New trimetallic catalysts supported on coprecipitated MgAl$_2$O$_4$ for n-paraffins selective dehydrogenation processes

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ABSTRACT

Trimetallic PtSnIn and PtSnGa catalysts supported on coprecipitated MgAl$_2$O$_4$ display better behaviors in n-butane conversion, selectivity to butenes and deactivation due to coke formation, than bimetallic PtSn/MgAl$_2$O$_4$ catalysts, and much better than the mometallic catalyst. The addition of Sn and In to Pt produces mainly an important decrease of the metallic particle sizes and geometric modifications of the metallic phase, these facts being the cause for the excellent performance. For PtSnGa/MgAl$_2$O$_4$, not only geometric but also electronic effects on the metallic phase would be present.

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1. Introduction

MgAl$_2$O$_4$ is a material with suitable properties to be used as a catalytic support for different reactions [1–6]. Some of these characteristics are the low acidity and the good interaction with the supported metals, which are very important in paraffin dehydrogenation processes [2,3]. The preparation of MgAl$_2$O$_4$ from traditional ceramic method leads to a material with low specific surface area and chemical inhomogeneity. However, other synthesis methods like the coprecipitation allow to obtain a material with higher specific surface area and chemical homogeneity [6].

With respect to the nature of the metallic phase of dehydrogenation catalysts, it can be noted that PtSn catalysts supported on different materials show both a high dehydrogenation activity and a high selectivity to olefins [3,4,7,8]. The addition of a third metal to PtSn/SiO$_2$ could improve the catalytic behavior in n-hexane dehydrogenation. In fact, Homs et al. [9] reported for PtSnIn catalysts a high selectivity for dehydrogenation, according to the characterization results, while the selectivity pattern of the PtSnGa/SiO$_2$ catalyst was different. Previously, Passos et al. [7] found that the addition of In to Pt/Al$_2$O$_3$ was more effective on the decrease of the hydrogenolysis activity than Sn. The study of tri and multimetallic catalysts is a new research field for n-paraffins dehydrogenation. These catalysts have been applied for catalytic reforming and other reactions [10–13], but very few papers were reported for n-paraffins dehydrogenation [9,14].

The objective of this paper is to compare the effect of In and Ga addition to PtSn/MgAl$_2$O$_4$ catalyst in the catalytic performance for n-butane dehydrogenation. Besides a complete characterization of bimetallic PtSn and trimetallic PtSnIn and PtSnGa catalysts supported on the MgAl$_2$O$_4$ spinel prepared by coprecipitation is carried out.

2. Experimental

The MgAl$_2$O$_4$ was synthesized by coprecipitation technique, using Mg(NO$_3$)$_2$ · 6H$_2$O, Al(NO$_3$)$_3$ · 9H$_2$O and ammonia solution as reagents [6].

The Pt(0.3 wt%)/MgAl$_2$O$_4$ catalyst was prepared by impregnation of the support with an aqueous solution of H$_2$PtCl$_6$ at 25 °C for 6 h. The Pt(0.3 wt%)Sn(0.3 wt%)/MgAl$_2$O$_4$ catalyst was obtained by impregnation of the monometallic one with an aqueous solution of SnCl$_2$ in HCl medium at 25 °C for 6 h. The Pt(0.3 wt%)Sn-(0.3 wt%)In(0.28 wt%)/MgAl$_2$O$_4$ and Pt(0.3 wt%)Sn (0.3 wt%)Ga-(0.17 wt%)/MgAl$_2$O$_4$ catalysts were obtained by impregnation of the bimetallic one with an aqueous solution of In(NO$_3$)$_3$ or Ga(NO$_3$)$_3$ at 25 °C for 6 h. The In and Ga concentrations are equimolar. Finally, mono, bi and trimetallic catalysts were dried at 120 °C and calcined in air at 500 °C for 3 h.

The n-butane dehydrogenation tests were carried out in a continuous flow reactor at 530 °C for 2 h. The catalyst bed (0.2 g) was fed with 18 mL min^{-1} of the reactive mixture (n-C$_4$H$_{10}$ + H$_2$, H$_2$/n-C$_4$H$_{10}$ molar ratio = 1.25). Prior to the reaction, catalysts were reduced with H$_2$ at 530 °C for 3 h. The reactor effluent was analyzed

in a GC–FID equipment. Carbon contents of the used catalysts were determined by Thermogravimetric Analysis (TGA).

