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Article

Transition Metal-based Bimetallic Catalysts for the Chemoselective Hydrogenation of Furfuraldehyde

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Neste trabalho foi estudada a hidrogenação quimiosseletiva em fase líquida do furfural, empregando-se catalisadores baseados em Pt, Rh e Ni. Sistemas bimetálicos, contendo diferentes quantidades de estanho, foram obtidos por meio de reações de superfície controlada entre um catalisador monometálico e $Sn(C_4H_9)_4$. Quando foram utilizados catalisadores monometálicos, os resultados obtidos sugerem uma relação entre as propriedades do metal e da atividade e seletividade. Todos os sistemas permitiram a obtenção do álcool furfurílico com alta seletividade (99, 97 e 76% com catalisadores de Pt, Rh e Ni, respectivamente). A adição de estanho tem efeitos diferentes sobre os três sistemas, tanto em termos de conversão quanto na seletividade. Um resultado interessante foi obtido para os catalisadores baseados em Ni, para os quais a adição de estanho levou a um aumento significativo da seletividade do álcool furfurílico e, dependendo da razão Sn/Ni, também há um aumento na atividade catalítica do sistema.

In this work, the liquid-phase chemoselective hydrogenation of furfural was studied, employing Pt, Rh and Ni-based catalysts. Bimetallic systems, containing different amounts of tin, were obtained by means of controlled surface reactions between a monometallic catalyst and $Sn(C_4H_9)_4$. The results obtained when monometallic catalysts were employed suggest a relationship between metal properties and the activity and selectivity obtained. All systems allowed obtaining furfuryl alcohol with high selectivity (99, 97 and 76% were achieved with Pt, Rh and Ni catalysts, respectively). The addition of tin has different effects on the three systems, both in terms of conversion and selectivity. An interesting result was obtained for the Ni-based catalysts, for which the addition of tin led to a significant increase in furfuryl alcohol selectivity and, depending on the Sn/Ni ratio, also to an increase in the catalytic activity of the system.

Keywords: furfural, furfuryl alcohol, hydrogenation, bimetallic catalysts, PtSn

Introduction

The hydrogenation of furfural is an important reaction in the chemical industry as it is the main way of obtaining furfuryl alcohol.[1] This product is widely used in the production of resins, as an intermediate in the manufacture of lysine, vitamin C and lubricants, and to obtain tetrahydrofurfuryl alcohol, among other applications.[2-4]

Due to the large variety of products that can be obtained from the hydrogenation of furfural, this reaction represents a great challenge from the point of view of its chemoselectivity. As shown in Figure 1, in addition to the products coming from the hydrogenation of the C=O bond and/or the furan ring, there are numerous compounds derived from side reactions (hydrogenolysis of the C=O bond, decarbonylation, hydrogenation and ring opening, condensation reactions, etc.).[3,5]

In chemoselective hydrogenation reactions using heterogeneous catalysts, the choice of the active metal is a key factor, since its influence on the resulting activity and/or selectivity is well-known. Frequently, the addition of a second metal leads to more efficient systems that allow obtaining the desired product.[6] The liquid-phase hydrogenation of furfural has been studied using catalysts based on Ni, Co, Ru, Pd and, to a much lesser extent, Pt. Sometimes another metal or promoter is added to improve the catalytic performance of the systems.[3,7] In this regard, systems based on Ni or Co, modified with Cu, Fe, Ce

