

PtSn/ γ -Al₂O₃ isobutane dehydrogenation catalysts: The effect of alkaline metals addition

Guillermo J. Siri^{a,b,*}, Guillermo R. Bertolini^a, Mónica L. Casella^a, Osmar A. Ferretti^{a,b}

^aCentro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. Jorge Ronco” (CINDECA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata-CONICET, 47 N°257, 1900 La Plata, Argentina

^bFacultad de Ingeniería, Universidad Nacional de La Plata, 1 esq 47, 1900 La Plata, Argentina

Received 23 August 2004; accepted 9 March 2005

Available online 31 March 2005

Abstract

In this work, the modifying effect of alkaline metals (Li, Na and K) is studied on the acid properties of the support and on the behavior of PtSn/ γ -Al₂O₃ catalytic systems, in the isobutane dehydrogenation. The isopropyl alcohol transformation rate decreases sharply with the addition of alkaline metals, according to the sequence Li < Na < K. For the dehydrogenation reaction, the addition of K improves the stability level of the catalyst, and, as a result, PtSnK1.7 catalyst presents the best performance activity/selectivity/stability.

© 2005 Elsevier B.V. All rights reserved.

Keywords: PtSn catalysts; Alkaline metals; Isopropyl alcohol reaction; Organometallic chemistry; Isobutane dehydrogenation

1. Introduction

The catalytic dehydrogenation of light paraffins, due to the endothermic character of these reactions, presents thermodynamic difficulties and for this reason it has to be carried out at high temperatures (above 773 K for the isobutane case). This fact, apart from representing a high energetic cost, favors the appearance of undesirable lateral reactions such as formation of coke and light hydrocarbons by cracking. Taking dehydrogenation reaction of isobutane as an example, the skeletal isomerization is also an important cause of selectivity decrease to isobutene. This reaction is strongly favored by acid sites present in the γ -alumina usually used as support. The neutralization of these sites by adding alkaline metals is a way to decrease the formation of lineal hydrocarbons from isobutane or from isobutene [1–3]. Previous studies performed by our group

demonstrated that the methodology of alkaline modifier incorporation has an important influence on the catalyst final properties [4,5].

Tin is the most widely used modifier of platinum in catalysts for direct alkane dehydrogenation, leading to a system with higher selectivity to olefins and higher stability [2,3,6–10]. The most important tin effects on these catalysts are: (i) the strong inhibition of cracking due to a geometrical effect, and (ii) the decrease of the deactivation rate, either by a decrease of the coke formation rate or by a modification of the nature of the coke formed. The accurate nature of supported PtSn systems is very complicated, and numerous factors affect the characteristics of these catalysts, such as the support acidity, preparation procedure, nature of the precursor compounds, etc. Preparation techniques play a significant role in controlling the type of interactions that occur between tin and platinum and between them and the support. Surface Organometallic Chemistry on Metals (SOMC/M) procedures applied to the synthesis of bimetallic catalysts lead to stable and highly dispersed systems, as it has been reported in the literature [2]. These techniques involve the reaction of organotin compounds, such as tetra-*n*-butyltin (SnBu₄), with a transition metal supported on SiO₂ or Al₂O₃ [11–13].

* Corresponding author. Centro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. Jorge Ronco” (CINDECA), Facultad de Ciencias Exactas, Universidad Nacional de La Plata-CONICET, 47 N°257, 1900 La Plata, Argentina.

E-mail address: gsiri@dalton.quimica.unlp.edu.ar (G.J. Siri).

In this work, the modifying effect of alkaline metals (Li, Na and K) was studied on the acid properties of the support and on the behavior of catalytic systems PtSn/ γ -Al₂O₃, in the isobutane dehydrogenation. The analysis of the influence of the alkaline metal addition on the solid acidity was carried out by means of the isopropyl alcohol transformation. In this case, the study was performed on the modified γ -Al₂O₃ (Li,Na,K)/ γ -Al₂O₃ and not on modified bimetallic systems (PtSn(Li,Na,K)/ γ -Al₂O₃), due to the fact that the isopropyl alcohol is dehydrogenated in presence of Pt, which masks the results referred specifically to acid–base properties of the support.

2. Experimental

A high purity commercial γ -Al₂O₃ with a BET surface area of 184.1 m²/g has been used. Before impregnation, alumina was calcined for 2 h at 773 K in air. Two series of alkali/alumina samples were prepared by impregnating alumina (60–100 mesh) with aqueous solution of the alkali metal precursors (LiOH, NaOH, KOH, Merck, p.a.). After impregnation, samples were dried at 378 K overnight and calcined in air at 773 K. The alkali metal concentrations of the different samples are shown in Table 1.

