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Hydrogenation of crotonaldehyde on Rh-Sn/SiO_2 catalysts prepared by reaction of tetrabutyltin on prereduced Rh/SiO_2 precursors

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Abstract

Rh and Rh-Sn/SiO_2 catalysts have been prepared, characterized and used in the crotonaldehyde hydrogenation reaction. New bimetallic Rh-Sn catalysts were prepared by reaction of $Sn(n\text{-}C_4H_9)_4$ over a prereduced Rh-SiO_2 precursor. It was observed that the temperature of the preparation reaction also plays an important role in the nature of the Rh-Sn active sites. Thus, at lower temperatures, 363 K, $Rh(SnBu_{4-x})_y$ species remain adsorbed on the silica surface whereas at 773 K, the organometallic residue decomposes leading to Rh-Sn bimetallic catalysts. Tin addition causes a significant drop in hydrogen chemisorption capability but only a slight increase in metal particle size. Electron diffraction detected the presence of Rh^0, $RhSn_2$ and SnO_2 phases for the bimetallic catalysts and Rh^0 for the monometallic ones. XPS shows an important surface enrichment in tin suggesting that SnO_x species would migrate and deposit on the metal crystals. The active sites generated upon these treatments allow the polarisation of the carbonyl group and consequently an enhancement in the selectivity to crotyl alcohol is obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst preparation; Organometallic compounds; Rh-Sn-silica; Crotonaldehyde hydrogenation; Characterization

1. Introduction

Hydrogenation reactions are of great interest in the field of fine chemicals, as processes to obtain either intermediates or final products. They usually involve the selective catalytic hydrogenation of certain chemical bonds to obtain the desired products. The selective hydrogenation of carbonyl groups in the presence of olefin groups in α, β unsaturated aldehydes is an important step in the preparation of various fine chemicals used in perfumes, flavorings, and pharmaceuticals [1–3].

From an industrial point of view, the most important product is the unsaturated alcohol and the reaction requires a preferential C=O hydrogenation of the α, β unsaturated aldehydes [4–8]. Research has been devoted to improve the selectivity of heterogeneous supported metal catalysts in these reactions [9–13]. Several research groups have reported catalysts able to selectively reduce certain conjugated aldehydes such as crotonaldehyde and cinnamaldehyde to the corresponding unsaturated alcohols [14–19]. Fig. 1 displays reaction pathway of the hydrogenation of crotonaldehyde.

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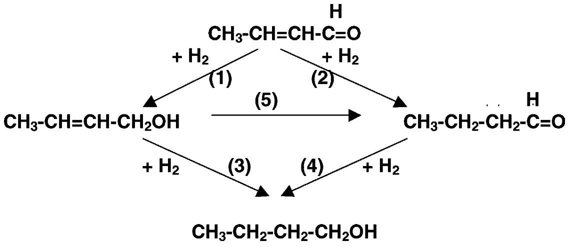


Fig. 1. Reaction pathway for crotonaldehyde hydrogenation.

Selectivity towards the allylic alcohol is highly dependent on the nature of the precious metal used as a catalyst [20]. The design of a new catalyst with a high selectivity for the reduction of the carbonyl bond, however, usually requires the creation of polar sites that interact with the C=O bond and thus lead to its preferential activation.

This may be achieved by using bimetallic catalysts or supported noble metals on partially reducible oxides. Gallezot and Richard [21] have classified this effect into three groups: (i) Catalysts where metallic promoters are added in ionic form. This process may result in the formation of the cationic species deposited on the metal crystals or, due to the hydrogenation conditions, these cationic species can be reduced producing bimetallic particles; (ii) Catalysts involving bimetallic particles, usually prepared ex situ, where electropositive metal atoms are associated in the same particle with metal atoms of higher redox potential (usually, platinum-group metals); and (iii) Catalysts involving oxidised metal species at the metal-support interface, usually produced by migration of partially reduced support species to metal crystals, producing decoration of metallic species. As a result of the induced modifications in the metal crystals, a polarization in the C=O bond is obtained, thus producing an enhancement in the selectivity to the unsaturated alcohol.

With regard to the bimetallic systems involving a platinum-group metal and a second metal, usually having lower catalytic activity, many studies have been carried out with the aim to investigate the chemical state of both metals. Thus, Pt, Os, Ir, Pd, Rh, and Ru catalysts among others have been studied, using Fe, Co, Ni, Ge, and Sn as second metal. Most of the studies have shown that the second metal after reduction remains as a cationic species associated with the platinum-group metal [11,22–26], these sites being responsible or the selectivity improvements to the allylic alcohol. Thus, the promoting effect of tin on Pt catalysts, prepared by the impregnation procedure with solution of H_2PtCl_6 and $SnCl_2$, produces a significant increase in the selectivity to the unsaturated alcohol during cinnamaldehyde and acrolein hydrogenation [27,28]. A similar effect was observed in crotonaldehyde hydrogenation by Marinelli et al. [29] for Pt-Sn/SiO_2, by Coloma et al. Pt-Sn/C catalysts [30] and by Neri et al. [31] for citral hydrogenation on Pt-Sn-C catalysts. The observed behavior was attributed to the electrophilic activation of the C=O bond by cationic tin on the platinum surface.

