

Preparation of Highly Dispersed Ru-Sn Bimetallic Supported Catalysts from the Single Source Precursors $\text{Cp}(\text{PPh}_3)_2\text{Ru-SnX}_3$ ($\text{X} = \text{Cl}$ or Br)

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In this work highly dispersed Ru-Sn bimetallic catalysts have been prepared from organobimetallic $\text{Cp}(\text{PPh}_3)_2\text{Ru-SnX}_3$ ($\text{X} = \text{Cl}$ or Br) complexes. These single source precursors can be easily impregnated in high surface area supports, such as activated carbon and sol-gel SiO_2 , and upon controlled thermal treatment the ligands are released as volatile products resulting in the formation of the bimetallic system Ru-Sn. Catalytic reactions, such as hydrodechlorination of CCl_4 and chlorobenzene and TPR (Temperature Programmed Reduction) experiments carried out with these RuSn catalysts suggested a strong interaction between Ruthenium and Tin. Mössbauer measurements showed that these materials when exposed to air are immediately oxidized to form Sn (IV). It was shown that upon controlled reduction conditions with H_2 it is possible to reduce selectively Sn to different oxidation states and different phases. The Sn oxidation state showed significant effect on the catalytic hydrogenation of 1,5-cyclooctadiene. The use of these single source precursors with a controlled decomposition/reduction procedure allows the preparation of unique catalysts with an intimate interaction between the components ruthenium and tin and the possibility of varying the Sn oxidation state around the Ru metal.

Keywords: bimetallic catalyst, ruthenium, tin, hydrogenation

1. Introduction

Bimetallic catalysts have been used in industrial process for many years due to their unique catalytic properties¹. However, only recently an understanding of the structure dependence on the preparation method and treatment has been developed²⁻⁵. An important application of bimetallic catalysts, which has been extensively investigated in the last years is the selective hydrogenation of C=O group in α,β -unsaturated aldehydes, such as crotonaldehyde, acrylaldehyde and citral⁶. These reactions should produce the respective unsaturated alcohols which are fine chemicals of great importance to the cosmetic and pharmaceutical industry^{7,8}. These catalysts are generally based on a noble metal, e.g. Pt, Rh or Ru, which catalyzes the reaction, and a second metal usually Sn, Fe, Pb, Ni, Co or Ge which is mainly responsible for the selectivity in the hydrogenation⁹⁻¹⁶. Among these promoters, Sn has shown the best re-

sults in selectivity for the carbonyl hydrogenation, what has been explained in terms of a strong interaction between the C=O group with the tin oxide¹⁵. Therefore, two factors are essential to produce an active and selective catalyst: (i) the proximity of Sn to the noble metal and (ii) the Sn oxidation state. The bimetallic system Ru and Sn has been pointed out recently as one of the most active and selective catalyst for these hydrogenation¹⁷. These catalysts have been prepared by the co-impregnation of two different ruthenium and tin precursors, typically RuCl_3 and SnCl_4 . However, the co-impregnation method produces mostly the segregation of the metals resulting in a poor interaction of Ru and Sn.

In this work, Ru-Sn catalysts have been prepared from a single source precursor containing both metals $\text{Cp}(\text{PPh}_3)_2\text{Ru-SnX}_3$ ($\text{X} = \text{Cl}$ or Br). The Ru-Sn chemical bond in the precursor should result in a close proximity of the two metals throughout the catalyst preparation steps lead-

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ing to a much better interaction compared to materials prepared by the traditional co-impregnation method.

2. Experimental

The preparation of the bimetallic complexes $\text{Cp}(\text{PPh}_3)_2\text{Ru-SnX}_3$ ($\text{X} = \text{Cl}$ or Br) is described in detail elsewhere¹⁸.

The Ru-Sn supported catalysts have been prepared by impregnation on activated carbon (100 mg, Aldrich Norit, $S_{\text{BET}} = 950 \text{ m}^2/\text{g}$) with a dichloromethane solution (100 mg in 2 ml) of the complexes $\text{Cp}(\text{PPh}_3)_2\text{Ru-SnX}_3$ ($\text{X} = \text{Cl}$ or Br). The CH_2Cl_2 was removed by vacuum at room temperature. The amount of the precursor was adjusted in order to produce a metallic content in the catalysts of 5 wt% ruthenium and 6 wt% of tin. The material was heated at $10 \text{ }^\circ\text{C}/\text{min}$ under hydrogen flow (15 ml/min) and kept at $500 \text{ }^\circ\text{C}$ for 60 min.

