Role of catalyst preparation on determining selective sites for hydrogenation of dimethyl adipate over RuSn/Al2O3

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Abstract

The hydrogenation of dimethyl adipate over RuSn/Al2O3 catalysts was studied. Attention was given to the effects of the preparation method and pretreatment conditions on the selective production of 1,6-hexanediol. The catalysts were prepared by co-impregnation and sol gel methods. The liquid phase catalytic reaction revealed that hexanediol can only be produced over the catalyst obtained by co-impregnation and calcined at low temperature. This system allowed 49% selectivity at practically total ester conversion. No diol could be formed when the same system was formerly calcined at 600 °C or over the sol gel catalyst. Mössbauer spectra revealed the occurrence of the same tin species in all catalysts; the distinct performance was thus attributed to the location of such species on the surface as evidenced by XPS. The results presented in this work indicated that alumina-supported Ru–Sn bimetallic catalysts may indeed be appropriate for 1,6-hexanediol production from DMA. However, the generation of tin oxidic species is not solely decisive for the formation of catalytically active sites. A suitable preparation method must be applied in order to better localize the SnOx moieties and tailor the required Ru–SnOx selective sites.

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1. Introduction

Diols are industrially important as they are used as raw materials for a wide variety of fine chemicals, pharmaceuticals and biodegradable polymers. Their synthesis by the hydrogenation of dicarboxylic acids and their esters is thus interesting for the industry but also in academia as the hydrogenation of such carbonyl compounds is more difficult to accomplish whether a ketone or an aldehyde is considered.

Drastic conditions are often used though in the manufacturing processes to achieve an acceptable productivity. By using the conventional copper chrome-based catalysts, which consist of an approximately equimolar mixture of cupric oxide and cupric chrome [1], diol can be produced at hydrogen pressures of around 20–30 MPa and temperatures at around 150–250 °C. Manufacture of diol under mild reaction conditions would require 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. Therefore, the development of a suitable catalyst that could allow the selective formation of alcohols and diols from carboxylic and dicarboxylic acids at relatively low pressure and temperature is still needed.

Monometallic noble metal-based catalysts are not suitable for obtaining alcohols [2–6]. Nevertheless, their catalytic properties can be modified when a second metal is added. Indeed, we have recently reported the performance of simple noble metal based catalysts as well as the effects brought about by adding some potential promoters on 1,6-hexanediol selective production from dimethyl adipate hydrogenation [2]. It was found that ruthenium catalysts promoted by cobalt, zinc and tin may lead to diol formation. However, only the bimetallic RuSn system exhibited appreciable selectivity towards diol. It has been gen-
eraly accepted that the promising performance of tin-promoted metallic catalysts over alcohol production from carbonyl compounds hydrogenation is bound to Sn$^{n+}$ species. The model used to explain this effect is based on the activation of the O=O bond through the interaction of ionic tin and the carbonyl oxygen [7,9].

The catalytic properties may also be drastically modified according to the preparation method applied and yet, following a similar procedure, they may change due to different preparation parameters such as calcination temperature, aging, and so on. Several examples may be found in the current literature concerning such aspects in selective hydrogenation reactions. In the early 1990s, catalysts prepared by surface organometallic reaction of Sn[n-C$_4$H$_9$]$_4$ on rhodium particles showed that they could be extremely active and selective in the reduction of citral to geraniol and nerol [10,11]. That was a remarkable finding as rhodium-based systems were claimed to be mostly selective to saturated aldehydes [7]. Shortly after, such method was successfully used for obtaining Rh/SiO$_2$ catalysts modified by tetra-n-butyl germanium and lead [12]. A later systematic study carried out by Coupé et al. [13] on such catalysts revealed that other preparation techniques, namely coimpregnation and successive impregnation were also able to create active sites suitable for the formation of unsaturated alcohols.

Ruthenium–tin catalysts, similarly prepared from the reaction of organometallic tin with the corresponding Ru/SiO$_2$ system, were found to be very selective for the hydrogenclysis/hydrogenation of ethyl acetate to ethanol [14]. These catalysts, prepared by sol gel methodology, were selective on the oleic alcohol production from its corresponding fatty acid as well (15–17). As a matter of fact, such bimetallic systems prepared via more conventional routes have also been reported as promising to the production of unsaturated alcohols from unsaturated aldehydes and fatty acids [5,18] and their esters. As regarding dicarboxylic acids, RuSn-based catalysts have already been successfully used in the hydrogenation of such compounds [2,3,19]; however, the benefits of choosing a suitable preparation method have not been studied in detail so far even though it has long been recognized its importance when it comes to chemoselectivity.