However, the oxidation state of the metals in the bimetallic systems is strongly affected by the preparation procedure. The presence of alloys or intermetallic compounds in supported catalysts is difficult to be detected if metal particle size is too low. Beccat et al. [32] reported the hydrogenation of methylcrotonaldehyde on a $Pt_{80}Fe_{20}$ single-crystal phase. These authors found that an increase in the rate of formation on the unsaturated alcohol was obtained by alloying platinum with iron. A similar finding was observed for Pt-Co colloidal particles during cinnamaldehyde hydrogenation [23]. The bimetallic phase was invoked to be responsible for the enhancement in the selectivity. With regard to supported catalysts, several contributions by Candy et al. [33–35], dealing with the use of organometallic compounds for preparing bimetallic catalysts, have been reported. These authors claimed that the use of surface organometallic chemistry (SOMC) may lead to catalysts having surface, bulk and catalytic properties which may be ascribed to the formation of alloys. Particularly, the selective reaction of organometallic complexes of group IVa elements with group VIII metal-supported catalysts have been widely studied. The catalysts obtained via SOMC, exhibit unusual activities and selectivities [33–35]. Thus, tetra-*n*-butyl tin ($Sn(n\text{-}C_4H_9)_4$) reacts with metal surface of silica-supported rhodium to give a bimetallic Rh-Sn catalyst which exhibits high selectivity and activity in several reactions such as the hydrogenation of α, β unsaturated aldehydes, nitrobenzene, acrilonitrile and olefins [34]. The nature of these new catalytic materials depend strongly on the reactivity of the organometallic compounds with the metallic surface. SOMC can yield a metallic surface covered with adatoms or surface organometallic fragments, or an alloy having the desired composition [36].

The present work is aimed to study bimetallic Rh-Sn/SiO$_2$ catalysts prepared by the SOMC for the selective hydrogenation of crotonaldehyde. The Rh/SiO$_2$ catalysts were obtained by the sol–gel method and by impregnation of a sol–gel silica with rhodium precursors. Tin was introduced by specific reaction between Rh/SiO$_2$ and tetra-*n*-butyltin. The performance of the bimetallic catalysts is studied on two type of modified systems: (i) the activation in hydrogen does not exceed 363 K; and (ii) the activation in hydrogen is carried out at 773 K. The catalytic reaction was carried out in liquid phase and the catalysts were characterized by specific surface area, H$_2$ chemisorption, transmission electron microscopy, electron diffraction and X-ray photoelectron spectroscopy in order to correlate chemical structures with performance. The evolution of hydrocarbons from the organometallic compounds chemisorbed on the bimetallic surface during the preparation reaction was monitored by gas chromatography.

2. Experimental

2.1. Catalysts preparation

The Rh/SiO$_2$ catalyst was obtained from the sol–gel using the following procedure [37]. A mixture of tetraethyl orthosilicate (TEOS) with ethanol and Rh(AcAc)$_3$ dissolved in acetone to give a Rh loading of 0.5 wt.% was stirred and refluxed at 318 K. The gelation pH was 5. The reflux was maintained until gel formation was achieved, then the temperature was increased to 353 K and kept constant for 1 h. The obtained solid was dried at 383 K for 6 h, calcined in air at 723 K for 4 h and reduced in situ at 773 K for 2 h, prior characterization or the catalytic test. Additionally, 0.5 and 1.0 wt.% Rh/SiO$_2$ catalysts were prepared by impregnation with acetone solution of Rh(AcAc)$_3$ on a silica ($S_{BET} = 700\,m^2\,g^{-1}$, pore volume $0.58\,cm^3\,g^{-1}$) prepared by the sol–gel method at pH = 5 as described previously. TG and DSC have shown that the complete decomposition of rhodium acetylacetonate into rhodium oxides takes place at temperatures lower than 673 K. The preparation of the bimetallic systems consisted of the reaction of a solution of tetra-*n*-butyltin (Sn(n-C$_4$H$_9$)$_4$) in a paraffinic solvent (*n*-heptane) with the reduced Rh/SiO$_2$ catalyst at 363 K under flowing hydrogen. After 4 h under reaction, the liquid phase was separated and the solid was repeatedly washed with *n*-heptane and subsequently dried in air at 363 K. The solid obtained after this procedure, labelled as organobimetallic catalyst (RhSn-OM) still had butyl groups grafted to the surface. The variation of SnBu$_4$ concentration was analyzed using a Varian 3400 gas chromatograph equipped with a flame ionization detector using a 10% OV-101 column (1/8 in i.d. and 0.5 m length).

The bimetallic phases (RhSn-BM) were obtained by removal of the organic groups by treatment of RhSn-OM catalysts in flowing hydrogen at 773 K for 2 h. The rhodium loading is given in brackets.

