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# Bimetallic PtSn catalyst for the selective hydrogenation of furfural to furfuryl alcohol in liquid-phase

Andrea B. Merlo, Virginia Vetere, José F. Ruggera, Mónica L. Casella *

*Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. Jorge J. Ronco" (CINDECA) (CCT La Plata-CONICET, UNLP),*
*Universidad Nacional de la Plata, Facultad de Ciencias Exactas, 47 N° 257, 1900 La Plata, Argentina*

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ABSTRACT

Bimetallic PtSn catalysts, containing different amounts of tin, were obtained by means of controlled surface reactions and used in the liquid-phase hydrogenation of furfural. All the studied systems allowed to obtain fufuryl alcohol with high selectivity (96–98%). A minor product was detected when alcoholic solvent were employed, coming from the reaction between furfuryl alcohol and the solvent. Nonalcoholic and non-polar solvents caused a drastic activity decrease.

When used in consecutive hydrogenation reactions, the bimetallic catalysts showed a certain deactivation (25% between the first and third cycle), but still they were very selective to furfuryl alcohol. The most efficient system was the catalyst with the lowest tin content ($PtSn_{0.3}$).

## 1. Introduction

Furfuryl alcohol, the main product from the hydrogenation of furfural, is widely employed in the chemical industry. One of its main uses is as an additive or solvent in the production of resins of different characteristics. It is also used as a chemical intermediate to manufacture lysine, vitamin C, lubricants, dispersing agents and to obtain tetrahydrofurfuryl alcohol, among other applications [1–3].

Fig. 1 shows the possible hydrogenation products of furfural, arising from the reduction of the C=O group and/or the furan ring. In addition, many other compounds derived from secondary reactions, such as hydrogenolysis of the C–O bond, decarbonylation, hydrogenation and furan ring opening, may appear. The formation of some condensation products of high molecular weight has also been reported [2,4]. Due to the wide variety of compounds available, it is attractive to design systems that are highly selective to the desired product, furfuryl alcohol.

The hydrogenation of furfural has been carried out in either liquid or vapor phase. The industrial process is conducted at high temperature and pressure, employing a Cu–Cr catalyst, which exhibits a moderate activity towards furfuryl alcohol [5–7]. With this type of catalyst, Vannice et al. found that the selectivity to furfuryl alcohol over copper chromite pretreated at 573 K was 70% for 64% of furfural converted [6]. The main drawback of this system is the toxicity of the catalyst, due to the presence of $Cr_2O_3$, which may have important consequences for the environment [3]. Therefore, the design of active and selective catalytic systems for obtaining the unsaturated alcohol is an issue of interest, which still presents great challenges.

Hydrogenation of furfural in the liquid-phase has been widely studied using catalysts based on Ni, Co, Ru and Pd, sometimes with the addition of a second metal or a promoter to improve the activity and/or the selectivity [2,8]. In this sense, systems based on Ni or Co modified with Cu, Fe, Ce or heteropolyacids have proved to be very successful, reaching 98% selectivity to the unsaturated alcohol, at almost total conversion [9–13]. However, in some cases, the main disadvantage is that the catalyst cannot be reused [9].

Pt-based catalysts have been much less employed, so little information is available in the open literature. The systems most commonly used are Pt/C and $Pt/Al_2O_3$ [2,8]. One of the main problems in the application of Pt-based catalysts in the hydrogenation of furfural is the often observed side reactions (hydrogenolysis of the C–O bond, decarbonylation, hydrogenation and furan ring opening, etc.), which decrease the selectivity to the desired product. In this regard, modifying the base catalyst, either by adding a more electropositive metal (Fe, Ga, Sn), by deposition of Pt on some partially reducible oxides ($TiO_2$, $ZrO_2$), or by controlling the size of Pt crystals, has been reported as giving good results in increasing the selectivity to furfuryl alcohol [2].

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* Corresponding author.
*E-mail address:* casella@quimica.unlp.edu.ar (M.L. Casella).

