Catalyst characterization Ni-Sn nanoparticles supported in Al₂O₃ and MgO: Acetophenone hydrogenation

Yasna León-Gutiérrez¹ and Galo Cárdenas-Triviño²

Abstract
Monometallic and bimetallic Ni and Sn catalysts were prepared in different ratios by the Solvated Metal Atom Dispersed (SMAD) method for the catalytic hydrogenation of acetophenone to 1-phenylethanol. The preparation of the catalysts was carried out by evaporation of Ni and Sn metal atoms and subsequent co-deposition at 77 K using 2-isopropanol as solvent on alumina and magnesium oxide as supports. X-ray photoelectron spectroscopy (XPS) analysis showed a high percentage of nickel atoms in zero valence, while the tin phases were founded in reduced and oxidized form. The average size of the nanoparticles measured by transmission electron microscopy (TEM) ranged from 8 to 15 nm while the metal dispersion on the surface measured by hydrogen chemisorption ranged from 0.07% for Ni1% Sn0.3%/MgO to 3.2% for Ni5%/MgO. Thermogravimetric analysis shows that γ-Al₂O₃ catalysts exhibit higher thermal stability than MgO catalysts. The catalysis results showed that the best support is MgO reaching 66% conversion in Ni5% Sn0.5%/MgO catalyst.

Keywords
metal nanoparticles, metal vapor, catalytic properties, electron microscopy, surface properties

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Introduction
The hydrogenation of acetophenone for the production of 1-phenylethanol is a model reaction of great interest because not only the ketone function is susceptible to being reduced by hydrogenation, but also the phenyl ring. Thus, the non-selective hydrogenation of acetophenone can lead, in addition to 1-phenylethanol, to the production of acetylcyclohexane, methylcyclohexyl ketone, ethylbenzene, ethlycyclohexane and 1-cyclohexylethanol, showing the importance of selectivity in this reaction. Metallic catalysts used in selective hydrogenation are commonly based on Pt, Rh, Ru, and Pd however none of these metals, is for itself a good catalyst for selective reduction of carbonyl groups. In addition, since they are expensive metals, their massive use in catalytic processes involves additional economic costs. Other alternatives consider the use of more accessible metals, such as nickel. However, because of their less

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activity, it is common that higher pressures are required to achieve economically viable conversions.

The supported metallic catalysts often improve drastically when a small amount of a second metal is added, displaying not only an activity increase but also selectivity. Selectivity can be improved with the addition of elements like P, Sn or MgO introduced in the reactor. Nevertheless, Sn can modify the stability and selective function of the metallic catalyst in two ways, through a “geometric effect” to decrease the number of adjacent atoms by dilution avoiding deposits of undesirable carbonaceous materials on the active phase, and an “electronic effect” caused by the formation of alloys or inter-metallic compounds.

The results found in the literature reveal the tin active type is ionic in cationic state Sn(II). Li and Klabunde prepared the Pt-Sn catalyst system in SiO$_2$ and Al$_2$O$_3$ supports through Solvated Metal Atom Deposition (SMAD) method. This method allows the production of very small zero-value bi-metallic particles. It implies the simultaneous vapor in a reactor under high vacuum followed by condensation at 77 K in presence of Al$_2$O$_3$ or MgO depending on the support used, for 1.5 hours after which the matrix turns black at the end of co-deposition. The mixture was thawed for 1 hour at room temperature under vacuum until reaching 5–10 μm of Hg while the crucibles are heated to red heat producing the sublimation of the metals.

A Dewar flask with liquid nitrogen was placed around the reactor and Ni, Sn, and 100 mL of 2-propanol were simultaneously deposited at 77 K in presence of Al$_2$O$_3$ or MgO depending on the support used, for 1.5 hours after which the matrix turns black at the end of co-deposition. The mixture was thawed for 1 hour at room temperature under vacuum through the elimination of liquid nitrogen from the Dewar. Finally, the solvent dispersed metal colloid was kept stirring for 24 hours in the reactor at room temperature under an inert atmosphere of N$_2$ (g).

