Catalysis Letters 22 (1993) 123–133

Catalysts for the selective dehydrogenation of high molecular weight paraffins

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Selective dehydrogenation of high molecular weight linear paraffins is an important process step for the production of biodegradable detergents. Pt, PtSn, PtGe and PtPb supported on γ-Al_2O_3 doped with alkaline metals were characterized and tested in the *n*-decane dehydrogenation reaction. When alkaline metals are added to Pt/Al_2O_3 a promoting effect on the selectivity to olefins in the *n*-decane dehydrogenation is observed. Regarding $PtSn/Al_2O_3$-doped catalysts their performance depends on the alkaline metal used as dopant, the Sn content and the preparation method. Moreover these bimetallic catalysts show a better olefin yield and a lower selectivity to gases and aromatics than the monometallic platinum catalysts. PtGe and PtPb based catalysts have an analogous behavior to the PtSn one but its selectivity to olefins is lower.

Keywords: *n*-decane dehydrogenation; Pt–Sn/Al_2O_3 catalysts; Pt–Ge/Al_2O_3; Pt–Pb/Al_2O_3; bimetallic catalysts

1. Introduction

Linear olefins of high molecular weight (C_{10}–C_{14}), which are raw materials for the production of biodegradable detergents, can be obtained by dehydrogenation of the corresponding paraffins.

Despite the economic importance of the dehydrogenation process of paraffins, relatively few studies on catalysts, their characterization and performance are available in the scientific literature. Thus, Timofeeva et al. [1] studied the influence of Pt concentration in Pt/Al_2O_3 and Pt/Al_2O_3–Li catalysts on the dehydrogenation of high linear paraffins. They found that selectivity to monoolefins depends on the presence of Li but not on the concentration of Pt. The effect of the addition of different Li concentrations (0.2–4 wt%) to $Pt(0.5\%)/Al_2O_3$ catalysts on the *n*-dodecane dehydrogenation was studied by Tyupaev et al. [2], who found that Li reduces both the Pt dispersion and the catalyst activity. However, the selectivity to olefins was improved because of the inhibition of the cracking reactions. Besides, Isagulyants et al. [3] reported that the alkaline additives not only reduced the catalyst acidity and suppressed the isomerization and hydrocracking reactions, but also decreased the aromatization capacity. On the other hand, the addition of Sn to Pt/Al_2O_3 catalysts improves the activity and selectivity to olefins in the *n*-dodecane dehydrogenation reaction, also increasing the catalyst stability [4].

The objective of this paper is to make a contribution to the formulation, preparation, characterization, and evaluation of Pt–Sn, Pt–Ge and Pt–Pb supported on γ-Al_2O_3 doped with alkaline metals for the *n*-decane dehydrogenation process taking into account the research work developed in the INCAPE.

2. Experimental

All the catalysts were prepared using a commercial γ-Al_2O_3 support ($S_{BET} = 180\ m^2/g$). The alumina samples doped with Li, Na and K were obtained by impregnating the support with an aqueous solution of the respective alkaline metal hydroxide. Besides, Pt(0.3%)/Al_2O_3, Pt(0.3%)/Al_2O_3–Ma (Ma = Li, K) catalysts, and Pt(0.3%)–M/Al_2O_3–Ma (M = Sn, Ge, Pb; Ma = Li, K) catalysts were prepared with different contents of M (0–0.3 wt%) and the same molar content of Ma (0.43 mmol/g Al_2O_3). These latter catalysts were obtained either by co-impregnation or by successive impregnation of the doped alumina (deposition of the M precursor, drying, deposition of the Pt precursor). The metallic precursors employed were H_2PtCl_0, $SnCl_2$, $GeCl_4$ and $Pb(NO_3)_2$. After impregnation, the samples were dried at 120°C, calcined in air at 500°C and reduced in H_2 at the same temperature.

The acidic properties of pure and doped alumina were studied by ammonia thermodesorption and IR spectroscopy. These samples were also evaluated in the isopropanol dehydration reaction ($T = 150$–$400°C$, H_2/isopropanol molar ratio = 18 and space velocity = 32 h^{-1}) and in the cracking reaction of *n*-decane at 460–520°C and H_2/*n*-decane molar ratio = 13.

