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Surface Organometallic Chemistry on Metals: Selective Dehydrogenation of Isobutane into Isobutene on Bimetallic Catalysts Prepared by Reaction of Tetra *n*-Butyltin on Silica-Supported Platinum Catalyst

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The selective dehydrogenation of isobutane into isobutene was studied on silica-supported bimetallic Pt-Sn. Several bimetallic catalysts were carefully prepared by selective hydrogenolysis of $Sn(n\text{-}C_4H_9)_4$ on Pt. Previous EXAFS studies have shown that this hydrogenolysis is a stepwise transformation of a $Pt\text{-}Sn(n\text{-}C_4H_9)_3$ fragment into a surface alloy. It was shown that after hydrogen treatment at 550°C, tin and platinum are in reduced form (zerovalent oxidation state) and that the tin atoms are located on the surfrace of the metallic particles. The presence of tin on platinum caused a decrease in hydrogen or carbon monoxide chemisorption, but an increase of the oxygen consumption. The decrease of H_2 and CO chemisorption is explained by the decrease of the number of accessible platinum atoms due to the increased number of surface tin atoms. The increase in the O_2 chemisorption was explained by the following reaction which represents a phase segregation: $Pt_sSn_x/SiO_2 + 1/2(y + xy')O_2 \rightarrow (PtO_y)_s(SnO_{y'})_x/SiO_2$. The values of y and y′ was about 1 and 2 at respectively 25°C and 300°C. Thermodesorption of adsorbed CO on several reduced PtSn catalysts showed no shift of the ν (CO) frequency, suggesting negligible electronic effect of tin atoms on the platinum atoms when both are reduced. At 550°C under atmospheric pressure of hydrogen and isobutane, the presence of tin increases drastically, both the selectivity and the activity of the isobutane conversion into isobutene (for $Sn/Pt_s = 0.85$, the selectivity is higher than 99% and the TOF, based on total platinum atoms, is greater than 6 s^{-1}). The increase in selectivity could be explained by the "site isolation effect" and the increase in activity could be due to the inhibition of the coke formation (which poisons the active surface). A mechanism of dehydrogenation and hydrogenolysis of isobutane based on elementary steps of organometallic chemistry has been proposed which accounts both for the high selectivity and activity of the bimetallic catalysts as compared to pure Pt/SiO_2. © 1998 Academic Press

INTRODUCTION

Bimetallic platinum–tin catalysts are now widely used to dehydrogenate paraffins to olefins and particularly isobutane into isobutene (1–3). When compared to the monometallic platinum catalysts the platinum–tin systems are more selective toward isobutene and more stable toward oxidative regeneration. It has been proposed that the tin atoms have several positive effects: they prevent the hydrogenolytic properties of the platinum (4), leading to a better selectivity for the dehydrogenation process; they diminish the sintering process and then stabilise the size of the metallic particles (5); they diminish the rate of coke formation and thus increase the life time of the catalyst (6–8). In most cases, the bimetallic catalysts are prepared by the classical co-impregnation method (9–12). This co-impregnation method usually consists of impregnating a support simultaneously with platinum and tin salts. After adequate drying, the system is reduced under flowing hydrogen at high temperature. It is not always certain that this procedure will lead to the exclusive formation of bimetallic particles. It may well be that monometallic tin and platinum particles co-exist on the support surface. It is expected that the selectivity and the stability of the catalysts will drastically depend on the repartition of the two metals on the support. It is evident that the presence of unmodified platinum particles could drastically destroy the selectivity of the catalyst. In the same way, the presence of tin in excess, located on the support could drastically modify or eventually destroy the activity of the catalyst by migration onto the particles during the dehydrogenation process. It is therefore interesting to find a way to prepare selectively bimetallic particles in such a way that the two metals are located **in the same particle**.

The reaction of a tin organometallic compound with platinum and rhodium surface has been first proposed respectively and simultaneously by Margitfalvi *et al.* (13) and Travers *et al.* (14) in 1984. Previous results in this area were obtained by Yermakov and Ryndin in the 1970s (15). Surface organometallic chemistry on metals is now a new route to generate real bimetallic catalysts in a more controlled manner. The reason for such assessment is the following: when a reduced platinum particle is deposited on an inert support, the hydrogenolysis of an organotin compound will occur selectively on the reduced metal surface and not on the support. Recently, Ferretti *et al.* (16) obtained

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selectivity as high as 96% for the dehydrogenation of isobutane into isobutene at 450°C on silica-supported rhodium catalyst modified by reaction with tetrabutyltin. Note that the reaction led to complete decomposition of isobutane to methane and coke when Rh/SiO_2 catalyst is used. In a recent publication (17) we have studied the reaction of tetrabutyltin ($Sn(n\text{-}C_4H_9)_4$) with silica-supported platinum, at various temperatures and at various coverages of the metal. The stoichiometry and kinetics of the reaction was followed by a careful analysis of reagents and products, including the extraction of unreacted reagents and elemental analysis of the samples at various time of the reaction. The various surface species formed were characterized by electron microscopy (CTEM and TEM EDAX) and EXAFS analysis. Possible structures of the surface organometallic fragments were considered using molecular modelling. At 50°C, the hydrogenolysis reaction of $Sn(n\text{-}C_4H_9)_4$ occurs selectively on the platinum surface with exclusive evolution of *n*-butane. There is first the formation of a $Sn(n\text{-}C_4H_9)_3$ fragment grafted on the platinum particle which undergoes a further stepwise cleavage of two tin-carbon σ-bonds to form a stable $Pt_s\text{-}Sn(n\text{-}C_4H_9)$ fragment. Regardless of the reaction time, surface coverage, or loading, the number of grafted butyl fragments per platinum is never greater than unity; that is to say that when $Sn(n\text{-}C_4H_9)_3$ is formed, the platinum coverage by tin is 0.3, whereas when $Sn(n\text{-}C_4H_9)$ is formed the platinum coverage is closer to 1. It has been suggested, therefore, that the surface composition is governed by the bulkiness of the *alkyl chains* which are "close packed" on the surface. Thermal treatment at 300°C under hydrogen of $Pt_s\text{-}Sn(n\text{-}C_4H_9)$ leads to alkyl-free tin atoms which are located at the periphery of the particle as evidenced by Sn-K edge EXAFS (Pt-Sn distance of 2.75 Å with a coordination number of ca 4). Even if the organotin fragments are grafted on Pt with a coverage of unity, after their complete hydrogenolysis at 300°C, despite the fact that tin does not chemisorb H_2, about 40% of the platinum is still accessible to H_2 chemisorption. This could be explained by the increase of the particle diameter (+0.5 Å) which prevents a close packing of the tin atoms around the particle and leaves some platinum atoms still accessible to the hydrogen. After treatment of the catalyst at higher temperatures, typically 500°C, the structure of the catalyst is slightly changed since the tin atoms migrate into the first monolayer of the particle, as evidenced by a significant increase of the tin coordination number (ca 4.4–5.6) as determined by EXAFS. Surface structures have been proposed based on EXAFS data as well as molecular modeling of platinum particles covered by various surface organotin fragments.