Ru-Sn/SiO₂ catalysts have been prepared by mixing TEOS (tetraethoxysilane), ethanol and water in a 1/3/10 molar ratio, with HCl and HF as catalysts. $\text{Cp}(\text{PPh}_3)_2\text{Ru-SnCl}_3$ (1 mol%) was added to the starting solution during preparation. The solution was kept under stirring at room temperature for two hours for homogenization and left still for gelation. The wet gels, prepared in monolithic shape, were dried at $110 \text{ }^\circ\text{C}$ for 24 h.

Some of the catalyst after reduction were embedded with liquid benzene, before they were exposed to the atmosphere, in order to hinder metal oxidation by air.

Thermogravimetric analyses were carried out in a Mettler TA 4000. The samples were heated from room temperature to $750 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C}/\text{min}$ under air or nitrogen flow. Scanning electron microscopy analyses were obtained in a Jeol JXA-8900RL.

Mössbauer analyses were obtained at 23 K in a transmission geometry equipment with a ¹¹⁹Sn source in CaSnO_3 . A least squares fitting program was used to analyze the spectra and to calculate the chemical shifts, quadrupole splitting and area of each component.

The TPR analyses were carried out in a Micromeritics TPR/TPD 2900 equipment. The samples were heated from room temperature to $800 \text{ }^\circ\text{C}$ under 50 ml/min H_2/N_2 (10% v/v H_2) flow. The samples were pre-treated from room temperature to $500 \text{ }^\circ\text{C}$ ($10 \text{ }^\circ\text{C}/\text{min}$) under He flow.

The hydrogendechlorination reactions have been carried in a fix bed reactor using 30 mg of Ru-Sn catalysts under H_2 flow (30 ml/min). CCl_4 or chlorobenzene were introduced in the H_2 stream by a controlled temperature saturator at $0 \text{ }^\circ\text{C}$, producing vapor pressures of 29 mmHg and concentration of $30 \text{ } \mu\text{mol}/\text{l}$ for CCl_4 and 2.5 mmHg and concentration of $3 \text{ } \mu\text{mol}/\text{l}$ for chlorobenzene. The diolefin hydrogenation reactions were carried in an autoclave using 40 mg of supported Ru-Sn catalysts and 40 ml of

1,5-ciclooctadiene (COD)/benzene solution (0,4 mol/l), under hydrogen pressure (20 atm). The reaction products were analyzed by gas chromatography (Shimadzu/GC 17 A) with a FID detector and capillary column Carbowax 20M ($25 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ } \mu\text{m}$).

3. Results and Discussion

3.1 Thermal Decomposition of the Complexes

The thermogravimetric (TG) profiles of the precursor $\text{RuCp}(\text{PPh}_3)_2\text{SnCl}_3$, pure and supported on activated carbon, in a nitrogen atmosphere, are shown in Fig. 1.

It can be observed a weight loss of ca. 74%, in the temperature range $250\text{-}650 \text{ }^\circ\text{C}$. This weight loss suggests the decomposition of the complex with the formation of the pure metals and elimination of the ligands as volatile products:



Similar results were obtained for the $\text{RuCp}(\text{PPh}_3)_2\text{SnBr}_3$ complex with a weight loss of 76% in the same temperature range.

The expected weight losses for the decomposition described in Eq. 1 are 76 and 79% for the Cl and Br derivatives, respectively, which are very similar to the experimental value of 74 and 76%.

TG profiles were also obtained for the organometallic precursors supported on activated carbon (Fig. 1). It was observed an initial weight decrease probably related to the presence of residual water and CH_2Cl_2 adsorbed on the carbon. From 250 up to $450 \text{ }^\circ\text{C}$, the complex supported on the carbon surface seems to decompose with the expected weight loss of approximately 22%.