Mono- and bi-metallic catalysts were characterized by test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), H_2 chemisorption, temperature programmed reduction and finally tested in the *n*-decane dehydrogenation reaction at 460–520°C, H_2/*n*-decane molar ratio = 13 and space velocity = 32 h^{-1}.

3. Results and discussion

3.1. EFFECT OF THE ADDITION OF Ma TO ALUMINA

Table 1 shows the distribution of sites with different acid strengths, obtained by ammonia thermodesorption on alumina and doped alumina samples. It can be

Table 1
Distribution of sites with different acid strength in samples of alumina and doped alumina. T_d = temperature of NH_3 desorption

Catalyst	Amount of NH adsorbed (meq/g)			
	weak[a]	medium[b]	strong[c]	total
γ-Al_2O_3	0.120	0.148	0.136	0.404
Al_2O_3–Li (0.05%)	0.118	0.146	0.124	0.388
Al_2O_3–Li (0.30%)	0.110	0.134	0.100	0.344
Al_2O_3–Na (0.15%)	0.102	0.128	0.102	0.332
Al_2O_3–K (0.25%)	0.096	0.101	0.042	0.239
Al_2O_3–K (1.67%)	0.056	0.061	0.031	0.148

[a] $T_d = 300°C$.
[b] $T_d = 400°C$.
[c] $T_d = 500°C$.

observed that the addition of Li, Na or K decreases the total acidity, mainly affecting the strongest acid sites and, to a lesser degree, those with medium and weak strength. However, for the same molar content of the alkaline metal, the poisoning effect is higher for potassium than for Na or Li.

Moreover, it was observed by means of IR spectroscopy using pyridine as a probe molecule) that the intensities of the characteristic bands of the Lewis acid sites (1447–1460 cm^{-1}) decrease after the alkaline metal addition to the alumina surface. Characteristic bands of the Brønsted acid sites were not observed (1485, 1540 and 1640 cm^{-1}).

The poisoning effect of the alkali-metals on the acidic properties of the alumina was also studied by means of the isopropanol dehydration to di-isopropylether and propylene. Fig. 1 shows that the isopropanol conversion decreases as the amount of Na increases. It can also be observed that very low molar contents of Na and K produce an almost total inhibition of the dehydrating capacity, whereas much higher contents of Li are required to produce the same effect. Likewise, as fig. 2 shows, the selectivity to di-isopropylether displays an analogous behavior. Taking into account that the ether formation would require strong acid sites [5], the results obtained in the isopropanol dehydration would be in agreement with the higher poisoning capacity of K and Na on the stronger acid sites.

Samples of Al_2O_3–Ma with the same Ma content (0.022 mmol/g Al_2O_3) were also tested in cracking of *n*-decane. Fig. 3 shows the relative conversion (conversion on Ma–Al_2O_3/conversion on Al_2O_3). It can be observed that the alkali-metal addition inhibits the cracking of *n*-decane, this effect being more important at higher reaction temperatures. The selectivity (x_G/x_L) defined as conversion to [C_1–C_4] gases/conversion to [C_5–C_9] liquids is shown in fig. 4. It can be noted that the cracking capacity to produce smaller hydrocarbon molecules is more affected by K or

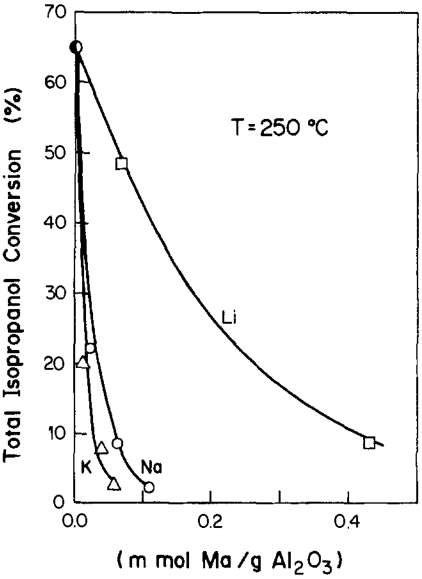

Fig. 1. Total isopropanol conversion as a function of the Ma content in Al_2O_3–Ma.

Na addition than by Li addition. This behavior can be explained by the higher poisoning effect of K or Na on the stronger acid sites.

3.2. EFFECT OF THE ADDITION OF Pt AND Pt–M TO THE DOPED ALUMINA

The alkaline metals employed for these studies were Li and K which, according to the above-mentioned results, appear as the weakest and the strongest poison of the acid sites, respectively.