The aim of this publication is to expose the catalytic properties of these relatively well-defined $PtSn/SiO_2$ bimetallic catalysts (17) in the case of isobutane dehydrogenation to isobutene. In particular, we wish to explore the structure–reactivity relationship and to see the origin of the high selectivity of such catalysts in a simple reaction of dehydrogenation.

EXPERIMENTAL PART

The silica-supported platinum catalyst precursor is prepared by cationic exchange of platinum tetramine complexes $[Pt(NH_3)_4(OH)_2]$ (purshased from Aldrich) with the proton of the silanol groups of the silica surface, following the procedure already described for silica supported rhodium (18):

$$\begin{aligned}&[Pt(NH_3)_4]^{2+}\,2[OH]^- + 2\equiv SiOH\\&\quad\rightarrow [\equiv SiO]_2^-[Pt(NH_3)_4]^{2+} + 2H_2O. \qquad [1]\end{aligned}$$

The silica support, Aerosil 200 from Degussa, has a surface area of 200 m^2/g.

The catalyst precursor is decomposed under flowing $N_2/0_2$ (4/1) at 500°C and then reduced at the same temperature under flowing hydrogen.

The bimetallic $Pt\text{-}Sn/SiO_2$ catalysts are obtained by the surface organometallic chemistry route (13,14,19). A given amount of silica-supported catalyst is reduced under flowing hydrogen at 500°C. The reactor is then sealed under 30 mbar of hydrogen and the desired amount of tetrabutyltin ($Sn(n\text{-}C_4H_9)_4$) is introduced (without any solvent). The temperature of the reactor is stabilised at 50°C for 24 h. The butane evolved is trapped at the liquid nitrogen temperature in a adequate part of the apparatus. After complete reaction, the sample is treated under flowing hydrogen at 550°C for 10 h. After cooling down to room temperature, the samples are kept under air. Blank experiments performed by washing the samples with *n*-heptane after the reaction of $Sn(n\text{-}C_4H_9)_4$ during 24 h at 50°C (and before the treatment under hydrogen at 550°C) showed that (i) with the silica support alone, the total amount of $Sn(n\text{-}C_4H_9)_4$ introduced can be fully removed, (ii) with Pt/SiO_2, all the amount of $Sn(n\text{-}C_4H_9)_4$ introduced (Sn_{int}) is fixed on the surface, as long as Sn_{int}/Pt_s is lower or equal to 0.85. This procedure is completely different from that described by Margitfalvi *et al.* (13). These authors used the "controlled surface reactions" (CSRs), where the first step is the exclusive formation of the primary surface complex (PSC). In this case, the platinum is reduced under hydrogen at 400°C and then purged in nitrogen at 25°C in order to elimimate the reversible part of the adsorbed hydrogen. The reaction with the tetraethyltin is performed under nitrogen in benzene (or *n*-hexane) at 50°C. In our case, the reaction between the tetra *n*-butyl tin and the reduced platinum surface is performed under hydrogen and without solvent. We consider that it is a selective hydrogenolysis of an organotin molecule on a metallic surface, leading to well-defined surface organometallic fragments.

The characterization of the monometallic and the bimetallic catalysts has been performed by elementary analysis, electron microscopy, hydrogen or oxygen adsorption, and infrared spectroscopy of adsorbed CO. Electron microscopy (C.T.E.M.) was performed by mean of a JEOL 100CX electron microscope. Chemisorption measurements were carried out using conventional static volumetric equipment as already described (18). Prior to any adsorption measurement, the samples were reduced under flowing hydrogen at 500°C in the volumetric apparatus. The amount of surface platinum atoms (Pt_s) of the particles was deduced from the amount of hydrogen or oxygen chemisorbed, assuming that 1.8 H and 1 O are adsorbed on each Pt_s (under 150 mbar at 20°C) (20,21).

The infrared spectroscopy was performed with a Nicolet 325 Fourier transform instrument. All the experiments were carried out under controlled atmosphere. The samples (self-supporting wafers) were placed in a sample holder which could move inside a closed reactor from the treatment position (located in an oven) to the analysis position (located between two CaF_2 windows in the infrared beam).

Dehydrogenation of isobutane was carried out in a dynamic reactor working under atmospheric pressure at 550°C with a ratio hydrogen/isobutane of 1/1 (mol/mol). The flow rate of hydrogen and isobutane, $f(H_2)$ and $f(iC_4^i)$, (mol/s) are measured and controled by mass flow controlers (Brooks). The flow rate of isobutane introduced $f(iC_4^i)$ is expressed by the amount (mol) of isobutane introduced per second (s). The products are analysed "in line" by gas phase chromatography of samples taken at regular intervals of time. The respective molar fraction of the observed products are represented by $[C_1]$ for methane, $[C_2]$ for ethane, $[C_2^{=}]$ for ethylene, $[C_3]$ for propane, $[C_3^{=}]$ for propene, $[C_4]$ for *n*-butane, $[C_4^{=}]$ for *n*-butene, $[\text{i-}C_4]$ for isobutane, and $[\text{i-}C_4^{=}]$ for isobutene.