Temperature Programmed Reduction (TPR) experiments were performed in a flow reactor. Samples were heated at 6 °C min^{-1} from 25 °C up to 550 °C. The reductive mixture (5 v/v% H$_2$–N$_2$) was fed to the reactor with a flow rate of 10 mL min^{-1}.

Cyclohexane dehydrogenation (CHD) and cyclopentane hydrogenolysis (CPH) were carried out at 300 and 500 °C, respectively, in a differential flow reactor. In both reactions the H$_2$/hydrocarbon molar ratio was 26. Prior to these reactions, samples were reduced with H$_2$ at 500 °C. The activation energy values for CHD (E_{CH}) were determined by measuring the initial CH dehydrogenation rate at three different temperatures.

The hydrogen chemisorption measurements were carried out in a volumetric equipment at room temperature. Samples were previously reduced with H$_2$ at 500 °C.

TEM measurements were carried out on a JEOL 100CX microscope, operated with an acceleration voltage of 100 kV, and magnification ranges of 80,000x and 100,000x. For each catalyst, a very important number of Pt particles (approximately 200) were observed and the distribution of particle sizes was done. The mean particle diameter was calculated as: $d = \Sigma ni.di/\Sigma ni$, ni: number of particles of diameter i.

3. Results and discussion

The synthesis of the support by coprecipitation led to a pure MgAl$_2$O$_4$ spinel with neutral characteristics, mean pore sizes between 140 and 160 Å, pore volume of 0.33 cm^3 g^{-1} and surface area of 108 m^2 g^{-1}.

Fig. 1 shows the n-butane conversion versus the reaction time (t) in a flow reactor for Pt/MgAl$_2$O$_4$, PtSn/MgAl$_2$O$_4$, PtSnIn/MgAl$_2$O$_4$ and PtSnGa/MgAl$_2$O$_4$ catalysts. The deactivation parameter (ΔX) along t was defined as: $\Delta X = 100 * (X_0 - X_f)/X_0$, where X_0 is the initial conversion (at $t = 10$ min) and X_f is the final conversion (at $t = 120$ min). The Pt/MgAl$_2$O$_4$ catalyst displays low X_0 (17%) and high ΔX (48%), while the PtSn/MgAl$_2$O$_4$ catalyst shows higher X_0 (25%) and the ΔX strongly decreases (24%). Both trimetallic catalysts display better behaviors in activity and deactivation than the bimetallic sample. Thus, PtSnIn and PtSnGa show higher initial n-butane conversions (29% and 26%, respectively) and lower deactivation parameters (3% and 12%, respectively).

The activity fall along the reaction time (measured by ΔX value) is mainly caused by the carbon deposition on the catalysts. In fact, carbon contents in the used catalysts followed a similar sequence than the deactivation parameters:

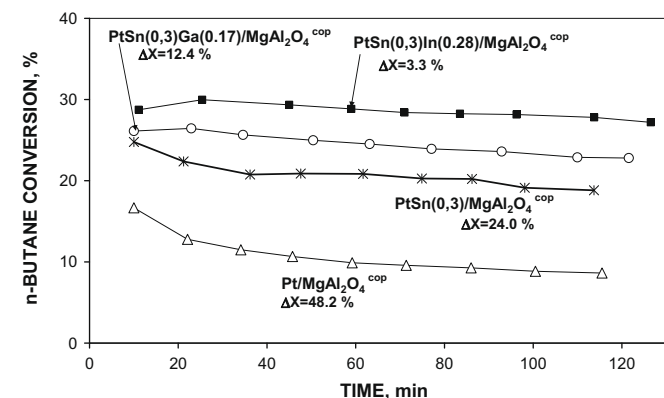Pt (4.2 wt%C) > PtSn (3.5 wt%C) > PtSnGa (2.0 wt%C) > PtSnIn (1.8 wt%C)

Fig. 2 shows the selectivity values to all butenes (1-butene, 2-butenes and butadiene) obtained for the different catalysts. PtSnIn and PtSnGa catalysts display very high selectivities along t (92–96%), the bimetallic PtSn/MgAl$_2$O$_4$ catalyst shows slightly lower selectivities (86–93%), while the values for Pt/MgAl$_2$O$_4$ are lower than 82%. These results clearly show the beneficial effect of the In or Ga addition to PtSn/MgAl$_2$O$_4$ catalyst, in the n-butane dehydrogenation. In this sense the initial yields to butenes, defined as the product between the initial conversion and the initial selectivity, increases in the following way:

