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Surface Organometallic Chemistry on Metals

II. Characterization of New Bimetallic Catalysts Generated by Reaction of $Sn(n\text{-}C_4H_9)_4$ with Silica-Supported Rhodium

J. P. CANDY,* O. A. FERRETTI,† G. MABILON,‡ J. P. BOURNONVILLE,‡
A. EL MANSOUR,* J. M. BASSET,* AND G. MARTINO‡

**Institut de Recherches sur la Catalyse, Laboratoire Propre du CNRS, conventionné à l'Université Claude Bernard, Lyon I, 2 Avenue Albert Einstein, 69626 Villeurbanne Cédex, France; †CINDECA (UNLP-CONICET), 47 No. 257, 1900 La Plata, Argentina; and ‡Institut Français du Pétrole, 2 Avenue de Bois-Préau, 92506 Rueil Malmaison Cédex, France*

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Reaction of $Sn(n\text{-}C_4H_9)_4$ with Rh supported on silica results in a new bimetallic Rh–Sn catalyst which is extremely active and selective in the reduction of ethyl acetate to ethanol. Whereas Rh/SiO_2 gives rise to a selectivity for ethanol of 57%, the Rh–Sn catalyst obtained by the organometallic route results in a higher activity and a selectivity to ethanol as high as 98%. Above a Sn/Rh value of 0.3, the activity varies linearly with the tin content which suggests that the enhanced catalytic activity is due to a new intermetallic phase. The catalysts have been characterized at various steps of the preparation. The starting reduced catalyst Rh/SiO_2 **A** with CO exhibits the typical infrared absorption bands of linear and bridged CO. Reaction of oxidized **A** with $Sn(n\text{-}C_4H_9)_4$ in refluxing heptane occurs mostly between Rh_2O_3 and the organotin compound to give an unreduced $Rh^{III}\text{–}SnR_x$ bimetallic surface complex **B**, the existence of which has been suggested from mass balance, STEM, and IR spectroscopy. Reduction of **B** at 773 K under H_2 leads to bimetallic particles with an average size of 2.2 nm and which do not contain any organic fragment (catalyst **C**). **C** chemisorbs only 0.1 H/Rh_t and 0.4 CO/Rh_t which is in sharp contrast with the values obtained with **A** (1.1 H/Rh_t and 1.1 CO/Rh_t). CO chemisorption on **B** gives only a single absorption band at 2000 cm^{-1} corresponding to linear coordination of CO. The presence of tin has apparently three effects: (i) it decreases significantly the amount of CO and H_2 adsorbed; (ii) it apparently isolates rhodium atoms from their neighbors; (iii) it increases slightly the electron density on rhodium. Redox behavior of the $Rh\text{–}Sn/SiO_2$ toward O_2 and silanol groups of silica has also been observed. With a fully reduced catalyst **C**, $Rh^{(0)}$ and $Sn^{(0)}$ are fully oxidized by O_2 to Rh_2O_3 and SnO_2. Thermal treatment of catalyst **C** under flowing He results in an oxidation of tin by surface silanol (or adsorbed water) to give a partially oxidized Sn species. H_2 is evolved during this oxidation process. The origin of the high activity and high selectivity (without hydrogenolysis property) of these catalysts is ascribed to the presence of a new catalytic phase in which rhodium atoms are isolated from their neighbors without any "ensemble" able to cleave the C–C and C=O bonds of ethyl acetate.

INTRODUCTION

A great variety of bimetallic catalysts has been used in heterogeneous catalysis (*1*), one of the major applications being catalytic reforming of crude oil (*2*). Among the large variety of bimetallics studied, tin associated with a Group VIII metal has been one of the most frequently used. Usually Group VIII metals, especially platinum, when they are associated with tin exhibit higher selectivity and stability in hydrogenation (*3*) and dehydrocyclization (*4*) reactions; they also exhibit a higher stability toward sintering (*5*). It has been suggested that the higher selectivities of those "modified" catalysts were due either to a geometric effect of tin which would reduce the size of the metallic "ensembles," so that hydrogenolysis would be suppressed (*6*), or to an electronic effect of tin toward the Group VIII metal (*7*).

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We report here that the addition of tin to supported rhodium results in a catalyst which is highly selective in the hydrogenation of esters to alcohols; a preliminary account of this observation has already been published (*8*). The particular features of this catalyst come from its very specific preparation which involves the reaction of the organostannic compound, $SnBu_4$, with the surface of rhodium supported on silica. This observation raises the question of the origin of the selectivity of these bimetallic catalysts: are we dealing with an electronic or a geometric effect or with a new class of intermetallic catalyst where the association of rhodium and tin via surface organometallic chemistry results in a new active phase? In order to answer these questions it appeared necessary to study the surface organometallic chemistry of the interaction between $SnBu_4$ and supported rhodium. In this paper we describe the preparation, characterization, catalytic properties, and redox properties of the $Rh-Sn/SiO_2$ system and we give evidence for a geometric effect of dilution of Rh atoms by tin atoms.