In this work, the studies were focused on the liquid phase hydrogenation of dimethyl adipate (DMA), a six-carbon dicarboxylic derived ester, on bimetallic alumina supported Ru–Sn catalysts. DMA was chosen as model reaction also considering the industrial relevance of the catalytic hydrogenation of C$_{5}$–C$_{6}$ dicarboxylic acids in the production of a wide variety of fine chemicals. The catalysts were obtained using different preparation methods, namely coimpregnation and sol gel. Chemoselectivity was evaluated considering the effects of such methods and pretreatment conditions.

2. Methods

2.1. Impregnated catalysts

The monometallic and bimetallic catalysts were prepared by impregnation and coimpregnation, respectively. A commercial γ-Al$_2$O$_3$ (104 m$^2$/g) was used as support. The metal precursor salts were hydrated ruthenium chloride (Aldrich) and tin (II) chloride (Aldrich). All catalysts were prepared so as to obtain a ruthenium content of 2 wt.%, and a tin content of 4.7 wt.%. Alumina was slurried with ethanolic solutions of the required amounts of the precursors in a rotary evaporator at room temperature for 15 h. Next, the solvent was slowly removed by evaporation under vacuum. The powders were dried overnight at 120 °C, calcined under an air stream of 50 mL min$^{-1}$ for 4 h at 400 or 600 °C. Finally, the catalysts were reduced with hydrogen flow of 40 mL min$^{-1}$ at 400 °C for 2 h. The samples herein labeled according to their composition and calcination temperature, for instance RuSn/Al-400 stands for a bimetallic catalysts calcined at 400 °C.

2.2. Sol gel catalysts

Sol gel catalysts were prepared according to a protocol described elsewhere [5,18]. Aluminium iso-propoxide was used as Al$_2$O$_3$ precursor and the surface area obtained was 375 m$^2$/g after calcination at 450 °C. Ruthenium and tin precursors were the same used in the coimpregnation method. Solvents used were ethanol and hexylene glycol. A ruthenium/alumina (RuAl), with a nominal metal loading of 2 wt.%, hexylene glycol was slowly added to a solution of RuCl$_3$ in ethanol at 45 °C. The mixture was maintained at 90 °C for 30 min, then aluminum iso-propoxide was added and the mixture was stirred at 90 °C for 4 h. A homogeneous solution was obtained. An amount of water and ethanol were then added to the solution and the resultant mixture was dried at 170 °C under vacuum. Similar procedures were used for the other sol gel catalysts. The catalysts were calcined at 450 °C for 4 h, and further reduced with a hydrogen stream at 400 °C during 2 h prior the reaction. These samples are also named according to their composition except that the slash was omitted to appoint the sol gel method. RuSnAl refers thus to a bimetallic catalysts obtained via sol gel.

Table 1 collects all catalysts with their corresponding preparation methods and metal composition.

2.3. Catalyst characterization

2.3.1. Mössbauer spectroscopy

The samples spectra were obtained at temperature of liquid helium using a constant acceleration spectrometer with $^{119}$Sn (source of BaSnO$_3$). The samples were handled in inert atmosphere to avoid oxidation. The Mössbauer parameters were determined by Lorentzian lines computer fitted by the least squares method. One spectra of a calcined bimetallic catalyst was collected at N$_2$ liquid temperature. This spectrum was taken in order to compare to those reduced samples.

2.3.2. XPS

The surface atomic composition of calcined samples was analysed by XPS in a spherical analyser spectrometer HA 100 VSI using a non-monochromatized Al K$_\alpha$ radiation.
Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ru (wt.%)</th>
<th>Sn (wt.%)</th>
<th>Sn/Ru</th>
<th>Preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/Al</td>
<td>–</td>
<td>4.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SnAl</td>
<td>–</td>
<td>4.7</td>
<td>–</td>
<td>Sol gel</td>
</tr>
<tr>
<td>RuAl</td>
<td>2.0</td>
<td>–</td>
<td>–</td>
<td>Impregnation</td>
</tr>
<tr>
<td>RuAl</td>
<td>2.0</td>
<td>–</td>
<td>–</td>
<td>Sol gel</td>
</tr>
<tr>
<td>RuSn/Al-400 or RuSn/Al-600(^a)</td>
<td>2.0</td>
<td>4.7</td>
<td>2.0</td>
<td>Impregnation</td>
</tr>
<tr>
<td>RuSnAl</td>
<td>2.0</td>
<td>4.7</td>
<td>2.0</td>
<td>Sol gel</td>
</tr>
<tr>
<td>RuSn1/Al-400(^b)</td>
<td>2.0</td>
<td>2.4</td>
<td>1.0</td>
<td>Impregnation</td>
</tr>
</tbody>
</table>

\(^a\) The index 400 or 600 refers to the calcination temperature.