Pt (12%) < PtSn (21%) < PtSnGa (24%) < PtSnIn (27%)

With regard to the catalyst characterization, the TPR profile of the Pt/MgAl$_2$O$_4$ catalyst (Fig. 3) shows a reduction peak at 260 °C due to the reduction of oxychlorinated Pt species [15]. The TPR pro-
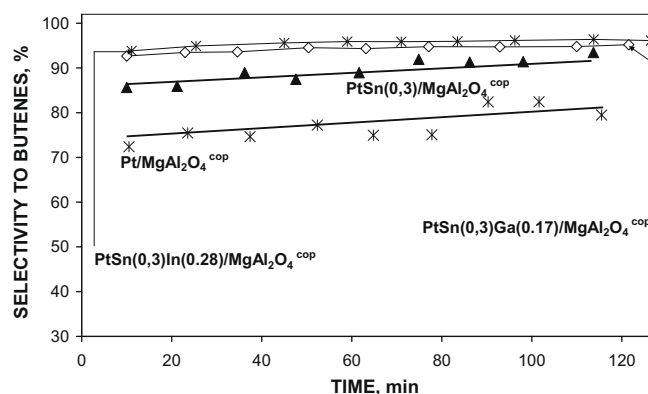
Fig. 2. Selectivity to all butenes vs. reaction time for the different catalysts.
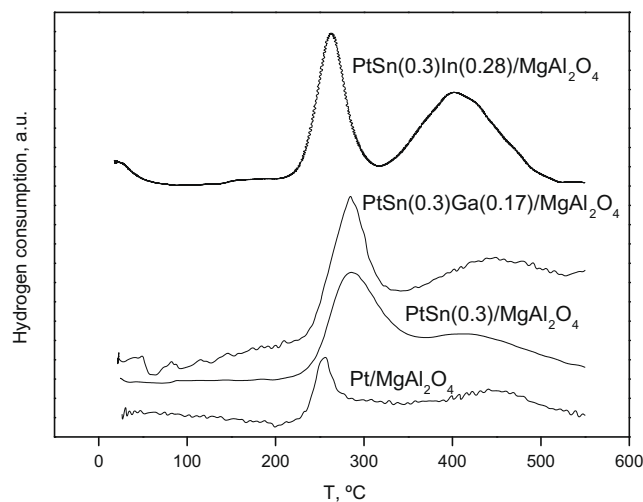
Fig. 3. TPR profiles of the different catalysts.

Table 1
Initial rates (R_{CH}) and Activation Energies (E_{CH}) for the cyclohexane dehydrogenation at 300 °C, initial rates (R_{CP}) of cyclopentane hydrogenolysis at 500 °C, and values of H$_2$ chemisorption (H) for the different catalysts.

Catalyst	R_{CH} mol CH h^{-1} g^{-1}	E_{CH} KJ mol^{-1}	R_{CP} mol CP h^{-1} g^{-1}	H μmol H$_2$ g^{-1}
Pt/MgAl$_2$O$_4$	68	67	6	2.4
PtSn/MgAl$_2$O$_4$	53	67	4.4	1.6
PtSnIn/MgAl$_2$O$_4$	11	75	2.5	0.1
PtSnGa/MgAl$_2$O$_4$	13	96	1.8	<0.1

Fig. 1. n-Butane conversion vs. reaction time for the different catalysts.

files of the fresh $Sn/MgAl_2O_4$, $In/MgAl_2O_4$ and $Ga/MgAl_2O_4$ catalysts (not shown in Fig. 3) displayed very small and non-well defined reduction zones at $T > 550\ °C$. Besides the TPR profile of $PtSn/MgAl_2O_4$ catalyst is similar to those reported by Passos et al. [7] for $PtSn/Al_2O_3$ catalysts, and shows an important reduction peak at 280 °C, corresponding to the simultaneous co-reduction of Pt and Sn. Besides, a small reduction zone at about 400 °C, probably due to free Sn species, is observed. The reduction profile of the PtSnIn catalyst shows a co-reduction peak at 265 °C and another important zone at about 400 °C, probably due to reduction of free Sn and In species. The TPR profile of the PtSnGa catalyst also shows a main reduction peak at 285 °C that could correspond to the co-reduction of Pt, Sn and Ga species, which could be interacting, and a small reduction zone at about 450 °C, corresponding to the reduction of free Sn and Ga species. The important differences in the second reduction zone (400–450 °C) of both trimetallic catalysts would be caused by a higher intermetallic interaction in PtSnGa than in PtSnIn. The quantification of consumed hydrogen from TPR experiments of the catalysts was done. The PtSn catalyst displays a H_2 consumption corresponding to the total reduction of oxidized Pt and Sn species to zerovalent state. The trimetallic catalysts also display high H_2 consumptions, and considering that all Pt was completely reduced, the percentages of Sn and In (or Ga) reduced to zerovalent state were 80% and 100% for PtSnIn and PtSnGa catalysts, respectively.