EXPERIMENTAL

Silica (Aerosil from Degussa) used as the support was treated, under reflux, with 3 *M* nitric acid for 24 h to lower the content of impurities to less than 10 ppm for each of the following elements: Al, Ca, Cu, Cr, Fe, and Na. After drying and calcination under flowing dry air at 773 K, for 2 h, the support exhibited a surface area of 200 $m^2\ g^{-1}$. The catalyst preparation is described under Results.

Electron Microscopy (CTEM and STEM)

Two types of experiment were carried out using conventional transmission electron microscopy (CTEM) and scanning transmission electron microscopy (STEM). CTEM and STEM experiments were made using JEOL 100 CX and Vacuum Generator HB5 electron microscopes, respectively. CTEM was used to determine the histogram of the Rh/SiO_2 samples before and after reaction with $Sn(n\text{-}C_4H_9)_4$ in order to calculate the dispersion (D is the number of surface atoms/number of total atoms, Rh_s/Rh_t). STEM experiments were carried out on the bimetallic catalyst to determine the composition of the particles (Rh, Sn).

Chemisorption Measurements

Two techniques (static and dynamic) were used, as follows.

Static volumetric measurements. These experiments were carried out using conventional equipment. The equilibrium pressures were measured with a Texas Instruments gauge working in the pressure range 0–1000 mbar (1 bar = 10^5 N m^{-2}) to an accuracy of ~1%. The vacuum was achieved by means of a turbomolecular pump, a procedure which avoided contamination of the catalyst with mercury. The gas phase present in the vessel was analyzed by means of a mass spectrometer (Supavac, from Vacuum Generators). The amount of adsorbed and/or consumed gas (O_2, H_2, or CO) was deduced from the amount of gas introduced (from a standard volume) and that remaining after the exposure to the catalyst. Pressure measurements were carried out at a temperature of 294 K. Under these conditions, the accuracy for the determination of adsorbed gases was close to 5%.

Dynamic measurements. Two types of experiment were carried out on equipment similar to that described by Falconer and Schwartz (*9*). These were: (i) temperature-programmed desorption (TPD) which allowed the determination of the amount of H_2 desorbed during a temperature-programmed desorption (10 K min^{-1}) under flowing argon (20 $cm^3\ min^{-1}$) and (ii) temperature-programmed reduction (TPR) which indicated the amount of H_2 consumed during a temperature-programmed experiment (10 K min^{-1}) under a flow of hydrogen + argon (H_2/Ar, 5/95; flow rate, 20 $cm^3\ min^{-1}$).

Infrared Spectroscopy

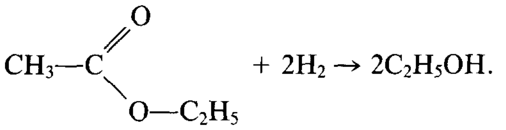
Infrared spectra were obtained with a

Nicolet 10 MX-1 Fourier transform instrument. Catalysis samples were placed on a sample holder which could be moved inside a closed reactor from a treatment position (located in an oven) to an analysis position located in the infrared beam (through CaF_2 windows).

The reactor could be evacuated or filled with H_2, O_2, and CO under a known pressure by means of a valve. The CO absorption bands were obtained by the difference between the IR spectrum of bare and CO-covered samples. Infrared spectroscopy was also used to evaluate the amount of alkyl groups present on the surface during reaction of Rh_2O_3/SiO_2 and $Sn(n\text{-}C_4H_9)_4$.

Catalytic Reactions

The reaction studied was the hydrogenation of ethyl acetate to ethanol:



$$CH_3{-}C({=}O){-}O{-}C_2H_5 + 2H_2 \rightarrow 2C_2H_5OH. \tag{1}$$

Various other products (CO, CO_2, CH_4, C_2H_6 and CH_3CHO) were identified, especially in the case of rhodium/SiO_2.

The reaction was carried out in a dynamic reactor working under differential conditions at 523 K under a pressure of 45 bar of hydrogen and 5 bar of ethyl acetate. The weight-hourly space velocity was 8 (w/w · h). The catalysts were first transferred in the open air into the reactor and treated under flowing pure H_2 (45 bar) at 723 K for 2 h. Then ethyl acetate was introduced into the reactor. Analysis for ethanol, acetaldehyde, CH_4, CO, CO_2, and other products was performed by gas chromatography. On tin-containing catalyst, the activity was constant after 30 min on stream. The activity was roughly constant for a period of 1 week. The sampling could be started after 5 min of reaction and after a small decrease in activity, the conversion and selectivity did not vary significantly. Preliminary experiments carried out with a catalyst prepared *in situ* without any contact with the open air indicated no change of activity and selectivity with respect to the previously described procedure.

Activity was defined as the number of moles of ethyl acetate transformed per gram of catalyst per hour. The selectivity was defined as the molar fraction of ethanol in the products (mol% $[C_2H_5OH]/([C_2H_5OH] + [CO_2] + [CH_4] + [C_2H_6] + [CH_3CHO]))$. The activity was stable over a period of more than 20 h. The sampling was carried out after 30 min at the desired temperature. It was possible to vary the range of temperature between 473 and 573 K and to obtain reproducible results for both activity and selectivity.

