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Catalysis Today 107–108 (2005) 250–257

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Performance of RuSn catalysts supported on different oxides in the selective hydrogenation of dimethyl adipate

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Abstract

Dimethyl adipate was chosen to probe the behaviour of RuSn catalysts supported on different oxides, namely alumina, silica, ceria, niobia and titania on selective hydrogenation. The bimetallic catalysts were prepared by co-impregnation and characterised by Mössbauer spectroscopy. The reaction was carried out in a liquid phase semi-batch reactor at 255 °C and a hydrogen pressure of 50 bar. The addition of tin promoted the formation of 1,6-hexanediol on all Ru–Sn-based systems, confirming the catalysts surface modification. Amongst the studied catalysts, the RuSn/TiO_2 was the most promising. The Mössbauer data allowed the conclusion that the oxidation state of tin as well as the tin–ruthenium and tin–support interactions are indeed rather different according to the support. The tin–support interaction appears to be more relevant with alumina; on titania, the metal–metal interaction seems to be favoured instead. The ionic tin forms, whether Sn^{4+} or Sn^{2+}, were credited for conducting the reaction to the formation of diol. It is suggested that the structure of the RuSn sites created over these catalysts acts differently on the dimethyl adipate activation when compared to the selective hydrogenation of aldehydes, ketones or fatty acids.

Keywords: Dimethyl adipate; 1,6-Hexanediol; RuSn; Titania; Alumina; Metal–support interaction

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1. Introduction

Alcohols synthesis from renewable raw materials has been motivating the research in the field of heterogeneous catalysis. They can be obtained through hydrogenation of α,β-unsaturated aldehydes or ketones [1–5], carboxylic acids, fatty acids/esters [6–15] and dicarboxylic acids and their esters [6,16–21]. In particular, production of diols from hydrogenation of dicarboxylic acids or their esters is one of the most attractive processes since they are valuable industrial intermediates for a wide variety of fine chemicals, pharmaceuticals compounds and biodegradable polymers.

Diols can be produced over the conventional copper chromite-based catalysts; however, extremely high hydrogen pressures (around 200–300 bar) are required to operate at temperatures around 150–250 °C [6]. Manufacturing processes under mild reaction conditions would demand the development of more active catalysts. Furthermore, the complexity of the reaction should also be considered as a wide range of other intermediate products can be formed, especially lactones, cyclic ethers, hydrocarbons and alcohols.

It has been reported that monometallic catalysts based on noble metals are not suitable for obtaining diols [16–21]. Nevertheless, it is well-known that such catalysts can alter their properties by introducing a second metal [16–21]. Our group has previously reported a systematic study concerning the use of different noble metals and some potential promoters on the hydrogenation of dimethyl adipate. The results indicated that some alternative catalysts based on noble

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doi:10.1016/j.cattod.2005.07.076

metal can be applied to synthesise diols at relatively low hydrogen pressures [20]. Ruthenium appeared as a promising active phase when modified by a second metal, especially tin.

Indeed, Ru–Sn systems have been successfully used to reduce the carbonyl group of fatty acids [11,12]. The widely accepted model used to explain such outstanding results is based on the activation of the C=O bond by tin ionic species through their interaction with the oxygen atom in the carbonyl group. Therefore, the oxidation state of tin is crucial for the catalyst chemoselectivity in such hydrogenation reactions. One should thus bear in mind that the formation and distribution of the required Sn^{n+} species are affected by the catalyst preparation procedure. It has been recently showed [21] that $RuSn/Al_2O_3$ samples with the same chemical composition but obtained by different methods, namely co-impregnation and sol–gel, presented the same distribution of tin ionic species. However, when they were applied in the hydrogenation of dimethyl adipate, the corresponding 1,6-hexanediol could not be equally detected over all catalysts. Such rather distinct performance was associated to the location of the ionic moieties on the surface.

Furthermore, the influence of some other factors, such as the influence of the support and metal/promoter ratio on tin oxidation state, has been widely reported in the literature and yet, a certain degree of uncertainty still prevails about this issue due to the quite different variables applied to obtain the catalytic systems. It has been stated that tin is mainly present as metallic Sn^0 and/or as metal–tin alloys when supported on activated carbon [22–24], silica [25,26], titania [25] and niobia [27]. It is otherwise observed in its ionic forms Sn^{4+}/Sn^{2+} over zirconia [25], magnesia [25,26] and alumina [7,21]. The most controversial results are undoubtedly related to the use of alumina, since some groups have identified both metallic and ionic species [7,28] on such oxides. It has also been observed that the reducibility of tin dioxide would be related to the acid-base properties of the support, especially the type and strength of the acidity [25].