The metallic phase of the different catalysts was characterized by the cyclohexane dehydrogenation test reaction, a structure insensitive one [16] and the results are shown in Table 1. It must be noted that $Sn/MgAl_2O_4$, $In/MgAl_2O_4$ and $Ga/MgAl_2O_4$ catalysts were inactive, while the $Pt/MgAl_2O_4$ one was very active. The addition of Sn to Pt slightly decreased the initial reaction rate (R_{CH}), whereas the addition of the third metal (In or Ga) drastically
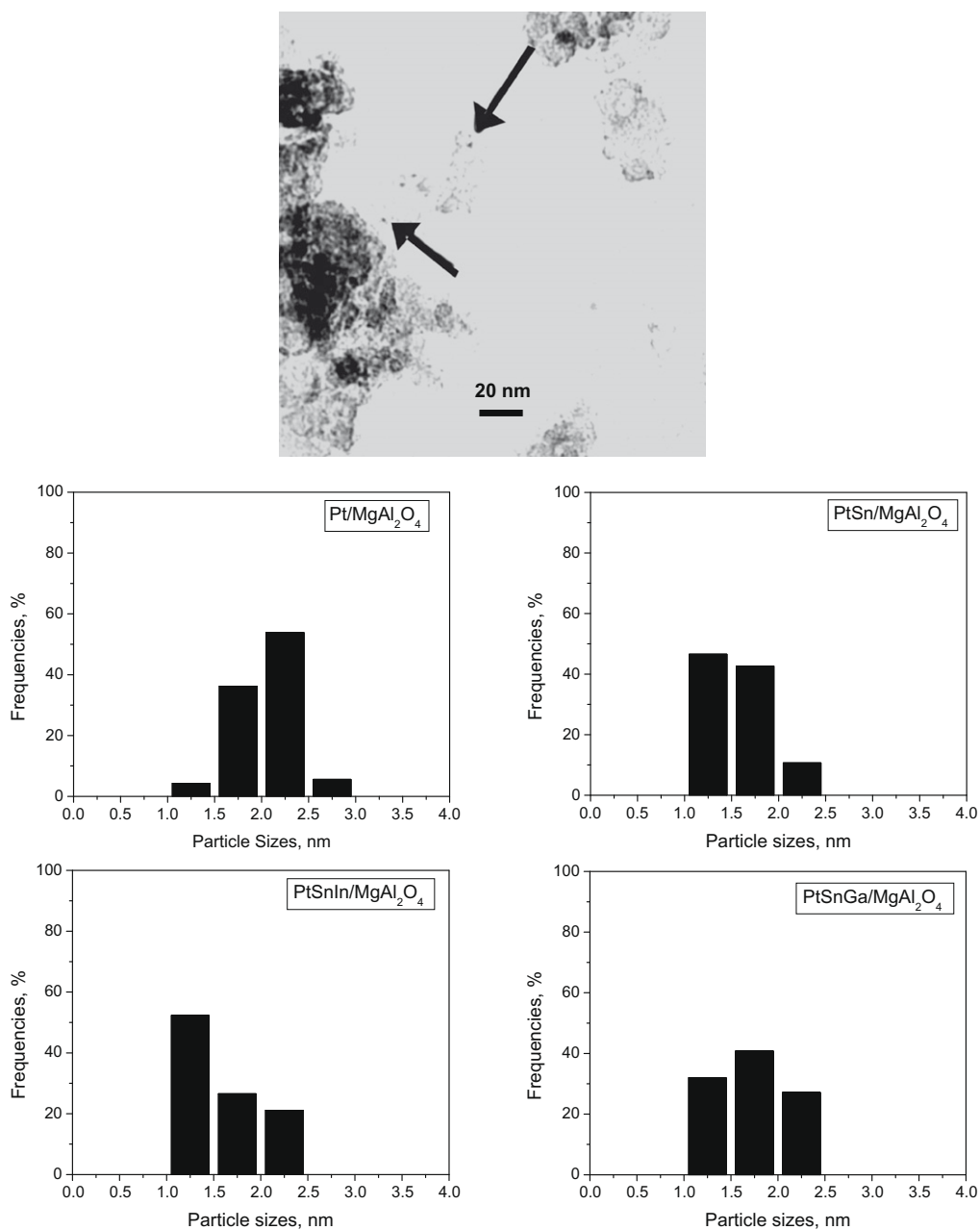