If m is the amount of catalyst introduced (g), Pt_s is the amount of surface platinum atoms per g of catalyst (mol/g), $f(iC_4^i)$ is the flow rate of isobutane (mol/s), and $[A] = [C_1]/4 + [C_2]/2 + [C_2^{=}]/2 + [C_3]/3 + [C_3^{=}]/3 + [C_4] + [C_4^{=}] + [\text{i-}C_4^{=}]$, one can define the conversion (Conv.), selectivity for isobutane (Sel.), and turnover frequencies (TOF) by the equations:

$$\text{Conv.}\ (\%) = 100 \cdot [A]/([A] + [\text{i-}C_4])$$

$$\text{Sel.}\ (\%) = 100 \cdot [iC_4^{=}]/[A]$$

$$\text{TOF}\ (s^{-1}) = f\left(iC_4^i\right) \cdot \text{Conv.}/(100 \cdot m \cdot Pt_s).$$

Prior to any catalytic reaction, the sample of catalyst was reduced under flowing hydrogen at 550°C for 1 h. It has been shown previously (17) that at such temperature, the tin is located just inside the first layer of the platinum particle.

The experimental conditions required to avoid any diffusional phenomena were determined. We verified that there is no effect of the pellet size ($\Delta < 200\ \mu m$ or $200 < \Delta < 400\ \mu m$). The amount of catalyst will be generally 50 mg and the flow rate is adjusted to the range 40–100 ml/min to obtain always less than 10% conversion.

In this range of flow rate and with 50 mg of pure silica, at 550°C, the reaction of isobutane gives methane, propene, and isobutene. These products are characteristic of homolytic cleavage of the carbon-carbon and carbon-hydrogen bonds. The conversion of isobutane is always lower than 0.25% and we did not correct the values obtained with mono and bimetallic catalysts (therefore 100% selectivity could never be obtained).

RESULTS AND DISCUSSION

Before presenting the catalytic results, we shall report the various characterizations of the Pt/SiO_2 and the resulting bimetallic $PtSn/SiO_2$. The starting silica-supported platinum catalysts FH560 contain 1.57 wt% platinum (80 μmol/g) as determined by elementary analysis. Several bimetallic Pt-Sn catalysts were prepared from this precursor with the following Sn/Pt ratios: 0.07, 0.21, and 0.31. The tin content and the amount of adsorbed hydrogen or oxygen on the different silica-supported monometallic (FH560) and bimetallic Pt-Sn catalysts are reported in Table 1. The particle size distribution measured by T.E.M. for the monometallic (FH560) and bimetallic (Sn/Pt = 0.21) catalysts are reported on Fig. 1. In both cases the distribution is narow, with a maximum around respectively 1.6 and 2.2 nm, but some larger particles appear which drastically decrease the dispersion. Assuming a cubo-octaedral shape for the metallic particles and according to Van Hardevel and Hartog (22), the dispersion of the FH560 monometallic catalyst could be estimated close to 0.34. The maximum of the metallic particle size distribution increases from 1.6 nm for the monometallic catalyst to 2.2 nm for the bimetallic

TABLE 1

Platinum and Tin Content of the Samples (wt%), Determined by Elemental Analysis

Sample	Pt/SiO_2	$PtSn_{0.07}/SiO_2$	$PtSn_{0.21}/SiO_2$	$PtSn_{0.31}/SiO_2$
Sn (%)	0	0.062	0.20	0.29
Sn/Pt	0	0.07	0.21	0.31
Sn/Pt_s (x)	0	0.2	0.6	0.85
H_2 chem. 25°C (μmol/g)	25	12.7	9.5	8.5
O_2 chem. 25°C (μmol/g)	14	16	22	26
O/Sn (y)		0.7	1.0	1.0
O_2 chem. 300°C (μmol/g)	28	32	42	48
O/Sn (y')		1.7	1.8	1.7

Note. Corresponding amount of tin atoms per total platinum atoms, Sn/Pt, or by surface platinum atoms, Sn/Pt_s. Amount of chemisorbed hydrogen (25°C, 150 mbar) and oxygen (25°C and 300°C, 150 mbar). Corresponding x, y, and y' values in Equation [2].

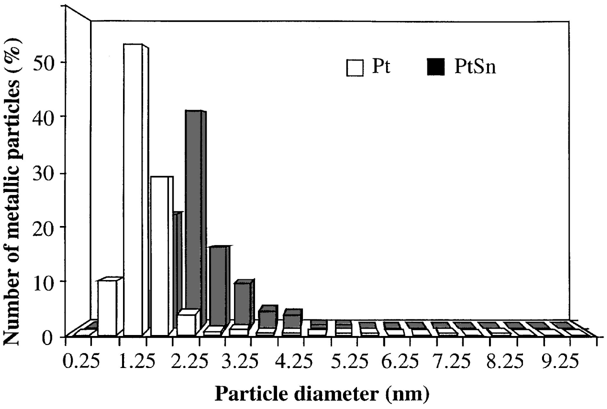


FIG. 1. Particles size distribution of Pt/SiO_2 and $PtSn_{0.21}/SiO_2$.

$PtSn_{0.21}/SiO_2$ sample. This observation confirms that the tin atoms have been added to the platinum particles (17).

Assuming the accepted stoechiometry of 1.8 H atoms chemisorbed per surface platinum atom and 1 O atom chemisorbed per surface platinum atom (20,21), the value of Pt_s measured by hydrogen or oxygen chemisorption are both equal to 28 μmol/g (dispersion, $Pt_s/Pt = 0.36$). This value is in good accordance with the value obtained by T.E.M.

For all the samples, the isotherm of adsorption shows a plateau above a hydrogen pressure of ca 50 mbar. Clearly, there is a decrease of the amount of adsorbed hydrogen on the surface when the tin content increases. This result is easily explained if we consider that tin is at least partially located on the metallic surface and does not chemisorb hydrogen at 25°C (23). On Fig. 2, we have reported the amount of hydrogen adsorbed at 25°C and 150 mbar versus Sn/Pt.