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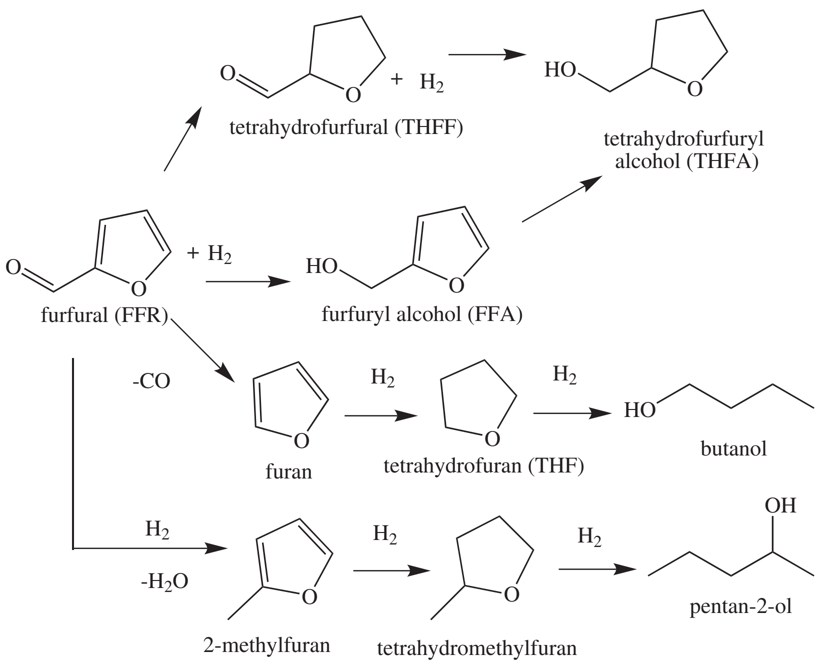

Figure 1. The hydrogenation path for furfural (FFR).

or heteropolyacids, have proved to be very successful, reaching 98% selectivity to the unsaturated alcohol at almost total conversion.[8-12] However, the disadvantage of some of these systems is that they cannot be reused or they promote unwanted side reactions. Therefore, for the industrial reduction of furfural, replacing the classical, highly toxic Cu-Cr catalysts remains a challenge.[13,14]

Concerning bimetallic catalysts, one way to obtain well-defined bimetallic phases is through controlled surface reactions using techniques derived from surface organometallic chemistry. In this regard, Zheng *et al.*[15] have studied the hydrogenation of furfural in the gas phase using Pt catalysts, supported on NaY zeolite, modified by the addition of $Sn(CH_3)_4$. According to their results, the use of bimetallic catalysts, PtSn/NaY, led to an increase in selectivity towards furfury alcohol compare to the monometallic catalyst Pt/NaY. The selectivities to the unsaturated alcohol, obtained at approximately 70% conversion, were 41 and 67% for the mono-and bimetallic system, respectively.

In this paper the liquid-phase hydrogenation of furfural has been investigated, using Pt, Rh and Ni catalysts, promoted with Sn. The objectives were to determine the influence of the base metal on the activity and selectivity achieved, and also to study the effect of the addition of Sn on the catalytic systems obtained. Preparation techniques derived from surface organometallic chemistry on metals (SOMC/M) were employed in order to obtain well-defined bimetallic catalysts.

Experimental

Preparation and characterization of the catalysts

The monometallic Pt catalyst was prepared by ion exchange, using SiO_2 (Evonik (previously Degussa) Aerosil 200, 180 $m^2\ g^{-1}$) as support. The silica was previously treated with ammonia solution and, once properly functionalized, it was contacted with an aqueous solution of $[Pt(NH_3)_4]Cl_2$ with an appropriate concentration so as to obtain *ca.* 1 wt.% Pt on the solid. After 24 h of exchange at room temperature, the solid was separated by filtration, washed, dried in an oven at 378 K, and subsequently reduced in H_2 at 773 K for 2 h.

Rh/SiO_2 (1 wt.%) and Ni/SiO_2 (2 wt.%) catalysts were prepared using the same procedure, the precursors being $[Rh(NH_3)_5Cl]Cl_2$ and $[Ni(NH_3)_6](NO_3)_2$, respectively. After the steps of washing and drying, the catalysts were reduced in H_2 flow at 673 K for 3 h in the case of Rh and at 923 K for 4 h, in the case of Ni.

Bimetallic PtSn, NiSn and RhSn catalysts were prepared by controlled surface reactions, using procedures derived from the SOMC/M. Following these techniques, the previously reduced monometallic catalysts were reacted with a solution of $Sn(C_4H_9)_4(SnBu_4)$ in a paraffinic solvent. The reaction was carried out in flowing H_2 for 4 to 6 h at 363 K (when *n*-heptane was used as solvent), at 393 K or 423 K (for *n*-decane), according to the Sn/M (M = Pt, Rh, Ni) atomic ratio looked for. After the reaction time had been completed, the solids were washed repeatedly with *n*-heptane in Ar flow and finally treated in H_2 at 773 K for 2 h. Bimetallic catalysts so obtained are designated MSn_y, where *y* represents the Sn/M atomic ratio.