In addition, the enhancement of the performance of those catalysts supported on reducible oxides (TiO_2, WO_3, MoO_3, Nb_2O_5, etc.) should be mentioned. It is generally attributed to the interaction of the C=O bond with the exposed cations of the oxide provided by the partially reduced moieties created during high temperature reduction, i.e. strong support–interaction effect (SMSI).

These compiled results of published data concerning different oxides evidence that the impact of the support on the reduction of tin, and consequently on the catalytic behaviour, must be carefully considered.

This contribution reports further studies on the production of diol over RuSn-based systems. Basically, the effect brought about by the support was investigated. Several supports were tested, including both unreducible (Al_2O_3, SiO_2) and reducible (CeO_2, TiO_2 and Nb_2O_5) oxides. However, the reducible supports were used under controlled conditions in order to prevent the SMSI effect, allowing evaluating, at this stage, the influence of their chemical nature. The dimethyl adipate molecule, a six-carbon ester derived from adipic acid, was chosen to probe such effects.

2. Experimental

The monometallic and bimetallic catalysts were prepared by impregnation and co-impregnation, respectively. The oxides used as supports were γ-alumina (Degussa, 104 m^2/g), Nb_2O_5 (CBMM, 78 m^2/g), CeO_2 (Aldrich, 24 m^2/g), SiO_2 (Aldrich, 258 m^2/g) and TiO_2 (Fluka, anatase $> 99\%$, 21 m^2/g). The metal precursor salts were hydrated ruthenium chloride ($RuCl_3$ Aldrich) and tin(II) chloride ($SnCl_2$, Aldrich). All catalysts were prepared so as to obtain a ruthenium content of 2 wt.%, while the tin content was 4.7 wt.% in order to keep a Sn/Ru atomic ratio of 2. Firstly, the commercial supports were treated under argon at 500 °C for 4 h; they were then slurried with ethanolic solution of the necessary quantities of the precursors in a rotatory evaporator at room temperature for 15 h. Afterwards, the solvent was slowly evaporated under vacuum. The powder was dried overnight at 120 °C, and then further dried under argon at the same temperature for 15 h. All samples were calcined under air stream for 4h at 400 °C. After calcination, the catalysts supported on Al_2O_3 and SiO_2 were reduced under a 2% H_2/N_2 flow at 400 °C while the catalysts supported on the reducible oxides (CeO_2, TiO_2 and Nb_2O_5) were activated at 250 °C to avoid their partial reduction, and consequently the establishment of SMSI effect.

The hydrogenation of dimethyl adipate (Aldrich, 99.9%) was carried out at 255 °C and hydrogen pressure of 50 bar. The catalyst (1.4 g) was mixed with dioxane used as solvent and preconditioned in situ at reaction conditions for 1 h. The reaction started by injecting 7.0 g of dimethyl adipate (DMA) in the reactor. The experiments were conducted with stirring of 1500 rpm to favour hydrogen diffusion and ensure kinetic control. Samples were taken periodically and analysed by gas chromatography; a Thermosquest/Trace CG equipped with a 30 m × 0.25 mm capillary columm (100% dimethyl-siloxane) was used. The products identification was carried out in a HP CG-MS 5988A. The reaction results were analysed in terms of selectivity:

$$S_j = \text{selectivity to product } j = 100 \times \frac{c_j}{\sum c_j}$$

The c_j is the concentration of the main identified hydrogenation products of DMA.

Mössbauer spectra were obtained at temperature of liquid helium using a constant acceleration spectrometer with a $BaSnO_3$ source. The samples were reduced following the same protocol applied before the catalytic tests. They were handled in inert atmosphere to avoid oxidation. The least-squares fits of the ^{119}Sn Mössbauer spectra yielded the mean electric quadrupole splitting (QS), the mean isomer shift (IS) and the relative resonance areas (area) of the different components of the spectra.