For low tin content, there is a strong decrease in the amount of hydrogen adsorption with the increase of the tin content. For higher Sn/Pt ratio, the amount of hydrogen adsorbed decreases slightly with the amount of tin. Similar results were found by Sinfelt (24) for hydrogen and CO adsorption on $Cu\text{-}Os/SiO_2$ catalysts. He concluded that the number of Os surface atoms in the osmium-copper system decreases by a factor of approximately four when the Cu/Os ratio is increased from 0 to 1 at a constant osmium content. On the unsupported platinum–tin system (Pt, Pt_3Sn, PtSn, and $PtSn_2$), Verbeek and Sachtler (23) found a drastic decrease in D_2 and CO adsorption when the Sn/Pt ratio increased. They concluded there was both a significant enrichment of the surface alloy in tin and on strong ligand effect, resulting in a drastic lowering of the heat of adsorption of hydrogen on the platinum atom of the alloy surface. On alumina-supported Pt-Sn catalysts, Lieske and Volter (25) also found a strong decrease for hydrogen adsorption with increasing tin content. They completly excluded a possible decrease of platinum dispersion and they proposed the formation of a PtSn alloy. On silica-supported Pt-Sn catalysts, Cortright and Dumesic (26) found also that addition of Sn to Pt reduces the number of sites that strongly interact with carbon monoxide or hydrogen. With the ruthenium–tin system, Coq *et al.* (27) observed that the addition of tin generates some differences in the amount of irreversibly adsorbed hydrogen (H_{irr}) as a function of Ru particle size. The ratio H_{irr}/Ru decreases linearly with the amount of tin on large particles of Ru, in the range expected, if one tin atom covers one surface ruthenium atom. However, on the smaller Ru particles, the "toxicity" of tin for hydrogen adsorption is initially much higher. This change might suggest a particular localisation of the tin atoms introduced first. The average particle size of our Pt/SiO_2 catalyst is much closer to the larger Ru/Al_2O_3 particles than to the smaller ones. Nevertheless, we observed a great "toxicity" of the tin atoms introduced first. These results seem to indicate that for low tin contents ($0 < Sn/Pt_s < 0.3$), the tin atoms are located on particular sites of the surface of the metallic particle. For higer tin content, a part of the tin atoms could migrate inside the particle or could even migrate on the support, in the close vicinity of the metallic particle.

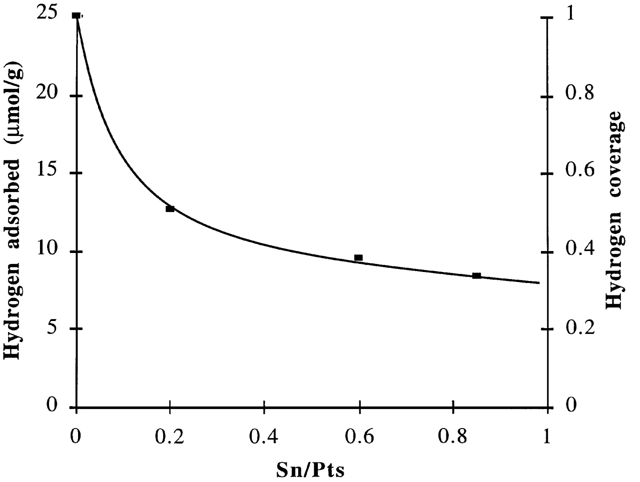


FIG. 2. Amount of adsorbed hydrogen at 25°C under 150 mbar as a function of Sn/Pt_s.

The amount of oxygen chemisorbed (at 25°C and at 300°C) on the reduced Pt and $PtSn_x$ samples is reported in Table 1. Let us recall that previous EXAFS data (17) carried out on the same sample have demonstrated that after reduction (hydrogen at 500°C), the tin atom has no detectable oxygen neigbours; before oxygen adsorption, the Pt and the Sn atoms of our samples are fully reduced. As can be seen on Table 1, the amount of chemisorbed oxygen increases with the tin content. If we assume that at 25°C, one surface platinum atom chemisorbs one oxygen atom and that one tin atom reacts with "y" oxygen atoms (following Eq. [2]), the obtained values of "y" are reported in Table 1.

$$Pt_sSn_x/SiO_2 + 1/2(xy + 1)O_2 \rightarrow Pt_sO(SnO_y)_x/SiO_2. \quad [2]$$

Clearly, the "y" values obtained at 25°C are close to unity. Apparently, at 25°C, the tin atoms react with oxygen to give

SnO. Let us remember that oxidation at room temperature of metallic tin leads to tin monoxide compound (28).

After oxidation at 300°C and if we assume that one surface platinum atom chemisorbs two oxygen atoms to form $(PtO_2)_s$, the "y" values in Eq. [3], Table 1, become close to 2:

$$Pt_sSn_x/SiO_2 + 1/2(xy' + 2)O_2 \rightarrow (PtO_2)_s(SnO_{y'})_x/SiO_2. \quad [3]$$

Apparently, at 300°C, there is mainly formation of SnO_2. These results seem to indicate that (i) after treatment at 300°C under oxygen, Pt and Sn are both in the +4 oxidation state; (ii) after reduction at 500°C, the main fraction of the two compounds is fully reduced; (iii) oxidation at 25°C of the latter species leads to $Pt^{(II)}$ and $Sn^{(II)}$. These results are quite different from the ones obtained with Pt/Al_2O_3. On this support, Lieske and Völter (25) found that after oxidation at 500°C, there is formation of $Pt^{(IV)}$ and $Sn^{(IV)}$ species, but, even after reduction at 500°C, most of the tin remains in the +2 oxidation state, likely under the form of an alumina-stabilized species. A small fraction of tin, probably located in a PtSn alloy is reduced to $Sn^{(0)}$. Adkins and Davis (29) found also no metallic tin in $PtSn/Al_2O_3$, but, in further studies, Davis *et al.* (30–32) measured by XPS and Mössbauer spectroscopy from 30 to 70% of $Sn^{(O)}$ mainly in the form of PtSn alloy. More recently, Barias *et al.* (33) found that the degree of reduction of tin at 600°C is only about 35% for $PtSn/Al_2O_3$ catalysts and reaches more than 60% for $PtSn/SiO_2$ catalysts. They conclude there is a possible PtSn alloy on $PtSn/SiO_2$, whereas tin in $PtSn/\gamma\text{-}Al_2O_3$ does not form metallic tin, at least to any significant degree. Therefore, we can suggest that in our samples, prepared by the SOMC/M route, the main part of the tin atoms are under the form of a PtSn alloy and could be fully reduced by treatment under hydrogen at 500°C or fully oxidized at 300°C under oxygen.

The carbon monoxide (CO) adsorption has been followed by infrared spectroscopy. Prior to introduction of CO in the reactor, the sample is reduced under hydrogen at 500°C for 4 h and then desorbed under vacuo (10^{-6} mbar) for 4 h. The CO adsorption was performed at room temperature, under 30 mbar of CO. In this condition we assumed that the sample is fully covered by chemisorbed CO. In order to vary the CO coverage, the sample was treated under vacuo at increasing temperatures (25, 100, 150, 200°C). The CO coverage of the samples was deduced from the ratio of the intensities of the bands obtained after treatment at various temperatures, with respect to the intensiy of the band obtained after treatment at 25°C. The spectra obtained with Pt/SiO_2 and $PtSn_x/SiO_2$ catalysts and for decreasing CO coverage are reported on Fig. 3.