The monometallic catalysts were characterized by atomic absorption spectrometry (AAS) (Instrumentations Laboratory IL 457), temperature programmed reduction (TPR) (Quantachrome, 25 cm^3 min^{-1}, 5% H_2 in N_2, heating rate 10 K min^{-1}, samples previously calcined at 773 K for 4 h) and H_2 and CO chemisorption using a catalyst characterization equipment RXM-100 (Advanced Scientific Designs Inc., USA).

The content of Sn in bimetallic catalysts was obtained both by AAS and gas chromatographic analysis (Varian CP-3800 gas chromatograph, equipped with a CP8907 FactorFour capillary column (VF-1ms, 15 m × 0.25 mm id., DF = 0.25)) following the consumption of $SnBu_4$ as a function of reaction time.

The metallic particle size distribution of the catalysts was determined by transmission electron microscopy (TEM), using a JEOL 100 Cx microscope, with a resolution of 6 Å and an accelerating voltage of 100 kV. The magnifications employed were 80000 and 100000.

Furfural hydrogenation

The hydrogenation of furfural was conducted in an autoclave-type reactor (Autoclave Engineers) at H_2 pressure of 1 MPa, 373 K and using a mass of catalyst of 0.25 g. In each test, 2 mL of furfural and 50 mL of propan-2-ol as solvent were employed (0.5 mol L^{-1}). The experimental conditions for the catalytic tests were chosen so that the reaction rate was not influenced by mass transfer.

The evolution of the reaction was followed by gas chromatography in a Varian CP-3800 chromatograph equipped with a capillary column CP wax 52 CB (30 m; 0.53 mm id.) and a FID detector. The reaction products were identified using a Shimadzu QP5050 computer GC/MS with a Supelco SPB-5™ (30 m; 0.25 mm id.) capillary column.

Results and Discussion

The metals chosen for this study were Pt, Rh and Ni. As is well-known, noble metals such as Pt and Rh are highly active in hydrogenation reactions. Besides, Ni, due to its low cost, is an interesting alternative, especially taking into account that there are numerous papers dealing with the hydrogenation of furfural employing Ni-based catalysts.[6] The monometallic catalysts M/SiO_2 (M = Pt, Rh, Ni) were characterized by atomic absorption spectrometry, temperature programmed reduction, H_2 and CO chemosorption and transmission electron microscopy. The results obtained are shown in Table 1. From chemisorption data, it can be seen that, for Pt and Rh, a high dispersion of the metallic phase could be obtained as a consequence of the strong interaction between the metal precursor and the support generated by the preparation method selected. With respect to the Pt/SiO_2 catalyst, it was reduced in H_2 at 773 K for 2 h before performing the chemisorption of H_2 and CO, which yielded similar values (H/Pt = 0.65 and CO/Pt = 0.55). This was not the case with the Rh/SiO_2 system, for which the differences found between H/Rh and CO/Rh may be due to the presence of Rh(I), which at the same time decreases the consumption of H_2 and increases the amount of CO adsorbed due to the formation of *gem*-dicarbonyls.[16] The Ni/SiO_2 catalyst resulted in a system with only a moderate dispersion. The results of TEM characterization for Pt/SiO_2, Ni/SiO_2 and Rh/SiO_2 are also presented in Table 1. It can be seen that the metal particle sizes determined by this technique are below 3.0 nm, in agreement with the presence of considerably dispersed metallic phases.

Table 1. Main characteristics of M/SiO_2 catalysts (M = Pt, Rh, Ni)

Catalyst	wt.% M	H/M	CO/M	d_{TEM}(nm)	TPR(K)*
Pt	1.0	0.65	0.55	2.5	523, 723
Rh	1.0	0.64	1.00	< 1.5	493, 623
Ni	2.2	0.16	-	2.8	873

*Maximum temperature of H_2 consumption peak.

