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# STUDY OF Pt AND Rh BASED SUPPORTED CATALYSTS MODIFIED WITH TETRABUTYLTIN FOR THE SELECTIVE HYDROGENATION OF 4-METHOXYACETOPHENONE

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**Abstract**

Catalysts based on Pt and Rh modified with $Sn(C_4H_9)_4$ were studied in the hydrogenation of 4-methoxyacetophenone. The selectivity to 1-(4-methoxyphenyl)ethanol was close to 100% at Sn/(Pt,Rh) = 1.0, however the catalytic activity decreased drastically. With respect to the balance between activity and selectivity the catalyst PtSnOM (Sn/Pt=0.4) showed the best performance.

*Keywords*: 4-Methoxyacetophenone hydrogenation, tin modified Pt and Rh catalysts, organometallic chemistry

## INTRODUCTION

The modification of supported metallic catalysts (M/support) by means of the specific reactions with organometallic compounds ($M'R_x$) and applying techniques derived from surface organometallic chemistry, leads to the generation of a special type of catalysts characterized by their efficiency and

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selectivity [1-3]. These catalysts were found to be active and selective in many reactions, such as the hydrogenation of α,β-unsaturated aldehydes to the corresponding unsaturated alcohols [4,5], dehydrogenation of isobutane to isobutene [6], hydrogenolysis of ethyl acetate to ethanol [7], enantioselective hydrogenation of ketones to alcohols [8,9]. The preparation of organobimetallic catalytic phases has been widely studied and it can be described by the following equations [4]:

$$M / Support + ySnR_4 + xy / 2H_2 \rightarrow M(SnR_{4-x})_y / Support + xyRH$$

$$M(SnR_{4-x})_y / Support + (4-x)y / 2H_2 \rightarrow MSn_y / Support + (4-x)yRH$$

With an appropriate selection of the hydrogenolysis conditions in the second stage (773 K in $H_2$ flow for 2 h), a bimetallic alloy type catalyst can be obtained. If, as in case of this work, the preparation reaction stops at the end of the first stage ($M(SnR_{4-x})_y$/Support), an organobimetallic catalyst is obtained. In both cases the solids obtained are catalysts with a specific interaction between the parent transition metal and the promoter.

The catalytic hydrogenation of acetophenone and its derivatives to obtain the corresponding alcohols has a great scientific and practical interest. For instance, the hydrogenation of *p*-isobutylacetophenone leads to the formation of 1-(*p*-isobutylphenyl) ethanol, is a key step of the synthesis of Ibuprofen®, a non-steroidal anti-inflammatory drug [10]. The hydrogenation of substituted aromatic ketones with –OH and -$OCH_3$ groups in the aromatic ring is a less studied, but not less interesting reaction, since the alcohols produced are compounds used as intermediates in organic syntheses [11].

In the present work, supported organobimetallic catalysts based on Pt and Rh and modified with $Sn(C_4H_9)_4$ were studied in the liquid phase hydrogenation of 4-methoxyacetophenone reaction. The properties of both metallic systems were analyzed and the influence of tin contents on the performance of the catalysts was also studied.

## EXPERIMENTAL

### Catalyst preparation

A non-porous $SiO_2$ (Aerosil 200 $m^2g^{-1}$) was used as a support in all preparations. Monometallic catalysts were obtained by ion exchange. In the preparation of 1 wt.% Pt/$SiO_2$ catalyst the precursor was an aqueous solution of the $[Pt(NH_3)_4]^{2+}$ ion. After ion exchange the solid was washed and dried at 373 K, then calcined at 773 K and reduced in a flow of $H_2$ at the same

temperature. 1 wt.% $Rh/SiO_2$ catalyst was prepared by using an aqueous solution of $[Rh(NH_3)_5Cl]Cl_2$ for ion exchange. Then the solid was washed and dried at 373 K, and calcined at 773 K. In this case, in order to preserve the dispersion of Rh, the reduction in flowing $H_2$ was carried out at 673 K [12].

