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Chemoselective hydrogenation of aromatic ketones with Pt-based heterogeneous catalysts. Substituent effects.

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Keywords: aromatic ketones, bimetallic catalysts, PtSn, Surface Organometallic Chemistry of Metals.

Highlights

PtSn catalysts were obtained by a surface reaction between Pt and SnBu₄.

PtSn systems have been active in the hydrogenation of aromatic ketones.

The substituents groups could influence in the adsorption mode of aromatic ketones.

PtSn catalysts lead to an increase in the selectivity to unsatured alcohol.

Sn presence favors the interaction through C=O, hindering the adsorption of ring.

ABSTRACT

Catalytic reduction of aromatic ketones is an interesting reaction that leads to the obtaining of alcohols. Some of these alcohols are employed as intermediaries to produce chemical fine compounds. The bimetallic catalysts are widely used in the chemoselective hydrogenation. The Surface Organometallic Chemistry on Metals (SOMC/M) is a methodology employed to obtain bimetallic systems.

In the present work the hydrogenation of ketones derived from acetophenone has been studied. The aim was observe the effect on activity and selectivity to aromatic alcohols by the presence of substituents in the ring. The chemical characteristics of substituents groups could influence the way aromatic ketones are absorbed on the metallic surface. This fact can be explained by a combination of geometric and electronic effects.

1. INTRODUCTION

The catalytic reduction of aromatic ketones is a reaction of considerable interest, since it leads to the production of alcohols used as intermediates in organic synthesis, in the manufacture of pharmaceuticals, flavors, and others. The hydrogenation of 1-phenyl-ethanone (acetophenone) to its corresponding alcohol (1-phenyl ethanol) obtained by reduction of carbonyl group is a classic example of these reactions [1, 2]. However, the selective hydrogenation of aromatic ketones is not easy due to the variety of products that can be obtained, both for the hydrogenation of C=O group and/or the aromatic ring as well as for the hydrogenolysis of alcohols generated in the first reaction step.

In general, reduction of unsaturated carbonyl compounds is usually carried out using supported metal catalysts. Monometallic systems including Pd, Pt, Rh, Ag, Ni and Ru have been employed in acetophenone hydrogenation [3, 4]. Rh-based catalysts, supported over C, allowed to obtain a selectivity to unsaturated alcohol in about 70 %, using moderate pressure [5]. Acetophenone hydrogenation over Ni/SiO₂ and Ni/Y catalysts resulted in high selectivity to phenylethanol (about 70 %). However, in some of them the conversion was less to 10 % [1].

Pt is one of the most employed metals in the hydrogenation of carbonyl and phenyl groups. Thereby, Chen et al. have been used Pt/SiO_2 catalyst like a model to study acetophenone hydrogenation. These authors have been studied the adsorbed species on Pt reduced by IR spectroscopy [4]. As will be discussed later, competitive

hydrogenation between the carbonyl and phenyl groups, and therefore the reaction selectivity, depends of adsorption mode of acetophenone molecule on metallic surface.

It is well known that the use of bimetallic systems may be advantageous to achieve higher activity, stability and/or selectivity to the desired product [3, 6]. Bimetallic catalysts such as Ru-Cr, Rh-Sn and Ni-Pt have been employed in the hydrogenation of acetophenone in liquid fase [3]. In the last case, bimetallic system produced an increase in the stability; however the selectivity to unsaturated alcohol is lower than achieved with monometallic catalyst [7].

There are different strategies for obtaining bimetallic systems [8]. One of the methodologies derived from Organometallic Surface Chemistry on Metals (SOMC/M). These techniques allow to prepare controlled catalytic phases, by reaction of a supported transition metal with an organometallic compound as $M'R_n$ (M' = Sn, Pb, Ge, Sb; R = Me, Et, Bu, etc.; n = 3, 4). These interactions lead to catalytic systems with good properties which have better activity and selectivity than the catalysts prepared by conventional methods [9].

In our research group, we have vast experience in the preparation of bimetallic catalysts based on Pt, Rh and Ni modified $SnBu_4$ using n-heptane or n-decane as a solvent. These systems proved to be active and selective in a wide range of hydrogenation reactions of interest in fine chemistry [10-12].