RESULTS

1. Preparation of the Catalysts

Rh/SiO₂ catalysts: ***A***$_1$ *and* ***A***$_2$. Rhodium is impregnated on silica at pH 10 by cationic exchange for 24 h of the chloroammine complex $[RhCl(NH_3)_5]^{2+}$ with the surface protons of silica. The solid is then washed, filtered, and dried under vacuum at 343 K. It is then calcined in flowing air (10 liters/h/g) up to 573 K and reduced in flowing hydrogen at 723 K for 2 h. Two samples **A**$_1$ and **A**$_2$ with rhodium contents of 1.2 and 2.6 wt% were prepared.

Rh–Sn/SiO₂ catalyst: ***B***. The reaction of increasing amounts of $Sn(n\text{-}C_4H_9)_4$ with catalyst **A**$_1$ is carried out at 370 K in refluxing *n*-heptane (blank experiments, when carried out in *n*-heptane, show no significant adsorption of $Sn(n\text{-}C_4H_9)_4$ with the silica support alone). The amount of tin fixed on the catalyst depends on the amount of $Sn(n\text{-}C_4H_9)_4$ introduced (Fig. 1). When the ratio Sn/surface rhodium is lower than ca. 2.5, approximately all the $Sn(n\text{-}C_4H_9)_4$ is adsorbed on catalyst **A**$_1$. Above this value a plateau is observed, indicating that no further surface reaction occurs between $Sn(n\text{-}C_4H_9)_4$ and catalyst **A**$_1$. In the following we shall call catalysts **B** the solids obtained by reaction of $Sn(n\text{-}C_4H_9)_4$ with the catalysts **A**

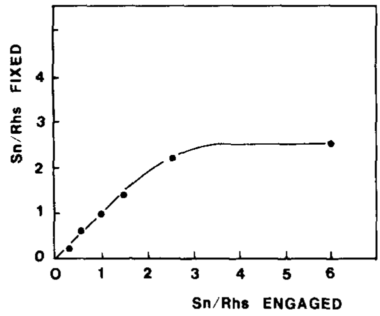


FIG. 1. Amount of tin fixed on catalyst A_I versus the amount of $Sn(n\text{-}C_4H_9)_4$ introduced.

at 370 K for 24 h followed by washing under Ar with boiling *n*-heptane to remove free $Sn(n\text{-}C_4H_9)_4$ and drying under flowing argon at the same temperature.

During the chemisorption of $Sn(n\text{-}C_4H_9)_4$ on catalysts **A**, approximately 1 mol of butane and 1 mol of butene (1-butene + *cis*- and *trans*-2-butenes) per mole of tin fixed are evolved. This suggests that a surface intermediate containing Rh and partially alkylated tin is formed.

The presence of some butyl groups remaining on the catalyst surface has been checked by infrared spectroscopy.

Rh–Sn/SiO$_2$ catalyst: ***C***. Catalyst **C** is obtained in the following way. Catalyst **B** is treated under H_2 at 723 K for 4 h in order to eliminate the remaining butyl groups of $Sn(n\text{-}C_4H_9)_4$ and then cooled under H_2 to room temperature and flushed at this temperature under flowing Ar.

After treatment of solid **B** under hydrogen at high temperatures, all the butyl groups are evolved as shown by the infrared spectra and by the mass balance experiment (all the butyl have been transformed into butenes and butane).

2. *Characterization of Catalysts **A**, **B**, and **C***

*Catalyst **A** (Rh/SiO$_2$)*. In order to determine the effect of tin on the chemisorption properties of supported rhodium, the chemisorption properties of two samples $\mathbf{A}_1$ and $\mathbf{A}_2$ of silica-supported rhodium have been studied.

The isotherms of H_2 and CO adsorption at 294 K on catalyst $\mathbf{A}_1$ are presented in Fig. 2. A plateau is observed for a partial pressure higher than ca. 50 mbar for CO and 400 mbar for H_2. We shall call H_{plat} and CO_{plat} the amount of H or CO adsorbed for an equilibrium pressure of 400 mbar (Table 1). By evacuation at room temperature, no CO and approximately one-half of the hydrogen previously adsorbed is desorbed. The remaining hydrogen (H_{ads}) is fully desorbed at 500 K *in vacuo* while CO needs higher temperatures (up to 770 K) to be fully desorbed.

Adsorption of CO on catalyst $\mathbf{A}_1$ at room temperature gives rise to two types of infrared band in the CO region (Fig. 3). A narrow band at 2055 cm^{-1} can be attributed to linear coordination of CO on a single rhodium atom (*10*). Another broader band of smaller intensity is observed at 1878 cm^{-1} ($\theta = 1$). This band is probably due to μ-coordination of CO to two surface rhodium atoms.