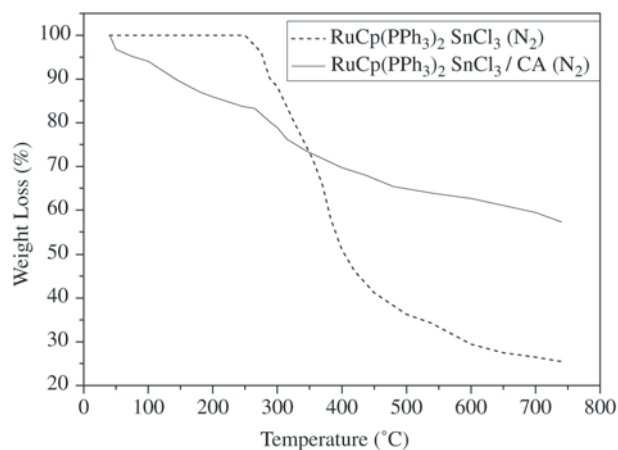


Figure 1. Thermogravimetric analyses of the precursor $\text{RuCp}(\text{PPh}_3)_2\text{SnCl}_3$ pure and supported on activated carbon.

3.2 Activated Carbon Supported RuSn Catalysts

The activated carbon supported catalysts have been obtained by impregnation methods resulting in a final ruthenium and tin content of 5 and 6 wt%, respectively. The following materials have been prepared: (i) Ru/AC, impregnation of RuCl₃ followed by reduction in H₂ at 500 °C, (ii) coimp-Ru+Sn/AC, prepared by co-impregnation of RuCl₃ and SnCl₂ followed by reduction in H₂ at 500 °C, and (iii) RuSn/AC prepared by the impregnation of the complex RuCp(PPh₃)₂SnX₃ followed by reduction in H₂ at 500 °C. For comparison, SnCl₂ was also impregnated on activated carbon and treated in H₂ at 500 °C (Sn/AC). An advantage the precursors RuCp(PPh₃)₂SnX₃ should offer over RuCl₃ and SnCl₃, is related to their hydrophobic character which will allow a much better interaction with the hydrophobic carbon support and consequently a better dispersion over the carbon surface.

3.3 SiO₂ sol-gel Supported RuSn Catalysts

The SiO₂ sol-gel supported catalysts have been obtained by dispersion of the different precursors during the sol-gel preparation, to obtain ruthenium and tin content of 1 and 1.2 wt%, respectively. The following materials have been prepared: (i) Ru/SiO₂, addition of RuCl₃ during the sol-gel preparation followed by reduction in H₂ at 500 °C, (ii) coadd-Ru+Sn/SiO₂, prepared by co-addition of RuCl₃ and SnCl₂ followed by reduction in H₂ at 500 °C, and (iii) RuSn/SiO₂ prepared by the addition of the complex RuCp(PPh₃)₂SnCl₃ followed by reduction in H₂ at 500 °C. For comparison,

SnCl₂ was also added during sol-gel preparation and treated in H₂ at 500 °C (Sn/SiO₂).

3.4 ¹¹⁹Sn Mössbauer Spectroscopic Studies

The Mössbauer data obtained for the activated carbon supported RuSn catalysts are shown in Table 1 and Fig. 2. The RuSn/AC sample was treated with H₂ at 500 °C and after cooling to room temperature it was exposed to air. Mössbauer analysis of this sample showed that Sn is completely oxidized to form Sn(IV). Similar results have been obtained by Stievano *et al.*¹⁹ who carefully treated carbon supported Ru 70% Sn 30% with H₂ at 400 °C and also observed the tin oxidation after exposure to air or moisture. The Mössbauer spectrum fitting suggests the presence of two different species with isomer shift (IS) of - 0.12 and 0.50 mm/s and quadrupole splitting (QS) of 0.48 and 0.4 mm/s, respectively, both related to Sn(IV). If the sample RuSn/AC treated with H₂ at 500 °C is protected with liquid benzene to hinder the oxidation by air, the spectrum can be fit with 4 Lorentzians indicating the presence of mainly Sn(II) and Sn(IV) with small amounts of Sn(0). These oxidized species are probably produced by the oxidation by traces of water in benzene and also to some oxygen diffusion through the liquid protection.

For the sample reduced at 900 °C it can be observed the presence of mainly Sn(IV) 54% and Sn(0) 16%. However, the Mössbauer spectrum seems to suggest the presence of three new phases: oxidic Ru-Sn, Ru₃Sn₁₅O₁₄ and Ru₃Sn₇. The oxidic Ru-Sn and Ru₃Sn₁₅O₁₄ prepared by Söhel *et al.*²⁰ under similar experimental conditions (900 °C) and have

Table 1. ¹¹⁹Sn Mössbauer parameters obtained at 23 K for the carbon supported RuSn catalysts submitted to different treatments.