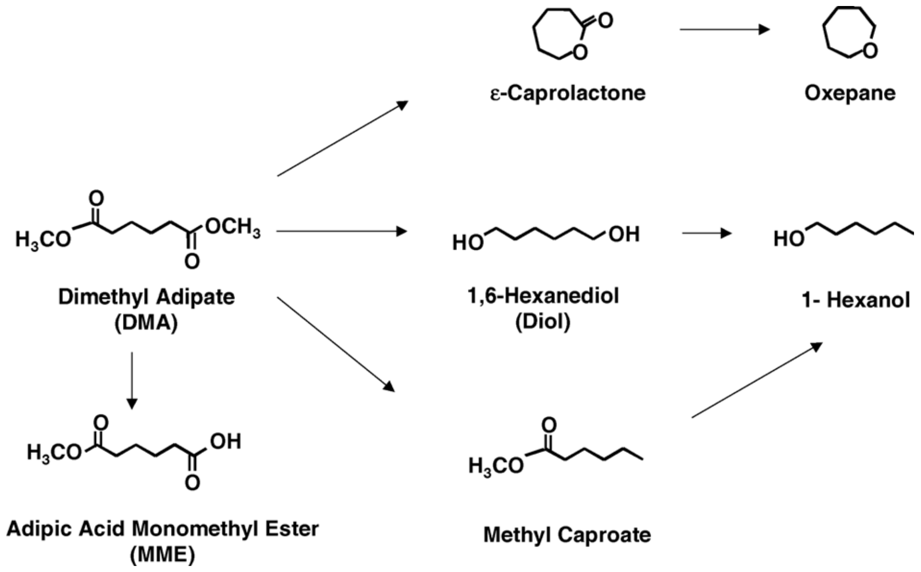

Fig. 1. A simplified reaction scheme for the hydrogenation of dimethyl adipate.

3. Results and discussion

A simplified reaction scheme for the hydrogenation of DMA is displayed in Fig. 1, pointing out only some relevant products. It can be seen that a wide range of products can be formed. 1,6-hexanediol is obtained by the hydrogenation of both carbonyl groups in the ester. However, several intermediate products are also likely to be produced, especially lactones, cyclic ethers, alcohols and hydrocarbons. The formation of the corresponding monoester is also possible.

The global catalytic activities of the prepared monometallic samples were compared by the DMA time-conversion profiles (Fig. 2). It could be thought that the activity difference found is related to a different metal crystallite distribution due to the distinct surface area of the supports. However, comparing the BET surface area given in Section 2 and the behaviour presented in Fig. 2, it can be concluded that the activity of the catalysts for the present case is more strongly determined by some other factors. In fact, it can be suggested that the chemical nature of the support plays a role in the catalyst performance. The system Ru/Nb_2O_5 sample was found to be the most active for the hydrogenation of DMA, reaching conversion of 92% after 10-h reaction. Ru/CeO_2, on the other hand, presented the poorest performance, only 18% of DMA conversion after the same reaction interval.

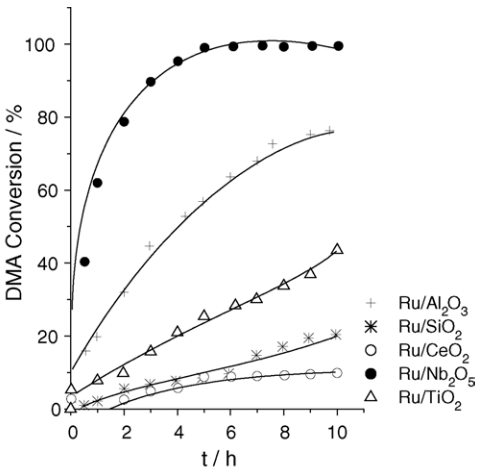

Fig. 2. DMA time-conversion profiles of the monometallic ruthenium catalysts.

No monometallic catalyst led to the formation of 1,6-hexanediol in agreement with previous results [17,18,20,21]. Nevertheless, a change in the products distribution was found according to the support used, evidencing its influence on the catalyst properties.