Transmission electron microscopy and selected area electron diffraction

Transmission electron microscopy images were obtained on a JEOL JEM 1200 EXII. The catalyst to be analyzed was placed in an agate mortar and dispersed in 2-propanol. A drop of each dispersion is dropped on a 150-mesh carbon-coated copper grid. The micrographs were obtained using 120 kV, 60 cm, and 4.209 Å wavelength. Calibration was carried out by diffracting electrons on a standard Au film (Aldrich Chemical 99.99%) evaporated over a copper grid. To study the particle size, representative regions of each sample were selected, and then between 80 to 100 particles were measured in each sample. Then using Origin 6.0 software (Microcal Software Inc.) a frequency histogram was made to determine the particle average size fitting both Gaussian and normal distribution functions.

Thermal studies

The thermogravimetric studies of the catalysts were performed under a nitrogen atmosphere using a TGA-7 from Perkin-Elmer. A sample mass between 5 to 10 mg was placed in a crucible on the thermal microbalance and heated using a program from 25°C to 550°C and a heating rate of 10°C min$^{-1}$, continuously recording the mass changes in the sample during the experiment.

Surface characterization by gas adsorption (H$_2$, N$_2$)

The hydrogen chemisorption was carried out at 373 K on a Micromeritics ASAP 2010 equipment provided with a
thermal conductivity detector. Before the analysis, the samples were reduced in situ under hydrogen flow (50 cm³ min⁻¹) at 673 K for 1 hour. Hereafter, the reactive gas was displaced with argon and the temperature was kept constant for 2 hours, then reduced to 373 K. Once the baseline was restored, different H₂ pulses were sent to the sample support until complete saturation of the metallic surface. The BET specific metallic surface area and the ratio H/Ni were obtained through the assessment of the chemically adsorbed amount of H₂ at 373 K. Nitrogen adsorption at 77 K was carried out to determine the specific surface area of the catalyst. Measures were done in the same apparatus. An amount between 100 and 200 mg of the catalyst was degassed in high vacuum at 350°C for 2 hours. The sample was then cooled to 77 K and analyzed automatically by the equipment evaluating the changes in equilibrium by sending successive pulses of nitrogen until the equilibrium pressure was reached.

**Infrared studies**

Infrared spectra were measured in solid solution on KBr discs by using an FT-IR Nicolet Change 330 spectrophotometer coupled to a PC with Omnis software analysis. Spectra were recorded at a resolution of 5 cm⁻¹ and 128 scans accumulated in the range from 400 to 4000 cm⁻¹.

**X-ray photoelectron spectroscopy**

Spectra were recorded in a Leybold HL 10 spectrometer with a mono-chromatized Mg Kα X-ray source (hv = 1253.6 eV) operated a 10 mA and 10 kV. All binding energies (BE) were referred to the C 1s line at 284.6 eV.

**Catalytic performance - acetophenone hydrogenation**

The acetophenone hydrogenation was performed in a 200 mL stainless steel vessel equipped with a pressure gauge and connected to a hydrogen tank (99.99% purity). The powdered catalyst was added to the reactor and a constant flow of H₂ gas was maintained to reduce the surface oxide that could be formed and then heated to 250°C for 1 h.

Once the catalyst has been properly prepared for catalytic testing, the reactor is cooled to room temperature and 70 mL of acetophenone 0.40 mol L⁻¹ in methanol solution was added homogenizing the mixture with a magnetic stirrer. The reactor was placed in a furnace with digital controlled temperature and heated at a rate of 5°C min⁻¹. The reaction progress was determined by taking samples periodically from the reaction system and immediately analyzed in a gas chromatograph HNU Systems GC 321 loaded with Carbopack B 80/120 6.6% Carbowax column and He flow of 25 mL min⁻¹ and thermal conductivity detector. The percentage conversion of acetophenone to 1-phenylethanol was determined using a calibration curve made with standard addition.