Sample	δ (mm/s) (± 0.05)	Δ (mm/s) (± 0.05)	Area (± 2%)	Species/phases
RuSn/AC treated at 500 °C/H ₂ and exposed to air at room temperature	-0.12	0.48	70	Sn (IV)
	0.50	0.40	30	Sn (IV)
RuSn/AC treated at 500 °C with H ₂ and not exposed to air	-0.02	0.77	30	Sn(IV)
	0.51	0.40	9	Sn(IV)
	3.16	1.82	55	Sn(II)
	2.50	-	6	Sn(0)
RuSn/AC treated at 900 °C with H ₂ and not exposed to air	0.25	0.69	54	Sn(IV)
	1.90	2.04	12	Oxidic Ru-Sn
	2.45	-	16	Sn(0)
	1.40	-	09	Ru ₃ Sn ₇
	0.7	2.46	09	Sn(IV)
Ru+Sn/AC, co-impregnated, treated at 500 °C/H ₂ and exposed to air at room temperature	0.07	0.55	45	Sn(IV)
	1.88	1.99	22	Sn(II)
	2.45	-	4	Sn(0)
	1.40	-	12	Ru ₃ Sn ₇
	0.7	2.46	15	Ru ₃ Sn ₁₅ O ₁₄

been described as RuSn alloys containing some oxygen into their structure. The formation of the Ru_3Sn_7 alloy has been reported previously^{19,21} in RuSn catalysts. These results suggested that the treatment at higher temperatures (900 °C) favors the formation of alloys containing Ru and Sn.

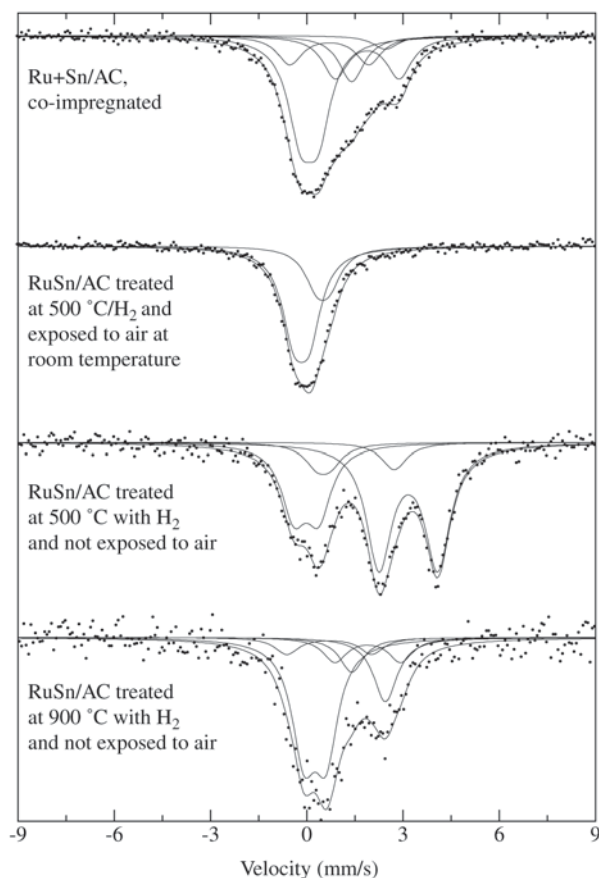


Figure 2. ^{119}Sn Mössbauer spectra obtained at 23 K for the carbon supported RuSn catalysts submitted to different treatments.

The activated carbon catalyst obtained by co-impregnation, coimp-Ru+Sn/AC, after treatment at 500 °C with H_2 and exposed to air at RT, showed the presence of the fully oxidized Sn(IV) (45%) and the reduced Sn(0) (4%). The Mössbauer fitting also suggests the presence of the phases $\text{Ru}_3\text{Sn}_{15}\text{O}_{14}$ 15% and Ru_3Sn_7 12% and a Sn(II) species. The formation of these Sn rich phases, i.e. $\text{Ru}_3\text{Sn}_{15}\text{O}_{14}$ and Ru_3Sn_7 , in the co-impregnated catalyst treated at temperature as low as 500 °C, might suggest that the impregnation method was not efficient in dispersing the tin throughout the carbon surface. This poor dispersion would originate Sn enriched regions which would favor the formation of the Sn rich phases observed.