2.2. Catalyst characterization

TG and DSC analyses of precursors of Rh catalysts were performed in a Polymer Laboratories model STA-625 TG, using an air flow of 20 cc min^{-1} at a temperature range 298 to 823 K and a heating rate of 10 K min^{-1}. Quantitative data obtained from TG allowed an evaluation of Rh loading. These results were confirmed by UV–VIS studies carried out on acetylacetonate rhodium solution in a Perkin-Elmer UV–VIS Lambda 12 Spectrometer analysing between 200 and 1000 nm with the maximum being at 319 nm.

The specific surface area of the catalysts studied was obtained from the nitrogen adsorption isotherms recorded at 77 K with a Micromeritics model Gemini 2370 apparatus. Hydrogen chemisorption at 298 K was carried out in a conventional greaseless volumetric adsorption system, equipped with a MKS Baratron 170 M pressure transducer. Before the chemisorption experiments, the samples were reduced in situ at 773 K for 2 h and then outgassed for 4 h at the same temperature.

Transmission electron micrographs and electron diffraction patterns were obtained with a Jeol JEM 1200 EXII microscope. The supported catalysts were ground in an agate mortar and dispersed in ethanol. A drop of each dispersion was placed on a 150 mesh copper grid coated with carbon. To obtain metal particle size, several magnifications were used in both bright and dark fields. For electron diffraction studies 120 kV and 60 cm were used as acceleration voltage and focus distance respectively and a gold standard (Merck 99.99% pure) was used for calibration. XPS spectra were recorded using a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a Mg Kα X-ray source ($h\nu = 1253.6$ eV). The system was provided with a reaction cell which allows pretreatment at high temperatures. The samples were pressed in a hydraulic die to form thin, smooth discs and placed in the cell. The samples were prereduced in hydrogen at 773 K for 1 h and then transported to the analysis chamber without contact with air. Rh and Sn peaks were decomposed into several components assuming that the peaks had Gaussian–Lorentzian shapes. Surface Rh/Si and Sn/Si ratios were estimated from the integrated intensities of Rh $3d_{5/2}$, Sn $3d_{5/2}$ and Si 2p lines after background subtraction and corrected by the atomic sensitivity factors [38]. The line of Si 2p at 103.4 eV was used as an internal standard.

2.3. Catalytic reactions

The catalytic reactions were carried out in a stirred batch reactor at 313 K and a pressure of hydrogen of 10 atm. The catalyst (1.00 g) was added to the reactor and mixed with 80 ml of a 0.15 M solution of crotonaldehyde in isopropanol. The analyses of reactants and products were performed using a Varian 3400 gas chromatograph equipped with a 30 m J&W DB-WAX capillary column and a flame ionization detector.

3. Results and discussion

Careful studies of the reaction between tetra-*n*-butyltin and a silica-supported group VIII metal M (M = Pt, Rh, Ru, Ni) have been performed [33–36]. The results indicate that when the reaction is carried out in the presence of molecular hydrogen on a reduced metallic particle, the process may be represented by a two-step scheme:

$$363\text{–}423\,\mathrm{K};\quad \mathrm{Rh/SiO_2} + y\,\mathrm{SnBu_4} + \tfrac{1}{2}xy\,\mathrm{H_2} \rightarrow \mathrm{Rh(SnBu_{4-x})_y/SiO_2} + xy\,\mathrm{BuH}$$

$$423\text{–}773\,\mathrm{K};\quad \mathrm{Rh(SnBu_{4-x})_y/SiO_2} + \tfrac{1}{2}(4-x)y\,\mathrm{H_2} \rightarrow \mathrm{RhSn_y/SiO_2} + (4-x)y\,\mathrm{BuH}$$

The extent of $SnBu_4$ chemisorbed on the rhodium surface was quantified from the initial and the final concentration in the impregnating solution. For both starting monometallic Rh/SiO_2 catalysts, prepared by either impregnation or sol–gel, the nominal Sn/Rh atomic ratio was 0.5. After the two-step reaction, the samples were analyzed and gave ratios of 0.40 and 0.47, respectively, close to the expected value. The higher value obtained for the sol–gel sample may be attributed to the preparation procedure. In fact, in sol–gel catalysts, the metal component remains trapped in the porous structure of the support, being likely to exhibit a high interaction with the organometallic tin precursor during surface reaction. After reaction in hydrogen in the temperature range of 363–423 K, a partial hydrogenolysis reaction takes place leading to $Rh(SnBu_{4-x})_y$ species. Only after reduction up to 773 K is the hydrogenolysis completed, leading to bimetallic Rh-Sn catalysts. The obtained Sn/Rh atomic ratios are in agreement with Rh dispersion, being higher in the catalyst prepared by the sol–gel procedure, as expected considering that the total amount of tin deposit on the catalyst is closely related to the surface Rh atoms, according the reaction previously described.

Table 1 summarizes metal loadings, H/Rh ratios and metal particle sizes for the catalysts study. Hydrogen chemisorption experiments at 298 K were carried out to evaluate available reduced metal surface area. Previous experiments have shown that tin does not chemisorb H_2, therefore the H_2 uptake may be assigned only to chemisorption on Rh atoms. It was found that higher H/Rh values existed for the monometallic Rh/SiO_2 samples (close to 0.4) compared with the bimetallic $Rh/Sn/SiO_2$ catalysts (ca. 0.10). This feature may be assigned either to a partial coverage of rhodium particles with tin or to the formation of bimetallic Rh-Sn phases. Thus, tin atoms are diluting rhodium ensembles producing an inhibitory effect in their capability to chemisorb hydrogen, in line with the previous explanations that the drop in H/Rh ratios would not be associated with changes in metal dispersion. Similar behavior has been reported previously by Claus [39] for $Rh/Sn/SiO_2$ catalysts in which a significant drop in H_2 chemisorption ability were found as tin content increases.