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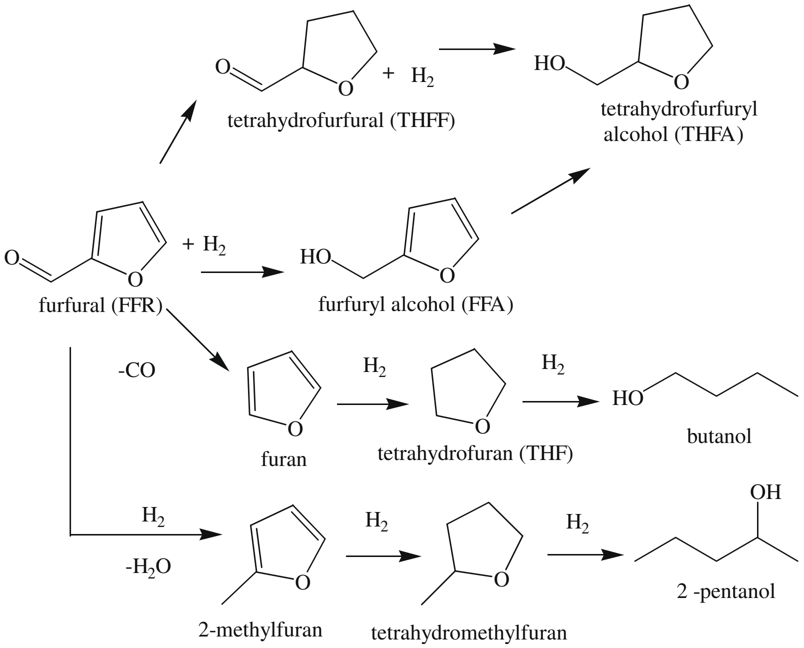

**Fig. 1.** Reaction pathway for furfural hydrogenation.

Previous studies conducted in our research group have shown that the addition of Sn to Pt-based systems leads to more efficient catalysts in the hydrogenation of many different unsaturated carbonyl compounds [14,15]. In this paper, we propose the systematic study of the effect of tin content on the activity, selectivity and stability of $Pt/SiO_2$ catalysts modified with $SnBu_4$ that are employed in the liquid-phase hydrogenation of furfural to furfuryl alcohol. In order to obtain well-defined bimetallic phases, surface-controlled reactions were used in the preparation of the catalysts.

## 2. Experimental

### 2.1. Catalysts preparation

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

Bimetallic PtSn catalysts were prepared by controlled surface reactions, using techniques derived from the Surface Organometallic Chemistry on Metals (SOMC/M) [16 and references cited therein]. According to this procedure, the monometallic catalyst, previously reduced, was reacted with a solution of $SnBu_4$ in a paraffinic solvent. The reaction was carried out in $H_2$ flow for 4 h at either 363 or 393 K, using *n*-heptane or *n*-decane, respectively, as solvent. After the reaction had finished, the resulting solid was washed repeatedly with *n*-heptane in Ar flow, and finally treated in $H_2$ at 773 K for 2 h. Bimetallic catalysts obtained are designated $PtSn_y$, where *y* represents the Sn/Pt atomic ratio.

### 2.2. Catalysts characterization

The monometallic catalyst was characterized by atomic absorption (Instrumentations Laboratory IL 457), temperature-programmed reduction (TPR) (Quantachrome, 25 $cm^3\,min^{-1}$, 5% $H_2$ in $N_2$, 10 K $min^{-1}$), and $H_2$ and CO chemisorption with a catalyst characterization equipment RXM-100 (Advanced Scientific Designs Inc., USA). The specific surface area of the support was also measured (Micromeritics ASAP 2020, $N_2$ adsorption at 77 K).

The content of Sn fixed in each bimetallic catalyst was obtained by chromatographic analysis of the solution containing the organometallic compound, as a function of reaction time, using a Varian CP-3800 gas chromatograph, equipped with a capillary column FactorFour CP8907 (VF-1 ms, 15 m × 0.25 mm *i.d.*, DF = 0.25) and a FID detector. These results were consistent with the values obtained from the analysis of the metal content of bimetallic PtSn catalysts carried out by atomic absorption spectrometry [17].

The metal particle size distribution of all catalysts used was measured by transmission electron microscopy (TEM), in a JEOL 100 Cx equipment.

### 2.3. Catalytic test

The hydrogenation of furfural was conducted in an autoclave type reactor (Autoclave Engineers) at 1.0 MPa $H_2$ pressure, a temperature of 373 K and using 0.25 g of catalyst. 2 mL of furfural in 50 mL of 2-propanol as solvent was used in each test. In addition, some experiments were performed using ethanol, *n*-heptane and toluene as reaction solvent. In all cases, the experimental conditions were the same as the above-mentioned.

The evolution of the reaction was followed by gas chromatography in a Varian CP-3800 gas chromatograph equipped with a capillary column CP wax 52 CB (30 m × 0.53 mm) and a FID detector. The reaction products were identified using a GC/MS Shimadzu QP5050 with a capillary column SUPELCO SPB$^{TM}$-5 (30 m, 0.25 mm *i.d.*).