The particle size distribution of catalyst $\mathbf{A}_1$ was determined by CTEM. A typical histogram is given in Fig. 4. The average value for the detectable particles (the resolution limit of the CTEM is 0.7 nm) is 1.5

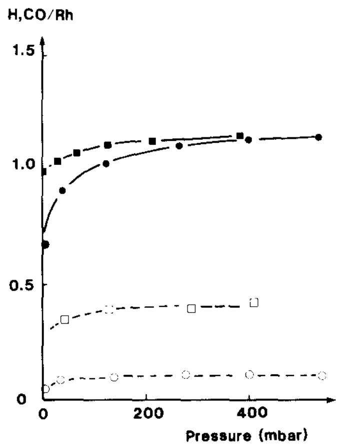


FIG. 2. Hydrogen (○,●) and CO (■,□) adsorption at 294 K on (—) catalyst $\mathbf{A}_1$ (Rh/SiO$_2$) and (---) catalyst $\mathbf{C}_2$ (Rh–Sn/SiO$_2$, Sn/Rh = 1.6).

TABLE 1

H_2, O_2, and CO Adsorption on Rh/SiO_2 and Rh–Sn/SiO_2

Catalyst	Rh (mmol g^{-1})	Sn (mmol g^{-1})	Treatment[a]	Q(O_2) (mmol g^{-1})	O/Rh[b]	O/Sn[b]	H/Rh[c]	CO/Rh[c]
$\mathbf{A}_1$	0.113	0.0	a	0.085	1.5	0.0	1.1	1.1
$\mathbf{C}_1$	0.113	0.130	a	0.209	1.5	1.9	0.1	—
$\mathbf{C}_1$	0.113	0.130	b	0.136	1.5	0.5	0.2	—
$\mathbf{C}_2$	0.113	0.180	a	0.260	1.5	2.0	0.1	0.4
$\mathbf{C}_2$	0.113	0.180	b	0.190	1.5	1.2	0.2	0.55
$\mathbf{A}_2$	0.252	0.0	a	0.189	1.5	0.0	0.8	0.7
$\mathbf{C}_3$	0.252	0.227	a	0.433	1.5	2.1	0.04	0.3
$\mathbf{C}_3$	0.252	0.227	b	0.350	1.5	1.4	0.1	0.4
$\mathbf{C}_4$	0.252	0.430	a	0.619	1.5	2.0	—	—
$\mathbf{C}_4$	0.252	0.430	a	0.610	1.5	2.0	0.03	0.1
$\mathbf{C}_4$	0.252	0.430	b	0.328	1.5	0.6	0.1	0.2

[a] Treatment: (a) flowing hydrogen at 773 K then cooling at 300 K under hydrogen; (b) flowing hydrogen at 773 K then evacuation (10^{-6} mbar) at 773 K for 4 h.

[b] O/Rh, O/Sn, calculated number of oxygen atoms fixed on Rh and Sn from oxygen consumption $Q(O_2)$ under oxygen at 673 K.

[c] H/Rh, CO/Rh, number of hydrogen atoms or CO molecules adsorbed on the sample at 295 K under 400 mbar (H_{plat} and CO_{plat}).

nm. This value corresponds to a dispersion *D* of 0.75, assuming that the particles have a cubooctahedral shape (*12*). These results are in good agreement with chemisorption measurements, assuming the respective stoichiometries: $H_{plat}/Rh_s = 1.5$ (*11–13*) and $CO/Rh_s = 1.5$ (*14*).

Temperature-programmed reduction (TPR) of catalyst $\mathbf{A}_1$ previously treated at 700 K under oxygen, studied in the range 300–873 K (Fig. 5), shows only one peak with a maximum of the TPR curve located at 370 K.

*Catalyst **B** (Rh–Sn/SiO$_2$).* Catalyst **B** has also been characterized by STEM. Most of the tin is present on the rhodium particles since the tin signal (LW for Sn = 3.44 keV) is detected only when the rhodium signal (LW for Rh = 2.69 keV) is observed and not on the support.

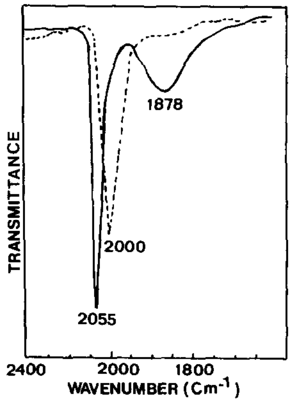


FIG. 3. Infrared spectra for CO adsorbed on catalysts $\mathbf{A}_1$ and $\mathbf{C}_2$. (—) $\mathbf{A}_1$ (Rh/SiO_2) and (–––) $\mathbf{C}_2$ (Rh–Sn/SiO_2, Sn/Rh = 1.6).

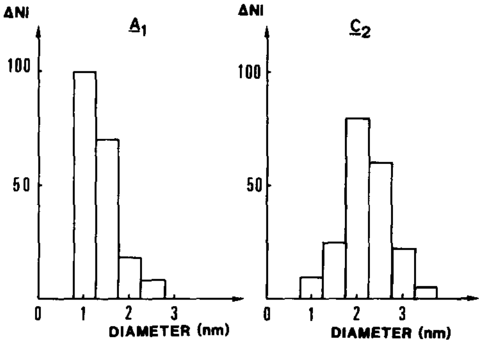


FIG. 4. Particle size determination of catalysts $\mathbf{A}_1$ (Rh/SiO_2) and $\mathbf{C}_2$ (Rh–Sn/SiO_2, Sn/Rh = 1.6).