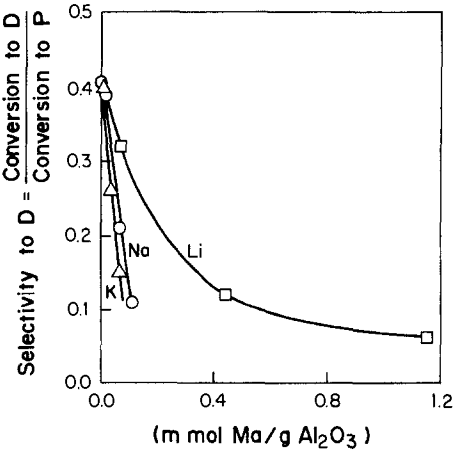

Fig. 2. Selectivity to di-isopropylether (conversion to ether (D)/conversion to propylene (P)) as a function of the Ma content in Al_2O_3–Ma.

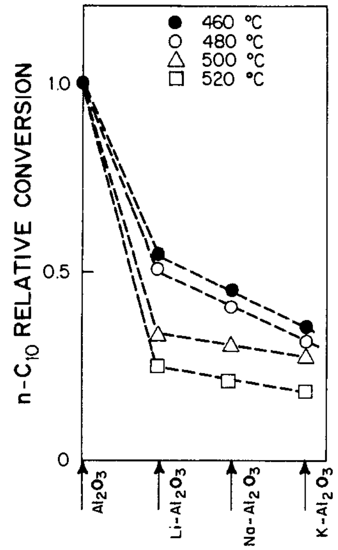

Fig. 3. Total relative conversion to alumina in samples of Al_2O_3–Ma (0.022 mmol/g) for cracking of n-C_{10}.

Table 2 shows the reaction rates for cyclohexane dehydrogenation and cyclopentane hydrogenolysis and platinum dispersion for monometallic catalysts. Considering Pt/Al_2O_3 as a reference, it can be observed that the dehydrogenating and hydrogenolytic activities of the metallic phase decreased by the Ma addition, but in different degrees depending on the alkaline metal. Taking into account the plati-

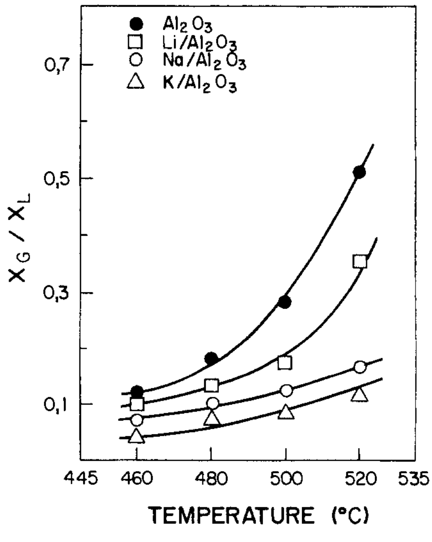

Fig. 4. X_G/X_L: conversion to gases/conversion to liquids for Al_2O_3 and Al_2O_3–Ma (0.022 mmol/g) as a function of temperature for cracking of n-C_{10}.

Table 2
Cyclohexane dehydrogenation (R_D) and cyclopentane hydrogenolysis (R_H) rates for mono- and bimetallic catalysts (co-impregnated)

Catalyst [a]	R_D (mol/h g Pt)	R_H (mol/h g Pt)	Pt dispersion (%)
Pt(0.30%)/Al_2O_3	116.6	7.96	47
Pt(0.30%)/Al_2O_3–Li	87.9	6.90	39
Pt(0.30%)/Al_2O_3–K	57.8	5.64	22
PtSn(0.3–0.1%)/Al_2O_3–Li	38.0	1.10	
PtSn(0.3–0.2%)/Al_2O_3–Li	16.5	0.76	
PtSn(0.3–0.3%)/Al_2O_3–Li	9.5	0.64	
PtGe(0.3–0.1%)/Al_2O_3–Li	20.0	0.72	
PtGe(0.3–0.2%)/Al_2O_3–Li	13.0	0.50	
PtGe(0.3–0.3%)/Al_2O_3–Li	5.0	0.38	
PtPb(0.3–0.1%)/Al_2O_3–Li	32.5	1.00	
PtPb(0.3–0.2%)/Al_2O_3–Li	16.5	0.58	
PtPb(0.3–0.3%)/Al_2O_3–Li	8.0	0.46	