TPR results obtained for the Pt/SiO_2 system showed the presence of two peaks: one at about 523 K and another at 723 K. According to the literature, the low temperature peak can be assigned to the presence of Pt(IV) species, generated during the calcination pretreatment. The high temperature peak may be assigned to species of the type $Pt\text{-}(O\text{-}Si\equiv)_y^{n-y}$ (n = 2^+ or 4^+), formed through the interaction of the metallic precursor and the support.[17] The peaks obtained were broad and presented shoulders, which could be due to the different environment of the ions on the support surface. In the case of the TPR test for the Rh/SiO_2 catalyst, the catalyst presented a main peak at 493 K, probably due to the reduction of Rh(III), present as Rh_2O_3.[18] A shoulder at about 623 K also appeared. Finally, the test for the Ni/SiO_2 catalyst presented a wide area H_2-peak consumption centered around 873 K, which was associated with the preparation method employed, which can lead to the formation of highly stable hydrosilicates having high reduction temperatures.[19] Literature data report that these hydrosilicates probably exist under structures of the type antigorite, $Ni_3(OH)_3Si_2O_5(OH)$, or talc, $Ni_3(OH)_2(Si_20_5)_2$.[20] This result could also explain the moderate dispersion obtained with this catalyst.

Tin-modified catalysts, MSn (M = Pt, Rh and Ni), were obtained by a controlled surface reaction between the monometallic catalyst, previously reduced, and a solution of $SnBu_4$ in a paraffinic solvent such as *n*-heptane or *n*-decane. This approach, derived from the SOMC/M, implies the selective reaction of organometallic compounds of several metals, such as Sn, Ge, Pb, with the surface of transition metals, giving rise to different types of surface structures, such as grafted organometallic fragments, adatoms or bimetallic alloys.[21-23]

The following equations describe the two stages of the reaction of tetrabutyl tin and silica-supported transition metal particles, M (M = Pt, Rh, Ni):

$$M / SiO_2 + ySnBu_4 + \tfrac{xy}{2} H_2 \rightarrow M(SnBu_{4-x})_y / SiO_2 + xyBuH$$

$$M(SnBu_{4-x})_y / SiO_2 + \tfrac{(4-x)y}{2} H_2 \rightarrow MSn_y / SiO_2 + (4-x)yBuH$$

The first stage is carried out at temperatures between 363 and 423 K and leads to a bimetallic system with organic groups anchored onto the surface, the second one occurs between 423 and 773 K, generating the formation of a bimetallic phase, with loss of all the organic fragments. Both supported systems obtained, the organobimetallic ($M(SnBu_{4-x})_y/SiO_2$) and the bimetallic (MSn_y/SiO_2), have shown interesting catalytic properties in terms of activity, selectivity and stability.[24-27]

In order to check on the specificity of the reactions that lead to the bimetallic catalysts obtained by SOMC/M methods, blank tests were performed, consisting of the reaction between $SnBu_4$ and the SiO_2 support. At temperatures between 298 and 423 K, there was neither evidence of change in the concentration of $SnBu_4$ with the reaction time (measured by gas chromatography), nor an appreciable amount of tin on the support after several hours of reaction (measured spectrophotometrically).[28] This allowed us to conclude that all the tin had been deposited selectively on the supported metal particles. These results are consistent with those reported for analogous systems, among others, by B. Didillon *et al.*,[29] who found, in the case of $RhSn/SiO_2$ catalysts studied by scanning transmission electron microscopy (STEM), that Rh signals were always accompanied by the corresponding Sn signal and that Sn could not be detected in those areas of the support that were not covered with metallic phase.