The hydrogenation of ketones derived from acetophenone has been much less studied. It has been reported in the literature the hydrogenation of phydroxyacetophenone, o-methylacetophenone and 2-methylpropyl-acetophenone on Nibased catalysts, however very low conversions have been achieved [1]. There are a few works about the influence of substituents of aromatic ring on activity and selectivity, but they study primarily enantioselective hydrogenations [13].

In this paper, we propose to study the hydrogenation of 1-(phenyl) ethanone (AP), 1-(4-metoxyphenyl) ethanone (4-MeOAP), 1-(4-chlorophenyl) ethanone (4-ClAP) and 1-(2-metylphenyl) ethanone (2-MeAP) using PtSn and Pt catalysts supported on silica. The objective is to analyze the influence of the chemical nature of the substituents groups on the aromatic ketones ring, as has been reported in literature that these groups can influence the selectivity and/or catalytic activity [14].

2. EXPERIMENTAL

2.1 Preparation of the catalysts

The Pt/SiO₂ monometallic catalyst was prepared by ionic exchange. The SiO₂ (Evonik, 180 m²/g) used as support was previously functionalized by treating it with an ammonia solution of pH 10.6, under continuous stirring for 30 minutes at room temperature. The resulting solid was contacted with an aqueous solution of the precursor, Pt(NH₃)₄Cl₂ (Aldrich), which has the appropriate concentration to obtain 1wt.% of Pt in the final catalyst. After 24 h of exchange, the solid was separated by filtration, dried in an oven at 105 °C, calcined in air at 500 °C and subsequently reduced in H₂ at 500 °C for 2 h. The catalyst so obtained was designated Pt.

For obtaining the bimetallic PtSn systems, techniques derived from Surface Organometallic Chemistry of Metals (SOMC/M) were used. These techniques consist of a controlled surface reaction between a reduced monometallic catalyst (Pt) and a solution of an organometallic compound (SnBu₄) in a paraffinic solvent. In this work, bimetallic systems with Sn/Pt atomic ratios 0.2 and 0.8 were prepared; those systems have been designated PtSn0.2 and PtSn0.8, respectively. The reaction between the monometallic catalyst and the organotin compound solution was carried out under a H₂ atmosphere for 4 h. The temperature used for the reaction was 90 and 120 °C for the preparation of the PtSn0.2 and PtSn0.8 systems, respectively. In the first case, n-heptane was used as solvent while for the catalyst with the highest tin content, n-decane was employed. The bimetallic systems obtained were then washed with n-heptane in flowing N₂, dried in an oven at 105 °C and finally reduced at 500 °C in H₂ flow for 2 h.

2.2 Catalysts characterization

The Pt content of the catalysts was determined by atomic absorption spectrometry (Varian Spectra AA55). The amount of Sn present in the catalysts was measured by gas chromatography analysis of the solution containing the organometallic compound, as a function of reaction time, using a Varian CP-3800 gas chromatograph, equipped with a FID detector and a Factor Four (VF-1 ms, 15mx0.25mm ID DF = 0.25) capillary column.

Temperature-programmed reduction (TPR) tests were performed on an instrument built in the laboratory, equipped with a thermal conductivity detector, using a mixture

having a composition of 5% H_2 in N_2 at a flow of 25 mL/min. The tests were conducted from 20 to 850 °C with a heating rate of 10 °C/min. For the measurement of H_2 adsorption the method of the static volumetric chemisorption at room temperature was used, employing an instrument from Advanced Scientific Designs Inc., USA.

The particle size distribution of the solids was determined by transmission electron microscopy (TEM) in a JEOL 100 CX microscope with a resolution of 6 Å and an accelerating voltage of 100 kV. The samples were prepared by its suspension in bidistilled water and subsequent dispersion in an ultrasonic bath.

Analysis by X-ray photoelectron spectroscopy (XPS) was performed on a multitechnical system (SPECS) equipped with a dual Mg/Al X-ray source and a PHOIBOS 150 hemispherical analyzer operating in FAT (fixed analyzer transmission) mode. Spectra were obtained with an energy flow of 30 eV, an Al-K α X-ray source operating at 100 W and 10 kV and at a pressure of the analysis chamber lower than 5x10⁻⁷ Pa. Data processing was performed with the XPS Casa program (Casa Software Ltd., UK). C1s signal that appears at 284.6 eV was used as reference.