Table 1 lists the selectivities of the most relevant products. It should be mentioned that the highly hydrogenated by-products, such as alcohols and hydrocarbons were all grouped for practical reasons and labelled as ‘‘others’’. As regarding product distribution, the reaction revealed to be strongly dependent on the support. It can be noted that the formation of adipic acid monomethyl ester is rather different over these samples. It is the main product detected along the whole experiment period over Ru/Al_2O_3 and Ru/TiO_2, indicating that the ruthenium metallic sites created on these oxides are able to selectively cleavage the O–CH_3 bond in the ester group [20]. It is worth noting, however, that no traces of adipic acid were detected at all. It implies that the hydrogenolysis reaction of both ester groups in the DMA molecule to their corresponding acid does not occur at the same rate over such systems. Additionally, it may be said that the sites responsible for the hydrogenolysis reaction are directly modified by the chemical nature of the support as different selectivities towards the adipic acid

Table 2
Catalytic performance of bimetallic catalysts in the hydrogenation of dimethyl adipate

Catalysts	Conversion (%)	Selectivity (%)					
		MME	MC	CPL	Diol	OXE	Others
RuSn/Al_2O_3	72	4	9	5	6	3	73
RuSn/SiO_2	78	1	23	4	8	–	64
RuSn/CeO_2	28	1	21	11	14	–	53
RuSn/TiO_2	64	–	29	9	29	–	33
RuSn/Nb_2O_5	72	4	23	6	7	–	60

MME: adipic acid monomethyl ester; MC: methyl caproate; CPL: ε-caprolactone; diol: 1,6-hexanediol; OXE: oxepane.

monomethyl ester were obtained. The rather low production of this monoester on silica and niobia-supported catalysts evidences the high activity of these systems to attack both DMA ester functions. It is consistent with the high formation of undesired by-products (Table 1) instead of some other specific possible product as illustrated in Fig. 1. Besides adipic acid monomethyl ester, methyl caproate and ε-caprolactone were also timidly formed over Ru/CeO_2 and Ru/SiO_2.

Table 2 collects the catalytic performances of bimetallic Ru–Sn samples on the hydrogenation of DMA after 10-h reaction. The addition of tin significantly changed both activity and product selectivity. The main aspect associated with the introduction of tin in the catalysts is the appearance of 1,6-hexanediol among the reaction products.

The selectivity to adipic acid monomethyl ester decreased over the bimetallic samples. This finding can be taken as an indicative of the modification of the surface sites by tin; the ruthenium atoms ensembles required for the hydrogenolysis reaction would now likely be in lower concentration. A drop of hydrogenolysis activity due to the addition of a second inactive metal is indeed well-reported in the literature [22,27,29,30].

Even though the experiments showed that selectivity towards diol was low, the promoting effect of tin on the ruthenium-based catalyst is unquestionable irrespective of the support, evidencing, once again, the catalysts surface modification. As a matter of fact, a quite significant selectivity to diol was achieved over all systems at longer reaction time, i.e. higher conversion. Fig. 3 displays such data after 15-h period. The performance of RuSn/TiO_2 is clearly superior to the others; it came up as the most selective sample reaching 45% at 81% conversion. This is a remarkable finding, especially due to the moderate reaction operating conditions used, particularly the low hydrogen pressure. We have previously reported similar result accomplished on alumina-supported catalyst but only after a longer experiment period (20 h), evidencing its lower activity to hydrogenate both C=O bonds [20].

Table 1
Catalytic performance of ruthenium monometallic catalysts in the hydrogenation of dimethyl adipate

Catalysts	Conversion (%)	Selectivity (%)				
		MME	MC	CPL	Diol	Others
Ru/Al_2O_3	76	68	–	–	–	32
Ru/SiO_2	21	16	12	9	–	63
Ru/CeO_2	18	38	3	3	–	56
Ru/TiO_2	44	59	–	–	–	41
Ru/Nb_2O_5	92	11	–	–	–	89

MME: adipic acid monomethyl ester; MC: methyl caproate; CPL: ε-caprolactone; diol: 1,6-hexanediol.

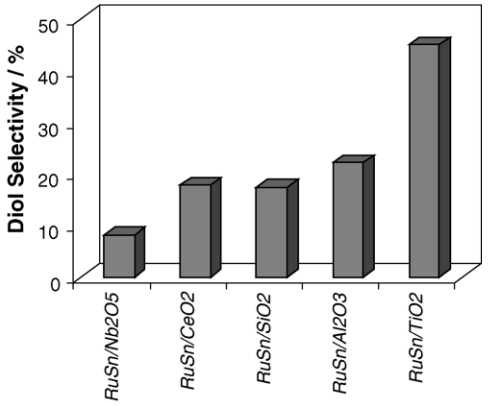

Fig. 3. Selectivity to 1,6-hexanediol after 15-h reaction.