[a] Alkaline metal content was 0.43 mmol/g Al_2O_3.

num dispersion estimated from hydrogen chemisorption, the dehydrogenation rate per exposed metallic atom is not noticeably modified with the Ma addition, which would agree with the "insensitive" nature of this reaction [6]. Instead, the cyclopentane hydrogenolysis rate per gram of metal decreases less with Ma addition than the metallic dispersion. Keeping in mind that the hydrogenolysis reaction requires an ensemble of several metallic atoms [7], the effect of the alkaline metal addition could be explained in terms of a growth of the metallic crystallites, thus favouring the hydrogenolysis reaction.

The effect of the addition of different amounts of Sn, Ge, or Pb on the cyclohexane dehydrogenation and cyclopentane hydrogenolysis rates is also shown in table 2. In all cases, the dehydrogenating and hydrogenolytic capacities of the metallic phase markedly decrease as the Sn, Ge or Pb amounts increase.

The deposition sequence of the metallic precursors in bimetallic systems can modify the characteristics of the metallic phase, even more in the case of Pt–Sn catalysts. In this system the metallic precursors are able to form a Pt–Sn complex which is adsorbed on the support when the co-impregnation method is used, but the Pt–Sn complex is not produced when the Al_2O_3 is first impregnated with Sn and then with Pt (successive impregnation) [8]. This justifies the studies on the effect of the deposition sequence upon the characteristics of the metallic phase in PtSn/Al_2O_3–Ma catalysts. Fig. 5 shows the behavior of the PtSn/Al_2O_3–Ma catalysts in the cyclohexane dehydrogenation and cyclopentane hydrogenolysis for different Sn/Pt molar ratios. Results indicate that catalysts prepared by successive impregnation exhibit an activity slightly higher than that obtained by co-impregnation. Catalysts containing K display a lower activity than those containing Li. It should be noted that, whatever the deposition sequence employed, the addition of increas-

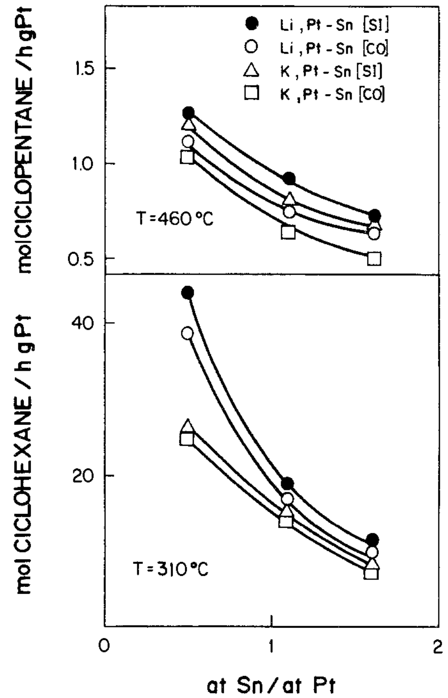

Fig. 5. Cyclohexane dehydrogenation and cyclopentane hydrogenolysis rate for PtSn/Al_2O_3–Ma (0.43 mmol/g) prepared by co-impregnation (CO) and successive impregnation (SI) as a function of at Sn/at Pt. Pt content = 0.3%.

ing quantities of Sn produces an important drop in the activity, which is more marked for hydrogenolysis than for dehydrogenation. These differences may reflect differences in tin oxidation state or Pt–Sn alloy formation, although it is clear that Sn, Ge and Pb all act as potent poisons for C–C bond breaking.

3.3. CATALYST BEHAVIOR IN THE *n*-DECANE DEHYDROGENATION

Fig. 6 shows the total conversion and selectivities to olefins, alkyl-aromatics and gases in the *n*-decane dehydrogenation for alumina, Pt/Al_2O_3 (doped and undoped) and different PtSn/Al_2O_3–Ma. The differences to reach 100% selectivity correspond to C_{10} isoalkanes and C_5–C_{10} hydrocarbons. It can be observed that the alumina only shows activity for cracking, typical of an acid support. On the other hand, the Pt/Al_2O_3 catalyst shows the characteristic behavior of a bifunctional catalyst. When alkaline metals are added to Pt/Al_2O_3, a decrease in the total conversion is observed because of the inhibition of the reactions which take place on the acidic function. The hydrogenolytic capacity of the metallic function also decreases, and its contribution to the formation of light paraffins is thus restricted.