Fig. 4. TEM microphotography of $PtSnIn/MgAl_2O_4$ catalyst. Distribution of particle sizes detected by TEM for the four catalysts.

diminished the activity with respect to PtSn/MgAl$_2$O$_4$. Results showed that the activation energy value for PtSn/MgAl$_2$O$_4$ is similar to that for the Pt catalyst (Table 1), which means that there is no electronic interaction between Pt and Sn. Besides the E_{CH} for PtSnIn/MgAl$_2$O$_4$ catalyst is slightly higher than for the Pt/MgAl$_2$O$_4$, while that corresponding to PtSnGa catalysts is much higher. These results indicate that there is a more important electronic interaction between Pt, Sn and Ga than between Pt, Sn and In. It must be noted that a higher intermetallic interaction in PtSnGa was observed in TPR profiles. In this sense, the effect of the In addition to PtSn would be different, probably by the dilution and blockage of the platinum sites, such as it was proposed by Passos et al. [7] for PtIn/Al$_2$O$_3$ catalysts. On the other hand, Ga could modify the Pt not only by geometric but also by electronic effects. In this sense, Jablonski et al. [17] postulated for PtGa/Al$_2$O$_3$ catalysts several effects including Ga blockage, and in a minor extension, an electronic modification of Pt sites. Moreover, Homs et al. [9] showed by FTIR of PtSnGa/SiO$_2$ catalysts, a slight shift in the ν(CO) towards higher values with respect to the monometallic one, pointing to an electronic effect. Finally Cao et al. [18] showed that Ga modifies the electronic properties of Pt by Pt–Ga interaction.

The catalysts were also characterized by cyclopentane hydrogenolysis reaction, which is a structure-sensitive one [19]. In this case, Sn/MgAl$_2$O$_4$, In/MgAl$_2$O$_4$ and Ga/MgAl$_2$O$_4$ catalysts were inactive. Table 1 displays that the Pt/MgAl$_2$O$_4$ was active for this reaction. The addition of Sn to Pt produced a diminution (27%) of the hydrogenolytic capacity, whereas the addition of In or Ga decreased the activity in a more pronounced way (59% and 70%, respectively). These results could be interpreted taking into account that, as this reaction requires larger Pt ensembles to be carried out, the presence of In or Ga geometrically modifies the metallic phase and produces a dilution of the Pt surface. In the case of PtSnGa, electronic effects could also be present. The effect of In or Ga on the hydrogenolytic activity is more pronounced than the influence of Sn. Taking into account that similar ensembles are necessary both for hydrogenolysis and for carbon formation, the higher stability of the trimetallic catalysts along the reaction time for n-butane dehydrogenation (see Fig. 1) would be caused by geometric modification of the metallic phase due to the In or Ga addition to the metallic phase.

Table 1 also displays the values corresponding to H$_2$ chemisorption. The addition of Sn to Pt/MgAl$_2$O$_4$ catalyst decreases the chemisorbed H$_2$, and this decrease is more pronounced when In or Ga are added. These results show that the addition of Sn, In and Ga strongly diminishes the number of Pt sites involved in the activation of H$_2$ molecule. In this sense, the drastic decrease of the H$_2$ chemisorption in both trimetallic catalysts can be attributed mainly to geometric effects (dilution and blocking), besides to probable electronic interactions in the case of PtSnGa. Another cause that could produce the decrease of the H$_2$ chemisorption would be the increase of the metallic particle sizes but this hypothesis was ruled out by TEM measurements.