2.3 Hydrogenation of aromatic ketones

The ketones chosen for the present study were 1-(phenyl) ethanone (AP), 1-(4metoxyphenyl) ethanone (4-MeOAP), 1-(4-chlorophenyl) ethanone (4-ClAP) and 1-(2metylphenyl) ethanone (2-MeAP). Hydrogenation reactions of the aromatic ketones were conducted in a batch reactor at 80 °C and a H₂ pressure of 1 MPa. In each catalytic test, 0.25 g of catalyst, a substrate concentration of 0.07 M and 2-propanol as solvent were used. The progress of the reaction was followed by gas chromatography on a Varian CP-3800 gas chromatograph equipped with a CP wax 52 CB (30 m, 0.53 mm ID) capillary column and a FID detector. The products were identified by GC/MS on a Shimadzu QP5050 instrument with a SUPELCO SPBTM-5 (30 m, 0.25 mm ID) capillary column.

3. RESULTS AND DISCUSSION

3.1 Results of catalysts characterization.

The catalysts Pt and $PtSn/SiO_2$ were characterized by atomic absorption, CO and H_2 chemisorption, temperature-programmed reduction and transmission electron microscopy. The results are shown in Table 1.

For monometallic catalysts preparation, the impregnation method by cation exchange was selected. This method allow to obtain reproducible systems with high dispersions (H/Pt = 0.65, CO/Pt = 0.55). This last feature is very important for obtaining bimetallic catalysts from controlled surface reactions.

The TPR assays results obtained for Pt catalyst system evidenced the presence of two peaks: one at about 250 °C and another at 450 °C. According to the literature, the low temperature peak can be assigned to the presence of Pt(IV) species, originated during the calcination pretreatment. The high temperature peak could be assigned to species of the type Pt-(O-Si \equiv)_y^{n-y} (n = 2⁺ or 4⁺), formed through the interaction of metallic precursor and the support [15].

The systems PtSn were prepared by a controlled surface reaction between the monometallic catalyst, previously reduced, and a solution of $SnBu_4$ in a paraffinic solvent. The reaction occurs in two stages. In the first, a system with organotin moieties anchored to the surface is obtained. In the second stage, at highest temperature, the organic fragments are eliminated and a bimetallic system is formed. The following equations represent the above-mentioned processes:

$$Pt/SiO_2 + ySnBu_4 + xy/2H_2 \rightarrow Pt(SnBu_{4-x})y/SiO_2 + xyBuH$$
(1)

 $Pt(SnBu_{4-x})/SiO_2 + (4-x)y/2H_2 \rightarrow PtSn_y/SiO_2 + (4-x)yBuH$ (2)

In the present work, catalysts with atomic ratios Sn/Pt of 0.2 and 0.8 were prepared. Regarding the first atomic ratio, n-heptane was used as solvent and the reaction proceeded at 90 °C. As regards the catalyst with higher tin content, n-decane was used as solvent and 120 °C as reaction temperature. The stoichiometry of the bimetallic catalyst was determined by chromatographic analysis, from the difference between the initial concentration of the organometallic solution and the concentration after four reactions hours [16].

Blank tests performed on the support demonstrated the specificity of the reactions which take place during the preparation of bimetallic catalysts through SOMC/M techniques, concluding that amounts of organotin modifier on SiO_2 were not detected.

TEM results for the three catalysts prepared are shown in Table 1. As can be seen, in all cases the mean particle size is about 2 nm. This value remains almost constant for the bimetallic catalysts, indicating that the addition of tin does not practically affect the particle size distribution with respect to the monometallic system. These results, consistent with other preliminary work, show the high specificity of the preparation method of bimetallic catalysts (SOMC/M). In the same way, tin addition decreases the value of chemisorbed H_2 (Table 1).