From each of the three monometallic catalysts, bimetallic systems having Sn/M atomic ratios of 0.2 and 0.8 were prepared. The stoichiometry of the bimetallic phase was determined by chromatographic analysis, from the difference between the initial concentration of tetrabutyl tin and the concentration after the completion of the reaction, that is, when the concentration of tetrabutyl tin remains constant. These results were consistent with the values obtained from the analysis of the metal content of the bimetallic catalysts MSn.[28]

In a first step, the monometallic catalysts were tested for the hydrogenation of furfural in the liquid phase. Figure 2 shows the conversion results as a function of reaction time for the three systems studied. As can be seen, although the level of activity was not very high in any of the three cases, the most active catalyst was Pt/SiO_2, which allowed obtaining a conversion of 46% after 8 h of reaction. In the same period, the conversion reached for Ni/SiO_2 and Rh/SiO_2 catalysts was 31 and 15%, respectively. Concerning the selectivity to furfuryl alcohol, values of 99, 97 and 76% were achieved with Pt, Rh and Ni catalysts, respectively (Table 2).

As is well-known, the activity and selectivity obtained for a heterogeneous catalytic hydrogenation process

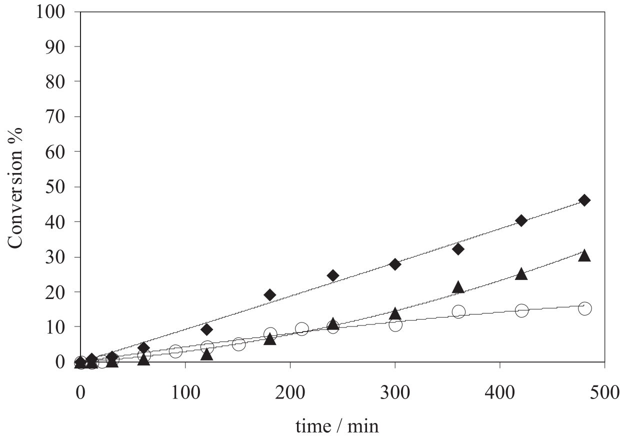

Figure 2. Evolution of overall conversion for furfural hydrogenation with reaction time at 373 K in propan-2-ol for Pt/SiO_2 (◆), Rh/SiO_2 (○) and Ni/SiO_2 (▲).

Table 2. Furfural hydrogenation at 373 K and P_{H2} = 10 MPa. Conversion and selectivity towards furfuryl alcohol (FFA) and tetrahydrofurfuryl alcohol (THFA) at 480 min of reaction

Catalyst	Conversion %	S_{FFA}%	S_{THFA}%	S_{other}%[a]
Pt	46	99	-	1
$PtSn_{0.2}$	100	96	-	4
$PtSn_{0.8}$	71	98	-	2
Rh	15	97	-	3
$RhSn_{0.2}$	14	96	-	4
$RhSn_{0.8}$	14	96	-	4
Ni	31	76	4	20
$NiSn_{0.2}$	43	78	-	22
$NiSn_{0.8}$	31	97	-	3

[a] 2-isopropoxymethylfuran. For Ni-based catalysts light products were also observed (for details, see the text).

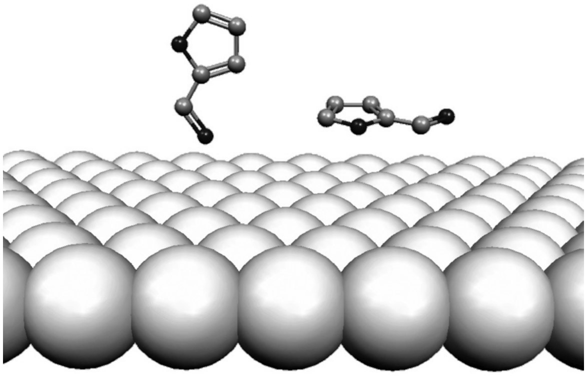

Figure 3. Adsorption geometries of furfural on a metal surface (adapted from reference 30).