TEM micrographs of $Rh\text{-}SiO_2$ catalysts show a narrow particle size distribution having an average

Table 1
Chemical analysis, H/Rh and rhodium particle size obtained from chemisorption and TEM data

Catalyst	Rh loading (wt.%)	Sn loading (wt.%)	(Sn/Rh) experimental	H-Rh	d, nm TEM
Rh(0.5)/SiO_2-SG	0.50	0	0	0.43	1.6
Rh(0.5)/SiO_2-I	0.50	0	0	0.40	1.7
Rh(1.0)/SiO_2-I	1.00	0	0	0.28	2.4
Rh(0.5)-Sn/SiO_2-OM-SG	0.50	0.27	0.47	–	–
Rh(0.5)-Sn/SiO_2-OM-I	0.50	0.23	0.40	–	–
Rh(0.5)-Sn/SiO_2-BM-SG	0.50	0.27	0.47	0.12	1.7
Rh(0.5)-Sn/SiO_2-BM-I	0.50	0.23	0.40	0.10	2.0
Rh(1.0)-Sn/SiO_2-BM-I	1.00	0.35	0.30	0.08	3.9

particle size close to 2.0 nm (1.6 and 2.4) for Rh(0.5) and Rh(1.0) respectively, (see Fig. 2).The electron diffraction of Rh-SiO_2 catalyst prepared by impregnation or sol–gel procedure showed both rings and spots, indicating the presence of a small quantity of small-sized crystal. Indexing this pattern, a good agreement with Rh^0 fcc was obtained. It should be mentioned that after rotating the sample and/or by changing the position of the beam, similar diffraction patterns were obtained, with the (1 1 1), (2 0 0) and (2 2 0) planes exhibiting a higher intensity. Additionally, the formation of hexagonal outlines, characteristic of most fcc metals including rhodium, suggests that the (1 1 1) plane is in contact with the support [40].

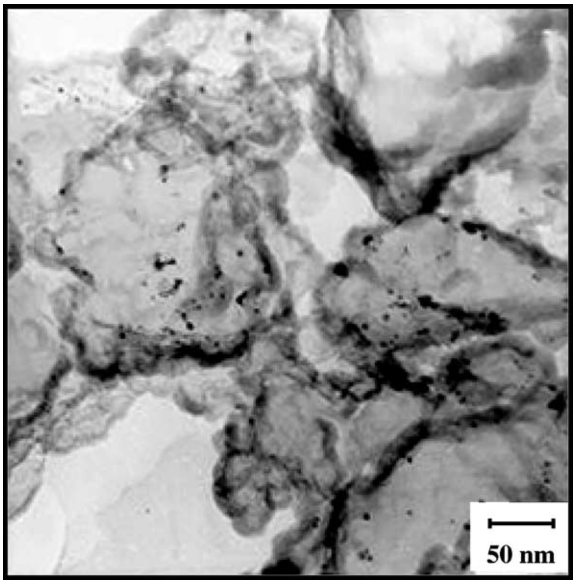
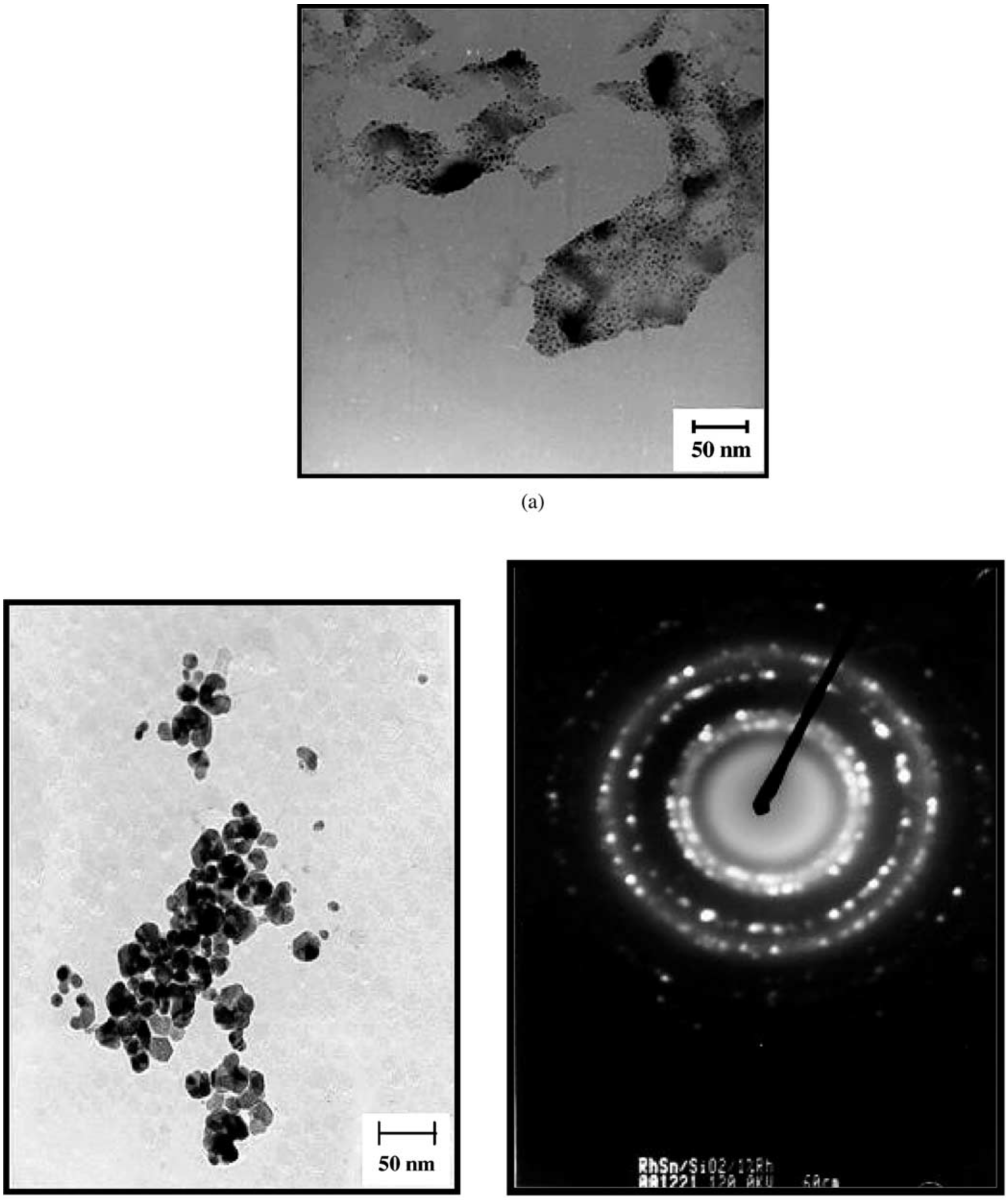