## 3. Results and discussion

The monometallic $Pt/SiO_2$ catalyst (Pt) was characterized by atomic absorption, temperature-programmed reduction, CO and $H_2$ chemisorption and transmission electron microscopy. The results are shown in Table 1.

**Table 1**
Characterization of $Pt/SiO_2$ and $PtSn/SiO_2$ catalysts.

| Entry | Catalyst | wt.% Pt | Sn/Pt[a] | H/Pt[a] | CO/Pt[a] | $d_{TEM}$ (nm) | TPR (K) |
|---|---|---|---|---|---|---|---|
| 1 | Pt | 0.6 | 0 | 0.65 | 0.55 | 2.0 | 523, 723 |
| 2 | $PtSn_{0.3}$ | 0.6 | 0.3 | – | – | 1.8 | – |
| 3 | $PtSn_{0.6}$ | 0.6 | 0.6 | – | – | 1.8 | – |
| 4 | $PtSn_{0.8}$ | 0.6 | 0.8 | – | – | 1.9 | – |
| 5 | $PtSn_{1.0}$ | 0.6 | 1.0 | – | – | 1.8 | – |

[a] Molar ratio.

From the chemisorption data a high dispersion of the metallic phase can be inferred, which is due to the strong interaction between the metal precursor and the support generated by the preparation method (ion exchange). With respect to the TPR test, the diagram presented two major peaks of $H_2$ consumption: one at ~523 K and the other at 723 K, in agreement with the literature information [18]. The first peak is usually assigned to a platinum oxide in weak interaction with the support, while the second one, with a significantly higher $H_2$ consumption, could be associated with a platinum oxide in strong interaction with the support.

Tin-modified catalysts, PtSn, 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. The reaction undergoes in two stages. The first takes place between 363 and 423 K and results in a system with organotin moieties anchored to the surface. The second step, occurring between 423 and 773 K, corresponds to the formation of a bimetallic phase in which all the organic fragments have been detached from the surface. The following equations represent the above-mentioned processes:

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

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

Preliminary work in our research group demonstrated the specificity of the reactions that take place during the preparation of bimetallic catalysts by means of SOMC/M techniques, concluding that all of the tin added is deposited selectively on supported platinum [17,19].

TEM results are shown in Table 1. From the analysis of the values obtained for the mean particle size, it can be seen that the addition of tin does not practically affect the particle size distribution with respect to the monometallic system. This is another indication of the specificity of the reaction between both metals. The Sn/Pt atomic ratio for each one of the prepared catalysts, as determined by chromatographic analysis of the solution containing the organometallic precursor, is also included in Table 1.

The results of conversion as a function of reaction time for the hydrogenation of furfural, using 2-propanol as solvent, are reported in Fig. 2. From the analysis of this figure it can be seen that PtSn systems have a higher activity than the corresponding monometallic catalyst.

PtSn-supported catalysts, similar to those employed here, have been thoroughly characterized by EXAFS, XANES and XPS in our research group [20,21]. Those studies revealed that in the bimetallic systems, there is a convergence of geometric (dilution of Pt sites) and electronic (increase of the electron density of Pt) effects, due to the presence of Sn, which modifies the characteristics of the base Pt catalyst. EXAFS studies confirmed the presence of two peaks assigned to the existence of PtSn alloys. Besides, the rest of the Pt is isolated by such alloys, and a percentage of ionic Sn (*ca.* 35%) also exists and it is probably located in the metal–support interface [21]. These ionic Sn species act as Lewis acid sites, promoting the attack of hydrogen to the carbonyl group of the furfural molecule and thus leading to greater activity. Taking into account that Sn(0) does not possess intrinsically hydrogenating properties, it seems reasonable to accept that PtSn alloys are not active in hydrogenation reactions and participate only in the isolation of the electronically modified Pt atoms.