depends, among other factors, on the structure of the substrate to be hydrogenated and on the geometric and electronic properties of the active metal. With regard to the structure of the substrate under study, two modes of adsorption of furfural molecules onto a metallic surface have been proposed in the literature.[30] On the one hand, as outlined in Figure 3, the molecule can be adsorbed in a planar form, through the C=C groups of the furan ring. Besides, the furfural molecule can approach the metal surface through the C=O group, being adsorbed in a vertical atop geometry, favorable to the formation of the desired product, furfuryl alcohol. As already mentioned, the preferential adsorption in one way or the other depends on the characteristics of the base metal. Theoretical results obtained by Delbecq and Sautet for the hydrogenation of α,β-unsaturated aldehydes suggest that the competitive adsorption of C=C and C=O groups is dependent on the radial expansion of the *d* orbitals of the metal.[31] Thus, the higher the expansion of the *d* orbitals, the greater the electronic repulsion with the C=C bond and therefore the lower the probability of adsorption through a planar geometry. The *d* band with of the metals selected for this study is Pt > Rh > Ni, then it is expected that for the Pt/SiO_2 system, the repulsive interaction with the C=C bond would be the greatest and so the adsorption of furfural molecule through the carbonyl group would be favored, thus obtaining a high selectivity to the unsaturated alcohol. On the other hand, the electronic properties of Ni may allow furfural molecules to approach the metal through the furan ring, resulting in a lower selectivity to the desired product. The results shown in Table 2 for the three monometallic systems are consistent with the above-given explanation. Moreover, only for the Ni/SiO_2 catalyst it was possible to obtain products from the hydrogenation of both the furan ring and the C=O group, tetrahydrofurfuryl alcohol.

With regard to the activity observed for the monometallic catalysts chosen, one should not rule out the influence of metal particle size on the results. It is well established that the catalytic properties may be strongly influenced by the size of metal particles.[32,33] Depending on whether or not the turnover frequency (TOF) is affected by the structure of the particle surface, Boudart coined the terms structure-sensitive or structure-insensitive reactions.[34] There are numerous studies indicating some structure sensitivity of hydrogenation reactions on Pt, Pd, Ni, Rh, Ru, and Au.[35-38] Concerning the origin of the particle size effect, various explanations have been forwarded, putting the emphasis on the electronic or the geometric parameters. [33,39] Regarding the electronic properties, the critical size above which the *d*-band structure appears is about 2 nm. At a lower size, the *d*-band becomes narrower with the appearance of discrete levels, leading to electron deficiency of small particles, where the small metal particles bind their core electrons more tightly.[40] Thus, the results found with the Rh-based catalyst, with very small particle size (Table 1), seem to agree with this explanation, as it has been the least active of the three systems studied.

Table 2 reports the results of conversion and selectivity obtained after 480 min of reaction for the tin-modified catalysts studied. From the analysis of the data, it can be seen that the addition of tin has different effects on the three systems. Thus, the Rh-based catalysts showed no significant changes due to the addition of Sn. The selectivity to furfuryl alcohol of both $RhSn_{0.2}$ and $RhSn_{0.8}$ catalysts maintained the same high level reached with the monometallic one (96%), but unlike data reported for other selective hydrogenation reactions using RhSn catalysts prepared by SOMC/M methods, there was no modification in the catalytic activity.[41,42] Probably, this result can also be assigned to the effect of the nanoparticles that constitute the metallic phase, as mentioned in the preceding paragraph.

In the case of Pt-based systems, it was observed that the addition of Sn allowed, as in Rh bimetallic systems, maintaining a high selectivity to furfuryl alcohol. With regard to activity, the system with the lower Sn/Pt ratio ($PtSn_{0.2}$) showed a significant increase in conversion, which was 100% at 480 min; on the other hand, the system with the highest level of tin added ($PtSn_{0.8}$) reached 71% conversion for the same time elapsed. Both bimetallic catalysts were more active than the monometallic one. XPS results obtained on both bimetallic catalysts (not shown) indicated the presence of Pt^0, Sn^0 and Sn(II,IV).[43] The presence of metallic tin in bimetallic catalysts is an indication of the existence of bimetallic PtSn phases (even alloys), as has been readily assessed by EXAFS analysis performed on analogous systems to the ones employed here.[44] The $PtSn_{0.8}$ catalyst showed a higher Sn^0/Pt ratio than the $PtSn_{0.2}$ system, a result that could be assigned to the following effects: (*i*) dilution of platinum by metallic tin, due to the formation of SnPt phases, (*ii*) coverage of superficial metal particles by oxidized tin species. The catalytic surface may be depicted by the coexistence of SnPt phases (maybe alloys), ionic tin located at the platinum-support interface and some segregated metallic platinum. Both the high selectivity towards C=O hydrogenation and the enhanced activity of the bimetallic catalysts compared to the monometallic catalyst are in perfect agreement with previously reported results for the hydrogenation of carbonyl compounds using PtSn bimetallic catalysts. This is attributed to the creation of a new type of active site, as a consequence of the specific interaction between $SnBu_4$ and the reduced Pt.[45]