It is interesting to note the different behavior of the RuSn/AC catalysts where Sn is completely oxidized whereas for the coimp-Ru+Sn/AC the Sn is only partially oxidized after reduction and exposure to air.

Mössbauer analyses have also been carried out for the RuSn catalysts supported on SiO_2 sol-gel matrix. The results are displayed in Table 2 and Fig. 3.

It can be observed similar spectra for both samples, RuSn/ SiO_2 and coadd-Ru+Sn/ SiO_2 , with the presence of Sn(IV), Sn(II) and Sn(0) species. On the other hand, the material RuSn/ SiO_2 showed a major contribution of Sn(II) species whereas coadd-Ru+Sn/ SiO_2 produced mainly Sn(IV).

3.5 Temperature Programmed Reduction (TPR) Studies

The TPR profiles for the activated carbon supported catalysts were obtained after reduction with H_2 at 500 °C and exposure to air at room temperature to reoxidize the metals. Figure 4 shows the TPR profiles obtained for coimp-Ru+Sn/AC, RuSn/AC and Sn/AC.

It can be observed for Sn/AC two peaks at the temperature 270 and 350-400 °C. According to the literature the first peak is probably related to the reduction of $\text{Sn}^{4+} \rightarrow \text{Sn}^{+2}$ which typically takes place in the temperature range

Table 2. ^{119}Sn Mössbauer parameters obtained at 23 K for the sol-gel SiO_2 supported RuSn catalysts submitted to different treatments.

Sample	δ (mm/s) (± 0.05)	Δ (mm/s) (± 0.05)	Area ($\pm 2\%$)	Species
RuSn/ SiO_2 treated at 500 °C/ H_2 and exposed to air at room temperature	-0.06	0.62	31	Sn(IV)
	0.33	0.80	10	Sn(IV)
	2.98	2.00	56	Sn(II)
	2.45	-	4	Sn(0)
Coadd-Ru+Sn/ SiO_2 treated at 500 °C/ H_2 and exposed to air at room temperature	-0.06	0.62	47	Sn(IV)
	0.33	0.80	24	Sn(IV)
	2.96	2.10	21	Sn(II)
	2.45	-	8	Sn(0)

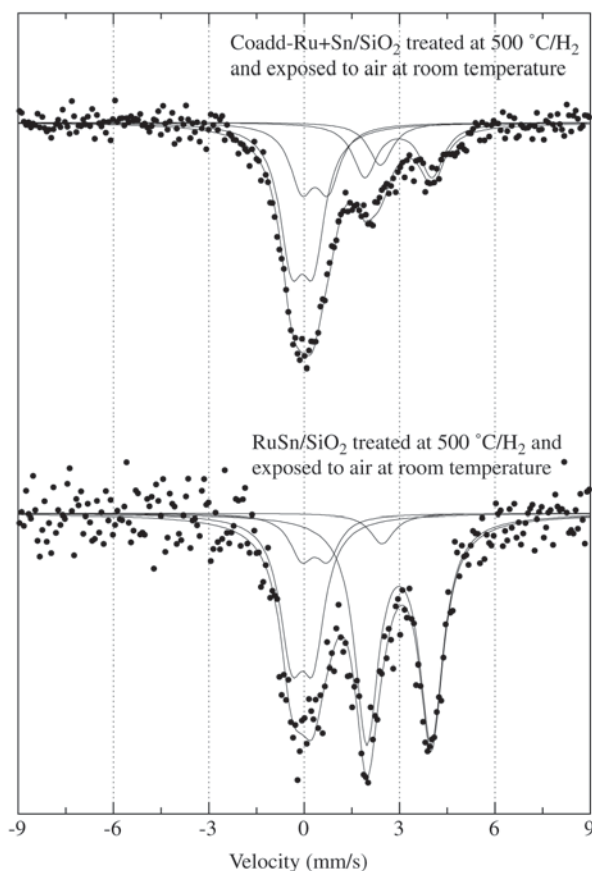


Figure 3. ^{119}Sn Mössbauer spectra obtained at 23 K for the sol-gel SiO_2 supported RuSn catalysts submitted to different treatments.