In Table 2 it is reported the binding energies (BE) of the Pt $4f_{7/2}$ and Sn $3d_{5/2}$ levels for Pt/SiO₂, PtSn0.2 and PtSn0.8 catalysts. For all the catalysts, the region corresponding to Pt $4f_{7/2}$ showed a single peak, which is characteristic of platinum in the metallic state [17]. It can also be seen that the BE undergoes a shift from 71.6 eV for the monometallic catalyst to 71.1 and 70.8 eV for PtSn0.2 and PtSn0.8 systems, respectively. The increase in the electronic density of platinum leads to the formation of polarized states of $Pt^{\delta-}$ and $Sn^{\delta+}$, which would be important in the chemisorption of reagents containing double C=O. This fact is indicative of the existence of an electronic effect of tin over platinum, in agreement with previous results obtained in studies performed with PtSn catalysts supported, prepared by SOMC/M techniques [18, 19]. The Sn 3d_{5/2} spectra for the bimetallics PtSn0.2 and PtSn0.8 present two bands, one centered at ca. 484 eV which can be ascribed to reduced tin, and another one at higher BE (486.3 and 487.3 eV for PtSn0.2 and PtSn0.8, respectively), which is attributed to oxidized tin (Sn(II) and Sn(IV)) [17, 20]. On the other hand, both bimetallic samples have similar $Sn(0)/Sn_{total}$ ratio (Table 2); the Sn(0)/Pt ratio increases when the amount of tin increases [16]. The presence of metallic tin in bimetallic catalysts is indicative of the existence of bimetallic PtSn phases (even alloys); as it has been readily assessed by EXAFS analysis performed on analogous systems as the ones here employed [18]. Tin oxidized species may be covering the metal particles in the metal-support interface.

3.2 Hydrogenation reaction

Figure 1 shows the main products from the hydrogenation of 1-(phenyl) ethanone (AP) and its derivatives. As can be seen, the hydrogenation of the C=O leads to the production of the corresponding aromatic alcohols, which are usually the desired product. Furthermore, if the aromatic ring is reduced, saturated ketones are produced. Finally, the saturated alcohols are obtained by the hydrogenation of either of the

products above. Other possible reaction products are ethyl benzene and ethyl cyclohexane, and their substituted derivatives.

The objective of this paper is to analyze the influence of the presence of substituents on the aromatic ring on the activity and selectivity achieved. For this reason, AP derivatives with substituents in different ring positions and/or electronic properties have been selected. Both effects would have influence at the adsorption mode on the metal surface. In this way, the results obtained can be explained from a balance between steric and electronic effects, result of presence of substituent on the aromatic ring.

The ketones selected for this work are AP, 2-MeAP, 4-MeOAP and 4-ClAP. As can be seen, the substituents of two of the ketones are in para- position and therefore far from the C=O group, whereas in the 2-MeAP the substituent is located very close to this group. As for the electrical characteristics, $-CH_3$ (-Me) and $-OCH_3$ (-OMe) groups are electron donors, while the -Cl group is an electron acceptor. Both effects would have influence at the adsorption mode on the catalyst surface.

It is important to emphasize that, in all the cases mentioned in this work, the reaction is initiated by the hydrogenation of the C=O group. The change of the reaction mixture composition as a function of time for the hydrogenation of AP, 2-MeAP, 4-MeOAP and 4-ClAP is shown in Figure 2, 3, 4 and 5, respectively. As can be seen, both the monometallic catalyst systems as well as PtSn initially formed 1-(phenyl) ethanol and its corresponding derivatives. As will be discussed further below, the figures show that the presence of tin produces changes in the activity and selectivity obtained.

In Table 3, the initial reaction rate and selectivity to the desired products (to 50% conversion), for the aromatic ketones and the catalysts studied, are reported. The different ways that the ketone molecules can approach the metal surface could explain the results. According to reported by Chen et al, there are two preferential modes of adsorption of AP molecule on Pt surface [4]. One of them considers that the molecule of 1-(phenyl) ethanone approaches to the metal surface through the oxygen of the C=O group (Figure 6a) and the aromatic ring, which is parallel to it, is susceptible to attack dissociated hydrogen on metal. The other mode of adsorption contemplates that the carbonyl group interacts with Pt via π electrons and the aromatic ring is tilted with respect to the metal surface (Figure 7a).