\(^b\) The index 1 refers to a Sn/Ru atomic ratio of 1.

(1986.6 eV). Experiments were carried out under vacuum of 2 \(\times 10^{-8}\) mbar.

2.4. Catalytic performance

The hydrogenation of dimethyl adipate (Aldrich, >99%) was carried out in the liquid phase in a PARR semi-batch steel reactor (300 mL) at 255°C and 5 MPa hydrogen. The experiments were conducted at 1500 rpm as it was seen to prevent hydrogen mass transfer and ensure kinetic control. An amount of 1.4 g of catalyst, mixed with 80 mL of dioxane, was preconditioned in situ at reaction conditions for 1 h. The reaction started by injecting 7 g of dimethyl adipate in the reactor. The pressure in the reactor was controlled during the reaction, while monitoring the hydrogen consumption. Samples were taken periodically in order to follow the reaction by chromatographic analysis. A metallic frit was used to collect clear liquid samples. A Thermoquest/Trace GC equipped with a 30 m \(\times 0.25\) mm capillary column (100% dimethyl-siloxane) was used. Some products were identified by a mass spectrometer CG/MS 5988 A.

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.

3. Results and discussion

3.1. Catalysts characterization

The catalysts were firstly characterized by Mössbauer spectroscopy in an attempt to identify the tin species. A selected \(^{119}\)Sn Mössbauer spectrum of the calcined RuSn/Al-400 sample is shown in Fig. 1. As can be seen, it is a quite simple spectrum, consisting of a quadrupole doublet associated to Sn\(^{4+}\) present as SnO\(_2\); any other tin oxidic species could not be observed, providing no evidence of any tin–alumina interaction at this stage.

Two quadrupole doublets are attributed to oxidic Sn\(^{4+}\) and Sn\(^{2+}\) species; an interaction between tin and alumina was now also detected by a spectral component with hyperfine parameters corresponding to SnAl\(_2\)O\(_5\) [20]. Another component with parameters comparable to hydrated Sn\(^{2+}\) oxides or hydroxides may also be distinguished. Such contribution has indeed been observed for other groups and is usually associated with tin species adsorbed onto the support with coordination shell containing hydroxyl ions [21].

![Fig. 1. Mössbauer spectra of calcined RuSn/Al catalyst.](image-url)

Table 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>Area (%)</th>
<th>Sn species</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuSnAl-400</td>
<td>0.00</td>
<td>0.50</td>
<td>8</td>
<td>Sn(^{4+})</td>
</tr>
<tr>
<td>2.82</td>
<td>2.04</td>
<td>65</td>
<td>Sn(^{2+})</td>
<td></td>
</tr>
<tr>
<td>1.74</td>
<td>1.67</td>
<td>22</td>
<td>RuSnO</td>
<td></td>
</tr>
<tr>
<td>RuSnAl-600</td>
<td>–0.04</td>
<td>0.50</td>
<td>14</td>
<td>Sn(^{4+})</td>
</tr>
<tr>
<td>3.03</td>
<td>1.99</td>
<td>70</td>
<td>SnAl(_2)O(_5)</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>0.69</td>
<td>4</td>
<td>SnAl(_2)O(_5)</td>
<td></td>
</tr>
<tr>
<td>1.91</td>
<td>1.80</td>
<td>12</td>
<td>RuSnO</td>
<td></td>
</tr>
<tr>
<td>RuSnAl</td>
<td>–0.04</td>
<td>0.50</td>
<td>20</td>
<td>Sn(^{4+})</td>
</tr>
<tr>
<td>2.85</td>
<td>2.01</td>
<td>52</td>
<td>Sn(^{2+})</td>
<td></td>
</tr>
<tr>
<td>1.60</td>
<td>1.74</td>
<td>12</td>
<td>RuSnO</td>
<td></td>
</tr>
<tr>
<td>Sn/Al-400</td>
<td>0.00</td>
<td>0.57</td>
<td>14</td>
<td>Sn(^{4+})</td>
</tr>
<tr>
<td>2.84</td>
<td>2.36</td>
<td>39</td>
<td>Sn(^{2+})</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>0.86</td>
<td>15</td>
<td>SnAl(_2)O(_5)</td>
<td></td>
</tr>
<tr>
<td>3.10</td>
<td>1.66</td>
<td>32</td>
<td>Sn(^{2+})-adsorbed</td>
<td></td>
</tr>
</tbody>
</table>
The Mössbauer spectra of the bimetallic catalysts also exhibited four different spectral components (Fig. 3). All samples presented the same distribution and, similarly to the reduced monometallic Sn/Al powder, Sn⁴⁺, Sn²⁺ and SnAl₂O₅ could be identified; however, their relative amounts varied as summarized in Table 2. The SnAl₂O₅ phase was mainly detected on the sol-gel sample, as could be expected due to the deeper interaction of the elements provided upon preparation. The fourth component presented hyperfine parameters similar to those reported by Stievano et al for RuSn/C systems [21], and was thus associated with an oxidic Ru–Sn species. These species have been described as an oxygen-bonded tin species with intermetallic bonds between ruthenium and tin; however, the accurate composition of this compound could not be established so far. It must be noted that no Ru–Sn alloy was detected in any sample.