Fig. 2. TEM micrographs of Rh(1.0)/SiO_2/I catalyst.

With regard to the bimetallic Rh-Sn samples, it should be mentioned that a significant heterogeneity of particle size was observed. Thus, by analyzing different areas of a grid, it was possible to observe areas of homogeneity in particle size, others in which small metal particles (close to 2.0 nm) and larger particles (in the range of 4.0–15 nm) were present, and a third area which essentially showed large particles. This fact makes difficult an appropriate evaluation of an average particle size; nevertheless, in the quantification, the three areas already mentioned were considered. Metal particle size distributions show a significant proportion of particles of comparable size with their monometallic counterparts, and also others with higher particle size. Fig. 3a and b show two different areas of a Rh(1.0)/Sn/SiO_2 sample. Only a slight increase in the average particle size compared with the monometallic counterpart was detected in the Rh/Sn samples, in agreement with results previously reported by Agnelli et al. [40] for silica-supported Rh, Ru, and Ni catalysts and by Humblot et al. [34] for Pt-Sn catalysts. More significant changes in particle size are expected at higher Sn-Rh ratios. Eventhough it is not possible to define precisely the morphology of the metallic particles, it seems that most of them are roughly hexagonal or close to spherical particles. Similar findings were reported by Chojnacki et al. [41] for the Pt/Rh system and for RhSn/SiO_2 catalysts [42]. The observed difference in contrast may be associated with differences in composition in the metallic particles. As the contrast in TEM images is proportional to the differences in electronic densities, and in this system, the atomic number of the metals involved are similar, no difference in contrast should be expected in Sn, Rh or RhSn particles. The observed differences may be attributed to the



(a)

(b)

(c)

Fig. 3. (a) and (b) TEM micrographs and (c) Electron diffraction pattern of Rh(1.0)/Sn/SiO_2-I catalyst.

presence of reduced species of a metal and oxidised species of the other. Thus it is likely that the metallic or intermetallic phases covered by SnO_x species exist.

Fig. 3c shows an electron diffraction pattern of a Rh(1)/Sn/SiO_2 catalyst obtained by impregnation. Under the specified conditions, an area of approximately one square micron ($1\,\mu m^2$) was examined, therefore the diffraction corresponds to all the crystals included in the selected area, in this case, that of the higher metal particle size (Fig. 3b). Changes in the intensity of the diffraction lines were a characteristic of the bimetallic samples studied in this work, with those corresponding to higher d values being more intense and showing at lower *d* values both weak and strong lines. The diversity of phases may be indicative of the presence of intermetallic phases in the bimetallic samples. The presence of Rh^0, Sn^0, SnO_x, and bimetallic compounds $RhSn_2$ and Rh_3Sn_2 were analyzed. The analyses of the different electron diffraction patterns of the bimetallic sample, revealed the presence of lines attributed mainly to $RhSn_2$ and lines due to Rh^0 in which the main face remains. Tin oxide, as SnO_2 (cassiterite) and metallic tin, as α-Sn and/or β-Sn phases could not be unambiguously assigned due to overlapping with lines of the other components.