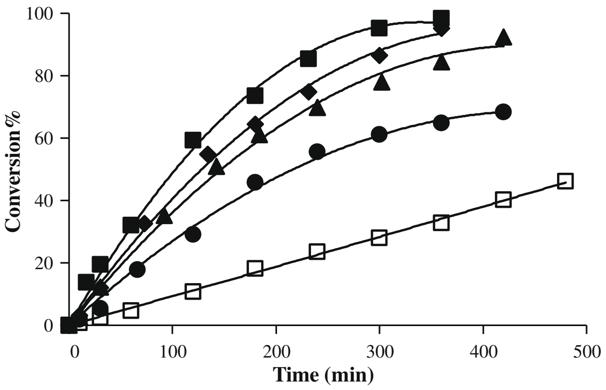

**Fig. 2.** Hydrogenation of furfural in 2-propanol. (□) Pt; (■) $PtSn_{0.3}$; (♦) $PtSn_{0.6}$; (▲) $PtSn_{0.8}$; (●) $PtSn_{1.0}$. (For experimental conditions, see the text.)

By analyzing the activity as a function of the Sn/Pt ratio, there seems to be a compromise between the dilution of Pt sites, active for the hydrogenation reaction, and the promoting effect of ionic Sn, yielding the highest hydrogenation rates for the lower Sn/Pt ratios. The effect of site isolation generated by tin favors the presence of species leading to FFA, mainly of types $\eta^1$-(O) and $\eta^2$-(C,O), according to the classical scheme of adsorption proposed in the literature for $\alpha,\beta$-unsaturated aldehydes [22]. The increase in the reaction rate when comparing PtSn bimetallic catalysts and $Pt/SiO_2$, has to be explained by a modification in the electronic nature of the active site, which agrees with XANES results of an electronic transfer from Pt to the PtSn bond [21].

The results of selectivity to different hydrogenation products of furfural, after 8 h of reaction, are gathered in Table 2. As can be seen, all the catalysts used are highly selective to the desired product, furfuryl alcohol. In addition, tin-modified catalysts allowed obtaining higher conversions than the $Pt/SiO_2$ catalyst (Fig. 2). An interesting result found during the analysis of the hydrogenation products of furfural, using 2-propanol as solvent, was the presence of an ether (2-isopropoxymethylfuran), product of reaction between furfuryl alcohol and 2-propanol. This product has not been reported so far in the literature for the hydrogenation of furfural in the liquid-phase. Therefore, other solvents were tested in order to evaluate their influence on the activity and selectivity in the hydrogenation of furfural. The $Pt/SiO_2$ catalyst was used with the three different solvents selected for this study: ethanol, toluene and *n*-heptane. As expected, when using ethanol, the ether was found among the products, as a consequence of the reaction between furfuryl alcohol and the solvent. Anyway, the selectivity to the unsaturated alcohol was *ca.* 98% at 36% conversion. When *n*-heptane and toluene were employed, there was no evidence of association between furfuryl alcohol and the solvent.

**Table 2**
Initial reaction rate and selectivity values at 480 min for the hydrogenation of furfural in 2-propanol.

| Entry | Catalyst | $r_i$[a] (mmol $g_{Pt}^{-1}$ $s^{-1}$) | $S_{FFA}$% | $S_{THFF}$% | $S_{THFA}$% | $S_{IPF}$%[b] |
|---|---|---|---|---|---|---|
| 1 | Pt | 0.38 | 98.70 | 0.00 | 0.00 | 1.30 |
| 2 | $PtSn_{0.3}$ | 2.30 | 96.18 | 0.00 | 0.22 | 3.60 |
| 3 | $PtSn_{0.6}$ | 1.82 | 96.89 | 0.05 | 0.06 | 3.00 |
| 4 | $PtSn_{0.8}$ | 1.63 | 98.24 | 0.00 | 0.10 | 1.66 |
| 5 | $PtSn_{1.0}$ | 1.15 | 98.20 | 0.25 | 0.00 | 1.55 |

[a] Reaction rate estimated between 0% and 10% conversion.
[b] IPF = 2-isopropoxymethylfuran.

Solvent effects in heterogeneous catalysis have been rationalized by correlating reaction rates and product distributions with solvent polarity or dielectric constant ($\varepsilon$) [23]. The nature of the solvent can influence the kinetics of competitive hydrogenation reactions of both polar and non-polar substrates: it has been found that a polar solvent enhances adsorption of the non-polar reactant while a non-polar solvent enhances the adsorption of a polar reactant [24]. Fig. 3 shows the results of activity obtained with each one of the solvents used in the present work. As is clear from the analysis of the figure, in spite of preventing the formation of the mentioned ether, the use of toluene and *n*-heptane makes the reaction become slower, reaching a conversion of ~12% after 8 h of reaction. Besides, the curves present a certain "flattening", that can be assigned to a deactivation process, may be due to the adsorption of the polar substrate in the non-polar solvents toluene ($\varepsilon = 2.0$) and *n-heptane* ($\varepsilon = 1.9$).