**Results and discussion**

**Transmission electron microscopy and selected area electron diffraction**

In Figure 1 the transmission electron micrographs for selected catalysts are presented. In Table 4, average particle sizes obtained by TEM and by H₂ chemisorption are summarized. In general, the size of the dispersed particles over Al₂O₃ is smaller than the ones supported on MgO. These sizes are comparable to the non-metallic and bimetallic nonsupported colloids obtained by this method on different organic solvents.²²,²³ The size difference between the two supports is attributed to the different interactions between the support and the particles.²⁴,²⁵ Tin-containing catalysts tend to show a larger particle size compared to monometallic catalysts. This nucleation is related in similar materials to the formation of binary intermetallic compounds.²⁶

In Figure 2 is presented the selected area electron diffraction patterns of the mono and bi-metallic Ni₅.0%/MgO series in MgO and γ-Al₂O₃. The formation of intermetallic compounds of nickel and tin was found in bimetallic catalysts in both supports. A summary of the observed crystallographic values for Ni₅%/MgO and Ni₅%/Sn₁.0%/MgO catalysts is presented in Table 1.

The crystalline planes and spacing found were allocated by comparison with the JCPDS database.²⁷ The presence of several metallic phases in the bimetallic catalysts has made it difficult to study the precise composition of the metallic nanoparticles. However, it has been possible to confirm the presence of metallic nickel phases in the monometallic catalysts. For the bi-metallic compounds the existence of Ni, Sn, SnO, and Nix-Sny phases are noticed, corroborating that the formation of inter-metallic compounds depends on the molar ratio Ni:Sn.²⁸

**Thermal studies**

In Figure 3 the thermogravimetric analysis for mono and bimetallic catalysts at 1% nickel in alumina and magnesium oxide is presented. Temperature decomposition intervals and percentage mass loss are summarized in Table 2. Alumina catalysts show higher thermal stability compared to those with MgO as support, displaying a slowly and steadily weight loss in a wide range of temperatures. In this set of catalysts, it was found that for higher tin content the thermal stability of the sample decreases. In the MgO catalysts, this trend is not observed, both bimetallic catalysts have shown higher stability than the respective nickel and tin monometallic catalysts. The difference observed
between Ni1% Sn0.3%/MgO and Ni1% Sn0.5%/MgO between 325°C and 400°C is attributed to the fact that in the former, according to the findings obtained by chemisorption which will be discussed later, the dispersion is lower in this sample, giving it higher thermal resistance. This could be related to the formation of new bimetallic phases as found by SAED for the Ni5% catalyst series.

The MgO support may be acting as a suitable surface for the formation of new bimetallic phases during the condensation of the solvated metal vapor in the synthesis of the metal nanoparticles. For both groups of catalysts, a higher tin content is related to a higher mass loss at low temperature, which is consistent with a higher amount of solvent incorporated. The solvent incorporation is considered to occur through an interaction of the oxygen atom of the 2-propanol with the metal particles on the catalyst surface, the higher tin-oxygen energy interaction compared to that of nickel-oxygen explains these differences.29,30

The information provided by the thermogram suggests that the interaction between the metal particles and the

Figure 1. Electron micrograph (100 K) for selected Ni5%/MgO and Ni1%/Al2O3 catalysts series. (A) Ni5%/MgO, (B) Ni5%Sn0.3%/MgO, (C) Ni5%Sn1%/MgO, (D) Ni1%/γ-Al2O3 (dark field), (E) Ni1%Sn0.3%/γ-Al2O3, (F) Ni1%Sn0.5%/γ-Al2O3.
Figure 2. Selected Area Electron Diffraction of selected samples.