After the reduction step, the monometallic catalysts were reacted with $Sn(C_4H_9)_4$ under a hydrogen atmosphere. The solvents applied were as follows: (i) *n*-heptane, when the reaction temperature was 313 K or 363 K for RhSnOM (Sn/Rh = 0.4) and PtSnOM (Sn/Pt = 0.4), respectively, (ii) *n*-decane for preparing (RhSnOM (Sn/Rh = 1) at 373 K, and (ii) *n*-dodecane for the preparation of PtSnOM (Sn/Pt = 1) at 423 K. Due to the higher hydrogenolysis activity of Rh than that of Pt [4], the surface reaction was performed at lower temperatures on the parent $Rh/SiO_2$ catalyst than on the Pt-containing one. The increase of the amount of tin introduced requires higher temperature for anchoring. Once the reaction was finished, the catalysts were washed with several portions of *n*-heptane in an Ar atmosphere. The resulting catalysts that correspond to solids containing butyl groups anchored onto the metallic surface are denoted as MSnOM catalysts.

## Catalyst characterization

The catalysts were characterized by their chemical composition, temperature programmed reduction (TPR), $H_2$ and CO chemisorption, X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The metal content of the parent catalysts was measured by atomic-absorption-spectroscopy. TPR, $H_2$ and CO chemisorption measurements were performed using a catalytic characterization equipment RXM-100 (Advanced Scientific Designs Inc., USA). The distribution of metal particle size was measured by TEM, using a JEOL CX100 instrument. To estimate the mean particle diameter, the particles were considered spherical and the second moment of the distribution was considered. The XRD spectra were taken using a Philips PW 105 diffractometer with $CuK_\alpha$ radiation. The tin content of catalysts was determined by spectrophotometry using a colorimetric technique.

## Hydrogenation experiments

The hydrogenation of 4-methoxyacetophenone was carried out in the liquid phase, in a batch reactor, at 1.0 MPa and 340 K, using in each experiment 0.25 g of the catalyst and 0.73 g of the ketone; and 60 mL of 2-propanol as a solvent. Identification and quantitative analysis of the reaction products was carried out in a GCMS-QP5050A Shimadzu gas chromatograph using a capillary column SUPELCO SPB$^{TM}$-5 of 30 m length and 0.25 mm diameter.

## RESULTS AND DISCUSSION

Monometallic $Pt/SiO_2$ and $Rh/SiO_2$ catalysts have been characterized by the chemisorption of $H_2$ and CO, TPR, TEM and XRD. Table 1 shows the results of dispersion measured by chemisorption, mean particle size determined by TEM and temperatures of the maxima of hydrogen consumption in the TPR tests.

**Table 1**

Characterization of the monometallic catalysts

| Catalyst | H/M | CO/M | $d_{TEM}$ | TPR (K) |
|---|---|---|---|---|
| $Pt/SiO_2$ | 0.19 | 0.21 | 4.8 nm | 450, 717 |
| $Rh/SiO_2$ | 0.64 | 1.00 | < 1.5 nm | 473, 543* |

* shoulder

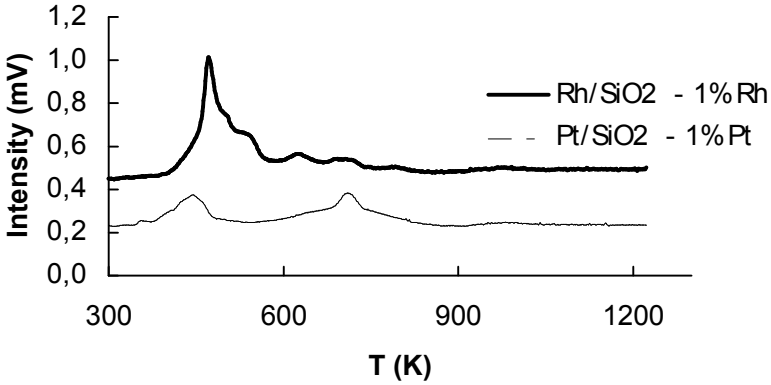


**Fig. 1.** TPR profiles of monometallic catalysts, $Pt/SiO_2$ and $Rh/SiO_2$

As seen from the TEM results in Table 1, with respect to the metal dispersion, both monometallic catalysts showed noticeable differences. In case of the $Rh/SiO_2$ catalyst reduced in $H_2$ at 673 K for 3 h, the H/Rh=0.64 and CO/Rh=1.0 ratios obtained indicate high dispersion, in agreement with XRD data, as no measurable Rh crystallites were detected in the spectrum. The higher CO/Rh value as compared to that of H/Rh, can be assigned to the presence of some