On the monometallic and on the bimetallic samples, at full coverage, only one band appears at respectively 2084 cm^{-1} and 2080 cm^{-1} which can be attributed to the linearly bond CO (34–36). The position of these bands shifts progressively with the decrease of the CO coverage, to reach the same value (2066 cm^{-1}) at zero coverage (Fig. 4).

At zero coverage of CO, the frequency of the band is the same on the monometallic and bimetallic samples. This rather surprising result was previously obtained on a RhSn catalyst with various Sn/Rh ratios. We can conclude that the shift of the band is due to the dipole–dipole effect (34–36) and that there is apparently and surprisingly no electronic effect of the tin on the platinum atoms. Similar conclusions were already reached in the case of silica supported Rh-Sn (37). These results seem to contradict Burch's (38) statement that there is no geometric effect without an electronic one. This statement came from studies carried out on $PtSn/Al_2O_3$ catalysts in which the major part of the tin atoms were in the ionic form ($Sn^{(II)}$) on the support. This is not the case in our studies where the tin atoms are in metallic form and, therefore, the conclusions are not contradictory.

These catalysts were tested in the catalytic dehydrogenation of isobutane into isobutene. On Figs. 5 and 6 we report the catalytic activity and selectivity of the monometallic FH560 and bimetallic catalysts as a function of the time on stream.

With the monometallic and bimetallic catalysts, a decrease of the activity is observed with time on stream (Fig. 5). This effect is probably due to the formation of coke which readily occurs on the surface of platinum and leads to poisoning of the catalyst (9,33). With the monometallic catalyst, the initial selectivity for isobutene is low (less than 91%) and slightly increases with the time on stream (Fig. 6). This effect could be also related to the coke formation which plays the role of a selective poison.

When tin is present, the selectivity for isobutene incre ases, as compared to pure platinum (to reach a value higher than 99%) and the activity remains more stable with time on stream. These results which have been already observed in several other cases (26,39–41) are remarkable and demonstrate the drastic effect of tin especially when it is exclusively located on the platinum particle. In Table 2 we report the catalytic activity (TOF) and the selectivity

TABLE 2

Selectivities and Turnover Frequencies for Isobutane Dehydrogenation (after 6 h on Stream), Based on the Number of Sites Determined from the Total Amount of Platinum Atoms (Col. 2) and from the Number of Pt Atoms Accessible to H_2 (Col. 3)

Sample	Sn/Pt_s	Selectivity (%)	TOF (s^{-1}) based on total Pt	TOF (s^{-1}) based on H_2 ads.
$PtSn/SiO_2$	0	92.8	1.9	5.5
$PtSn_{0.07}/SiO_2$	0.2	94.8	2.0	12.1
$PtSn_{0.21}/SiO_2$	0.6	96.1	7.0	19.9
$PtSn_{0.31}/SiO_2$	0.85	99.3	6.3	20.0

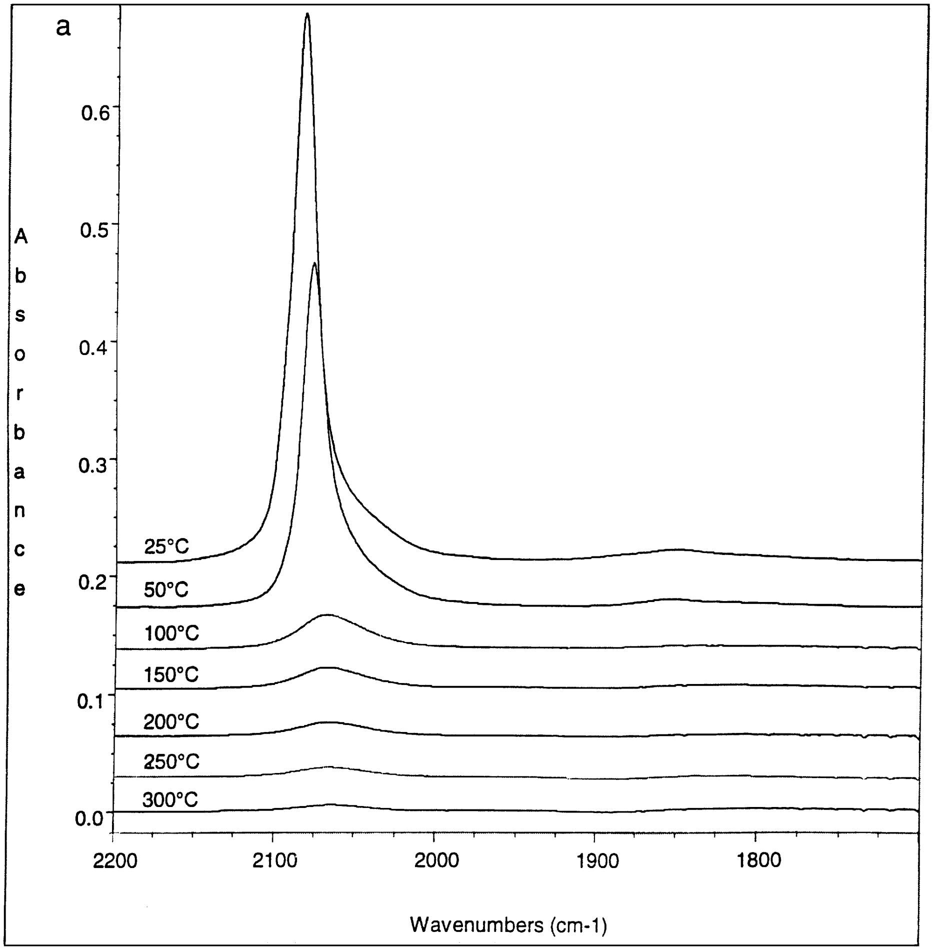


FIG. 3. Infrared spectroscopy of adsorbed CO on (a) Pt/SiO_2 and (b) $PtSn/SiO_2$ (Sn/Pt = 0,3). (The various spectra are taken after adsorption at room temperature under 30 mbar of CO and subsequent desorption at increasing temperatures: (1) 25°C, (2) 100°C, (3) 150°C, and (4) 300°C).

measured after 6 h of reaction with the different mono and bimetallic samples.