The Mössbauer results indicate that tin is mostly present as ionic species, around 70–80%, whether Sn⁴⁺ or Sn²⁺, according to the relative resonance areas collected in Table 2. These findings are indeed in close agreement with previous findings based on temperature-programmed techniques [5,6]. Moreover, it could also be inferred that interaction between tin and alumina is more relevant if compared to the interaction established between the two metal phases as oxidic Ru–Sn species could be assigned while no bimetallic alloy was identified. As regarding tin species distribution, it would be verified that the same sort of species was created over all samples, evidencing that the preparation method did not seem to bring up a significant change; their generation would thus be driven basically by their chemical affinity.

3.2. DMA hydrogenation

The liquid-phase hydrogenation of dimethyl adipate (DMA) is represented in Scheme 1. This reaction may give different products ranging from adipic acid monoester and lactone to alcohol and hydrocarbon as displayed in the simplified reaction scheme, which points out only some relevant products.

The global catalytic activity of the prepared samples was compared by the dimethyl adipate (DMA) time-conversion patterns depicted in Fig. 4. The presence of tin altered the catalytic performance of the ruthenium catalysts leading to a relatively small decrease in activity regardless of the preparation route used. It is well known that the addition of a second metal can markedly change the surface properties, affecting both the catalytic activity and selectivity for several hydrogenation reactions. Such effect is usually explained by a blockage of part of ruthenium surface sites by tin species, which do not dissociatively adsorb molecular hydrogen or hydrogen spilled over from adjacent ruthenium atoms [22,23]. Indeed, a blank test was carried out in our laboratory with Sn/Al powder and it exhibited a rather poor activity in this hydrogenation reaction, achieving only 16% after 10 h.

As regarding selectivity, no 1,6-hexanediol was formed over the monometallic ruthenium catalysts as already previously
Scheme 1. A simplified reaction scheme for the hydrogenation of dimethyl adipate.

Fig. 4. Dimethyl adipate consumption along the reaction over the mono and bimetallic catalysts.

Table 3
Hydrogenation of DMA over bimetallic Ru catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>f (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Adipic acid monomethyl ester</td>
<td>Methyl caproate</td>
</tr>
<tr>
<td>Ru/Al</td>
<td>76</td>
<td>68</td>
</tr>
<tr>
<td>Sn/Al</td>
<td>16</td>
<td>–</td>
</tr>
<tr>
<td>RuSn/Al-400</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>RuSn/Al-600</td>
<td>83</td>
<td>–</td>
</tr>
<tr>
<td>RuSn/Al</td>
<td>68</td>
<td>5</td>
</tr>
<tr>
<td>RuSn/Al-400</td>
<td>75</td>
<td>2</td>
</tr>
<tr>
<td>RuSn/Al-400c</td>
<td>98</td>
<td>–</td>
</tr>
</tbody>
</table>

* Experimental conditions—temperature: 255°C; pressure: 5 MPa; reaction time: 15 h.
* f: conversion.
* Reaction data collected after practically total conversion – reaction time 20 h.

report by us [2,19]. These systems showed that the metal sites are responsible for the selective cleavage of the O-CH₃ bond in the ester group, giving the adipic acid monomethyl ester. Indeed, such behavior was detected over both monometallic samples irrespective of the preparation method used as presented in Table 3.