In accordance with what was stated in the previous paragraph, for the monometallic catalyst, it is expected that the presence of electron donor groups (- CH_3)

and -OCH₃) (Figure 6b and 6c) increase the electronic repulsion between the ring and the metal surface and both favor the hydrogenation of the carbonyl group, compared with the AP. The selectivity results reported in Table 3 for the catalyst based on Pt shows one consequences of this. For 2-MeAP y 4-MeOAP the aromatic alcohol selectivity is superior to that achieved for the same AP conversion (74, 75 and 63%, respectively, at 50% conversion). On the other hand, it is expected that the electronic effect of substituents electron donors causes an increase in the initial reaction rate to AP, considering that we have observed that the hydrogenation starts by the attack to the C=O. In this way, in Table 3 can also be seen that the initial rate of hydrogenation for 4-MeOAP is higher than for AP. However, it is observed for the 2-MeAP a decrease in the initial activity respect to unsubstituted ketone. In Figure 7b it can be seen that the methyl group in ortho- position exerts a steric impediment, which could be responsible for the decrease in the observed rate for this substrate. This geometric impediment would have less significance in the case of the substituents in the para-position, furthest from C=O (Figure 7c and 7d).

For the 4-ClAP, the molecule has an electron attractor group (-Cl) to favor the adsorption by the aromatic ring (Figure 6d). In Table 3 can be seen that this fact affects both the activity and selectivity to the desired product. Thus, the initial reaction rate is less than half that achieved for AP (69 and 156 µmoles.gPtsup⁻¹.s⁻¹, respectively). Regarding to target product selectivity, the observed value was lower than the corresponding unsubstituted ketone (55 and 63%, respectively, 50% conversion).

As is known, the addition of a more electropositive metal on the Pt leads to geometric and electronic modifications that affect the activity and selectivity of the catalyst system. On the one hand, the blocking of active sites for hydrogenation can lead to decrease the reaction rate. Furthermore, the presence of electrophilic tin favor polarization of C=O group and hence the reduction [3]. Moreover, in our case, the geometric effect could difficult the ring adsorption of the aromatic ketones and modify the selectivity and the initial rate of hydrogenation.

As seen in Table 3, selectivity to corresponding unsaturated alcohols increases with the presence of tin for all tested ketones. Moreover it should be noted that the selectivity is higher for the catalyst with higher atomic ratio Sn/Pt (PtSn0.8). This could be attributed to the combination of the mentioned effects above: the C=O polarization by electronic effects and/or impediment of adsorption through the ring, by blocking active sites. It is also important to highlight that the most pronounced effect is evident

for the hydrogenation of 4-ClAP. In this case, the presence of -Cl (electron-acceptor group) promotes the ring adsorption on the monometallic catalyst surface. Blocking of active sites by the presence of Sn prevents this adsorption mode, leading to a marked increase in selectivity respect to monometallic system.

In Table 3, the initial rates for the catalysts PtSn are also reported. As can be seen in this Table, for AP, 2-MeAP and 4-MeOAP, the rate decreases as the Sn content increases, due to the blocking of active sites for hydrogenation. However, as shown in the Table, for 4-ClAP is observed a marked increase in the initial reduction rate. To explain this result we must remember that initially (less than 10 % of conversion) the only product formed comes from the hydrogenation of C=O. As has already been mentioned, the initial reaction rate for 4-ClAP is about half of the AP, on the monometallic catalyst. This fact can be attributed to the better attraction of the substituted aromatic ring on the metal surface. As some sites are blocked by the Sn, it would be harder to approach to the ring, favouring the hydrogenation of the carbonyl group and, therefore, increasing the initial speed (Figure 7d).

As a summary, in Table 4 can be seen the relationship between initial rate of hydrogenation of 1-(phenyl) ethanone and initial rates of substituted ketones. It can be observed, that in the presence of Sn the rate ratios for different ketones keep the tendency observed for Pt, but the relative rates approach each other with the Sn content increase. As noted above, these results might be due to a combination of steric and electronic effects, as a result of ring substituents.

4. CONCLUSIONS

The main conclusions that can be derived from this study are summarized below:

In the hydrogenation of 2-MeAP and 4-MeOAP, employing Pt/SiO₂ system, it was observed an increment in the selectivity to aromatic alcohol in relation to the one obtained for AP (74, 75 and 63%, respectively, at 50% of conversion). The initial rate for the hydrogenation of 4-MeOAP was higher than the one achieved for AP, whereas for 2-MeAP it was observed a decrease in the initial activity with respect to the non-substituted ketone.

The activity and selectivity to desired product in the hydrogenation of 4-ClAP were lower than those obtained for AP.

When Pt-based catalysts modified with $SnBu_4$ were employed for the hydrogenation of aromatic ketones, it was observed an increase in the selectivity to unsatured alcohol. This fact can be explained from geometric an electronic effects due to the presence of Sn. These effects encourage the interaction through C=O, hindering the adsorption of aromatic ring.