Increasing the amount of the Sn/Pt ratio increases the selectivity of the reaction for isobutene (Table 2). For a Sn/Pt_s ratio of 0.85, the selectivity becomes greater than 99%.

The increase of selectivity for isobutene formation with the amount of tin could be explained simply by the "site isolation" effect. It is generally admitted that coke formation and the hydrogenolysis process occurs on a large "ensemble" of surface platinum atoms (42) while dehydrogenation reactions would proceed on single Pt atoms (39). Kappenstein *et al.* (40) compared $PtSn/Al_2O_3$ catalysts prepared by the classical co-impregnation procedure or via a Pt-Sn complex precursor. They found that the specific rate of dehydrogenation of *n*-hexane into olefin at 420°C is higher on the latter catalyst. They conclude that there is lower amount of contiguous Pt atoms on the sample prepared via Pt-Sn complex precursor. They also observed that the apparent activation energy for the formation of olefin is greater on the latter catalyst and they suggest that there is some electronic interaction between tin and Pt in the latter catalyst. These results demonstrate, if necessary, the prominant role of the preparation procedure of bimetallic catalysts.

Cortright and Dumesic (26) prepared bimetallic $PtSn/SiO_2$ catalysts by evaporative impregnation of a tributyltinacetate/pentane solution on a monometallic Pt/SiO_2 catalyst. After impregnation with tin, the catalyst were dried overnight in air at 117°C and treated with flowing hydrogen at 500°C. For tin loading lower than 1:1 Pt/Sn there is exclusive formation of a PtSn alloy while for higher tin loading, some tin atoms are in the oxidized form $Sn^{(II)}$, even after reduction at 500°C. Isobutane dehydrogenation was conducted at 400°C under atmospheric pressure and a $H_2/iBu = 6$. They also found selectivities for isobutene close to 99% at ca 4% conversion, but the turnover frequencies based on total Pt were only 0.27, instead of 6 in this study (at 550°C). More recently, Stagg *et al.* (41) prepared bimetallic $PtSn/SiO_2$ catalysts by various methods and measured there catalytic activities and selectivities for

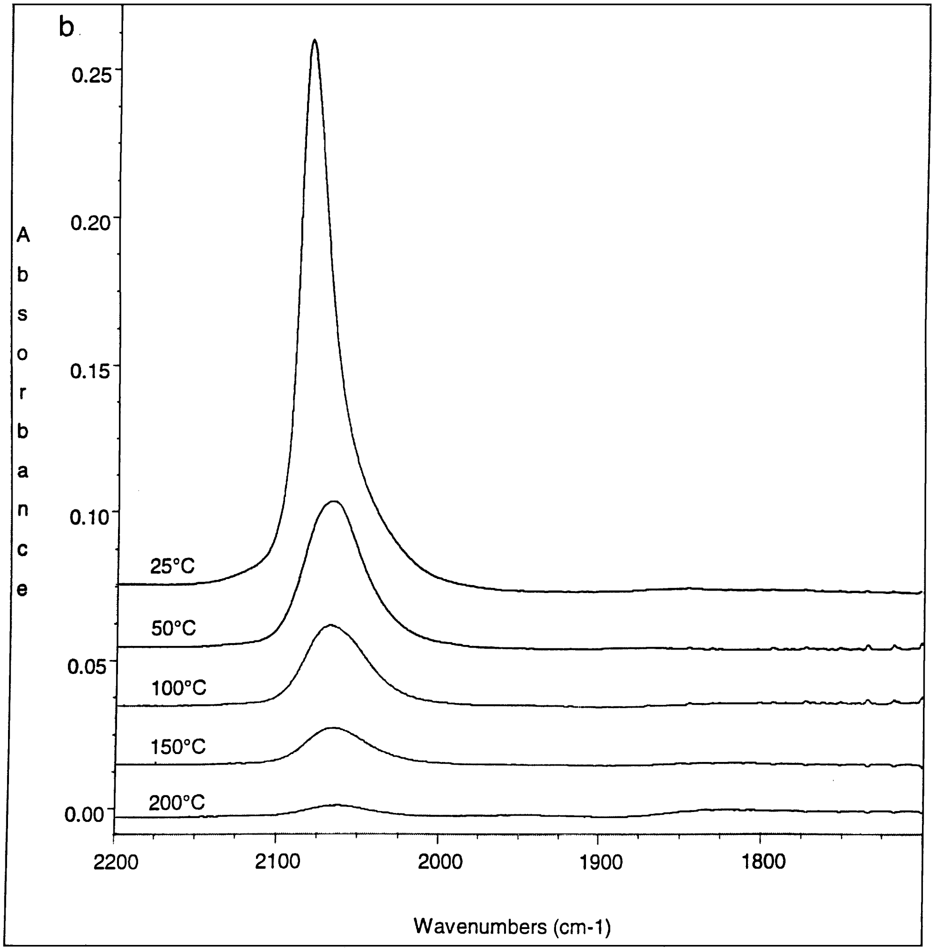
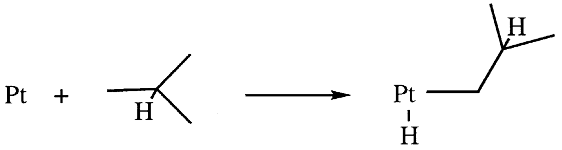
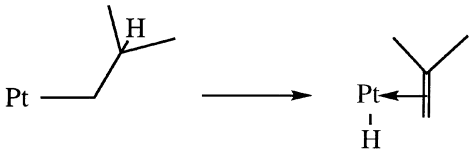