No diol was detected during the blank experiment with Sn/Al either. Despite the quite poor activity, the main product detected over this powder was e-caprolactone (Table 3), suggesting that this product does not require metal sites for its formation. As a matter of fact, this cyclic ester might be formed through the intramolecular esterification of DMA, an acid catalyzed step. It should be recalled that this product is conventionally synthesized by adding an inorganic acid in the organic media [24]. It is thus conceivable that the Lewis acid sites of alumina are the active sites of such sample.

A drastic change in the product distribution was found over the bimetallic catalysts (Table 3). The almost suppression of the hydrogenolysis reaction, i.e. the formation of adipic acid monomethyl ester, and the accessibility of the carboxylic groups
come up as the main aspects associated with the addition of tin in the catalyst composition. Nevertheless, some interesting points should be highlighted; the selectivity data summarized in Table 3 clearly reveal that the introduction of tin may not be solely credited with being responsible for the products distribution. As far as bimetallic systems are concerned the preparation methods as well as the experimental conditions applied can deeply influence the catalyst performance, particularly chemoselectivity.

The hydrogenation of the carboxylic group leading to the production of 1,6-hexanediol could only be effective over the catalyst obtained by coimpregnation and calcined at lower temperature (RuSn/Al-400). Even though the selectivity towards diol was low after 15-h reaction, it increased gradually and after 20 h it reached 50% at total ester conversion (Table 3). Interestingly, no diol could be formed when the same system was formerly calcined at 600 °C or when a similar sample was prepared via a sol gel route. A thoroughly distinct product distribution was registered over the different samples as depicted in Fig. 5.

The profiles obtained for the coimpregnated RuSn/Al-400 catalysts are displayed in Fig. 5A. It may be suggested that the formation of adipic acid monomethyl ester and ε-caprolactone occurs concomitantly by two side reactions from DMA; those reactions would take place over the isolated ruthenium metallic sites and the support Lewis acid sites, respectively, as suggested by the previous results obtained over both ruthenium and tin monometallic samples. The decrease of adipic acid monomethyl ester followed by the appearance of methyl caproate indicates that the monoester formed undergoes further hydrogenolysis in a series reaction.

Likewise, the production of ε-caprolactone was found to drop along the reaction, which may be associated with its hydrogenation to the cyclic ether, oxepane, especially at lower conversions. The production of 1,6-hexanediol over this sample must be highlighted. First it is curious to observe that the diol could only be detected after some reaction time period of around 6 h (>40% DMA conversion). It should also be noted that over this time a significant amount of by-products were formed, mainly alcohol.

![Fig. 5. Products distribution profiles along the reaction over (A) RuSn/Al-400; (B) RuSn/Al-600; (C) RuSnM.](image-url)
and hydrocarbon, which were grouped herein as “others” for simplicity.

Along with the diol formation, an additional increase in oxepane is also detected at this DMA conversion range. The cyclic ether should be, in this case, a consequence of the diol dehydration over alumina acid sites.

In summary, three sets of series reactions would take place over RuSn/Al-400:

\[
\begin{align*}
HCOOCH_2OH & \quad \rightarrow \quad HCOOCH_3 \quad \text{Adipic acid monoesterification} \\
HCOOCH_2OH & \quad \rightarrow \quad \text{O} \quad \text{Cyclic ether formation} \\
HCOOCH_2OH & \quad \rightarrow \quad HCO \quad \text{Adipic acid monomethyl ester formation}
\end{align*}
\]

The occurrence of these reactions is influenced by calcining the catalyst at higher temperatures (Fig. 5B). The formation of adipic acid monomethyl ester and subsequent hydrogenolysis to methyl caproate seems not to be significantly affected. Similarly, the intramolecular esterification of DMA to \( \varepsilon \)-caprolactone still takes place but its hydrogenation to oxepane is totally suppressed as a constant trend is registered within all DMA conversion range. More significantly, the other by-products were preferentially produced hindering the formation of diol.

Lastly, the sol gel catalysts presented a rather distinct trend. Fig. 5C suggests that, as a matter of fact, the formation of by-products proceeds from the hydrogenation of adipic acid monomethyl ester onto this catalyst. It might indicate that the cleavage of \( \text{O} - \text{CH}_3 \) bond is much faster over this system.