200-300 °C, whereas the second peak might be related to the reduction $\text{Sn}^{+2} \rightarrow \text{Sn}^0$.²²

The co-imp-Ru+Sn/AC catalyst showed a broad peak centered at 160 °C related to the reduction of ruthenium Ru^{+4} or $\text{Ru}^{+3} \rightarrow \text{Ru}^0$.²³ It can also be observed peaks for the reduction of Sn species similar to those observed for the Sn/AC sample, indicating that most of the Sn species present in the co-imp-Ru+Sn/AC catalyst are similar to those formed in the Sn pure sample Sn/AC. On the other hand, the TPR profile for the RuSn/AC showed significant differences. The Ru reduction peak is shifted to lower temperatures, 130 °C, whereas the reduction of Sn seems to occur in a broad peak in the temperature range 250-350 °C. Although the detailed explanation for these differences is not clear, they suggest that Ru and Sn species formed from the precursor $\text{Cp}(\text{PPh}_3)_2\text{Ru-SnX}_3$ are significantly different from those obtained by the impregnation methods with RuCl_3 and SnCl_2 . These TPR differences could be produced by a dif-

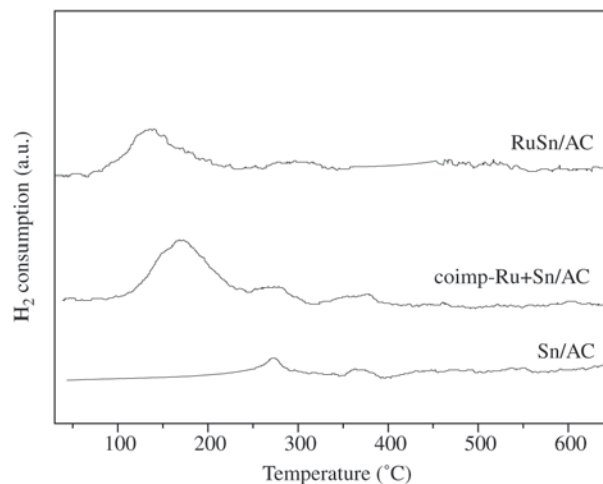


Figure 4. The TPR profiles for the catalysts Sn/AC, co-imp-Ru+Sn/AC and RuSn/AC.

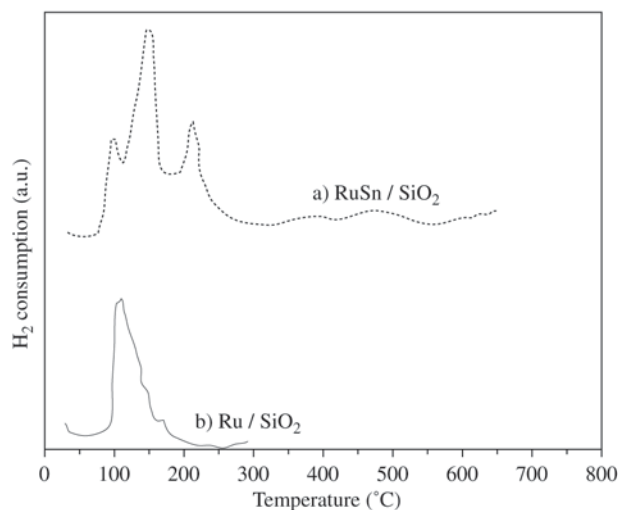


Figure 5. TPR profiles for the catalysts Ru/SiO₂ and RuSn/SiO₂ pretreated in air at 500 °C.

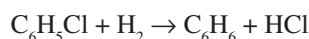
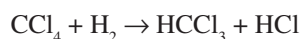
ferent dispersion or by a chemical interaction of the phases present on the surface of the activated carbon.

For the reduction experiments of the sol-gel SiO_2 supported catalysts (Fig. 5), all the samples were pre-treated in O_2 (air) flow at 600 °C for 30 min. TPR experiments with the sample Ru/SiO₂ showed only one intense peak at ca. 110 °C, related to the reduction of Ru^{+4} dispersed in the sol-gel matrix. On the other hand, it can be observed in the TPR profile of the catalyst RuSn/SiO₂ three well defined reduction peaks at 100, 150 and 210 °C and two broad peaks