FIG. 3—*Continued*

isobutane dehydrogenation at 500°C. They found that the best catalyst is prepared by impregnation with the complex $PtCl_2(SnCl_3)_2^{2-}$ and that in the presence of hydrogen in the stream $H_2/iBu = 1$, the turnover frequencies based on total Pt are close to 1.4 after 1 h on stream, but they do not give the corresponding selectivity for isobutene. Let us remark that without hydrogen in the stream, the observed selectivities were never greater than 95%. It seems to us that the procedure used in the present work gave better results in terms of activity and selectivity. This could be due both to the better repartition of the tin atoms on the platinum surface and to the precise control of the amount of tin introduced. It is generaly admitted (26,39–41,43) that the presence of tin atoms regularly distributed on the platinum surface diminishes the size of the "ensemble" as do copper atoms on nickel surfaces (44) or tin atoms on rhodium and nickel surfaces (45–48). Increasing the amount of tin then strongly inhibits the hydrogenolysis process but slightly affects the dehydrogenation reaction, leading to a catalyst which is almost fully selective for isobutene (98%). The explanation for the high selectivity for isobutene should be based on a relationship between the structure of the PtSn catalyst and the mechanism of the reaction. We have seen previously by EXAFS (17), as well as by other techniques, that in the reduced form the platinum atoms are surrounded mostly by tin atoms. A simple but nevertheless useful description of the surface alloy leads to the concept of "site isolation": an active platinum atom is surrounded by "inactive" tin atoms. By active, we mean active for C-H bond activation. We have previously studied and interpreted in terms of elementary steps of organometallic chemistry, the mechanism by which an alkane can react with metallic surfaces (49). This mechanism when applied to isobutane implies, first, the activation of one of the primary C-H bonds of isobutane:

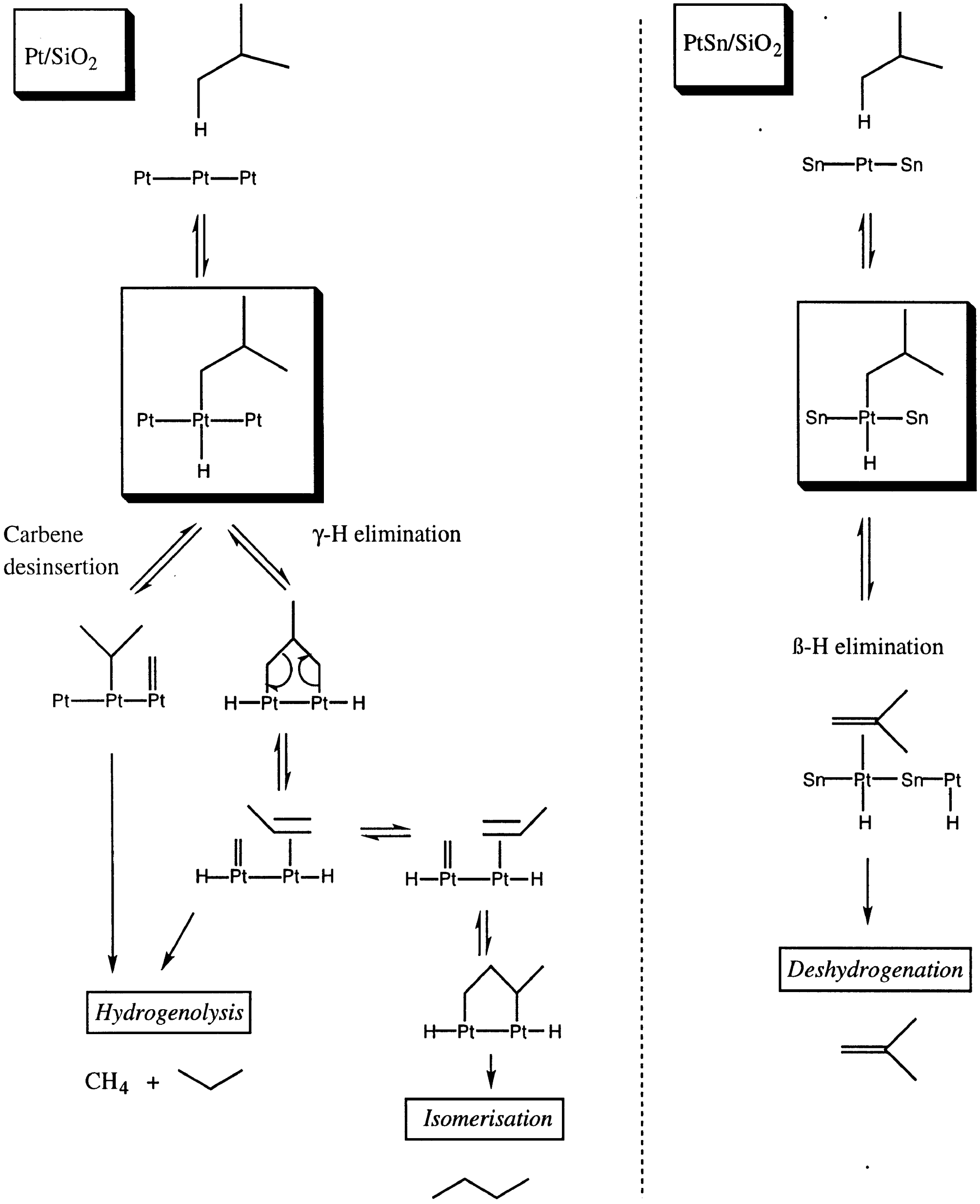


The elementary step leading to isobutene is just a β-H elimination:



However, from this isobutyl fragment it is possible to cleave one C-C bond and thus obtain fragments which may eventually give methane and propane (drop of selectivity) or give surface carbon (drop of activity with time on stream). A possible mechanistic explanation of the higher selectivity observed on Pt-Sn as compared with pure Pt may be:

Here we have represented the elementary steps leading to C-C bond cleavage from an isobutyl-platinum fragment. γ-H elimination by another platinum atom from the isobutyl-platinum fragment leads to a dimetallacyclobutane fragment (49). This metallacycle may rearrange to give a surface methylene and a propylene molecule. The methylene fragment leads either to methane and propane effectively observed as by-products or to *n*-butane by a secondary process of methylene attack on coordinated (and rotated) propylene molecule, followed by several steps of C-C bond formation and cleavage. Alternatively, and depending on the hydrogen pressure, the methylene fragment may dehydrogenate further to a surface carbyne and



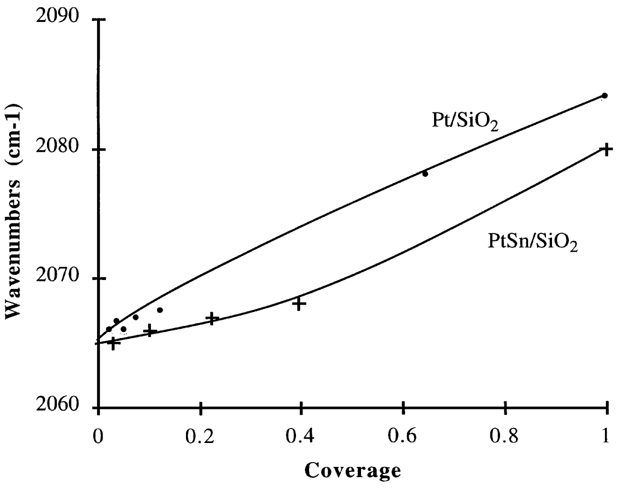


FIG. 4. ν(CO) frequency of adsorbed CO against CO coverage on Pt and PtSn/SiO_2 catalysts.

eventually carbon, leading to coke deposit (ageing with time on stream).