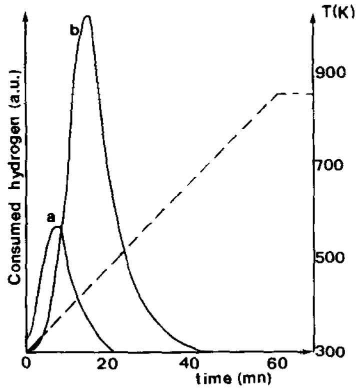


FIG. 5. Temperature-programmed reduction (TPR) under 5% H_2 + Ar of samples $\mathbf{A}_1$ (a) and $\mathbf{C}_2$ (b).

*Catalyst **C** (Rh–Sn/SiO₂).* After evacuation of catalyst **C** under 10 mbar at 473 K and then at room temperature, the resulting solid chemisorbs a smaller amount of hydrogen or CO at 300 K in comparison with catalyst **A** (Rh/SiO_2) (Fig. 2 and Table 1).

One should note that the decrease in CO adsorption capacity is not proportional to the decrease in H_2 adsorption capacity (H/Rh = 0.1 whereas CO/Rh = 0.4 for a Sn/Rh ratio of 1.6).

CO adsorption on catalyst **C** exhibits a single infrared peak at 2000 cm^{-1} corresponding to linear CO without any band below 2000 cm^{-1} which could arise from a bridged form of CO adsorbed. The decrease in frequency for linear CO (55 cm^{-1}) corresponds to an increased back-donation to the π^* orbitals of CO: Sn apparently increases the electron density on rhodium.

Analysis by CTEM indicates that the particle size increases from 1.2 to less than 2.0 nm as the Sn/Rh ratio rises from 0 to 2.5 (Fig. 4). The corresponding "apparent" decrease in the dispersion (from 75 to 56%) cannot account for the drastic decrease in chemisorption toward H_2 (the H/Rh ratio decreases from 1.0 to 0.1 when the Sn/Rh ratio increases from 0 to 2.4).

STEM analysis of catalyst **C** indicates that the particles are bimetallic with an average composition determined by the Sn and Rh signals, which is close to the expected value from chemical analysis. No tin is observed on the support.

After calcination of catalyst **C** under flowing oxygen at 600 K, the temperature-programmed reduction of the sample exhibited only one peak (Fig. 5). The maximum of the TPR curve is higher (450 K) for catalyst **C** than for catalyst **A** (370 K), but much lower than expected for tin oxide ($T_{red} > 950$ K) (*15*).

3. *Evidence for Tin Oxidation by Silanol Groups*

With Rh/SiO_2, temperature-programmed desorption of preadsorbed hydrogen leads to a single peak of desorption situated at ca. 350 K (Fig. 6, curve a). With catalyst **C**, H_2 is evolved in two steps (Fig. 6, curves b and c).

The first peak, centered at 350 K, very probably corresponds to the hydrogen adsorbed on "bare" Rh since it occurs at the same temperature as that observed for Rh/SiO_2. The amount of hydrogen evolved in this step, H_{ads}, decreases drastically with the Sn content (Fig. 7).

The second peak, observed at higher temperatures, does not exist with Rh/SiO_2.

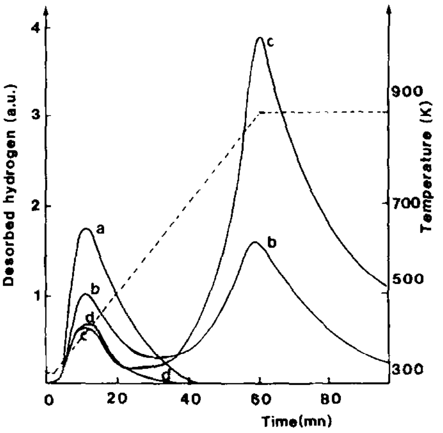


FIG. 6. Temperature-programmed desorption (TPD) under Ar of hydrogen chemisorbed on (a) catalyst $\mathbf{A}_1$ (Rh/SiO_2), H_2 adsorbed at 773 K; (b) catalyst $\mathbf{C}_1$ (Rh–Sn/SiO_2, Sn/Rh = 1), H_2 adsorbed at 773 K; (c) catalyst $\mathbf{C}_2$ (Rh–Sn/SiO_2, Sn/Rh = 1.6), H_2 adsorbed at 773 K; (d) catalyst $\mathbf{C}_2$ (Rh–Sn/SiO_2, Sn/Rh = 1.6), H_2 adsorbed at 294 K.