Rh(I) which, at the same time decreases the $H_2$ chemisorption and increases the CO chemisorption by formation of *gem*-dicarbonyls [13]. Chemisorption measurements carried out on $Pt/SiO_2$ catalyst reduced in $H_2$ at 773 K for 2 h, gave H/Pt = 0.19 and CO/Pt = 0.21 ratios indicating a moderate dispersion of the metallic phase. There is a good agreement between the dispersion of Pt measured by chemisorption and calculated from the average crystallite size measured by TEM. Accordingly, XRD results showed the presence of platinum crystallites with an average size around 10 nm. The difference between the average platinum crystallite size obtained by TEM and XRD, 4.8 and 10 nm, respectively can be attributed to the uncertainty of calculation emerged from the broad lines corresponding to metallic Pt in the XRD spectrum of $1\%Pt/SiO_2$ catalyst.

Figure 1 shows the TPR curves of monometallic catalysts. The hydrogen uptake for the calcined $Rh/SiO_2$ sample was 6.68 $cm^3/g_{sample}$, which corresponded to the reduction of *ca*. 95% of Rh(III), whereas the $H_2$ consumption of 3.51 $cm^3/g_{sample}$ and the two peaks for $Pt/SiO_2$ could be assigned to the reduction of $PtO_2$ and Pt species interacting more strongly with the support [14].

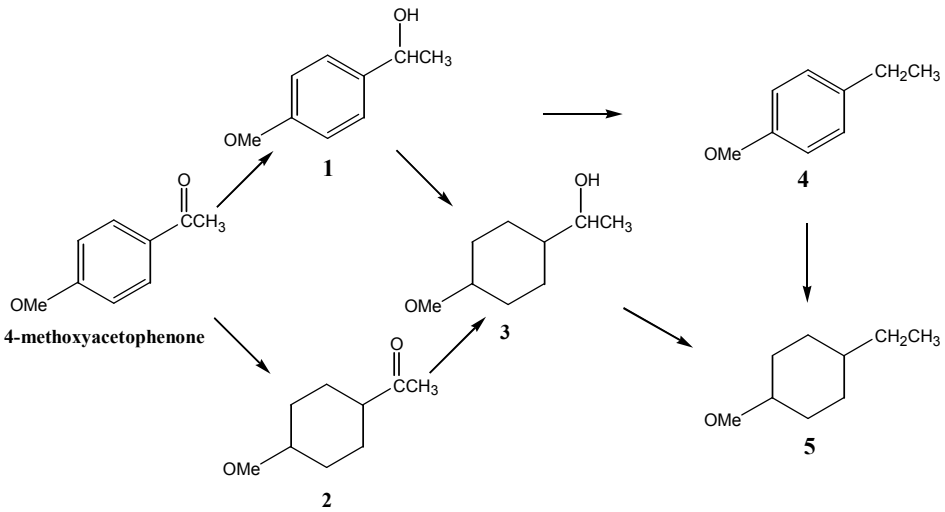


**Fig. 2.** Simplified reaction scheme for the hydrogenation of 4-methoxy-acetophenone

Figure 2 shows the scheme of the probable reaction routes and products in the hydrogenation of 4-methoxyacetophenone. Hydrogenation of the C=O group results in the formation of 1-(4-methoxyphenyl)ethanol (**1**), the desired

product in this study. The hydrogenation of the aromatic ring leads to the formation of 4-methoxycyclohexyl-methylketone (**2**). The subsequent hydrogenation of (**1**) and/or (**2**) leads to the formation of 1-(4-methoxycyclohexyl)-ethanol (**3**). From (**1**), it is also possible to obtain 4-ethylphenylmethylether (**4**) via hydrogenolysis, whose subsequent hydrogenation generates 4-ethylcyclohexylmethylether (**5**). This product can also be obtained by the hydrogenolysis of the C-OH bond of (**3**).