Bimetallic PtSn/ γ -Al₂O₃ catalysts were prepared by employing SOMC/M techniques [2,14]. To prepare the base monometallic catalyst, a solution of H₂PtCl₆, having a concentration to obtain 1% w/w Pt exchanged, was added onto the γ -Al₂O₃, according to the procedures described in references. The reduced monometallic catalyst was made to react with tetra-*n*-butyltin (SnBu₄) in *n*-decane solution under an H₂ atmosphere. The reaction temperature was 423 K; after approximately 6 h, the solid was filtered out, washed with several portions of *n*-heptane, and dried. The bimetallic phase PtSn/ γ -Al₂O₃ was obtained by eliminating all the organic moieties with a reduction treatment under H₂ flow at 773 K. For the experiments presented in this work, an Sn/Pt atomic ratio of 1.6 was selected.

In order to prepare alkali-modified systems (PtSnM_x.x; M: Li, Na, K; x.x: concentration wt.% of the alkaline metal), an aqueous solution of the alkaline promoter was introduced on the reduced PtSn/ γ -Al₂O₃ catalyst. The concentrations of the alkaline ions were the same as those employed to modify the support.

The surface and porous characteristics of the investigated samples were obtained by N₂ adsorption (77.4 K) in a conventional volumetric apparatus (Micromeritics ASAP 2000). Micrographs were obtained by using a Philips 505 Scanning Electron Microscope.

All the samples were tested in the isopropyl alcohol dehydration reaction, at atmospheric pressure in a flow reactor. The alcohol was fed into the reactor in an N₂ stream (30 cm³/min). The reaction temperature ranged between 373 and 676 K. Reaction products were analyzed through GC, by using a 1.2 m column packed with Carbowax 20M and a flame ionization detector. A sample weight of 100 mg was used in all the experiments.

Catalytic activity for isobutane dehydrogenation was measured in a conventional flow reactor at atmospheric pressure, 823 K, total feed flow of 50 cm³/min, and an H₂/*iso*-C₄H₁₀ ratio of 3. The composition of the feed flow and of the reaction products was analyzed through gas chromatography, by using a Carlo Erba Fractovap series 2150 gas chromatograph on line with the reactor. A 1/4 in. o.d. stainless steel column, 6 m in length, packed with tricresyl phosphate on Chromosorb W, operated at 353 K was employed for this work.

3. Results and discussion

As it was previously mentioned, competitive reactions of isomerization are favored by the presence of acid sites of the γ -Al₂O₃ used as support. In order to inhibit or decrease the strength of these sites, in a first stage, the addition effect of alkaline ions on the total acidity of the support was analyzed. Table 1 presents the composition of the prepared materials and their nomenclature; Li, Na and K concentrations were selected in order to be able to compare results at similar atomic concentrations.

Modified supports were analyzed from the point of view of their textural properties, taking into account that alkaline metals could act as fusing agents. It is clear that changes induced in these properties can have important influence on the final properties of the catalysts prepared with these supports. Table 1 presents values of BET (S_g) surface for different analyzed supports. From the analysis of this table, it appears that neither Na nor K significantly modifies the original S_g of γ -Al₂O₃, while Li modifies it by passing from

Table 1
Composition and BET area of modified and unmodified supports

Series	Support	Name	Li (wt.%)	Na (wt.%)	K (wt.%)	BET (m ² /g)
Series I	γ -Al ₂ O ₃		0	0	0	184.1
	γ -Al ₂ O ₃ +0.1% Li	ALi0.1	0.1	0	0	181.5
	γ -Al ₂ O ₃ +0.3% Na	ANa0.3	0	0.3	0	177.2
	γ -Al ₂ O ₃ +0.6% K	AK0.6	0	0	0.6	176.2
Series II	γ -Al ₂ O ₃ +0.3% Li	ALi0.3	0.3	0	0	164.1
	γ -Al ₂ O ₃ +1.0% Na	ANa1.0	0	1.0	0	180.8
	γ -Al ₂ O ₃ +1.7% K	AK1.7	0	0	1.7	178.2

184.1 to 164.1 m²/g when the γ -Al₂O₃ is compared with ALi0.3. Differences of textural properties observed in the Li-modified support are correlated with morphological characteristics that arise from the observation of SEM microphotographs of these materials. Fig. 1a–d show these microphotographs for the unmodified support and for the modified supports with the highest alkaline concentrations.