Fig. 4a and b shows the X-ray photoelectron spectra of the Rh 3d and Sn 3d core level, respectively of representative reduced catalysts. The BE of the Rh $3d_{5/2}$ peak at ca. 307.2 eV corresponding essentially to Rh^0 species is observed in the monometallic Rh/SiO_2 catalysts (sol–gel and impregnated). A slight shift was observed in the BE of the Rh $3d_{5/2}$ peak for the Rh-Sn catalysts suggesting a partial electron transfer from tin species. The Sn 3d profile for both $RhSn/SiO_2$ catalysts indicates the different species. In fact, curve fitting of the experimental spectra indicates both reduced tin species, Sn^0, (BE = 485.1 eV) and oxide species (ca. 488.0 eV). It is noted that discrimination between Sn^{2+} and Sn^{4+} species is extremely difficult, if not impossible, because the BE of the Sn $3d_{5/2}$ core-level is virtually the same for the two tin oxide species [43]. The proportion of reduced tin species is close to 50%, higher than those usually reported for Pt-Sn and Rh-Sn catalysts prepared by conventional impregnation methods [31]. These results were expected considering the strong interaction produced between the metal components during the surface reaction, as has been pointed out [33–36,44]. With regard to the Rh-Si atomic surface ratio, higher values are observed in the monometallic Rh/SiO_2 samples compared with the bimetallic Rh-Sn counterpart, in line with chemisorption results. The Sn-Rh surface atomic ratio in bimetallic samples is almost 10 times higher than the bulk ratios, indicating a surface enrichment in Sn in the metallic phase. These results are compiled in Table 2.

Crotonaldehyde hydrogenation was studied at 313 K and a H_2 pressure of 10 atm, and the obtained products were crotyl alcohol (CROH), butyraldehyde (BUHO) and butanol (BUOH). No formation of other byproducts was detected. The reaction was studied during a period in which a stable conversion level was reached. Fig. 5 shows the variation of the conversion level with time for the series prepared by SOMC on reduced silica-supported rhodium, prepared by the sol–gel method. Significant differences in conversion levels were found for the catalysts studied and activity increased in the sol–gel catalysts in the following order: Rh-Sn-OM < Rh-Sn-BM < Rh. The lower activity of the bimetallic samples may be attributed to the presence of tin atoms producing surface rhodium sites apparently isolated from their neighbors by tin atoms, thus changing drastically the hydrogenation capability.

Table 2
Binding energies (eV) of Rh $3d_{5/2}$ and Sn $3d_{5/2}$ core levels core levels and Rh-Si, Sn-Rh atomic surface ratios obtained from XPS

Catalyst	B.E. (eV)		$(Rh/Si)_s$	$(Sn/Rh)_s$
	Rh $3d_{5/2}$	Sn $3d_{5/2}$		
$Rh(0.5)/SiO_2$-SG	307.3	–	0.0014	–
$Rh(0.5)/SiO_2$-I	307.1	–	0.0019	–
$Rh(1.0)/SiO_2$-I	307.2	–	0.0023	–
$Rh(0.5)$-Sn/SiO_2-BM-SG	307.5	485.1(56) 487.9(44)	0.0013	3.92
$Rh(0.5)$-Sn/SiO_2-BM-I	307.5	485.0(53) 488.2(47)	0.0011	5.00
$Rh(1.0)$-Sn/SiO_2-BM-I	307.5	485.1(64) 488.1(36)	0.0021	3.05

The catalysts obtained from impregnation show similar trends, but have obvious differences in conversion levels. This feature emphasizes the importance of the experimental procedure to deposit the metal component, which has a strong influence on the catalytic behavior of the samples. Thus, Lopez et al. [45], have shown for Pt/SiO_2 catalysts that the interaction between metal precursor-support surface are stronger in the catalysts prepared by the sol–gel method compared with the impregnation ones. Studies by diffuse reflectance UV–VIS confirm that catalysts obtained by the former procedure exhibit two types of interaction: one strong, bulk interaction and another weaker on the surface. The stronger interaction exhibits a ligand exchange between the metal complex and the OH groups of the support. As a consequence of these interactions, the metal incorporates OH groups into its coordination sphere, and the metal symmetry is distorted. On the other hand, catalysts obtained by impregnation of the support lead only to the former species.

