with the tin content on the two series of catalysts investigated (with 0.2 and 0.35% platinum, respectively). Straight lines are obtained; the slopes and intercepts with the y-axis are

Fig. 3. Electron micrograph of platinum crystallites.

TABLE 3

Cycle of Adsorptions

Catalyst heated at 530°C (air)	→	Reduced by H_2 at 510°C (760 Torr)	→	Evacuation at 510°C (10^{-4} Torr)
				↓
Evacuation at room temperature (10^{-4} Torr)	←	Adsorption of H_2 at room temperature (100 Torr)	←	Evacuation at room temperature (10^{-4} Torr)
↓				
Adsorption of O_2 at room temperature (100 Torr)	→	Evacuation at room temperature (10^{-4} Torr)		

proportional to the platinum content. These results can be interpreted in three different ways.

According to a first hypothesis, in the vicinity of platinum atoms, tin would be submitted to a metallic influence represented by SnↃ where the adsorbed hydrogen atom would be localized as SnↃ-H and would further react with oxygen. Thus one assumes for hydrogen

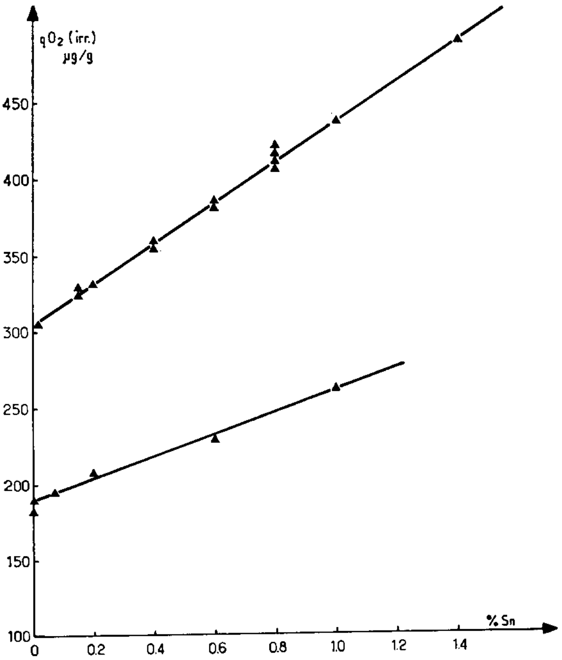


FIG. 4. Variation of the amounts of chemisorbed oxygen at room temperature as a function of tin content for catalysts with 0.20% Pt (lower curve) and 0.35% Pt (upper curve). Equations of the straight lines: q_{O_2}-irr. = 190 + 73.3% Sn (µg/g); q_{O_2}-irr. = 305 + 134% Sn (µg/g).

and oxygen adsorption on tin the same sequence of reactions which is assumed in the case of platinum (*13*):

$$\mathrm{Pt} + \tfrac{1}{2}(\mathrm{H_2})_g \rightarrow \mathrm{Pt\,H_{irr}} \tag{7}$$

$$\mathrm{Pt\,H_{irr}} + \tfrac{3}{4}(\mathrm{O_2})_g \rightarrow \mathrm{Pt\,O_{irr}} + \tfrac{1}{2}\mathrm{H_2O_{irr}} \tag{8}$$

Then the accessibility of Pt (or H/Pt) would be the sum of an intrinsic accessibility of platinum and of another one which would be a linear function of the tin content.

From the intercepts and slopes of the straight lines in Fig. 4 and from the theoretical weight uptake corresponding to Eq. (8) (430 and 245 μg/g for 0.35 and 0.20% Pt) the intrinsic accessibility of Pt is near 75%; 6.3 and 3.5% of the tin atoms are in the form of $\mathrm{Sn}\circlearrowright$ and involved in oxygen adsorption. The number of such tin atoms appears to be a function of two parameters, the tin content x and the platinum content y:

$$\text{Percentage of } \mathrm{Sn}\circlearrowright \; = 18x\cdot y,$$

where x and y are given in weight percent per gram of catalyst. Therefore, hydrogen atoms would not necessarily be localized on the metallic platinum atoms but could also migrate by a spill-over-type mechanism (*14–17*) on the $\mathrm{Sn}\circlearrowright$ atoms and then react with O_2, as has been demonstrated.

According to a second hypothesis, the stoichiometry of the titration reactions according to Eqs. (7) and (8) would not hold any more in the presence of tin. It may be supposed that the preadsorption of tin on the carrier increases the platinum dispersion in the platinum–tin/alumina catalysts. If one assumes that the very small platinum crystallites adsorb two hydrogen atoms instead of one, the stoichiometry of Eqs. (7) and (8) would be modified, and the higher adsorptivity of the Pt–Sn catalyst would be explained.

Finally, a third hypothesis would involve an oxygen spillover similar to the one postulated for hydrogen. Even if molecular oxygen cannot change the oxidation state of tin at room temperature, atomic oxygen formed on platinum and migrating to the $\mathrm{Sn^{II}}$ moiety could oxidize it according to Eq. (6). In this case the percentage of accessible tin would be 27 xy instead of 18 xy according to the different stoichiometries of Eqs. (6) and (8).

Of the three above hypotheses, the third one seems the least likely. At room temperature, after evacuation, a second adsorption of oxygen just after the first one is totally reversible; the water produced according to Eq. (8) is initially formed on a platinum metal site and then rapidly transferred to a hydrophilic center of alumina (*13*). Moreover, the oxygen atoms are strongly bonded as PtO (*18*) and cannot be involved in a migration process since only hydrogen treatment can break the Pt–O bond at room temperature.

The second hypothesis is also neglected because it does not explain the linear dependence of the adsorbed oxygen amount on the platinum and tin contents. Moreover, no correlation between the tin content and the distribution of platinum crystallite sizes as determined by electron microscopy has been found.

In conclusion, we may assume that the very specific spillover mechanism as postulated by the first hypothesis is the most probable. The mobility of hydrogen atoms between tin and platinum sites can explain the very high selectivity and stability of the industrial Pt–Sn reforming catalysts.

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