It is evident that the morphology is similar for γ -Al₂O₃ and γ -Al₂O₃ modified by Na or K, while γ -Al₂O₃ modified by Li morphology suffers important changes in its texture, noticing “patches” that originate blocking of pores and decrease of the BET surface. These “patches” are formed during the calcination stage carried out at 773 K. This behavior may be explained by the melting point of alkaline hydroxides which are 633, 591 and 743 K for KOH, NaOH and LiOH, respectively. The melting temperatures of NaOH and of KOH are quite below the temperature of calcination and that is why it is possible to assume that they melt completely, so they can be distributed uniformly on the alumina. In the LiOH case, a probable incomplete melting effect during the calcination stage may be the cause of a non-homogeneous redistribution resulting in these “patches”.

The study about the influence of the deposit of alkaline metals on the γ -Al₂O₃ acidity was carried out by means of the isopropyl alcohol transformation. The “test” reaction of the isopropyl alcohol (IPA) decomposition is an indirect determination for the characterization of acid and basic sites present on a solid surface, different from the case of adsorption–desorption of bases (complemented with IR spectroscopy) [15,16]. The decomposition of this alcohol involves dehydration and dehydrogenation

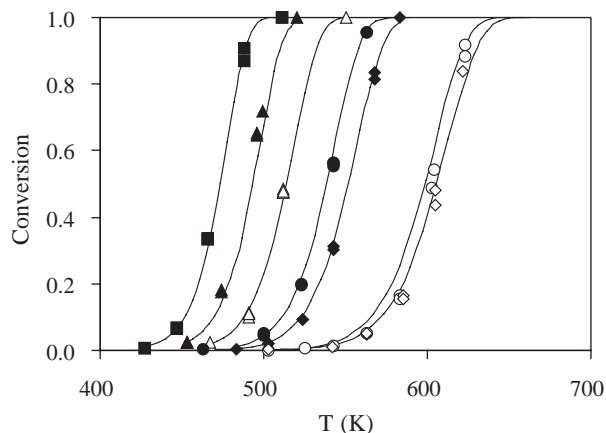


Fig. 2. Conversion of IPA as function of temperature: (■) γ -Al₂O₃, (▲) ALi0.1, (△) ALi0.3, (●) ANa0.3, (○) ANa1.0, (◆) AK0.6, (◇) AK1.7 (for the experimental conditions, see text).

reactions that occur by means of three mechanisms denominated E₁, E_{1CB} and E₂. The E₁ mechanism involves strong Brønsted or Lewis acid sites to give propene as reaction product. On the other hand, the E_{1CB} mechanism requires basic and weak Lewis acid sites, which act in a concerted mechanism producing also propene. Finally, the E₂ dehydration mechanism involves pairs of acid–base sites of similar strength. Di-isopropyl ether is also produced by this mechanism, by condensation followed by dehydration. The isopropyl alcohol dehydrogenation to ketone is produced through an E_{1CB} mechanism. From these considerations, the obtention of propene as main product (or propene plus di-isopropyl ether) suggests a support with predominant acid nature,