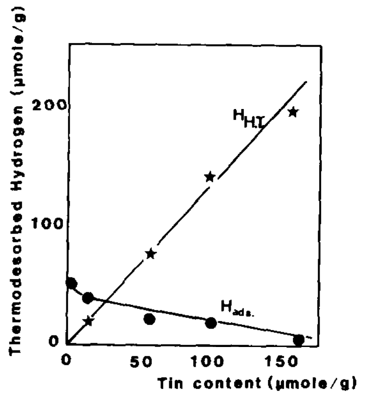


FIG. 7. Amount of H_{HT} and H_{ads} thermodesorbed versus tin content of catalysts **C**. (●) H_{ads}; (★) H_{HT}.

The amount of hydrogen evolved in this step, H_{HT}, is directly proportional to the Sn content (Fig. 7). It is therefore likely that this second TPD peak of H_2 is due to the presence of tin. Two hypotheses can be advanced to account for this evolution of H_2 at high temperatures:

—oxidation of zero-valent tin by silanol groups;

—desorption of a strongly adsorbed hydrogen from Rh–Sn alloy.

If this strongly adsorbed form of hydrogen exists, it is expected to react with oxygen to give water. If pure oxygen is introduced into a closed vessel on catalyst **C** previously desorbed at 480 K (in order to eliminate the H_{ads} form without removing the H_{HT} form) and samples of the gas phase are analyzed by mass spectrometry, no water is detected up to a temperature of 475 K. Water produced in the titration of hydrogen adsorbed on Rh/SiO_2 by O_2 is easily detected by mass spectroscopy at 473 K.

Chemisorption of O_2 on catalyst previously treated *in vacuo* at 480 K in order to eliminate adsorbed hydrogen (H_{ads}) can be used to determine the average oxidation state of rhodium and tin. With catalysts **A** the amount of adsorbed O_2 (Table 1, treatment a) at 600 K corresponds to the overall reaction

$$Rh^{(0)} + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}Rh_2O_3. \qquad (2)$$

With catalysts **C**, the amount of adsorbed O_2 at 673 K corresponds to the overall reactions

$$Rh^{(0)} + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}Rh_2O_3 \qquad (3)$$

$$Sn^{(0)} + O_2 \rightarrow SnO_2. \qquad (4)$$

Therefore in catalyst **C**, tin is in a zero-valent oxidation state.

When catalyst **C** is treated *in vacuo* (10^{-6} mbar) at 773 K for 4 h and cooled to room temperature, the amount of adsorbed oxygen is much lower than expected from reactions (3) and (4) (Table 1, treatment b). Assuming reaction (3) is total, the observed O/Sn ratios are much below the stoichiometry of Eq. (4) which suggests that Sn has already been oxidized during the treatment *in vacuo* at 773 K. This oxidation is very likely to be occurring via silanol groups of silica.

In order to check if tin in the rhodium–tin sample could be oxidized by reaction with water (or silanol groups), some water (18 mbar) is introduced on catalyst **C** previously treated *in vacuo* at 373 K. If the sample is heated in a closed vessel at 473 K for 2 h, mass spectroscopic analysis of the gaseous phase shows the presence of a large amount of hydrogen. Under the same conditions, Rh/SiO_2 does not give any hydrogen.

Thus we can propose an oxidation of zero-valent tin by the silanol groups of the surface, which explains the high-temperature desorption of hydrogen:

$$Sn^{(0)} + 2(\equiv Si{-}OH) \rightarrow (\equiv Si{-}O)_2Sn^{(II)} + H_2. \qquad (5)$$

4. *Hydrogenation of Ethyl Acetate*

Rh/SiO_2 is active in the hydrogenation of ethyl acetate in a temperature range 470–570 K but its selectivity to ethanol is rather low (57%). The main side reactions are hydrogenolysis to CH_4, CO, C_2H_6, and H_2O. The apparent activation energy is 75.2 kJ mol^{-1}.

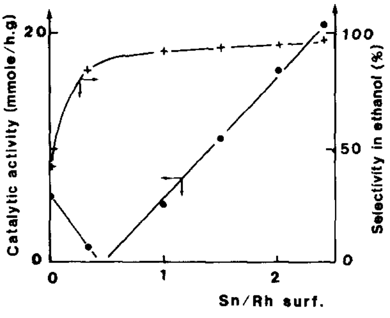


FIG. 8. Activity and selectivity in catalytic conversion of ethyl acetate versus tin content of catalysts **C**. Hydrogen pressure, 45 bar; ethyl acetate pressure, 5 bar; temperature, 523 K; contact time, 8 w/w/h.

For tin-containing catalysts two main features can be seen in Fig. 8. As the ratio Sn/surface rhodium increases from 0 to 0.5 the overall conversion of ethyl acetate decreases sharply, whereas the selectivity to ethanol increases significantly. Above a ratio Sn/surface rhodium of 0.5, the conversion of ethyl acetate increases linearly with tin content and simultaneously the selectivity for ethanol reaches very high values (up to 98%). Obviously the introduction of tin results in a new catalyst which exhibits unexpected selectivities for hydrogenation of an ester to an alcohol. Apparently, conversions and selectivities are comparable to those obtained with copper chromites (*14*). The apparent activation energy observed for this bimetallic system is 46 kJ mol^{-1}, quite different from that observed with pure rhodium (75.2 kJ mol^{-1}). The activation energy is varying quite drastically with tin content. It decreases very much above a Sn/Rh ratio of 0.3 (Fig. 9). This indicates a sharp modification of the rhodium due to the presence of tin which induces drastic changes in the overall reaction path and possibly reaction mechanism.