Fig. 4 shows the distribution of particle sizes (detected by TEM) corresponding to Pt, PtSn, PtSnIn and PtSnGa catalysts supported on MgAl$_2$O$_4$. As an example, a microphotography of metallic particles of the PtSnIn/MgAl$_2$O$_4$ catalyst is also shown in this Figure. The monometallic Pt catalyst shows a mean particle diameter of 1.83 nm, thus displaying a very high percentage (60%) of particle

sizes between 2 and 3 nm. Sn addition to Pt produces a decrease of the mean particle diameter whose value is 1.35 nm. In this catalyst there is an important decrease of the bigger particles (11%) and an increase of the particles with sizes <2 nm (89%). A decrease of the particle sizes in bimetallic Pt–Sn catalysts supported on different materials was also reported in the bibliography [20,21], and these authors concluded that Sn induces a larger dispersion of the metallic particles. With respect to the trimetallic catalysts, they also show a decrease of the mean particle size with respect to the monometallic Pt. In this sense the mean particle size corresponding to the PtSnIn catalyst is 1.38 nm. This catalyst, that displays the higher concentration (52%) of the smallest metallic particles (between 1 and 1.5 nm), shows the best performance in n-butane dehydrogenation. Finally, the PtSnGa catalyst shows a mean particle size of 1.51 nm, an intermediate value between that of the mono and the bimetallic catalyst. Besides, it shows lower concentration of the smallest particles (32%) than the PtSnIn catalyst. Hence, both bi and trimetallic catalysts have particles sizes smaller than the monometallic one, and this fact would be one of the reasons for their better catalytic behavior.

4. Conclusions

The influence of Sn and In on the catalytic performance of Pt/MgAl$_2$O$_4$ catalysts would be restricted mainly to geometric modifications of the metallic phase, thus producing important decreases of the metallic particle sizes, and this fact would cause the higher yield to olefins, lower deactivation parameter and lower carbon formation. For PtSnGa/MgAl$_2$O$_4$, not only geometric but also electronic effects on the metallic phase would be present, which produce a very good behavior in the n-butane dehydrogenation to olefins.

References

[1] G. Baudin, R. Martinez, P. Pena, J. Am. Ceram. Soc. 80 (1995) 1857.
[2] R. Rennard, J. Freel, J. Catal. 98 (1986) 235.
[3] H. Armendáriz, A. Guzmán, J. Toledo, M. Llanos, A. Vazquez, G. Aguilar-Ríos, Appl. Catal. A 211 (2001) 69.
[4] S. Bocanegra, A. Guerrero-Ruiz, S. de Miguel, O. Scelza, Appl. Catal. A 277 (2004) 11.
[5] J. Guo, H. Lou, H. Zhao, D. Chai, X. Zheng, Appl. Catal. A 273 (2004) 75.
[6] S. Bocanegra, A. Ballarini, O. Scelza, S. de Miguel, Mater. Chem. Phys. 111 (2008) 534.
[7] F. Passos, D. Aranda, M. Schmal, J. Catal. 178 (1998) 478.
[8] N. Nava, P. Del Angel, J. Salmones, E. Baggio-Saitovitch, P. Santiago, Appl. Surf. Sci. 253 (2007) 9215.
[9] N. Homs, J. Llorca, M. Riera, J. Jolis, J.L.G. Fierro, J. Sales, P. Ramírez de la Piscina, J. Mol. Catal. A 200 (2003) 251.
[10] Á. Fürcht, A. Tungler, S. Szabó, A. Sárkány, Appl. Catal. A 226 (2002) 155.
[11] C. Carnevillier, F. Epron, P. Marecot, Appl. Catal. A 275 (2004) 25.
[12] S. Hermans, M. Devillers, Appl. Catal. A 235 (2002) 253.
[13] S. Gobölös, J. Margitfalvi, M. Hegedus, Y. Ryndin, React. Kinet. Catal. Lett. 87 (2006) 313.
[14] S. de Miguel, E. Jablonski, A. Castro, O. Scelza, J. Chem. Technol. Biotechnol. 75 (2000) 596.
[15] G. Lietz, H. Lieske, H. Spindler, W. Hanke, J. Völter, J. Catal. 81 (1983) 17.
[16] A.D. Cinneide, J.K.A. Clarke, Catal. Rev. 7 (1972) 233.
[17] E. Jablonski, A. Castro, O. Scelza, S. de Miguel, Appl. Catal. A 183 (1999) 189.
[18] Y.C. Cao, X.Z. Jiang, J. Mol. Catal. A 242 (2005) 119.
[19] M. Boudart, Adv. Catal. 20 (1969) 153.
[20] A. Vazquez-Zavala, A. Ostoa-Montes, D. Acosta, A. Gómez-Cortés, Appl. Surf. Sci. 136 (1998) 62.
[21] G. Meitzner, G. Via, F. Lytle, S. Fung, J. Sinfelt, J. Phys. Chem. 92 (1988) 2925.