The comparison of the performance of RuSn-based catalysts on the selective hydrogenation of DMA allows the selection of a suitable system to produce 1,6-hexanediol. Nonetheless, by comparing the evolution of diol selectivity over the studied samples along the experiment (Fig. 4), some interesting aspects of the chemoselective reaction may be risen. It is curious to observe in Fig. 4 that the formation of diol begins only after an initial period of ~2–7 h. This fact might suggest an inductive time for the selective formation of diol over these systems.

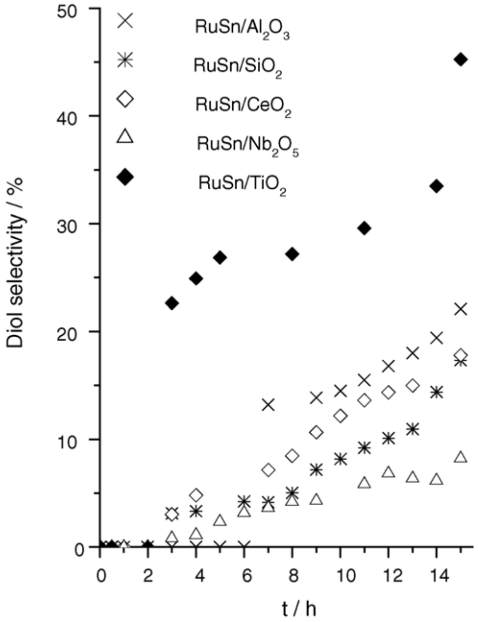

Fig. 4. Selectivity to 1,6-hexanediol as a function of reaction time.