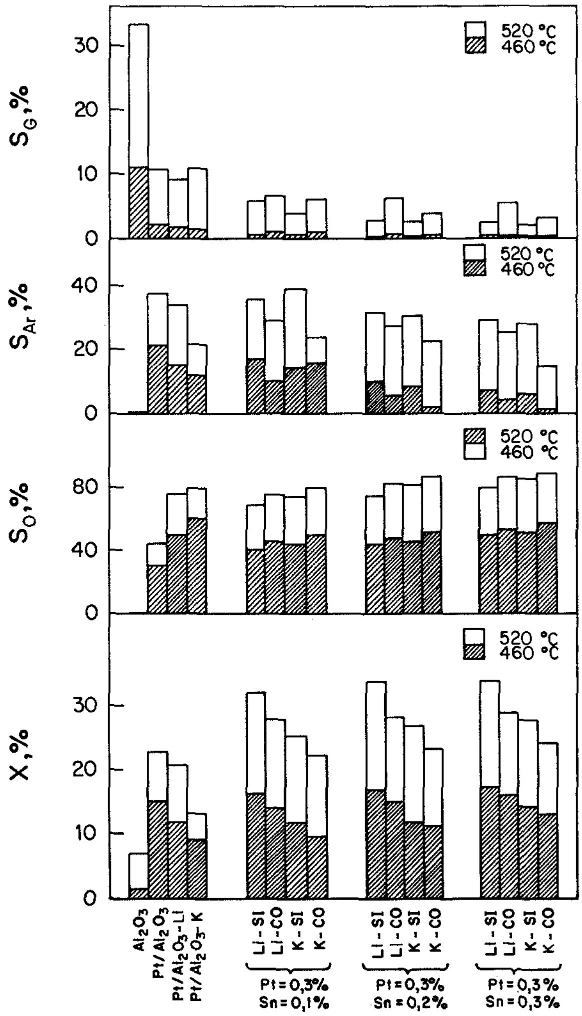

Fig. 6. Total conversion (X) and selectivities to olefins (S_O), alkyl-aromatics (S_{Ar}) and gases (S_G) for Al_2O_3, Pt/Al_2O_3–Ma and $PtSn/Al_2O_3$–Ma with different contents of Sn, prepared by co-impregnation (CO) and successive impregnation (SI), and equal Ma molar content.

The selectivity to alkyl-aromatics substantially decreases because of the poisoning of the acidic function, which is reflected in a smaller participation of the bifunctional path in the formation of aromatic products. On the other hand, the addition of alkaline metals seems to produce a promoting effect on the selectivity to olefins. Similar effects have been observed by Timofeeva et al. [1] and Tyupaev et al. [2]. With respect to the selectivity to gases it should be noted that it notably decreases when Pt or Pt–Ma are deposited on the alumina leading to catalysts with low selectivity to gases ($<5\%$ at 460°C).

Regarding PtSn/Al_2O_3–Ma catalysts their performance depends on the alkaline metal used as dopant, the Sn content and the preparation method. It is worth noticing that the gas formation is diminished by the Sn addition to Pt. This effect can be explained by taking into account that the Sn addition produces both an inhibition of the hydrogenolytic capacity of the metallic phase (according to the cyclopentane hydrogenolysis results) and additional poisoning of the acidity [9]. With respect to aromatization, there is a decrease in selectivity when the Sn content increases. This is a consequence of a lower contribution of the bi-functional path since the tin addition modifies the metallic phase and diminishes the acidity. Instead, the yield to olefin (defined as the product between conversion and selectivity to olefins) is favoured by the addition of increasing amounts of Sn to Pt. The promoting action of Sn on dehydrogenation is due not only to the inhibition of the other competitive reactions (gas and aromatic formation) but to the electronic modifications of Pt by tin. This effect would modify the interaction strength between the olefins and the metallic site, making it weaker and thus keeping the metallic surface more free of coke precursors [3,10] which improves the coke tolerance.