Table 1. Electron diffraction of the Ni5%/MgO and Ni5% Sn1.0%/MgO catalyst.

| Catalyst         | D (cm) | \(d_{(h,k,l)}\)_{exp} (Å) | Phases and \(hkl\) | \(d_{(h,k,l)}\)_{exp} (Å) |
|------------------|--------|----------------------------|---------------------|-----------------------------|
| Ni5%/MgO        | 1.971  | 2.172                      | Ni (0.0,2)          | 2.172                       |
|                  | 2.695  | 1.561                      | MgO (5,1,1)         | 1.560                       |
|                  | 4.319  | 0.974                      | Ni (0.1,1.4)        | 0.980                       |
| Ni5% Sn1.0%d/MgO| 1.942  | 2.167                      | Ni (0.0,2)          | 2.172                       |
|                  | 2.290  | 1.838                      | NiSn (11,1,1)       | 1.830                       |
|                  | 3.217  | 1.308                      | Sn (2,2,0)          | 1.309                       |
|                  | 3.855  | 1.092                      | Ni<sub>3</sub>Sn<sub>4</sub> (−2.2,4) | 1.090                       |
|                  |        |                            | MgO (8,0,0)         | 1.085                       |
|                  |        |                            | SnO (4,2,3)         | 1.095                       |
support is different for MgO and γ-Al₂O₃. The presence of electron-deficient metallic particles in γ-Al₂O₃ has been reported for Pd³¹ and Pt³² demonstrating that the nature of the support can induce the modulation of the electron density on the active sites. In the catalysts presented in this work, the difference in decomposition temperatures for both supports can be attributed to this effect.

**Surface characterization by gas adsorption (H₂, N₂)**

Table 3 summarizes the metallic area, the specific surface, the ratio H/Ni and the assessment of average particle size from the results of hydrogen and nitrogen adsorption of the catalysts. The ratio H/Ni is related to the dispersion of the metal nickel phase and was founded low for both supports.

In addition, it can be observed that for MgO the rate H/Ni in the monometallic Ni catalyst is slightly larger regarding the bi-metallic Ni-Sn catalysts. Consequently, although Ni and Sn enriched nanoparticles are produced in the reduced state during the synthesis, bimetallic NiₓSnᵧ alloys are also formed as observed by electron diffraction analysis. This leads to a decrease in the amount of hydrogen adsorbed during the experiment. Low dispersion can be attributed to a partial coating of Ni particles by SnOₓ species. This behavior has been reported by Asgardi et al.³³ and Antolini et al.³⁴ for PtSn catalysts.

It is also possible that the presence of organic matter from the trace solvent when in contact with the metal, gives rise to pseudo-organo-metallic compounds that prevent hydrogen chemisorption.³⁵ The existing particle size difference between the one determined by hydrogen chemisorption and TEM is because for chemisorption the size has been determined by the equation \( d = \frac{5 \times 10^{-4}}{S \cdot \rho} \), where \( d \) is the particle diameter (Å), \( S \) is the metallic surface (m² g⁻¹) area and \( \rho \) the specific gravity of the metal phase (g mL⁻¹). This model assumes cubic shape particles with five faces exposed to the gas and one to the support, which is not completely true considering the electron microscopy images, which show a rather spherical shape.

**Infrared Studies**

Table 4 shows the main absorption bands found for selected catalysts. When comparing the spectrum of the pure support with the corresponding mono or bimetallic catalysts, bands around 2960-2860 cm⁻¹ and 1475-1490 cm⁻¹ appear, attributable to asymmetric tension of the C-H bond in methyl groups and C-H flexion, respectively. Also, around 1260, 1098, and 1031 cm⁻¹ absorption bands related to hydroxyl O-H flexion and C-O stretching modes are found.
These observations are compatible with the presence of 2-propanol incorporated in the nanoparticles. Compared to the infrared fingerprint for the pure solvent, only small shifts are found, which can be originated from the interaction of the solvent with the metal surface through the oxygen atom.