centered at 380 and 480 °C. The peak at 100 °C is similar to that observed in the sample Ru/SiO₂. The intense peak at 150 °C, is related to a less reactive ruthenium species, which can be reduced only at higher temperatures. This species is only observed when the organometallic complex is used as precursor. As discussed above the broad peaks at 380 and 480 °C are likely related to the reduction of Sn species dispersed in the matrix²⁴. However, their peak areas are too small to account for the reduction of all tin present in the sample. Therefore, the peak at 210 °C is probably also related to the reduction of tin. These two shifted peaks at 150 °C (related to the reduction of Ru species) and at 210 °C (related to the reduction of Sn species) suggest a strong interaction of the Ru and Sn species. The increase in the ruthenium reduction temperature can be caused by the close proximity of the tin oxide. On the other hand, the significant decrease in the reduction temperature of the Sn species should occur via a spillover effect,²⁵ where the Ru⁰ metal activates H₂ and transfer to the surrounding Sn oxides species.

3.6 Catalytic Reactions

The catalytic activity of the activated carbon supported materials were investigated for the following hydrodechlorination reactions:



The activities presented by the different catalysts at 200 °C are shown in Fig. 6.

It can be observed that Ru/AC and Ru+Sn/AC show very

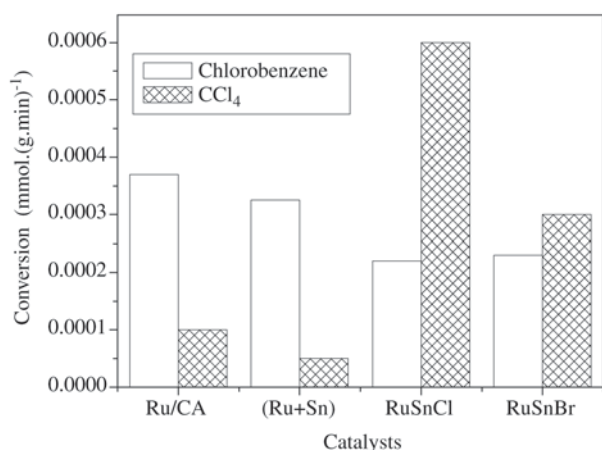


Figure 6. Hydrodechlorination of CCl₄ (at 200 °C) and chlorobenzene (at 300 °C) in the presence of different RuSn catalysts.

similar results with low CCl₄ conversions of approximately 0.1 μmol/g_{cat}.min. These results reinforces that in the catalyst prepared by co-impregnation Ru+Sn/AC the Ru is not interacting significantly with the Sn species, since it showed similar performance when compared to the pure Ru/AC catalyst. On the other hand, the catalysts RuSn/AC obtained from the organometallic precursors shows a much stronger effect of tin resulting in an activity of 0.3-0.6 μmol/g_{cat}.min, indicating a promoting effect of this metal. The results obtained for the hydrodechlorination of chlorobenzene also suggest a significant effect of tin on the catalytic activity of the catalysts RuSn/AC, but with a negative effect on the conversion.

3.7 The Effect of the Sn Oxidation State on the Catalytic Activity

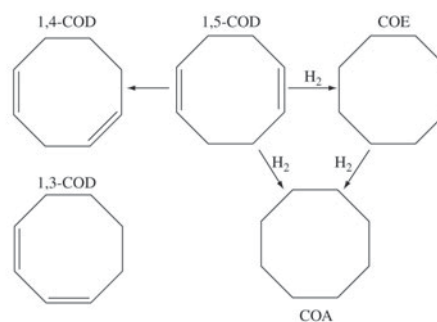
To investigate the effect of the Sn oxidation state on the catalytic properties of the catalyst it was studied the hydrogenation 1,5-cyclooctadiene in the presence of the catalyst RuSn/AC submitted to two different treatments:

- after thermal treatment the catalyst was exposed to air leading to the complete oxidation of tin to Sn(IV) as shown by the Mössbauer spectrum and treated with H₂ at 200 °C in order to reduce only the ruthenium to Ru⁰. This catalyst was named Ru⁰/Sn(IV)/AC;
- after thermal treatment, the catalyst was reduced with H₂ at 500 °C and not exposed to air. As suggested by Mössbauer experiments, this catalyst contains mainly Sn(II) with some Sn(0) and Sn(IV). This catalyst was named Ru⁰/Sn(II/IV)/AC.

The results are displayed in Fig. 7a and 7b.