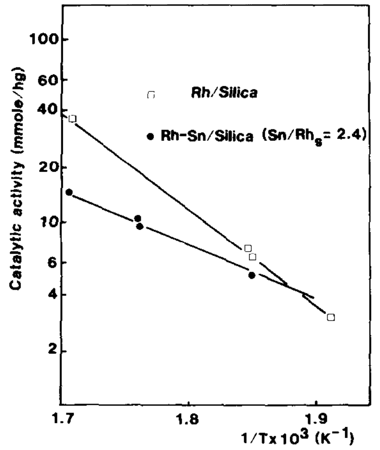


FIG. 9. Variation of catalytic activity in ethyl acetate hydrogenation versus temperature, for catalyst **A** and catalyst **C** (Sn/Rh = 1). Hydrogen pressure, 45 bar; ethyl acetate pressure, 5 bar; weight-hourly space velocity, 8 w/w/h.

DISCUSSION

The reaction of Sn(n-C_4H_9)$_4$ with solid **A** (Rh/SiO_2) results in a new kind of catalyst which exhibits very high selectivities and activities in the hydrogenation of ethyl acetate to ethanol (Fig. 8). This behavior, unexpected in the field of heterogeneous catalysis by metals, has prompted us to study in detail the preparation and characterization of such catalysts in the hope that it would be possible to correlate activity and/or selectivity with some characteristics of this new class of catalysts.

Three types of catalysts have been prepared and characterized, namely **A**, **B**, and **C**, and we can comment on their properties as follows.

Catalyst **A** (Rh/SiO_2) has been characterized by electron microscopy and chemisorption measurements. For the catalyst **A** containing 1.2 wt% rhodium, the particle size is close to 1.5 nm. This value corresponds to a dispersion of 0.75. These results are in good agreement with the amount of H_2 or CO chemisorbed (Fig. 2) assuming the respective stoichiometries H_{plat}/Rh_s = 1.5 and CO_{plat}/Rh_s = 1.5 at room temperature. This catalyst exhibits toward CO the typical bands of linear (2055 cm^{-1}) and bridged (1878 cm^{-1}) carbon monoxide (Fig. 3). H_2 is desorbed from this catalyst in a single step with a maximum at ca. 350 K. We do not discuss here the low-temperature peak of desorption which occurs at ca. 200 K, for which one should see the remarks in Part I (*12*). When **A** is oxidized to Rh_2O_3/SiO_2, there is only one peak of reduction under flowing H_2 which occurs at 370 K (Fig. 5).

Catalyst **B**, which is obtained by reaction of catalyst **A** with $Sn(n\text{-}C_4H_9)_4$ in heptane solution at 370 K, has been characterized by electron microscopy and IR spectroscopy. CTEM indicates a significant increase in particle size with respect to **A**. Moreover, these particles contain both Rh and Sn (STEM). This suggests that $Sn(n\text{-}C_4H_9)_4$ has reacted with the oxidized rhodium rather than with the silica support. A blank experiment carried out in heptane has shown no apparent reaction between $Sn(n\text{-}C_4H_9)_4$ and the silica surface. This chemical reaction between Rh_2O_3 and $Sn(n\text{-}C_4H_9)$ is confirmed by the fact that for a given amount of rhodium there is a maximum value for the amount of tin fixed (Fig. 1). This maximum is almost proportional to the amount of rhodium (Table 1). Infrared spectroscopy and mass balance measurements (*18*) suggest that **B** is an unreduced form of rhodium with very probably $(\gtrdot Rh{-}O{-})_xSnBu_y$ $(x + y = 4)$ ligands.

Catalyst **C** is obtained by reduction of **B** at 773 K under H_2. Again the metal particles of **C** contain both Rh and Sn (STEM). Their average size (2.2 nm, catalyst $\mathbf{C}_2$) is larger than those of **A** (1.5 nm). No butyl groups are present on **C** (IR spectroscopy). $\mathbf{C}_2$ chemisorbs only 0.1 H/Rh_t and 0.4 CO/Rh_t which is in sharp contrast with the values obtained with $\mathbf{A}_1$ (1.1 H/Rh_t and 1.1 CO/Rh_t). These strong modifications of the chemisorption properties are confirmed by the IR spectra of adsorbed CO. With **C**, only one peak at 2000 cm^{-1} is observed, corresponding to linear coordination of CO. The presence of tin has apparently three effects:

(i) it decreases significantly the amount of CO adsorbed;

(ii) it apparently isolates rhodium atoms from their neighbors (absence of bridged CO);

(iii) it increases slightly the electron density on rhodium (2000 cm^{-1} on **C** instead of 2055 cm^{-1} on **A**).