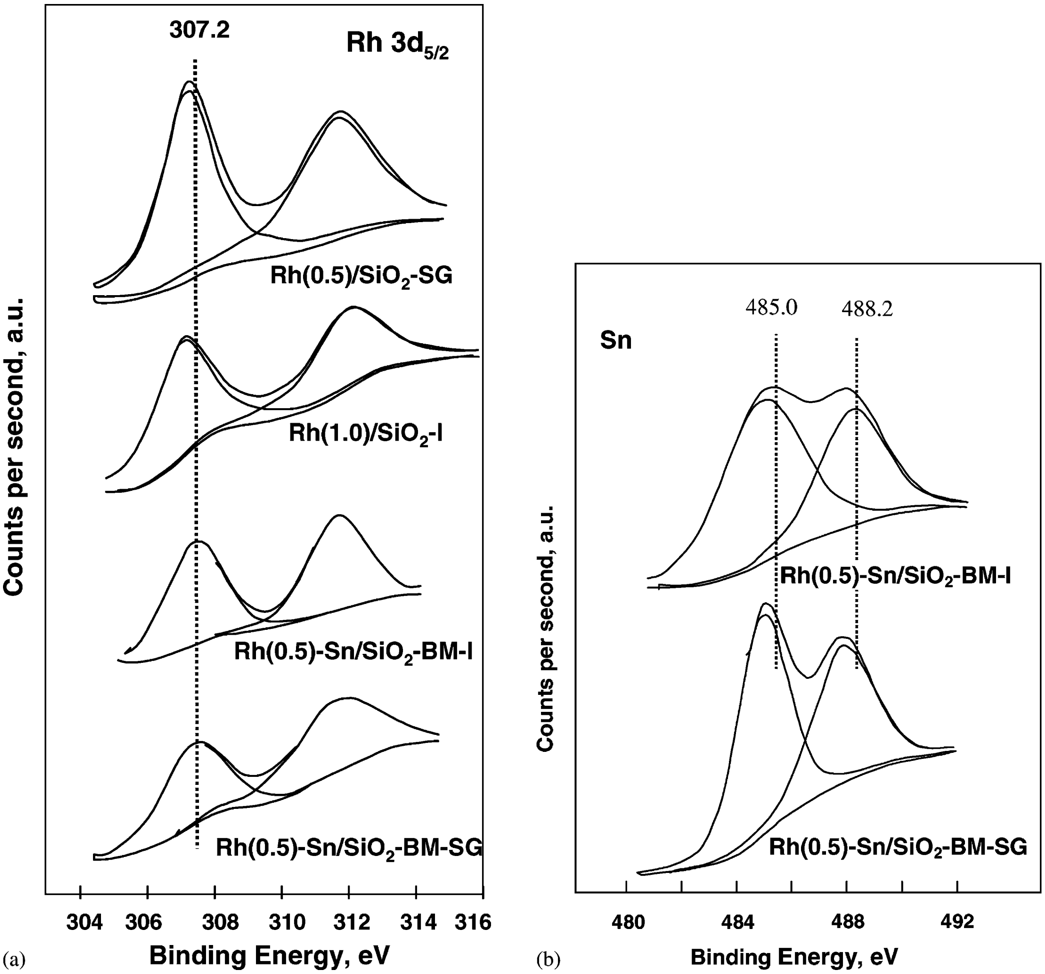


Fig. 4. XP spectra of reduced Rh/Sn/SiO$_2$/SG catalysts (a) Rh 3d and (b) Sn 3d core levels.

The series of catalysts with higher rhodium loading (1 wt.%) displays higher activities due to the larger amount of Rh surface atoms, therefore, these catalysts exhibit a larger hydrogenation activity.

Besides the differences observed in activity, important changes in selectivity were also detected in these catalysts. On Rh(0.5)/SiO$_2$ catalysts, the main product was butyraldehyde, with the other products below 9%. However, the Rh(1.0)/SiO$_2$ sample showed a drop in the selectivity to butyraldehyde and a significant increase in the selectivity to CROH. This fact may be assigned to a particle size effect, due to the later catalysts have a larger rhodium particle size compared with those of lower Rh loading. Similarly, an important enhancement in the selectivity to crotyl alcohol and butanol was detected in the Rh-Sn samples. The Rh-Sn-OM samples show selectivity to the unsaturated alcohol in the range of 10–16% whereas in the Rh-Sn-BM catalysts selectivities are close to 30%. The selectivity to the different products changes with the extent of conversion, however, these changes are not very significant for crotyl alcohol as it can be seen in Fig. 6 for the Rh(0.5)/Sn/SiO$_2$BM/SG catalyst. On the other hand, the selectivity to BUHO and BUOH exhibit different behavior. The former, decreases as conversion increases whereas the later increases with conversion. This trend is as expected, considering that BUOH is the completely saturated product and

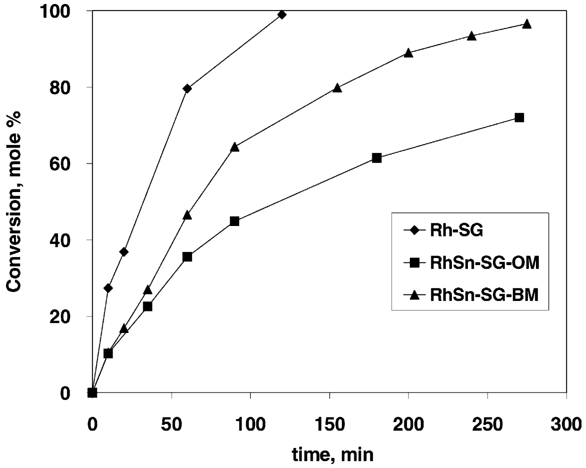


Fig. 5. Conversion vs. time for crotonaldehyde hydrogenation at 313 K and 10 atm on Rh(0.5)-Sn-SiO$_2$-SG catalyst.