It is interesting to notice that the catalysts obtained by co-impregnation show lower activity than those obtained by successive impregnation, using Li or K as dopant. This could be explained in terms of a higher dilution effect of the metallic phase in co-impregnated catalysts with respect to those obtained by successive impregnation. This would cause a decrease in the number of ensembles and therefore a lower participation of the direct path of aromatization on the metal phase, thus favouring the selectivity to olefins.

PtGe/Al_2O_3–Ma and PtPb/Al_2O_3–Ma catalysts exhibited an analogous behavior to that of the PtSn/Al_2O_3–Ma catalyst in the test reactions of the metallic phase, as shown in table 2. It was also found that the acidity of the support decreases with the addition of increasing quantities of group IVA metals. Likewise, the behavior of PtGe and PtPb catalysts in the *n*-decane dehydrogenation reaction shows a certain similarity with those in which Sn was used as additive.

In fig. 7 the performance of different bimetallic catalysts in the *n*-decane dehydrogenation is shown. It can be observed that for a given total conversion level, the Sn-based catalyst presents higher selectivity to olefins than the catalysts based on Ge and Pb.

These results would indicate that the three types of catalysts mentioned would have similar characteristics relative to the nature of their catalytic functions.

4. Conclusions

Alumina supported Pt–Sn bimetallic catalysts doped with alkali metals have a better olefin yield and a lower selectivity to gases and aromatics than the monome-

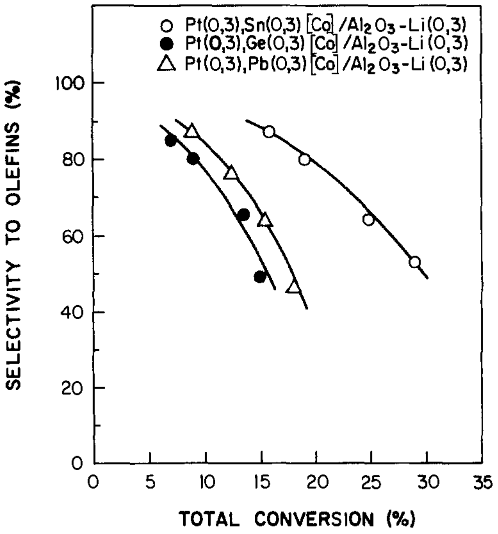

Fig. 7. Dehydrogenation of n-C_{10}. Comparison among different catalysts prepared by co-impregnation. The contents are expressed in wt%. The content of Li is equivalent to 0.43 mmol/g.

tallic platinum catalyst. PtGe and PtPb based catalysts have similar performance to the PtSn one, but their selectivity to olefins is lower.

Acknowledgement

The experimental results reported in this paper were obtained at INCAPE by the working group under my direction: S.R. de Miguel, O.A. Scelza and G. García Cortez. I am grateful to these persons for the experimental assistance. Besides I thank S.R. de Miguel and O.A. Scelza for critical discussions of this paper.

References

[1] E.A. Timofeeva, A.P. Tyupaev and G.B. Isagulyants, Izv. Akad. Nauk. SSSR Ser. Khim. 9 (1981) 2067.

[2] A.P. Tyupaev, E.A. Timofeeva and G.B. Isagulyants, Neftekhimiya 21 (1981) 186.

[3] G.B. Isagulyants, N.R. Bursian and A.A. Greish, Izv. Akad. Nauk. SSSR Ser. Khim 11 (1980) 2455.

[4] S.B. Kogan, N.M. Podkletnova, O.M. Oranskaya, I.V. Semenskaya and N.R. Bursian, Kinet. Katal. 22 (1981) 663.

[5] G. García Cortez, S.R. de Miguel, O.A. Scelza and A.A. Castro, J. Chem. Tech. Biotech. 53 (1992) 177.

[6] D.W. Blakely and G.A. Somorjai, J. Catal. 42 (1976) 181.

[7] C.R. Apesteguía and J. Barbier, *Proc. VII Simposio Iberoamericano de Catálisis*, Huelva España (1982) p. 751.

[8] G.T. Baronetti, S.R. de Miguel, O.A. Scelza, M.A. Fritzler and A.A. Castro, Appl. Catal. 19 (1985) 77.

[9] J.C. Luy, S.R. de Miguel, G.T. Baronetti, O.A. Scelza and A.A. Castro, React. Kinet. Catal. Lett. 32 (1986) 234.

[10] L. Lin, T. Zhang, J. Zang and Z. Xu, Appl. Catal. 67 (1990) 11.