Finally, it was observed that the rate decreases with the Sn content for the hydrogenation of AP, 2-MeAP y 4-MeOAP. This can be understood through blockage of the active sites for the hydrogenation. For 4-ClAP it was seen a marked increase of the initial reduction rate. In this case, the Sn presence could hinder the ring adsorption, encouraging the carbonyl group hydrogenation and therefore increasing the initial rate.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- R.V. Malyala, C.V. Rode, M. Arai, S.G. Hegde, R.V. Chaudhari, Appl. Catal., A 193 (2000) 71–86.
- [2] A.F. Trasarti, N.M. Bertero, C.R. Apesteguía, A.J. Marchi. Appl. Catal. A: General 475 (2014) 282- 291.
- [3] P. Mäki-Arvela, J. Hájek, T. Salmi, D.Yu. Murzin, Appl. Catal. A: General 292 (2005) 1–49.
- [4] Ch. Cheng, H. Chen, W. Cheng, Appl. Catal. A: Gen. 248 (2003) 117-128.
- [5] I. Bergault, P. Fouilloux, C. Joly-Vuillemin, H. Delmas, J. Catal. 175 (1998) 328-337.
- [6] W. Yu, M.D. Porosoff, J.G. Chen. Chemical Reviews 112 (2012) 5780-5817.
- [7] M.A. Keane, J. Mol. Catal. A: Chem. 118 (1997) 261-269.
- [8] O. S. Alexeev, B. C. Gates, Ind. Eng. Chem. Res. 42 (2003) 1571-1587.
- [9] O.A. Ferretti and M.L. Casella, in M. Basset, R. Psaro, D. Roberto, R. Ugo(Eds.), Modern Surface Organometallic Chemistry, Wiley VCH Verlag GmbH, Weinheim, 2009, pp.239-291.
- [10] V. Vetere, M.B. Faraoni, G.F. Santori, J. Podestá, M.L. Casella, O.A. Ferretti, J. Catal. 226(2) (2004) 457-461.

- [11] M.L. Casella, G.F. Santori, A. Moglioni, V. Vetere, J.F. Ruggera, G. Moltrasio Iglesias, O.A. Ferretti, Appl. Catal. A: General 318 (2007) 1-8.
- [12] V. Vetere, A.B. Merlo, J.F. Ruggera, M.L. Casella, J. Braz. Chem. Soc. 21 (2010) 914-920.
- [13] A. Vargas, T. Bürgi, M. von Arx, R. Hess, A. Baiker J. Catal. 209 (2002) 489-500.
- [14] R. Hess, T.Mallat, A.Baiker, J. Catal. 218 (2003) 453-456.
- [15] L.-W. Ho, C.-P. Hwang, J.-F. Lee, I. Wang, C.-T. Yeh, J. Mol.Catal. A: Chemical 136 (1998) 293–299.
- [16] A.B. Merlo, B.F. Machado, V. Vetere, J.L. Faria, M.L. Casella. Appl. Catal. A: General, 383 (2010) 43-49.
- [17] C.D. Wagner, NIST X-ray Photoelectron Spectroscopy Database, Gaithersburg, 1989.
- [18] J.M. Ramallo-Lopez, G.F. Santori, L. Giovanetti, M.L. Casella, O.A. Ferretti, F.G. Requejo, J. Phys. Chem. B 107 (2003) 11441–11451.
- [19] G.J. Siri, J.M. Ramallo-López, M.L. Casella, J.L.G. Fierro, F.G. Requejo, O.A. Ferretti, Appl.Catal. A: General 278 (2005) 239–249.
- [20] J.A. Rodriguez, T. Jirsak, S. Chaturvedi, J. Hrbek, J. Am. Chem. Soc. 120 (1998) 11149 - 11157.

Figure Captions

Figure 1. Main products from the hydrogenation of acetophenone and its derivatives.