### Table 3. Metallic area, specific surface, H/Ni, and particles size determined for chemisorption and TEM of mono-metallic and bi-metallic catalyst supported in MgO and Al2O3.

| Sample                  | \(S_{\text{BET}}\) | \(S_{\text{Metallic}}\) | H/Ni | d \(_{\text{Ni}}\) (H2) | d \(_{\text{Ni}}\) (TEM) |
|-------------------------|---------------------|--------------------------|------|--------------------------|---------------------------|
| \(\gamma\)-Al2O3        | 124                 | —                        | —    | —                        | —                         |
| Ni1%\(\gamma\)-Al2O3    | 119                 | 7.7                      | 1.2  | 73.3                     | 4.9                       |
| Ni1% Sn0.3%/\(\gamma\)-Al2O3 | 121              | 5.6                      | 0.8  | 100.1                    | 5.0                       |
| Ni1% Sn0.5%/\(\gamma\)-Al2O3 | 119              | 10.1                     | 1.5  | 55.6                     | 4.5                       |
| Sn1.0%/\(\gamma\)-Al2O3  | 111                 | —                        | —    | —                        | —                         |
| Ni5%/\(\gamma\)-Al2O3    | 110                 | 3.8                      | 0.6  | 147.4                    | 9.3                       |
| Ni5% Sn0.5%/\(\gamma\)-Al2O3 | 108              | 3.5                      | 0.6  | 136.0                    | 10.9                      |
| Ni5% Sn1.0%/\(\gamma\)-Al2O3 | 109              | 4.1                      | 0.5  | 162.8                    | 12.2                      |
| MgO                     | 195                 | —                        | —    | —                        | —                         |
| Ni1%/MgO                | 175                 | —                        | a    | —                        | b                         |
| Ni1% Sn0.3%/MgO         | 184                 | 0.5                      | 0.07 | b                        | 6.9                       |
| Ni1% Sn0.5%/MgO         | 183                 | 3.7                      | 0.6  | 152.9                    | 7.7                       |
| Sn1.0%/MgO              | 194                 | —                        | —    | —                        | —                         |
| Ni5%/MgO                | 185                 | 21.5                     | 3.2  | 26.2                     | 13.6                      |
| Ni5% Sn0.5%/MgO         | 192                 | 16.2                     | 2.4  | 34.2                     | 12.9                      |
| Ni5% Sn1.0%/MgO         | 185                 | 5.1                      | 0.8  | 110.0                    | 14.6                      |

*It could not be determined.

bValues out of range.

### Table 4. FT-IR analysis of the support \(\gamma\)-Al2O3 and MgO, and catalysts Ni5%/\(\gamma\)-Al2O3 and Ni5% Sn0.5%/MgO.

| Catalyst bands                  | Solvent assignment | Support bands |
|---------------------------------|--------------------|---------------|
| Ni5% / \(\gamma\)-Al2O3         |                    | \(\gamma\)-Al2O3 | 3448 |
| 3456                            |                    | \(\gamma\)-Al2O3 | 3448 |
| 2962*                           | \(\nu_{\text{asym}}\) CH\(_3\) | 3645 |
| 2925*                           | \(\nu_{\text{asym}}\) C-H, CH\(_2\) | 3647 |
| 2859*                           | \(\nu_{\text{sym}}\) C-H, CH\(_2\) | 3442 |
| 1637                            |                    | \(\gamma\)-Al2O3 | 1643 |
| 1475*                           | \(\delta\) CH\(_3\) | 3700           |
| 1407*                           | \(\delta\) CH\(_3\) | MgO            | 3698 |
| 1260*                           | \(\delta\) O-H     | 800            |
| 3700                            |                    | MgO            | 3698 |
| 3645                            |                    |                | 3647 |
| 3442                            |                    |                | 3442 |
| 2960*                           | \(\nu_{\text{asym}}\) CH\(_3\) | 1629           |
| 2924*                           | \(\nu_{\text{sym}}\) CH\(_3\) | 1490           |
| 2859*                           | \(\nu_{\text{sym}}\) CH\(_2\) | 1426           |
| 1629                            |                    |                | 1633 |
| 1490                            |                    |                | 1486 |
| 1426                            |                    |                | 1424 |
| 1261*                           | \(\delta\) O-H     | 1098*          |
| 1098*                           | \(\nu\) C-O        | 3700           |
| 1031*                           | \(\nu\) C-O        | MgO            | 3698 |