In order to study the effect of the tin modifier, in a first step, the hydrogenation of the 4-methoxyacetophenone over monometallic catalysts $Rh/SiO_2$ and $Pt/SiO_2$ was studied. Results given in Table 2 indicate that the $Rh/SiO_2$ catalyst has a similar activity (measured as TOF) to that of the $Pt/SiO_2$ catalyst. Both monometallic systems showed moderate selectivity values to 1-(4-methoxyphenyl)ethanol due to the appearance of a variety of products. Figures 3a and 3b show the changes in the composition of the reaction mixture as a function of reaction time for both monometallic systems. In case of the $Rh/SiO_2$ catalyst (Fig. 3a), the amount of 1-(4-methoxyphenyl)ethanol is small and reacts quickly to give other products, mainly 4-ethylphenylmethylether, 4-ethylcyclohexylmethylether, ethylcyclohexane, methoxycyclohexane and 4-ethylcyclohexanone. This is in agreement with the higher hydrogenating and hydrogenolyzing activity of Rh, as it was observed in the hydrogenation of esters to alcohols, in which the selectivity loss is due to the cleavage of the C-OH bond in the presence of hydrogen [15,16]. For the $Pt/SiO_2$ catalyst (Fig. 3b), a higher selectivity to 1-(4-methoxyphenyl)ethanol is observed, although the contribution of consecutive reactions of hydrogenation and hydrogenolysis leads to different products, principally 4-ethylphenylmethylether, 4-ethyl-1-methoxycyclohexane, ethylcyclohexane and 1-cyclohexylethanol. The concentration of different products shown in Figs 3a and 3b indicate that on the two monometallic catalysts, 1-(4-methoxyphenyl)ethanol is the only primary product of the hydrogenation reaction; the other products are always secondary products formed in consecutive reactions from **1**. The inhibition of the hydrogenation of the aromatic ring leading to the formation of **2** has already been observed in the hydrogenation of 3,4-dimethoxyacetophenone by using $Pt/SiO_2$ catalysts [9,17,18]. This behavior can be explained by the increase of repulsion between the aromatic ring and the catalyst surface, due to the presence of an electron-donating group such as the $-OCH_3$ group in the ring.

Hydrogenation of 4-methoxyacetophenone was also performed over the tin modified $Rh/SiO_2$ and $Pt/SiO_2$ catalysts. Tin was introduced by means of a controlled surface reaction between $Sn(C_4H_9)_4$ and the previously reduced monometallic catalysts. As seen from the data given in Table 2 the bulk Sn/M atomic ratio was adjusted to 0.4 and 1.0 by varying the condition of preparation (temperature and concentration of $Sn(C_4H_9)_4$ solution). Due to the lower dispersion of Pt than that of Rh, the $Sn/M_{surface}$ ratios were found to be

significantly higher for the Pt organobimetallic catalysts (PtSnOM).