Figure 2. Concentration profiles (mol%) as a function of time for the hydrogenation of AP (a) Pt; (b) PtSn0.2 and (c) PtSn0.8. (**n**) 1-(phenyl) ethanone, (\bigstar)1-(cyclohexyl) ethanol, (\bigstar) 1-(phenyl) ethanol, (\times) 1-(ethyl) benzene, (\times) 1-(ethyl) cyclohexane

Figure 3. Concentration profiles (mol%) as a function of time for the hydrogenation of 2-MeAP (a) Pt; (b) PtSn0.2 and (c) PtSn0.8. (\blacksquare) 1-(2-methylphenyl) ethanone, (\blacklozenge) 1-(2-methylcyclohexyl) ethanone, (\bigstar) 1-(2-methylcyclohexyl) ethanol, (\blacklozenge) 1-(2-methylphenyl) ethanol.

Figure 4. Concentration profiles (mol%) as a function of time for the hydrogenation of 4-MeOAP (a) Pt; (b) PtSn0.2 and (c) PtSn0.8. (\blacksquare) 1-(4-methoxyphenyl) ethanone, (\blacklozenge) 1-(4-methoxycyclohexyl) ethanol, (\blacklozenge) 1-(4-methoxycyclohexyl) ethanol, (\blacklozenge) 1-(4-methoxyphenyl) ethanol, (\times) 1-(4-methoxy)-ethyl benzene, (\times) 4-ethenylcyclohexyl methyl ether.

Figure 5. Concentration profiles (mol%) as a function of time for the hydrogenation of 4-ClAP (a) Pt; (b) PtSn0.2 and (c) PtSn0.8. (**n**) 1-(4-chlorophenyl) ethanone, (\blacktriangle)1-(4-chlorocyclohexyl) ethanol, (\blacklozenge) 1-(4-chlorocyclohexyl) ethanone, (\blacklozenge)1-(4-chlorocyclohexyl) ethanol.

Figure 6. Adsorption mode of aromatic ketones through the oxygen of the C=O group. (a) AP; (b) 2-MeAP; (c) 4-MeOAP; (d) 4-ClAP.

Figure 7. Mode of adsorption contemplates with C=O interacts with Pt via π electrons. (a) AP; (b) 2-MeAP; (c) 4-MeOAP; (d) 4-ClAP.

Catalyst	Sn/Pt	H/Pt	Pt/CO	d _{TEM} (nm)
Pt	-	0.65	0.55	2.2
PtSn0.2	0.2	0.25	n.d.	2.2
PtSn0.8	0.8	0.20	0.25	2.1

 Table 1. Catalysts characterization.

n.d. not determined

Catalyst	В	inding Energ	Sn _{total} /Pt	Sn(0)/Sn _{total} %		
	Pt $4f_{7/2}$ Sn ⁰ $3d_{5/2}$		${\rm Sn}^{n+} {\rm 3d}_{5/2}$			
Pt	71.6	-	-	-	-	
PtSn0.2	71.1	484.1	486.3	0.20	55	
PtSn0.8	70.8	484.2	487.3	0.79	59	

Table 2.	XPS	testing	result	for P	t and	PtSn	cataly	sts.
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Entry		Sustrate	rate Product Catalyst		Selectivity %	r _i *
а		0	ОН	Pt	63	156
1	b			PtSn0.2	71	162
	с			PtSn0.8	84	125
	a	0	ОН	Pt	74	102
2	b			PtSn0.2	86	92
	с			PtSn0.8	96	86
	a	0	ОН	Pt	75	215
3	b			PtSn0.2	84	187
	с	MeO	MeO	PtSn0.8	90	143
	a	O II	ОН	Pt	55	69
4	b			PtSn0.2	96	90
	c	cı l	cı T	PtSn0.8	98	94

Table 3. Hydrogenation of the aromatic ketones results at 80 °C, a H_2 pressure of 1 MPa and 50% of conversion.

*r_i: initial rate (μ mol g⁻¹_{Ptsup} s⁻¹)

Catalyst	r _{i AP} /r _{i 2-MeAP}	r _{i AP} /r _{i 4-MeOAP}	r _{i AP} /r _{i 4-ClAP}
Pt	1.53	0.72	2.26
PtSn0.2	1.76	0.87	1.80
PtSn0.8	1.45	0.87	1.33

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Table	4.	The	initial	relative	rates	$r_{iAP}\!/r_{iX}$	of	the	substituted	ketones	for	the	study
catalyt	ic s	vsten	ns.										



Adsorption modes of aromatic ketones on Pt surface.







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a-







d-

 \mathbf{i}