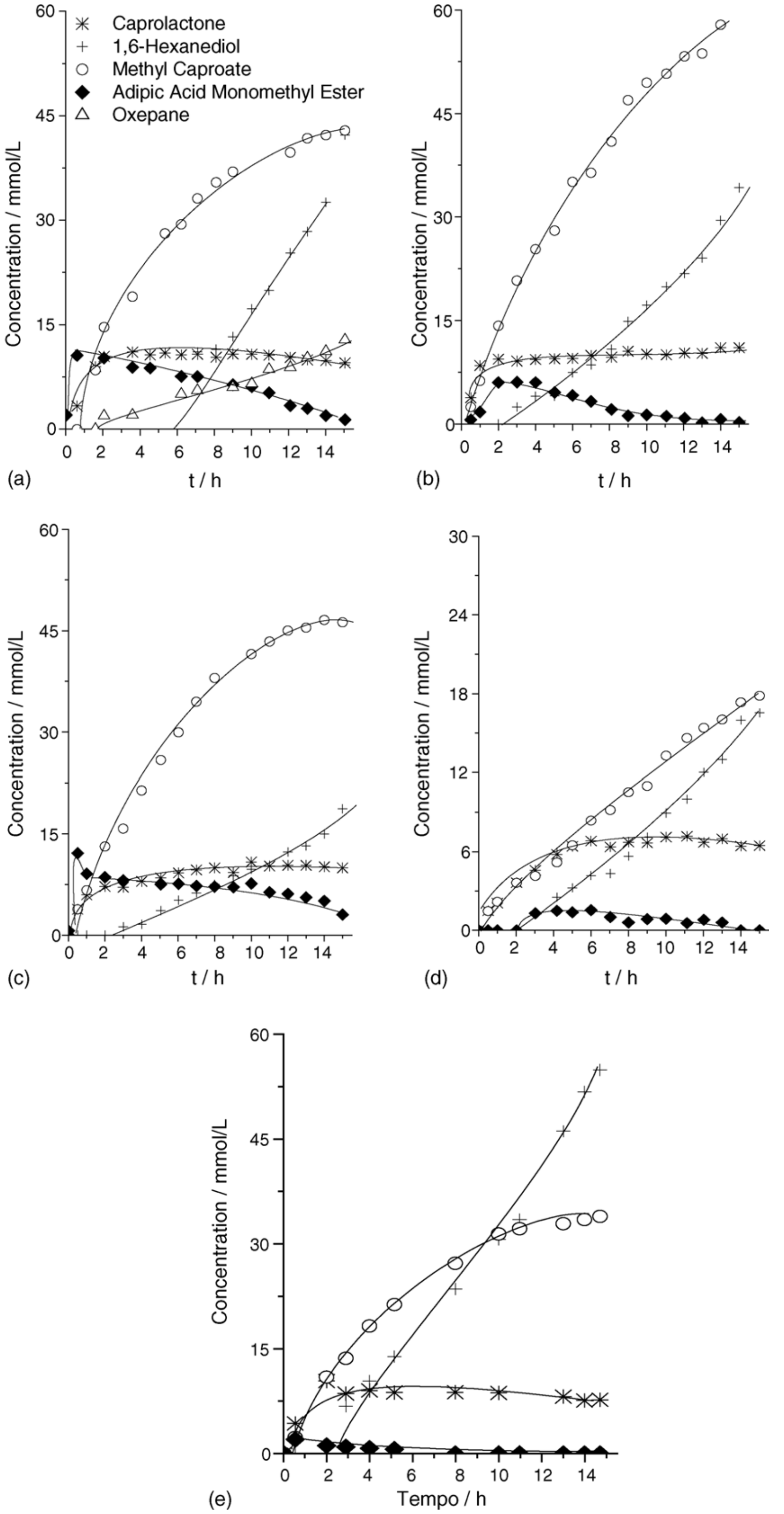

Fig. 5. Products concentration profiles along the reaction on: (a) RuSn/Al_2O_3, (b) RuSn/SiO_2, (c) RuSn/Nb_2O_5, (d) RuSn/CeO_2 and (e) RuSn/TiO_2.

Fig. 5 depicts the products concentration profiles obtained over the studied samples. It may be noted that similar distributions were registered irrespective of the support; all samples produced adipic acid monomethyl ester, ε-caprolactone, methyl caproate and hexanediol. It must be outlined, though that titania-supported catalyst provided a narrower distribution since the production of the adipic acid monomethyl ester was totally suppressed. Oxepane, a cyclic ether, could only be detected on alumina-supported sample. It may also be observed that its formation follows a fairly similar pattern of that registered for hexanediol. It might suggest that oxepane proceeds from the alcohol dehydration reaction due to the surface acid sites of alumina. It is worth mentioning that the expected acidic features of niobia were inhibited by the calcination temperature applied before preparing the catalyst [31]. The formation of ε-caprolactone and methyl caproate does not seem to be dependent of any other compound, which indicates that they are probably formed concomitantly by side reactions from DMA (Fig. 1). Adipic acid monomethyl ester, on the other hand, showed a fairly particular profile. It is mostly produced at the very first minutes of reaction but its consumption is clear after around 1–2 h. As a matter of fact, this monoester may also be considered as a substrate for the catalysts tested as this molecule features an acid and an ester group, which are both likely to be hydrogenated under the operating conditions according to paths similar to those presented in Fig. 1 from DMA.

Based on the catalytic performances observed in the above-presented results, regarding particularly the significant selectivity towards 1,6-hexanediol, two selected samples, namely RuSn/Al_2O_3 and RuSn/TiO_2, undertook a more detailed study. They were characterised by Mössbauer spectroscopy in an attempt to identify the tin species.

Figs. 6 and 7 present the Sn Mössbauer spectra obtained from reduced catalysts supported on alumina and titania, respectively. As can be seen in Fig. 6a, the monometallic sample Sn/Al_2O_3 exhibited four spectral components. Two can be attributed to oxidic Sn^{4+} and Sn^{2+} species; an interaction between tin and alumina was detected by a spectral component with Mössbauer parameters comparable to $SnAl_2O_5$ [28]. A strong component with parameters comparable to hydrated Sn^{2+} oxides or hydroxides can also be distinguished. Such contribution is associated with Sn species adsorbed onto alumina with a nearest coordination shell containing hydroxyl ions [23]. The determined Mössbauer parameters and the respective tin species present on reduced samples are summarised in Table 3.

The data of the Mössbauer bimetallic catalyst also required four components to fit the spectrum. This sample presented a similar distribution when compared to the reference Sn/Al_2O_3 powder, where Sn^{4+}, Sn^{2+} and $SnAl_2O_5$ could be identified. A fourth different component was attributed to an oxidic Ru–Sn species, described in the literature [23] as an oxygen-bonded tin species with intermetallic bonds between ruthenium and tin.