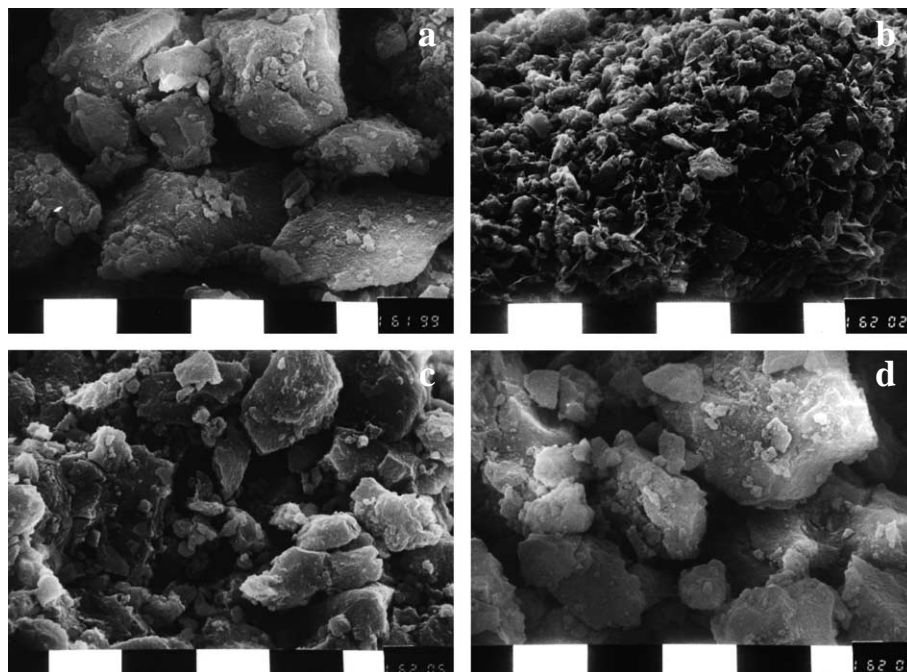


Fig. 1. SEM micrographs of γ -Al₂O₃ (a), ALi0.3 (b), ANa1.0 (c) and AK1.7 (d) (scale bar=1 μ m).

Table 2

Activation energy and pre-exponential factor for the IPA reaction on the studied supports

Support	Activation energy (kJ/mol)	Pre-exponential factor (s^{-1})
γ -Al ₂ O ₃	152.7	$2.11 \cdot 10^{17}$
ALi0.1	150.5	$2.48 \cdot 10^{16}$
ALi0.3	152.3	$8.84 \cdot 10^{15}$
ANa0.3	156.8	$4.65 \cdot 10^{15}$
ANa1.0	160.9	$3.19 \cdot 10^{14}$
AK0.6	156.8	$2.00 \cdot 10^{15}$
AK1.7	158.8	$1.42 \cdot 10^{14}$

while the ketone presence clearly indicates the existence of basic sites.

Fig. 2 presents conversion curves as a function of the reaction temperature for the IPA transformation on the different studied supports. The IPA transformation rate sharply decreases with the addition of alkaline metals; at higher concentration of alkaline metal, the penalizing effect is higher. When the three alkaline metals are compared at equivalent atomic concentrations, the inhibiting sequence follows the order $Li < Na < K$.

Considering a first order reaction rate expression, apparent activation energies and pre-exponential factors were calculated and are shown in Table 2.

In the unmodified support as well as in modified supports, for the lower concentration level in Li, Na or K (Series 1), the propene is the main product, detecting also di-isopropyl ether (it decreases as the temperature increases) and ketone (it increases with temperature). For these systems, the generation of basic sites is still incipient and for this reason the ketone contribution to the final products is not significant.

When the concentration of alkaline metals increases (Series 2), larger ketone amounts appear indicating an increase in the basicity and a decrease in the acidity of γ -Al₂O₃; the appearance of basic sites together with weak acid sites would be responsible for the dehydrogenation to ketone (E_{1CB} mechanism). Results obtained are conclusive

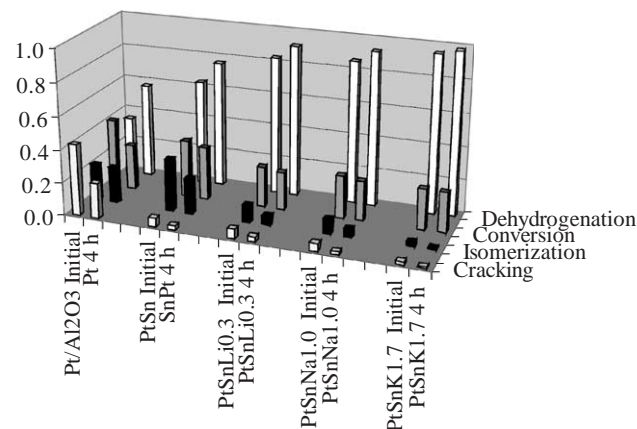


Fig. 3. Activity results for different catalysts on the dehydrogenation of isobutane reaction at initial time after 4 h on stream (for the experimental conditions, see text).

with respect to an important inhibition of the activity of acid sites of the support following the sequence $K > Na > Li$, as it appears from the values of the pre-exponential factor. Ionic radii of K, Na and Li are 0.133, 0.097 and 0.068 nm, respectively; at larger ionic radius, there is larger blocking of the support acid sites. Table 3 shows the selectivities to the different products for γ -Al₂O₃ and Series 2 modified supports at 3 levels of temperature.

Values of activation energy between 150 and 160 kJ/mol were obtained for all systems suggesting that no changes are observed in the mechanism of the isopropyl alcohol transformation. Values of the same order for the IPA transformation are reported by Trikalitis and Pomonis in the case of perovskites catalysts [17].