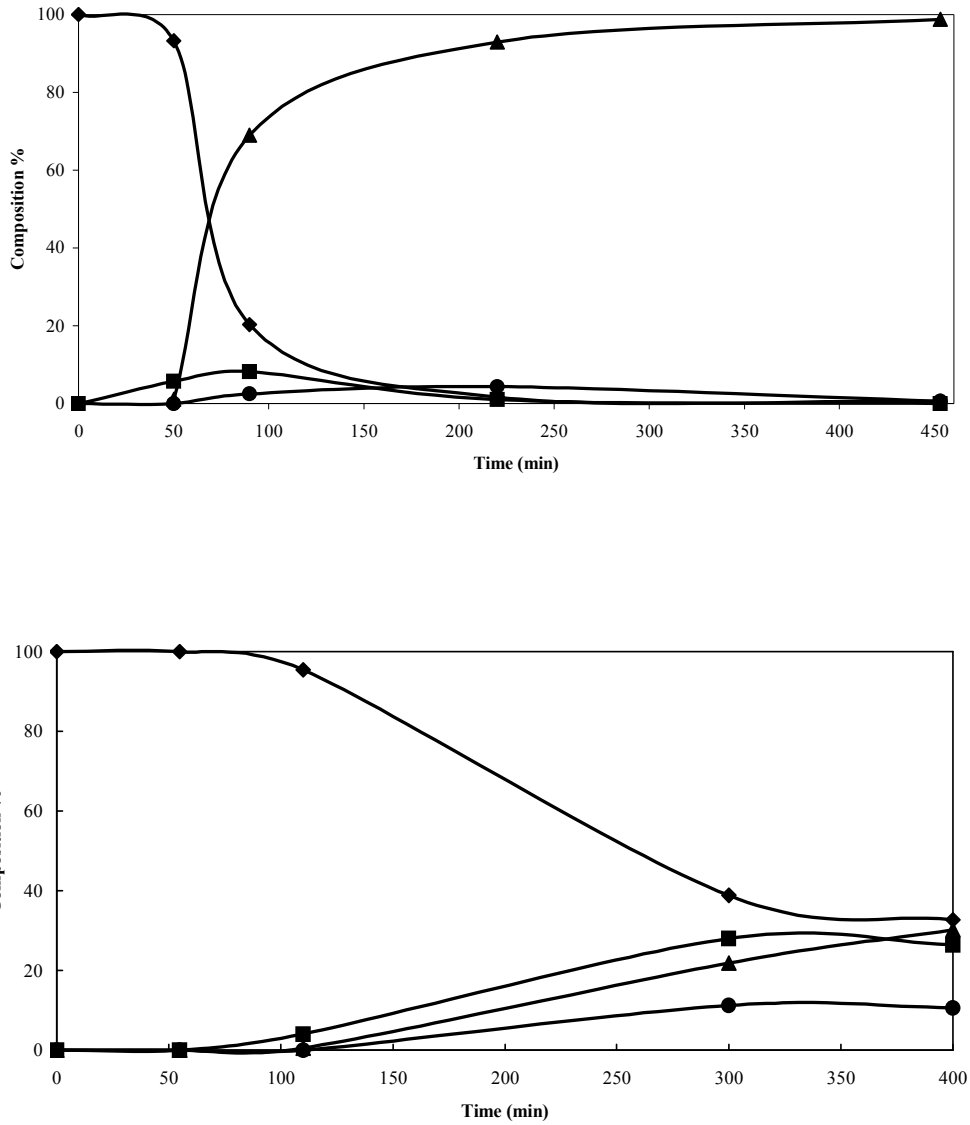


**Fig. 3.** Hydrogenation of 4-methoxyacetophenone. Concentration profiles along the reaction time on **(a)** $Rh/SiO_2$ and **(b)** $Pt/SiO_2$. (◆)4-methoxyacetophenone; (ν)1-(4-methoxyphenyl)ethanol; (●)(1-methylethyl)-1-(4-methylphenyl) ethyl ether; (σ)other reaction products (described in the text). For reaction conditions, see the text

The presence of tin changes considerably the catalytic performance, both in terms of activity and selectivity. TOF values related to the total Group VIII metal content of the catalysts are also listed in Table 2. The reaction rate for supported organobimetallic catalysts is significantly lower than the one corresponding to monometallic catalysts and the reaction rate is a function of the amount of tin anchored on the parent metal. In Figs 4a and 4b the evolution of the composition of the reaction mixture is shown as a function of time for RhSnOM (Sn/Rh = 0.4) and PtSnOM (Sn/Pt = 0.4), respectively. The presence of tin enhances the selectivity to the desired product. This behavior can be attributed to the effect of a "dilution" of M atoms together with an electronic modification of Group VIII metal by the presence of tin. This was already evidenced by XPS, EXAFS/XANES and Mössbauer spectroscopy for similar catalytic systems [4,19,20]. The existence of $Sn(C_4H_9)_x$ fragments on the catalytic surface of MSnOM systems results in an additional steric effect. These effects favor the interaction of the substrate with the catalyst surface, more precisely with the promoter atom, via the C=O group facilitating the formation of 1-(4-methoxyphenyl)ethanol.