A general problem encountered in the hydrogenation of aldehydes using an alcohol as solvent is the formation of secondary products of the type of acetals, due to a reaction between the substrate and the solvent [25]. This reaction has been reported for the liquid-phase hydrogenation of furfural using Ir-based systems where, by mass spectroscopy analysis, the presence of 2-furaldehyde diethyl acetal was detected [26]. With the catalysts used in the present work, and under the experimental conditions previously mentioned, the presence of products of acetylation between furfural and the alcohol used as solvent has not been detected, proving an additional advantage of the catalytic systems proposed here.

A valuable property of heterogeneous catalysts, in addition to their activity and selectivity, is the possibility to reuse them, looking forward to their practical application. Therefore, stability tests were performed on some of the studied systems, choosing 2-propanol as solvent. In each experience, after completing a hydrogenation test, the catalyst was washed with solvent and used again, completing three cycles of hydrogenation. The results of the conversion of furfural after 480 min of reaction, for three of the systems studied, are reported in Fig. 4. As shown, in the first cycle the monometallic catalyst reached a conversion of 46% at 480 min of reaction, while for the same time elapsed, in the second and third cycles a conversion of ~30% was reached. These results indicate that the Pt/SiO$_2$ catalyst suffers a certain deactivation. This observation is consistent with that reported for other systems used in the hydrogenation of furfural, which suggests that there may be a catalyst poisoning due to the adsorption of furfural and/or any of the reaction products on the active metal [6,27]. With regard to the tin-modified catalysts, it can be seen that they also present some deactivation. However, despite this deactivation, the catalyst designated PtSn$_{0.3}$ resulted to be the most active, reaching a high level of conversion, even after three hydrogenation cycles. Besides, the selectivity to furfuryl alcohol was kept more or less at the same value during the three cycles of reaction (96%).

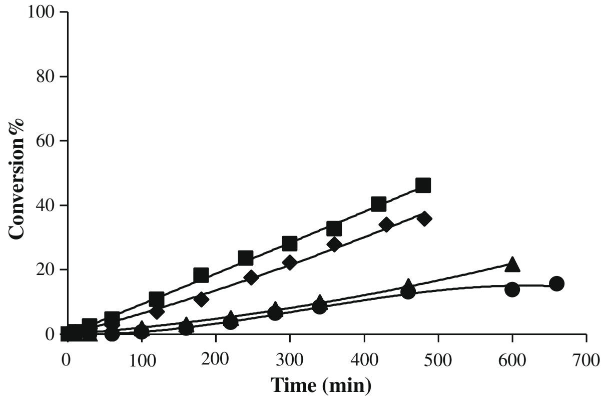

**Fig. 3.** Hydrogenation of furfural with Pt/SiO$_2$. (■) 2-propanol; (♦) ethanol; (▲) toluene; (●) *n*-heptane. (For experimental conditions, see the text.)

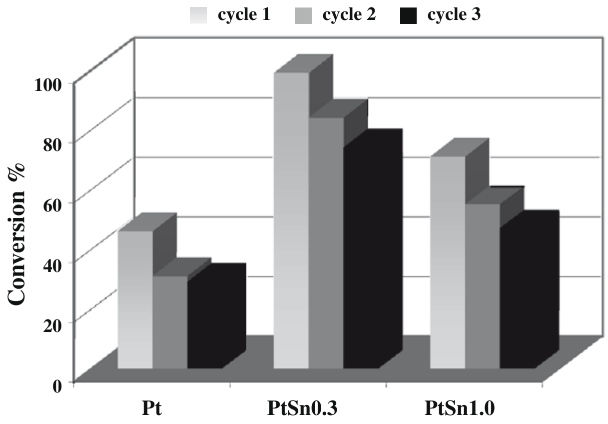

**Fig. 4.** Activity of Pt, PtSn$_{0.3}$ and PtSn$_{1.0}$ for the furfural hydrogenation, in successive reactions.

## 4. Conclusions

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

- It was possible to use Pt-based systems, modified with SnBu$_4$, in the liquid-phase selective hydrogenation of furfural to furfuryl alcohol. All the catalysts were highly selective to the desired product.
- PtSn systems were more active than the monometallic catalyst. The highest reaction rate was obtained for the lowest Sn/Pt atomic ratio studied.
- The study of the stability of the catalysts used in the hydrogenation of furfural in 2-propanol showed that, although there is some deactivation in all the systems, the catalyst PtSn$_{0.3}$ gave a high level of conversion after three reaction cycles. Besides, the selectivity to unsaturated alcohol was kept during the three hydrogenation cycles.