The 1,5-COD hydrogenation affords mainly two products: the selective hydrogenation compound cyclooctene (COE) and the total hydrogenation molecule cyclooctane (COA) (Scheme 1).

Very small amounts of the isomerization products 1,3-COD and 1,4-COD were also detected (yields < 1%).



Scheme 1. 1,5-COD reactions.

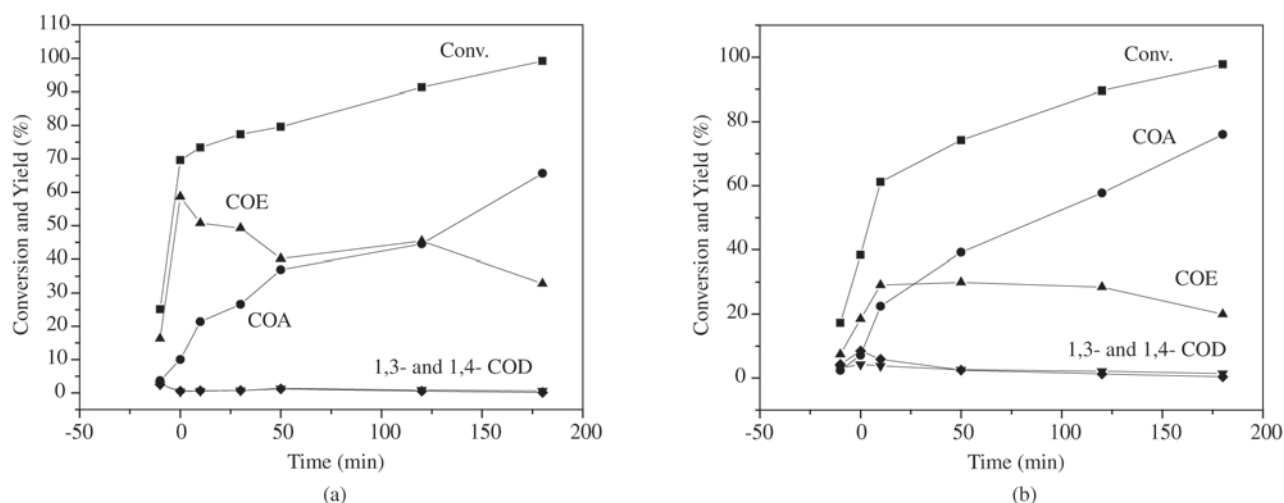


Figure 7. Catalytic hydrogenation of 1,5-cyclooctadiene in the presence of (a) catalyst RuSn/AC exposed to air and reduced with H₂ at 200 °C; (b) catalyst RuSn/AC treated at 500 °C with H₂ not exposed to air (the conversion and product formation at 0 min takes place within the time taken to reach the reaction temperature, 80 °C).

From Fig. 7a and 7b it can be observed similar conversions for both catalysts Ru⁰/Sn(IV)/AC and Ru⁰/Sn(II/IV)/AC. However, it is interesting to note that these catalysts showed significantly different product distribution during the reaction. Ru⁰/Sn(IV)/AC showed much better selectivity for the production of COE, with *ca.* 60% yield in the beginning of the reaction. For longer reaction times this yield will decrease due to hydrogenation of the COE to COA. On the other hand, the catalyst Ru⁰/Sn(II)/AC produces mainly the total hydrogenation compound COA.

These results show that the oxidation state of tin does not affect the catalyst activity but it has a significant effect on the product selectivity. The effects of Sn species around the Ru metal catalytic center are likely related to electronic and steric effects⁷.

4. Conclusion

Supported RuSn bimetallic catalysts can be prepared by impregnation and thermal decomposition of the organometallic precursors Cp(PPh₃)₂Ru-SnX₃ (X = Cl or Br). Catalysts prepared by these precursors and by the co-impregnation method showed significantly different properties, as revealed by the catalytic hydrogenodechlorination of CCl₄ and chlorobenzene, TPR experiments and Mössbauer spectroscopy. These differences could be related to a better metal dispersion and a stronger interaction of ruthenium with tin. The interaction Ru-Sn in the prepared catalysts is favored by the chemical bond Ru-Sn existent in the organometallic precursor which will keep the two metals in a close proximity throughout the catalyst preparation. With these

catalysts it is also possible to have some control of the Sn oxidation state which showed a significant effect on the catalytic hydrogenation of 1,5-cyclooctadiene.

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