**Table 2**

TOF ($s^{-1}$) in the hydrogenation of 4-methoxyacetophenonene

| Catalyst | $Pt/SiO_2$ | PtSnOM | PtSnOM | $Rh/SiO_2$ | RhSnOM | RhSnOM |
|---|---|---|---|---|---|---|
| $Sn/M_{bulk}$ | 0 | 0.4 | 1.0 | 0 | 0.4 | 1.0 |
| $Sn/M_{surface}$ | 0 | 2.1 | 5.3 | 0 | 0.63 | 1.6 |
| TOF ($s^{-1}$) | 0.094 | 0.030 | 0.001 | 0.095 | 0.015 | 0.002 |

Experimental conditions are given in the text

In all cases an ether (1-methylethyl)-1-(4-methylphenyl) ethyl ether) appears among the reaction products formed in the reaction between the alcohol as primary product (**1**) and the solvent (2-propanol). The presence of the $–OCH_3$ group in *para*- position increases the reactivity of the -OH group of 1-(4-methoxyphenyl)ethanol favoring in this way the etherification reaction.

The selectivity to 1-(4-methoxyphenyl)ethanol was significantly higher on catalysts with Sn/M = 0.4 ratio than over the monometallic catalysts (Fig. 5). The selectivity of the desired alcohol **1** was higher than 80 % on platinum based organobimetallic catalysts in the whole range of conversions measured. On the contrary, in case of rhodium-based organobimetallic catalysts, consecutive hydrogenolysis reactions take place, resulting in products such as **4** and **5**, thus decreasing the selectivity to alcohol **1**. Over the catalysts with the largest tin loading (Sn/M = 1.0), selectivity to the desired product reached almost 100%

but the catalytic activity decreased drastically. The very low activity of these catalysts can be explained by the high $Sn/M_{surface}$ atomic ratios and the poisoning effect of tin organic moieties.