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## References

[1] B.M. Nagaraja, V. Siva Kumar, V. Shasikala, A.H. Padmasri, B. Sreedhar, B. David Raju, K.S. Rama Rao, Catal. Commun. 4 (2003) 287–293.
[2] J. Kijenski, P. Winiarek, T. Paryjczak, A. Lewicki, A. Mikołajska, Appl. Catal. A: Gen. 233 (2002) 171–182.
[3] B.M. Nagaraja, A.H. Padmasri, B. David Raju, K.S. Rama Rao, J. Mol. Catal. A: Chem. 265 (2007) 90–97.
[4] H.Y. Zheng, Y.L. Zhua, B.T. Teng, Z.Q. Bai, C.H. Zhang, H.W. Xiang, Y.W. Li, J. Mol. Catal. A: Chem. 246 (2006) 18–23.
[5] J. Wu, Y. Shen, C. Liu, H. Wang, C. Geng, Z. Zhang, Catal. Commun. 6 (2005) 633–637.
[6] R. Rao, A. Dandekar, R.T.K. Baker, M.A. Vannice, J. Catal. 171 (1997) 406–419.
[7] L.J. Frainier, H. Fineberg, US Patent 4,302,397, 1981.
[8] P.D. Vaidya, V.V. MahajaniInd, Ind. Eng. Chem. Res. 42 (2003) 3881–3885.
[9] N. Merat, C. Godawa, A. Gaset, J. Chem. Technol. Biotechnol. 48 (1990) 145.
[10] H. Li, H. Luo, L. Zhuang, W. Dai, M. Qiao, J. Mol. Catal. A: Chem. 203 (2003) 267–275.
[11] X. Chen, H. Li, H. Luo, M. Qiao, Appl. Catal. A: Gen. 233 (2002) 13–20.
[12] H. Li, S. Zhang, H. Luo, Mater. Lett. 58 (2004) 2741–2746.
[13] L. Baijun, L. Lianhai, W. Bingchun, C. Tianxi, K. Iwatani, Appl. Catal. A: Gen. 171 (1998) 117–122.
[14] G.F. Santori, A.G. Moglioni, V. Vetere, G.Y. Moltrasio Iglesias, M.L. Casella, O.A. Ferretti, Appl. Catal. A: Gen. 269 (2004) 215–223.

[15] M.L. Casella, G.F. Santori, A. Moglioni, V. Vetere, J.F. Ruggera, G. Moltrasio Iglesias, O.A. Ferretti, Appl. Catal. A: Gen. 318 (2007) 1–8.

[16] O.A. Ferretti, M.L. Casella, in: Basset et al. (Eds.), Modern Surface Organometallic Chemistry, Wiley-VCH, Weinheim, 2009 (Chapter 6).

[17] V. Vetere, Ph.D. Thesis, University of La Plata, Argentina, 2007.

[18] E. Merlen, P. Beccat, J.C. Bertolini, F. Delichere, N. Zanier, B. Didillon, J. Catal. 159 (1996) 178–188.

[19] G. Santori, Ph.D. Thesis, University of La Plata, Argentina, 2000.

[20] G.J. Siri, J.M. Ramallo-López, M.L. Casella, J.L.G. Fierro, F.G. Requejo, O.A. Ferretti, Appl. Catal. A: Gen. 278 (2005) 239–249.

[21] J.M. Ramallo López, G.F. Santori, L. Giovanetti, M.L. Casella, O.A. Ferretti, F.G. Requejo, J. Phys. Chem. B 107 (2003) 11441–11451.

[22] P. Claus, Top. Catal. 5 (1998) 51–62.

[23] U.K. Singh, M.A. Vannice, Appl. Catal. A: Gen. 213 (2001) 1–24.

[24] L. Cerveny, V. Ruzicka, Catal. Rev.-Sci. Eng. 24 (1982) 503–566.

[25] P.G.N. Mertens, F. Cuypers, P. Vandezande, X. Ye, F. Verpoort, I.F.J. Vankelecom, D.E. De Vos, Appl. Catal. A: Gen. 325 (2007) 130–139.

[26] H. Rojas, G. Borda, D. Rosas, J.J. Martínez, P. Reyes, Dyna 155 (2008) 115–122.

[27] M.V. Twigg, M.S. Spencer, Appl. Catal. A: Gen. 212 (2001) 161–174.