An interesting result that emerges from the analysis of Table 2 is that for Ni-based catalysts, the addition of tin leads to a significant increase in furfuryl alcohol selectivity and, depending on the Sn/Ni ratio, also to an increase in the catalytic activity of the system. As mentioned above, during the hydrogenation of furfural with the Ni/SiO_2 catalyst, the formation of a significant proportion of light by-products from secondary reactions (hydrogenolysis, decarbonylation, etc.) was observed, as shown in Figure 1. This same behavior was noted with the $NiSn_{0.2}$ system, but in terms of activity, this bimetallic catalyst allowed obtaining the best results. For the catalyst with the highest content of tin ($NiSn_{0.8}$), the selectivity to furfuryl alcohol reached 97%, with an activity level similar to that of the monometallic catalyst. Undesirable reactions of hydrogenolysis and decarbonylation have been almost completely eliminated in this system. It has been previously demonstrated that the addition of small quantities of tin can considerably attenuate the hydrogenolysis activity of a supported iron group metal. This effect is especially pronounced when tin is added using methods of surface organometallic chemistry.[46-48] XANES studies conducted on NiSn catalysts similar to those studied here have shown a decrease in the intensity of the white line at the Ni K edge for samples containing tin, as compared to monometallic systems.[49] This is an indication of an increase in the electron density of Ni due to the presence of Sn alloyed with it or in its immediate vicinity. This would lead to the existence of $Sn^{\delta+}$ species that lead to the activation of the C=O group, favoring the interaction of the furfural molecule through the carbonyl group, rather than through the furan ring, facilitating the formation of unsaturated alcohol. These results are attractive from a practical point of view, since the use of nonprecious metals such as nickel in this type of reaction has significant economic benefits due to the lower cost of these metals. It is worth mentioning that for all the catalysts tested in the furfural hydrogenation under the experimental conditions stated, the selectivity to furfuryl alcohol did not vary significantly with conversion.

Finally, it is interesting to note that, for all catalysts used, a product of the reaction between furfuryl alcohol and the reaction solvent (propan-2-ol), 2-isopropoxymethylfuran, has been obtained. In a recent study conducted by our research group we showed that although the use of solvents that do not contain an alcohol function prevents the formation of this ether, the catalyst activity decreases dramatically, proving propan-2-ol to be a suitable solvent for this reaction.[50]

Conclusions

In this paper the liquid-phase hydrogenation of furfural has been investigated, using Pt, Rh and Ni catalysts, promoted with Sn added through the surface organometallic chemistry on metals techniques. Two levels of Sn/M atomic ratios were selected: 0.2 and 0.8.

The monometallic catalysts showed a level of activity that was not very high in any of the three cases. The order of activity was $Pt/SiO_2 > Ni/SiO_2 > Rh/SiO_2$ (46, 31 and 15% conversion after 8 h of reaction, respectively). Concerning the selectivity to furfuryl alcohol, values of 99, 97 and 76% were achieved with Pt, Rh and Ni catalysts, respectively. Both electronic (radial expansion of *d* orbitals of the metals) and geometrical properties (metal particle size) seem to be responsible for the observed behavior.

The addition of tin has different effects on the three systems, both in terms of conversion and selectivity. Whereas the Rh-based catalysts showed no significant changes due to the addition of Sn, Pt-based systems, showed a significant increase in conversion, keeping a high selectivity to furfuryl alcohol. For the Ni-based catalysts, the addition of tin leads to a significant increase in furfuryl alcohol selectivity and, depending on the Sn/Ni ratio, also to an increase in the catalytic activity of the system. These results are attractive from a practical point of view, since the use of nonprecious metals such as nickel in this type of reaction has significant economic benefits.

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