In order to have some insight on the effect brought about by tin loading, another sample prepared by coimpregnation was tested and its behavior is also collected in Table 3. As can be seen, its performance is quite poor and the selectivity towards 1,6-hexanediol was only 5% after 15-h reaction. Comparing the two samples prepared at exactly the same conditions, it can be easily noted that the tin content in these bimetallic systems significantly affects the chemoselectivity. Higher Sn/Ru ratios seem to favor the production of 1,6-hexanediol from DMA. Such trend differs from the optimal ratio earlier reported for the selective hydrogenation of the corresponding six-carbon dicarboxylic acid, adipic acid [3]. Interestingly, a similar contrast has been previously presented by some authors concerning the hydrogenation of fatty acids and their respective esters. A high Sn/Ru ratio was found to be necessary to produce alcohols from fatty esters (Sn/Ru = 8) whereas a ratio of 2 showed to be suitable for their corresponding acids [8,9]. These findings give more evidences of the strong effect of functional group on catalysts chemoselectivity.

The effects of tin as promoter on selective hydrogenation have been widely discussed in the literature over several carbonyl and carboxyl compounds. The better performance has been attributed to the presence of Lewis acid sites, Sn**, on the surface of the metal, which activate the \( \text{C} - \text{O} \) bond. Accordingly, such effect was clearly seen in this work as monometallic ruthenium led to the formation of adipic acid monomethyl ester by the cleavage of \( \text{O} - \text{CH}_3 \) bond. By adding tin, and creating thus Lewis acid sites capable of interacting with the lone electron pair of the carbonyl group oxygen, the \( \text{C} - \text{O} \) bond in the ester could be split to obtain diol. However, even though all systems have the same ionic species, as revealed by their hyperfine parameters, diol could not be equally detected over them. Hence the rather distinct performance is likely bounded to their location on the surface as Mössbauer spectroscopy would only provide information on the bulk catalysts.

The catalysts surface was therefore analysed by XPS with special attention to the information regarding relative surface concentrations. The Sn/Ru surface ratios are given in Table 4 and they clearly show that the catalyst surface composition is deeply affected by the preparation variables. The Sn/Ru atomic concentration of the coimpregnated catalysts was found to be twice and almost four times higher than the bulk value, evidencing a surface enrichment with tin. Such phenomenon has been often reported in the literature dealing with bimetallic particles containing tin [21]. It may be explained either by the broken-bond model [25], whereby the surface of the particles is enriched by the component with the lower heat of sublimation, or by the size-different model [26], which predicts that the larger atomic volume goes to the surface.

However, as outlined in Table 4, the tin surface concentration drops significantly by increasing the calcination temperature of Table 4

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Binding energy (eV)</th>
<th>Sn/Ru*</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuSn/Al</td>
<td>464.2</td>
<td>487.9</td>
</tr>
<tr>
<td>RuSn/Al-600</td>
<td>461.3</td>
<td>488.0</td>
</tr>
<tr>
<td>RuSnAl</td>
<td>462.2</td>
<td>487.0</td>
</tr>
</tbody>
</table>

* Bulk Sn:Ru atomic ratio = 2.
the coimpregnated catalysts. Similar behavior has indeed been reported before for different bimetallic tin-containing alumina-supported catalysts [27,28]. IRTEM and XPS experiments suggested that high temperatures could enhance tin oxide mobility favoring its redispersion and the oxide could even be inserted into the support structure, particularly when supported onto alumina [27,28].

A Sn/Ru ratio deviation was also seen when sol gel method was used to prepare the catalyst. A further decrease of tin surface concentration was found over RuSnAl, suggesting that most of the Sn\(^{n+}\) might be located in the bulk interacting with alumina.

The results presented in this work indicate that alumina-supported Ru–Sn bimetallic catalysts may indeed be appropriate for 1,6-hexanediol production from DMA. However, the generation of tin oxidic species is not solely decisive for the formation of catalytically active sites. A suitable preparation method must be applied in order to better localize the SnO\(_x\) moieties and tailor the required Ru–SnO\(_x\) selective sites.

4. Conclusions

The catalyst performance confirmed that the presence of tin species is essential to promote chemoselectivity. The spectroscopic results suggested that the localization of Sn\(^{n+}\) moieties at the particles surface, generating Ru–SnO\(_x\), selective sites, is determined by the preparation method applied. Coimpregnation method showed to be effective for 1,6-hexanediol production over RuSnAl\(_2\)O\(_x\) catalysts.

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