\*X-Ray Photoelectron Spectroscopy

A summary of the binding energies for Ni 3p\(_{3/2}\) and Sn 3d\(_{1/2}\) is shown in Table 5. Literature assign binding energies values of 853.8 ± 0.1 eV to Ni 3p\(_{3/2}\) levels in the metallic state and 853.6 ± 0.1 eV for nickel in the +2 oxidation.
In the case of metallic tin, the binding energy is 484.6 ± 0.1 eV, while for the oxidized species it is approximately 487 eV. Nickel in the alumina catalysts presents a peak at 853.5 eV which can be assigned to both Ni⁰ and Ni⁺² since the energy difference between both species is only 0.2 eV. In the case of tin, the 485 eV spike can assign the species Sn⁰ while the highest binding energy around 487 eV is attributed to the presence of tin oxides of Sn⁺² or Sn⁺⁴ valences. Previous reports show that alumina strongly interacts with tin impeding its reduction, and this effect could be the reason to promote tin oxidation. Bi-metallic catalysts supported on MgO present the same signals as those supported on γ-Al₂O₃. The Sn/Ni surface atomic ratios determined by XPS suggest that Sn is mainly found in the top layers of the catalyst.

### Catalytic performance - acetoephone hydrogenation

The pressure for the reaction was set at 100 psi at a temperature of 80°C, being. It has been found that for the same reaction, similar conversion yields have been obtained but using higher temperatures and pressures. For example, with 15% m/m Ag catalysts supported on molecular sieves Yadav and Mewada have obtained the same conversion percentage reached in this work but at a higher pressure of 147 psi and a higher temperature of 160°C. Tanash et al. achieved lower pressures for the catalytic hydrogenation of acetoephone using ruthenium catalysts supported on alumina with conversions of up to 80% at pressures between 43 and 87 psi and temperatures in the range of 58 to 86°C. However, the process presents a low selectivity, obtaining secondary products such as acetylcylohexane and 1-cyclohexylethanol. A better selectivity has been reported by Costa et al. using nickel-based catalysts at 145 psi and 80°C to favor the hydrogenation reaction at the C=O bond more than the C=C, however, they have only reached a 30% conversion rate. In the series of catalysts tested in this work, the best conversion of acetoephone to 1-phenylethanol occurs with Ni⁵% Sn⁰.5%/MgO catalysts, since they showed higher metal surface area in the hydrogen chemisorption measurements. In Figure 4 it can be observed a high level of conversion when Ni⁵% Sn⁰.5%/MgO catalyst is used, reaching 66% after 7 reaction hours, however when using a 1.0% Sn catalyst the activity decay.

This effect is consistent with the findings obtained from the surface characterization of the catalysts. It can be observed that Ni⁵% Sn⁰.5%/MgO catalyst, with a higher Sn content, leads to a 70% decrease in metal surface area, in addition to an increase in nanoparticle size and a noticeable decrease in the H/Ni ratio in comparison with Ni⁵% Sn⁰.5%/MgO. The decrease in exposed nickel surface area leads to lower activity in the conversion of acetophenone to 1-phenylethanol. On the other hand, the conversion rate found for Ni⁵% Sn⁰.5%/MgO in this work may be related to the surface polarity. From the TGA results, it can be observed that Al₂O₃ catalysts, compared to those of MgO, seem to retain a higher amount of solvent as observed in the mass loss at low temperatures, which may be associated with a higher surface polarity. A less polar surface favors the adsorption of acetoephone which once hydrogenated generates 1-phenylethanol, a molecule of higher polarity and therefore lower affinity to the catalyst, leaving the surface free to continue the catalytic cycle. The monometallic catalyst supported on MgO shows no activity, independently from having a higher dispersion. The same effect has been shown by alumina-supported catalysts, which also show low dispersion. It has been reported that