On platinum-tin the only reaction which can occur on a platinum atom surrounded only by tin atoms is the β-H elimination from the platinum-isobutyl surface fragment. This process of β-H elimination leads to the selective formation of isobutene. The concept of site isolation means that once the isobutane molecule has been transformed to Pt-isobutyl by a C-H bond activation process, the resulting isobutyl fragment, even if it can rotate around the Pt-C bond, can no longer have a γ-H in a favorable position which can lead to a metallacycle formation. Evidently the β-H elimination also occurs as a predominant process on platinum but with a degree of competing γ-H elimination which is much larger than on Pt-Sn (50). The "site isolation" concept explains at a molecular level why a single platinum atom can lead to very selective catalysts. Some other examples have been found previously in the laboratory where single Rh atoms lead to a selective cleavage of bonds in molecules. The most striking one is the hydrogenolysis of esters to alcohols (14,19,47) or the selective hydrogenolysis of acids to aldehydes (51,52).

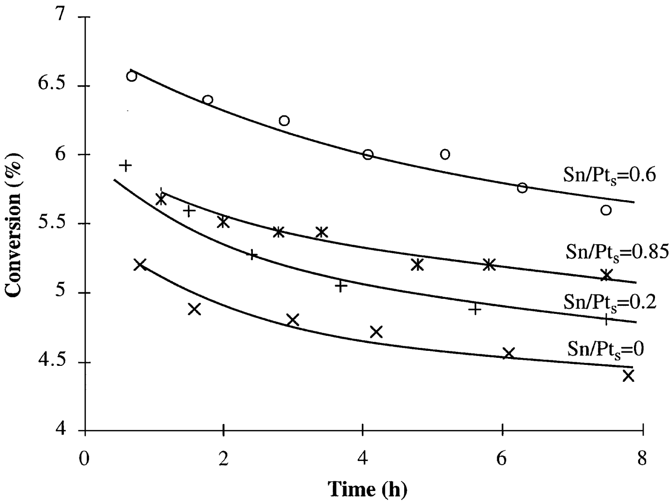


FIG. 5. Isubutane conversion of various bimetallic catalysts $PtSn_x$/SiO_2 (prepared from FH560) at 550°C, wwh = 500, and $H_2/iC_4 = 1$.

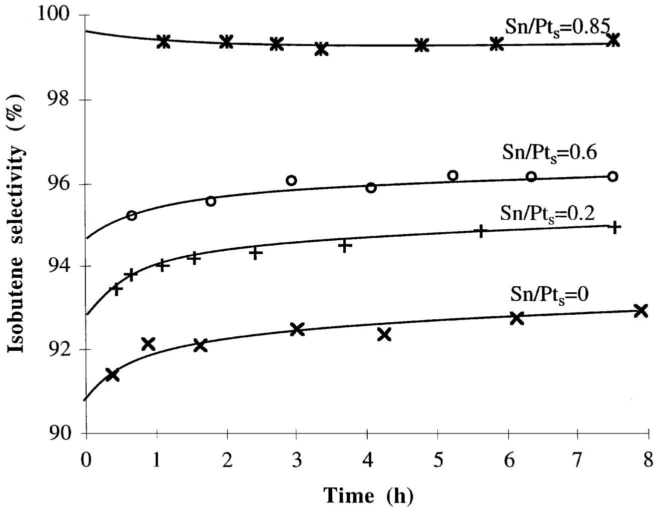


FIG. 6. Selectivity for isobutene of various bimetallic catalysts $PtSn_x$/SiO_2 (prepared from FH560) at 550°C, wwh = 500, and $H_2/iC_4 = 1$.

The effect of tin on the catalytic activity expressed as turnover frequencies (TOF) is more complex (Table 2). When Sn/Pt_s increases from 0 to 0.85, the catalytic activity based both on the total number of Pt atoms or even on surface Pt atoms (Pt_s) first increases drastically. The increase of activity with the addition of tin (from $Sn/Pt_s = 0$ to 0.6) could be explained by the inhibition of the coke formation (which poisons the active surface). Above a ratio of 0.6 the activity of the catalyst based on total Pt atoms begins to decrease but the activity based on Pt_s remains roughly constant. This result can be explained assuming that the catalytic activity for alkane dehydrogenation is structure insensitive (39,53,54). This is reasonable in view of the last mechanism depicted above: all isolated Pt atoms can achieve the C-H bond activation leading to a Pt-isobutyl fragment and a β-H elimination leading to isobutene. Above the ratio of 0.6 the rate of the reaction depends only on the number of surface platinum atoms and, then, the TOF based on Pt_s remains constant.

CONCLUSION

Bimetallic platinum-tin catalysts were prepared by surface organometallic chemistry on metals. The controlled reaction under hydrogen between tetra *n*-butyl tin and the platinum surface leads to well-defined bimetallic PtSn particles which exhibit remarkable properties for isobutane dehydrogenation to isobutene. Selectivities greater than 99% can be obtained with an increase of the catalytic activity

(TOF). According to the EXAFS data, the tin atoms are located on the first layer of the metallic particle, leading to a complete "site isolation" of the platinum by surface tin atoms. Hydrogenolysis processes leading to lower alkanes or eventually to carbon deposit are then almost fully inhibited. The catalyst becomes then extremely selective for the dehydrogenation processes. Its increased activity is thus explained by the inhibition of the coke formation.

Elementary steps of organometallic chemistry applied to the mechanism of isobutane dehydrogenation and hydrogenolysis fully account for the improved activity and selectivity of PtSn catalysts.

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