The behavior of PtSn/ γ -Al₂O₃ catalytic systems, unmodified and modified by the K, Na and Li addition, was studied in the isobutane dehydrogenation reaction at atmospheric pressure, 823 K and a feed composition of H_2 /isobutane = 3/1.

Fig. 3 shows isobutane conversion values (initial and after 4 h of reaction), for all analyzed systems. Taking the

Table 3

Selectivities for modified and unmodified supports at several temperatures for the IPA transformation

Catalysts	Temperature (K)	Sel. propene	Sel. di-isopropyl ether	Sel. acetone	Conversion
Al ₂ O ₃	443	0.71	0.29	0	0.05
Al ₂ O ₃	463	0.87	0.13	0	0.25
Al ₂ O ₃	483	0.96	0.04	0	0.78
ALi0.3	463	0.80	0.20	0	0.01
ALi0.3	483	0.84	0.16	0	0.07
ALi0.3	503	0.92	0.08	0	0.27
ALi0.3	523	0.99	0.01	0	0.73
ANa1.0	583	0.70	0	0.30	0.26
ANa1.0	603	0.71	0	0.29	0.59
ANa1.0	623	0.75	0	0.25	0.92
ANa1.0	643	0.83	0	0.17	0.99
AK1.7	563	0.76	0	0.24	0.06
AK1.7	583	0.71	0	0.29	0.18
AK1.7	603	0.63	0	0.37	0.45
AK1.7	623	0.65	0	0.35	0.81

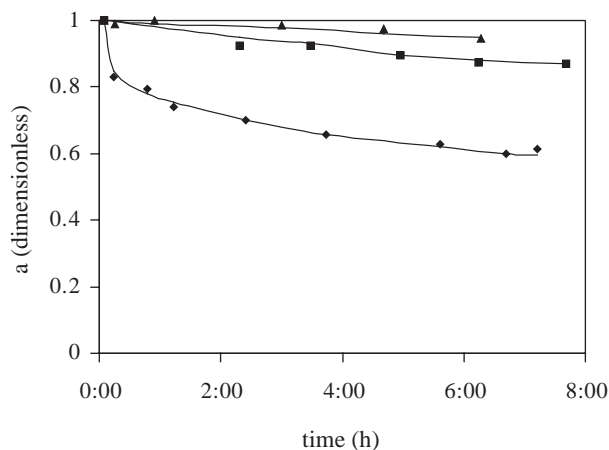


Fig. 4. Activity coefficient vs. time on stream for the dehydrogenation of isobutane reaction: (♦) Pt/γ-Al₂O₃, (■) PtSn/γ-Al₂O₃, (▲) PtSnK/γ-Al₂O₃.

Pt/γ-Al₂O₃ catalyst as basis for comparison, it is possible to observe that this system presents the highest initial activity, but it decreases markedly after 4 h on stream. When tin is added, the initial conversion for all systems is slightly lower but in contraposition, its value is maintained without important variations in the course of time, especially in the systems modified by adding alkaline metals.

Also in Fig. 3, initial values and values after 4 h of reaction are represented, for selectivities to cracking, isomerization and dehydrogenation. The selectivity to isobutene after 4 h on stream was noticeably improved by adding Sn, raising from 57% for Pt/γ-Al₂O₃ to 76% for PtSn/γ-Al₂O₃, due to the decrease of cracking and isomerization reactions. This is a well known fact studied in the literature and explained by a combination of geometric and electronic effects [2,3,7]. However, the contribution of isomerization reactions in the PtSn/γ-Al₂O₃ system is still important.

The fact that the selectivity to isomerization products for this catalyst is almost unaffected in relation to Pt/γ-Al₂O₃ system indicates that, due to the specificity of SOMC/M techniques, tin might not be modifying the support acidity. As it is shown in Fig. 3, the presence of alkaline metals as modifiers produces a marked decrease of isomerization reactions, being the effectiveness order is K>Na>Li, in agreement with results obtained for support acidity studies. Thus, the K addition to PtSn/γ-Al₂O₃ catalyst results in a catalyst able to produce isobutane dehydrogenation with a selectivity to isobutene >98%.

Results arising from this study show that the presence of alkaline metals affects basically isomerization reactions, carried out principally on acid sites of the support and in a lesser proportion to the reactions catalyzed by the metallic phase. This indicates that conclusions obtained from the study of the isopropyl alcohol transformation on γ-Al₂O₃ modified in relation to its acid–basic properties can be extrapolated to the modified bimetallic systems.