The analysis of the spectra collected for the catalysts supported on TiO_2 (Fig. 7) revealed that different metal–metal and metal–support interactions were accomplished. The reference sample Sn/TiO_2 (Fig. 7a) exhibited three spectral components, two quadrupole doublets related to the Sn^{4+}, Sn^{2+} species and a third single line, which was

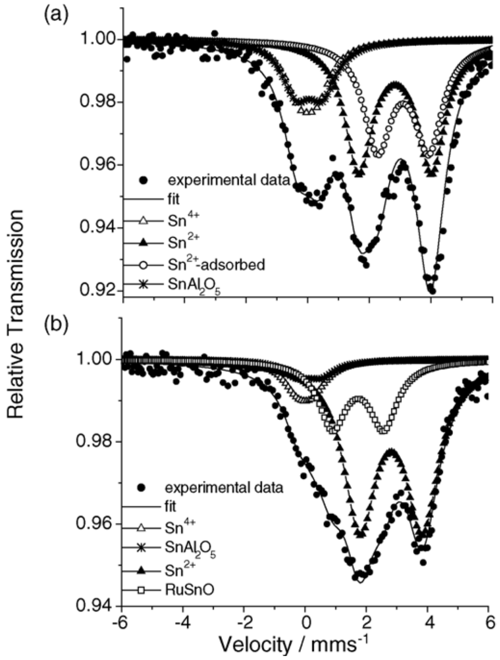

Fig. 6. (a and b) ^{119}Sn Mössbauer spectra of alumina-supported catalyst: (a) Sn/Al_2O_3; (b) RuSn/Al_2O_3.

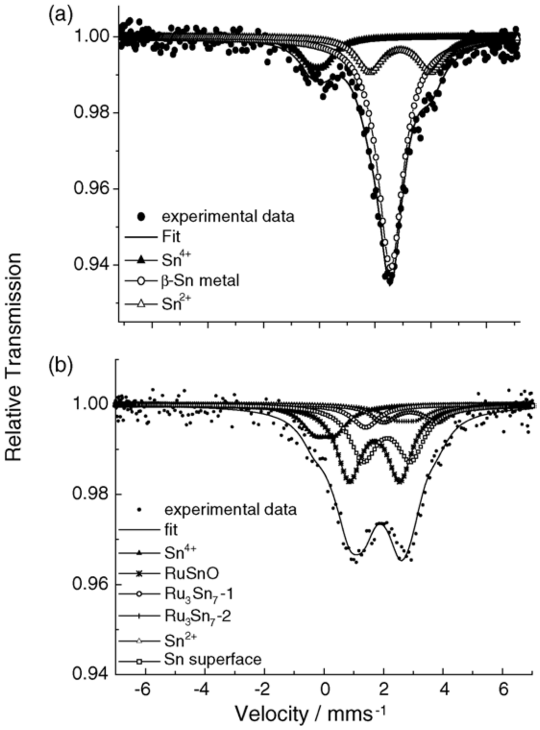

Fig. 7. (a and b) ^{119}Sn Mössbauer spectra of titania-supported catalyst: (a) Sn/TiO_2; (b) RuSn/TiO_2.

Table 3
^{119}Sn Mössbauer parameters of Ru–Sn-supported catalysts

Catalyst	IS (mm/s)	QS (mm/s)	Area (%)	Sn species
Sn/Al$_2$O$_3$	0.00	0.57	14	Sn^{4+}
	2.84	2.36	39	Sn^{2+}
	0.05	0.86	15	SnAl$_2$O$_5$
	3.10	1.66	32	Sn^{2+}-adsorbed
RuSn/Al$_2$O$_3$	0.00	0.50	8	Sn^{4+}
	2.82	2.04	65	Sn^{2+}
	0.15	0.80	5	SnAl$_2$O$_5$
	1.74	1.67	22	Oxidic Ru–Sn
Sn/TiO$_2$	0.00	0.51	11	Sn^{4+}
	2.90	2.20	20	Sn^{2+}
	2.56	–	69	β-Sn
RuSn/TiO$_2$	0.06	0.70	13	Sn^{4+}
	2.90	1.80	9	Sn^{2+}
	1.70	1.70	36	Oxidic Ru–Sn
	1.40	0.00	6	Ru$_3$Sn$_7$-1
	2.70	0.70	7	Ru$_3$Sn$_7$-2
	2.15	1.59	29	Surface Sn

associated with metallic tin (β-Sn). This phase is actually the major species (69%) according to the relative resonance areas collected in Table 3.