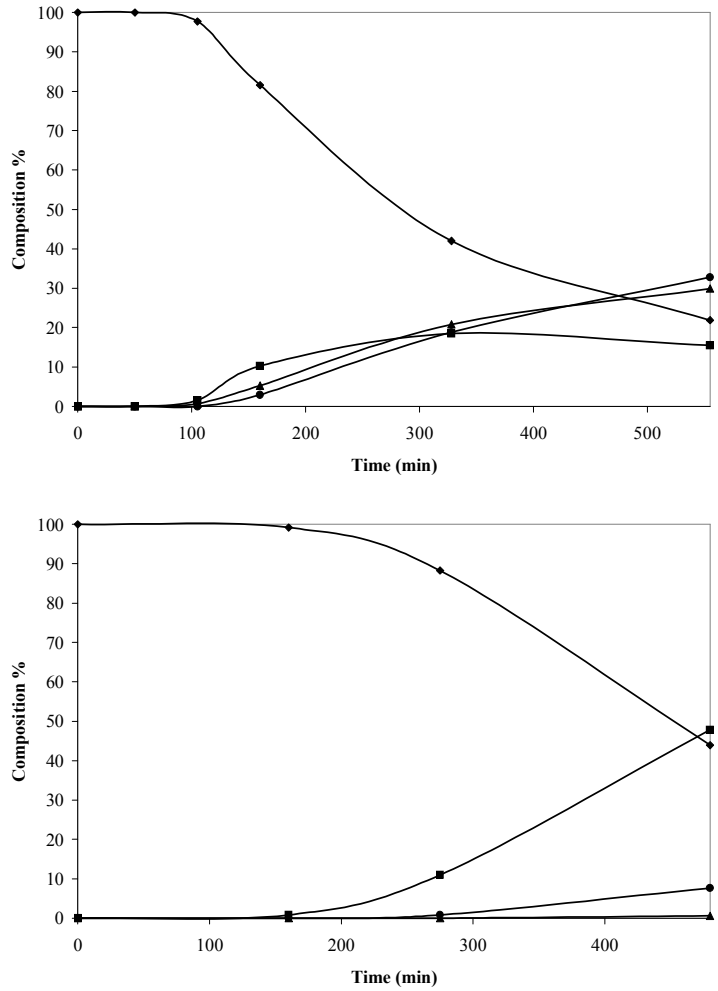


**Fig. 4.** Hydrogenation of 4-methoxyacetophenone. Concentration profiles along the reaction time on **(a)** RhSnOM (Sn/Rh=0.4) and **(b)** PtSnOM (Sn/Pt=0.4). (◆)4-methoxyacetophenone; (ν)1-(4-methoxyphenyl)ethanol; (●)(1-methylethyl)-1-(4-methylphenyl) ethyl ether; (σ)other reaction products (mainly 4-ethylphenylmethylether; in the case of RhSnOM small quantities of 4-ethylcyclohexylmethylether, ethylcyclohexane, methoxycyclohexane and 4-ethylcyclohexanone). For reaction conditions, see the text.

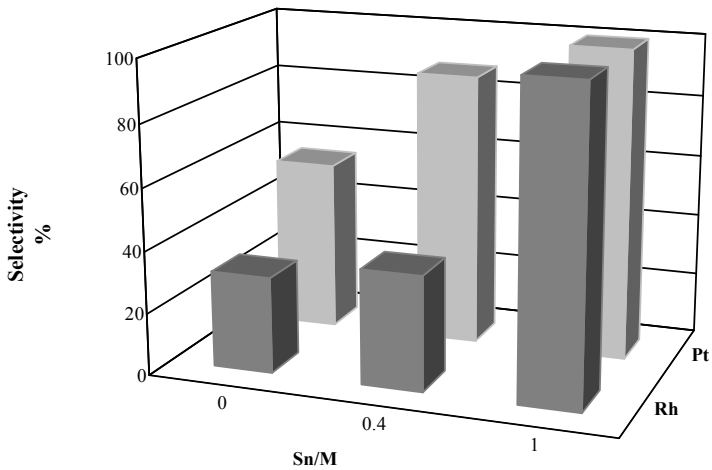


**Fig. 5.** Selectivity to 1-(4-methoxyphenyl)ethanol at 50% conversion for all catalysts studied (in the case of MSnOM catalysts having Sn/M = 1, the selectivities were measured at 1% conversion). Experimental conditions are given in the text

## CONCLUSIONS

The main conclusions of this work can be summarized as follows:

Monometallic $Rh/SiO_2$ and $Pt/SiO_2$ catalysts are highly active in the liquid phase hydrogenation of 4-methoxyacetophenone. Because of their high hydrogenating capacity, the monometallic catalysts are unselective to the desired product, *i.e.* 1-(4-methoxyphenyl)ethanol.

$Rh/SiO_2$ and $Pt/SiO_2$ catalysts modified with $Sn(C_4H_9)_4$ were more selective to 1-(4-methoxyphenyl)ethanol. The modification of platinum catalysts with tin allowed to achieve more than 90% selectivity to the desired alcohol in the whole conversion range studied. On the contrary, in the case of rhodium-containing catalysts, consecutive hydrogenolysis reactions decreased the selectivity to alcohol **1**.

The presence of tin and $Sn(C_4H_9)_x$ fragments on the catalyst surface are responsible for the activation of the C=O group of substrate, and thus for the formation of 1-(4-methoxyphenyl)ethanol with high selectivity.

The activity of catalysts modified by tin depends strongly on the Sn/M (M=Pt, Rh) atomic ratio. The selectivity to the desired alcohol was almost 100 %, but the catalytic activity decreased drastically when Sn/M = 1.

Taking into account both the activity and selectivity values, it was found that the PtSnOM (Sn/Pt = 0.4) catalyst showed the best performance in the hydrogenation of 4-methoxyacetophenone to 1-(4-methoxyphenyl)ethanol.

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