A very unusual behavior of **C** can be observed by TPD experiments. The usual peak of H_2 desorption observed on catalyst **A** is still present on **C** but the corresponding amount is decreasing sharply with tin content (Figs. 6a–6c and 7). Increasing the amount of tin results in a new high-temperature peak of H_2 evolution at 873 K, the amount of H_2 evolved being proportional to the amount of tin introduced (Figs. 6 and 7). It is possible to eliminate this high-temperature peak of H_2 evolution if catalyst **C** is treated under flowing helium at 873 K and then contacted with H_2 at room temperature (Fig. 6d). High-temperature desorption of hydrogen from bimetallic catalysts containing Sn has been previously observed by Kuznetsov and Yermakov (*16*), but without explanation. Two hypotheses have been advanced to account for this evolution of H_2 at high temperatures:

(a) oxidation of zero-valent tin by silanol groups:

$$x\ Si{-}OH + Sn^{(0)} \rightarrow (\equiv Si{-}O)_xSn^{(x+)} + x/2\ H_2 \quad (6)$$

(b) desorption of a strongly adsorbed hydrogen from Rh–Sn alloy.

The absence of water evolution by reaction of this (hypothetical) strongly adsorbed hydrogen with oxygen rules out the existence of such hydrogen.

Recently, Duprez and Miloudi (*17*) demonstrated that water evolved from a Rh or Pt on alumina catalyst during a TPD experiment could be decomposed by a reducing system (Fe powder) to produce a hydrogen desorption peak at about 670 K.

It is therefore likely as in their case that tin is oxidized by surface water or silanol groups at high temperatures to form hydrogen. The average oxidation state of tin resulting from high-temperature desorption can be estimated from the amount of H_2 evolved (Fig. 7) (1.3 H_2/Sn).

Although the results are not very accurate, the calculated value for the average oxidation state (2.6 ± 0.5) suggests two possibilities:

(i) total oxidation of $Sn^{(0)}$ by water to $Sn^{(IV)}$ (with some $Sn^{(0)}$ remaining on the particles):

$$H_2O_{(ads)} + Sn^{(0)} \rightarrow Sn^{(IV)}O_2 + 2H_2 \quad (7)$$

(ii) partial oxidation by silanols of all the $Sn^{(0)}$ to $Sn^{(II)}$:

$$2Si\text{-}OH + Sn^{(0)} \rightarrow (\equiv Si\text{-}O)_2Sn^{(II)} + H_2. \quad (8)$$

When using O_2 as an oxidizing agent (rather than surface protons) it is possible to demonstrate the occurrence of total oxidation of $Sn^{(0)}$ and $Rh^{(0)}$ to $Sn^{(IV)}O_2$ and $Rh_2^{(III)}O_3$ (Table 1). With a fully reduced catalyst the amount of O_2 adsorbed corresponds to the overall oxidation process:

$$Rh^{(0)} + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}Rh_2^{(III)}O_3 \quad (9)$$

$$Sn^{(0)} + O_2 \rightarrow Sn^{(IV)}O_2. \quad (10)$$

The presence of a partially oxidized tin after high-temperature desorption can be proved by further oxidation by O_2 (Table 1, treatment b). The amount of O_2 adsorbed on a sample which has been thermally desorbed at high temperatures is much less than that on a fully reduced sample. This seems to be in agreement with an incomplete tin oxidation.

It is impossible to make a clear distinction between the two possible equations, (7) and (8). It is very likely that both can occur simultaneously depending on the respective amount of molecular water adsorbed and silanol groups on the silica surface. It seems unreasonable that tin can be oxidized above $Sn^{(III)}$ by surface silanols. Molecular water was effectively found to react with catalyst **C** to give H_2 and therefore oxidized tin.

In conclusion, we may try to summarize at this stage of investigation the state of catalyst **C**. **C** seems to be a bimetallic alloy with the possible formulation $RhSn_2$. In this alloy the surface rhodium sites are apparently isolated from their neighbors by tin atoms. It is this isolation with no metallic ensemble which renders these catalysts selective for ester hydrogenation to alcohols without significant hydrogenolysis. This confirms the fact that hydrogenolysis requires ensembles of metal atoms (*6*). This also suggests that ester hydrogenation occurs on a single rhodium atom surrounded by tin atoms which not only have a geometric effect of dilution but also coordinate to rhodium with favored surface configuration for the coordination and reaction of ethyl acetate on the surface. One should also consider the fact that these catalysts chemisorb a very small amount of H_2 and a higher amount of CO. The reason for such a difference is not clear. The phenomenon cannot be accounted for only by a geometric effect. The still hypothetical intermetallic phase "$RhSn_2$" probably has a specific affinity for H_2 and CO which deserves further studies.

In addition to the reduced form, a redox behavior between tin and surface OH or water has been demonstrated. Zero-valent tin can be oxidized at high temperatures by surface protons and this process can be reversed under H_2. It is not yet clear whether tin migrates totally or partially from the particle to the silica surface or if water from the surface oxidizes the tin of the bimetallic particle to SnO_2 which would remain "above" the particles. It is possible that both phenomena occur depending on the hydroxyl content of the silica and the Sn/Rh ratio.

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