Regarding stability, it was demonstrated in previous works that the principal deactivation mechanism is produced by the coke deposition. This coke is deposited on the metallic phase and also on the support through a migration process. In order to quantify the stability, an activity coefficient *a* was defined (ratio between the catalyst activity at reaction time *t* and the initial activity). Fig. 4 shows results corresponding to Pt/γ-Al₂O₃, PtSn/γ-Al₂O₃ and PtSnK1.7 catalysts, noticing that in presence of Sn a marked stability increase is produced.

As a conclusion, the addition of potassium improves even more this stability level of the catalyst and as a result, PtSnK1.7 catalyst presents the best performance activity/selectivity/stability in the isobutane dehydrogenation reaction.

4. Conclusions

- ✓ The addition of Na and K on γ-Al₂O₃ support does not modify its textural properties, while Li modifies the *S_g* value, due to a probable incomplete melting effect during the calcination stage generating “patches” on the support surface.
- ✓ The isopropyl alcohol transformation rate sharply decreases when adding alkaline metals, according to the sequence Li<Na<K. These results are conclusive with respect to an important inhibition of the activity of the support acid sites: at larger ionic radius, there is a larger blocking effect.
- ✓ For the dehydrogenation reaction, the addition of K improves the stability level of the catalyst, and as a result, PtSnK1.7 catalyst presents the best performance activity/selectivity/stability.

Acknowledgments

This work has been sponsored by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina) and the Agencia Nacional de Promoción Científica y Técnica (ANPCYT, Argentina).

References

- [1] S. de Miguel, A. Castro, O. Scelza, J. Soria, Catal. Lett. 32 (1995) 281.
- [2] G.J. Siri, M.L. Casella, G.F. Santori, O.A. Ferretti, Ind. Eng. Chem. Res. 36 (1997) 4821.
- [3] R.D. Cortright, J.M. Hill, J.A. Dumesic, Catal. Today 55 (2000) 213.
- [4] M.L. Casella, G.J. Siri, G.F. Santori, O.A. Ferretti, M. Ramirez de Agudelo, Langmuir 13 (2000) 5639.
- [5] G.J. Siri, M.L. Casella, O.A. Ferretti, J.L.G. Fierro, Stud. Surf. Sci. Catal. 139 (2001) 287.
- [6] E. Merlen, P. Beccat, J.C. Bertolini, P. Delichère, N. Zanier, B. Didillon, J. Catal. 159 (1996) 178.
- [7] Z. Paál, A. Gyory, I. Uszkurat, S. Olivier, M. Guérin, C. Kappenstein, J. Catal. 168 (1997) 2463.

- [8] C. Kappenstein, M. Guérin, K. Lázár, K. Matusek, Z. Paál, *J. Chem. Soc., Faraday Trans.* 94 (1998) 2463.
- [9] S.M. Stagg, C.A. Querini, W.E. Alvarez, D.E. Resasco, *J. Catal.* 168 (1997) 75.
- [10] J.M. Hill, R.D. Cortright, J.A. Dumesic, *Appl. Catal., A Gen.* 168 (1998) 9.
- [11] J. Margitfalvi, M. Hegedüs, S. Göbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó, F. Nagy, *Proc. 8th Int. Congr. Catal., Berlin*, vol. 4, 1984, p. 903.
- [12] O. Ferretti, L. Bettega de Pauli, J.P. Candy, G. Mabilon, J.P. Bourmonville, *Stud. Surf. Sci. Catal.* 31 (1987) 713.
- [13] O.A. Ferretti, C. Lucas, J.P. Candy, J.M. Basset, B. Didillon, F. Le Peltier, *J. Mol. Catal.* 103 (1995) 125.
- [14] G.F. Santori, M.L. Casella, G.J. Siri, H.R. Adúriz, O.A. Ferretti, *Appl. Catal., A Gen.* 197 (2000) 141.
- [15] S. de Miguel, A. Caballero Martínez, A. Castro, O. Scelza, *J. Chem. Technol. Biotechnol.* 65 (1996) 131.
- [16] A. Gervasini, J. Fenyvesi, A. Auroux, *Catal. Lett.* 43 (1997) 219.
- [17] P.N. Trikalitis, P.J. Pomonis, *Appl. Catal., A Gen.* 131 (1995) 309.