Table 3

Initial turnover frequency and selectivity to reaction products in crotonaldehyde hydrogenation at 313 K on Rh/SiO$_2$ Rh/Sn/SiO$_2$ catalysts, at constant conversion level (30%)

Catalyst	TOF (s^{-1})	Selectivity (%)		
		BUHO	BUOH	CROH
Rh(0.5)/SiO$_2$-SG	0.15	97.0	1.8	1.2
Rh(0.5)/SiO$_2$-I	0.08	91.3	6.4	2.3
Rh(1.0)/SiO$_2$-I	0.10	72.5	12.5	15
Rh(0.5)-Sn/SiO$_2$-OM-SG	–	78.0	6.4	15.6
Rh(0.5)-Sn/SiO$_2$-OM-I	–	76.5	12.5	11.0
Rh(0.5)-Sn/SiO$_2$-BM-SG	0.28	47.4	19.1	33.5
Rh(0.5)-Sn/SiO$_2$-BM-I	0.34	53.2	13.6	27.4
1 Rh(1.0)-Sn/SiO$_2$-BM-I	0.21	49.0	21.0	30.0

its formation is favored at higher time on stream and higher conversion. Nevertheless, it is worthwhile to compare both, the activity and the selectivity to the different product levels, as given in Table 3. It shows the initial turnover frequency (TOF), expressed as the number of molecules converted per second per surface rhodium atom, obtained from the plot conversion versus time plots, extrapolated to $t = 0$ over the first 30 min on stream. It can be seen a significant enhancement in the activity per site in the bimetallic catalysts. These results clearly indicate that upon the addition of the organometallic tin compound new and more appropriate sites are developed.

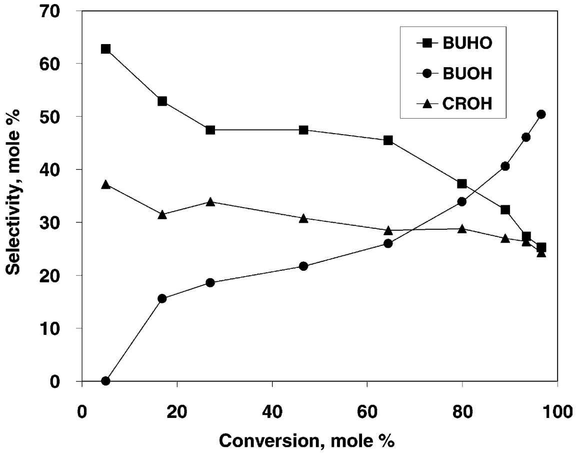


Fig. 6. Product distribution vs. conversion for crotonaldehyde hydrogenation at 313 K and 10 atm on Rh(0.5)-Sn-SiO$_2$-SG catalyst.

In the Rh-Sn-OM samples, the presence of butyl groups contributes to a significant increase in the selectivity to CROH due to both electronic and steric effects: electronic due to that in the active site, the Sn atoms are bonded to two butyl groups and to a Rh atom and additionally, part of Sn is also in the metallic state (as detected by XPS). It is likely that this later increases the electronic density of Rh as it was proposed for Pt-Sn catalysts [36]; and steric due to fragments of butyl groups that make easier the adsorption of crotonaldehyde through the C=O bond. In the Rh-Sn-BM catalysts, the presence of ionic tin and intermetallic Rh-Sn compounds lead to a significant enhancement in the selectivity to CROH. This behavior may be explained considering mainly the electronic effect: the difference in electronegativity in rhodium and tin in the metallic phase contributes strongly to polarize the carbonyl group and therefore favors the formation of the allylic alcohol.

Claus [39] studying Rh-Sn catalysts prepared via SMOC on a commercial silica aerosil, has reported much higher selectivity to CROH, close to 70% in crotonaldehyde hydrogenation. However, in that work the experimental conditions were different: the reaction was carried out in gas phase, rhodium loading was four times higher and different Sn loadings were used. Therefore, the catalysts posses different metal particle size, surface composition and consequently different catalytic behavior should be expected. It is well known [8] that higher metal particle size, which may be obtained with this preparation procedure at higher metal loading, induces an increase in the selectivity to CROH.

4. Conclusions

The activity and selectivity of Rh-supported catalyst were strongly modified by tin incorporation by a surface organometallic reaction between tetra-*n*-butyl tin and reduced Rh/SiO_2 catalysts. Depending on the pretreatment temperature in H_2, catalysts having fragments of organometallic tin bonded to the metallic phase, Rh-Sn-OM or only the metallic components, Rh-Sn-BM, were obtained. Surface characterization by H_2 chemisorption and XPS revealed a tin enrichment on the surface of the metallic phase and electron diffraction confirmed the presence of Rh^0, $RhSn_2$, and SnO_2 in the BM samples. XPS indicates that in the BM samples the proportion of oxide tin species is close to 45%. The presence of these new species modifies the nature of the active sites through electronic and steric effects, thus contributing to an increase in the selectivity to crotyl alcohol.

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