| Catalyst                | Binding energy (eV) | Surface atomic ratios |
|-------------------------|---------------------|-----------------------|
|                         | Ni 3p₃/₂  | Sn 3d₁/₂  | Ni/support | Sn/support | Sn/Ni |
| Ni¹%/Al₂O₃              | 853.4    | —         | 0.016     | —          | —     |
| Ni¹% Sn⁰.3%/γ-Al₂O₃     | 853.5    | 484.8     | 487.2     | 0.015     | 0.0027 | 5.7   |
| Ni¹% Sn⁰.5%/γ-Al₂O₃     | 853.5    | 484.2     | 487.8     | 0.017     | 0.0030 | 4.8   |
| Sn¹.0%/γ-Al₂O₃          | —        | 484.4     | —         | 0.0074    | —     | —     |
| Ni¹%/MgO                | —        | —         | —         | —         | —     | —     |
| Ni¹% Sn⁰.3%/MgO         | 853.4    | 484.7     | 487.3     | 0.023     | 0.0012 | 19.2  |
| Ni¹%Sn⁰.5%/MgO          | 853.4    | 484.0     | 487.5     | 0.013     | 0.0021 | 6.06  |
| Sn¹.0%/MgO              | —        | —         | —         | —         | —     | —     |

*Not determined.

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state. In the case of metallic tin, the binding energy is 484.6 ± 0.1 eV, while for the oxidized species it is approximately 487 eV. Nickel in the alumina catalysts presents a peak at 853.5 eV which can be assigned to both Ni⁰ and Ni⁺² since the energy difference between both species is only 0.2 eV. In the case of tin, the 485 eV spike can assign the species Sn⁰ while the highest binding energy around 487 eV is attributed to the presence of tin oxides of Sn⁺² or Sn⁺⁴ valences. Previous reports show that alumina strongly interacts with tin impeding its reduction, and this effect could be the reason to promote tin oxidation. Bi-metallic catalysts supported on MgO present the same signals as those supported on γ-Al₂O₃. The Sn/Ni surface atomic ratios determined by XPS suggest that Sn is mainly found in the top layers of the catalyst.
the addition of a secondary nonactive metal, could improve the activity and selectivity of the hydrogenation reactions.45

Conclusions

Two catalyst series have been synthesized using MgO and γ-Al2O3 as supports on which metallic nanoparticles were deposited through the SMAD method. TEM micrographs have revealed that the average particle size range from 8 to 15 nm detecting the presence of metallic nickel phases while tin it has been found oxidized in Sn(II) and Sn(IV) states. The size differences are attributed to the different interactions of these metals with both supports. The tin-containing catalysts show in general a larger particle size and a higher degree of crystallinity compared to those monometallic ones. Also depending on the proportion of Ni and Sn used the presence of NiSn type intermetallic phases has been detected with a higher presence in the MgO catalysts which may be acting as an appropriate surface for the formation of these species during the condensation of the solvated metal atoms through the SMAD method. The addition of Sn to the catalysts has proved to be an initiator of hydrogenation of the acetophenone through the C=O bond, increasing selectivity for 1-phenylethanol production. The best conversion of acetophenone to 1-phenylethanol was achieved at 100 psi and 80°C reaching 66% with the Ni5% Sn0.5%/MgO catalyst which represents an improvement compared to other catalysts used for this same hydrogenation reaction that require more drastic pressure and temperature conditions to achieve higher yields.

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