The registered spectrum of the bimetallic RuSn/TiO$_2$ catalyst was quite complex (Fig. 7b). Besides the Sn^{4+}, Sn^{2+} and oxidic Ru–Sn species also observed on alumina-based sample, three others could be fitted. Taking into account the hyperfine parameters they were attributed to the so-called surface Sn and two intermetallic Ru$_3$Sn$_7$ compounds [23]. Surface tin is generally described as a monolayer of metallic Sn covering the metallic ruthenium surface [23]. The two intermetallic compounds (Ru$_3$Sn$_7$-1 and Ru$_3$Sn$_7$-2) differ basically in the position that the tin atoms occupy in the crystal lattice [32].

The Mössbauer data allow the conclusion that the oxidation state of tin as well as the tin–ruthenium and tin–support interactions in RuSn/Al$_2$O$_3$ and RuSn/TiO$_2$ are indeed rather different as initially suggested. The tin–support interaction appears to be more relevant with alumina hindering its reduction. On the other hand, when deposited on titania, the metal–metal interaction seems to be favoured instead, leading to the formation of Ru–Sn intermetallic compounds as well as the existence of metallic surface tin. In fact, it is in accordance with our previous conclusions based on the temperature-programmed reduction profiles of similar catalysts [12].

By facing the catalytic behaviour and the Mössbauer results, it should be appreciated that 1,6-hexanediol could be produced over both alumina and titania-supported catalysts even though distinct tin species were formed. As the ionic tin forms, whether Sn^{4+} or Sn^{2+}, were the common species detected in both samples, it is conceivable that the selectivity towards diol is related to the well-described C=O activation effect brought about by the presence of promoter-cations, the Lewis Sn^{n+} acid sites.

The occurrence of different induction periods (Fig. 4) over these systems is quite intriguing though. Indeed, such periods have been observed for several authors when dealing with a noble metal-based catalyst modified by tin for selective hydrogenation [33–37]. This fact is referred to as ‘‘reaction induced catalyst activation’’. It assumes that the catalyst surface modifies during the initial stage of the hydrogenation due to the total or, at least, partial oxidation of Sn^0 present in the catalyst. Such oxidation would be induced by the reaction mixture itself. This explanation relies on the presence of metallic tin in the RuSn catalysts either isolated or as an intermetallic compound and yet that such Sn^0 moieties would not promote the C=O hydrogenation.

This approach has satisfactorily fitted several experimental results collected from different chemical substrates (α,β-unsaturated aldehydes [35–37] and fatty acids [11,12]) and also observed by some spectroscopic studies [36]. Nonetheless, it seems to fail to the hydrogenation of ester derived from dicarboxylic acids. The occurrence of only ionic tin on alumina-supported catalyst is not consistent with the observed induction period if the reaction induced catalyst activation model is considered. As the experimental reaction data pointed to a thoroughly opposite way, it could be speculated that this phenomenon might be associated to some mechanistic issues due to the structure of the dicarboxylic ester molecule. This would imply that the structure of the RuSn sites created over these catalysts acts differently on the molecule activation when compared to the selective hydrogenation of aldehydes, ketones or fatty acids.

4. Conclusion

The addition of tin provided the formation of 1,6-hexanediol on all Ru–Sn-based system. Amongst the studied catalysts the RuSn/TiO$_2$ was the most promising of all. The ionic tin forms, whether Sn^{4+} or Sn^{2+}, were credited for conducting the reaction to the formation of diol. This work suggests that even though similar RuSn active sites are present in a catalyst, they will act differently according to the molecular structure of the substrate. The creation of active bimetallic sites may be controlled by the use of a suitable support.

Acknowledgments

The authors are indebted to Dr. Marco A. Morales and Dr. Elisa M. Baggio-Saitovitch from CBPF for the Mössbauer spectroscopy measurements.

S.M.S and A.M.S. acknowledge the financial support from CNPq and CAPES.

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