Tungsten–palladium selective hydrogenation catalysts

P.C. L'Argentière and N.S. Fígoli

INCAPE, Instituto de Investigaciones en Catálisis y Petroquímica, Santiago del Estero 2654, 3000 Santa Fe, Argentina
E-mail: nfigoli@fiqus.unl.edu.ar

Received 18 March 1998; accepted 3 June 1998

The activity and sulfur resistance of palladium–tungsten supported catalysts having different W/Pd ratios is compared. The maximum was found for the catalyst having a W/Pd ratio 6. The existence of a Pd–WO_x interface, more active and sulfur-resistant, is suggested. Regeneration of bimetallic catalysts at mild temperatures was studied.

Keywords: W–Pd catalysts, selective hydrogenation, sulfur resistance, regeneration

1. Introduction

Palladium supported on alumina has turned out to be an effective catalyst for the selective hydrogenation of poly-unsaturated hydrocarbons to partial-hydrogenated ones. However, several attempts have been made in order to increase Pd/Al_2O_3 activity and selectivity [1], for example, by the addition of a second metal.

It is well known that sulfur compounds are poisons of metallic catalysts [2]. The regeneration of these poisoned catalysts, especially in the case of palladium-containing ones, has not been fully studied; nevertheless, several alternatives have been proposed [3–6].

It is the objective of this paper to study the modifications in catalytic activity, selectivity, sulfur resistance and regenerability produced by the addition of different concentrations of tungsten to a Pd/Al_2O_3 catalyst.

2. Experimental

2.1. Catalysts preparation

Alumina CK 300, cylinders of 1.5 mm diameter, with a BET surface area of 180 $m^2\,g^{-1}$ and a pore volume of 0.52 $cm^3\,g^{-1}$ was used as a support. It was calcined in air at 500 °C for 3 h prior to catalyst preparation. An aqueous solution of $Pd(NO_3)_2$ was used for impregnation in a suitable concentration such as to obtain a catalyst containing 0.3% palladium. The catalyst was then dried and calcined at 350 °C for 3 h within an air flow rate of 480 $cm^3\,h^{-1}\,g_{cat}^{-1}$ and, finally, reduced at 120 °C for 5 h using a hydrogen flow rate of 480 $cm^3\,h^{-1}\,g_{cat}^{-1}$.

Tungsten–palladium alumina catalysts were prepared by wet impregnation of Pd/Al_2O_3 with aqueous $H_3PO_4{\cdot}12WO_3$ solutions of an appropriate concentration such as to obtain W/Pd atomic ratios 3, 6 and 12. The bimetallic catalysts will be called WPd-x ($x = 3$, 6 and 12, respectively). After washing with bidistilled water, the solids were dried at 110 °C for 24 h and calcined at 550 °C for 7 h. The calcination temperature used ensures the complete elimination of phosphorus from the catalyst [7]. The material was finally reduced at 120 °C for 5 h.

2.2. Catalysts characterization

2.2.1. Dispersion

Dispersion was determined by hydrogen chemisorption following the method of Benson et al. [8], in order to ensure that the samples were free from the formation of β-PdH. To corroborate the previous results, dispersion was also measured by CO chemisorption following the technique described by Martin et al. [9] using a CO_{ads}/Pd stoichiometry of 1.15/1 as previously reported [10].

2.2.2. X-ray photoelectron spectroscopy (XPS) analyses

XPS analyses were carried out on a Shimadzu ESCA 750 electron spectrometer coupled to a Shimadzu ESCAPAC 760 data system. The C 1s line was taken as an internal standard at 285.0 eV and was used to correct possible deviations caused by an electric charge of the samples. After reduction, the samples were introduced into the preparation chamber of the XPS equipment following an operation procedure previously described [11], in order to avoid superficial reoxidation of palladium. The possibility that during thermal treatments the palladium particles became decorated by WO_x species was investigated by ion sputtering using an Ar^+ ion source at 3.5 keV. Before the Ar^+ etching, the sample was heated in vacuum (550 °C) in order to remove contaminants from their surfaces. The determinations were carried out in the preparation chamber of the XPS equipment for different periods of time and, after each one, an XPS determination was performed in order to determine the variation of the atomic ratios. This procedure was repeated until a stationary state was reached. Determinations of the atomic ratios were made by comparing the areas under the peaks after background subtraction and corrections due to differences in escape depths and in photoionization cross sections [12].

2.2.3. Catalytic activity and selectivity

Catalytic activity and selectivity were determined in a stirred tank reactor operated at 80 °C and stirring velocity 700 rpm; the weight of catalyst was 0.4 g and the reactor volume was 300 cm^3. No diffusional limitations were observed under these conditions [13]. During each run, the reactor was connected to a hydrogen cylinder and the pressure was maintained constant at 22 $\mathrm{kg\,cm^{-2}}$ throughout the experiment. The selective hydrogenation of styrene to ethylbenzene was used as a test reaction. Ethylbenzene can be further hydrogenated to ethylcyclohexane, and polymerization of styrene can also occur as a side-reaction. A 5% styrene in toluene solution, or solutions containing either 1000 or 2000 ppm thiophene, were used as feed. Reactants and products were chromatographically analyzed by means of a flame ionization detector and a DC 200 column. The catalytic activity and the selectivity to ethylbenzene (% of styrene molecules converted to ethylbenzene) were calculated from the chromatographic data; benzene was added to the reaction mixture as an internal standard to follow the polymerization reaction.

Regeneration experiments were carried out over the catalysts poisoned with the highest thiophene concentration (2000 ppm). After running with the poison-containing feed, temperature was decreased to room temperature and liquid was drained; then hydrogen was introduced at 10 $\mathrm{kg\,cm^{-2}}$ pressure, temperature was raised up to 200 °C and the system was left for 4 h. Finally, the regenerated catalyst was run with the poison-free feed. In order to ensure that changing for the unpoisoned feed does not produce the regeneration, a similar procedure was followed without the intermediate hydrogen treatment.

3. Results and discussion

Palladium dispersion in $\mathrm{Pd/Al_2O_3}$ is 28%, calculated from hydrogen and CO chemisorption (3.90 and 3.73 $\mu\mathrm{mol\,g_{cat}^{-1}}$, respectively). For the bimetallic catalysts, both hydrogen and CO chemisorption were very low (about 0.29 $\mu\mathrm{mol\,g_{cat}^{-1}}$). Furthermore, an attempt to determine the metal particle size by TEM failed because of the interference of the support, as previously reported [13]. The very low hydrogen and carbon monoxide chemisorption capacities of the bimetallic catalysts can be ascribed to a decorative effect of WO_x moieties over Pd, as also reported in the literature for platinum–tungsten [14] and palladium–lanthanum [10] systems. The existence of a decorative effect may be also suggested from the Ar^+ sputtering results presented in figure 1 for WPd-6; it can be noted an increase in the Pd/Al atomic ratios and a decrease in the W/Al atomic ratios, respectively, until a stationary state was achieved at 4 h. It is well established in the literature [15] that ion bombardment induces structural and chemical effects which may cause important changes in the superficial composition as well as in the electronic properties of the species remaining on the surface. Segregation and preferential sputtering have been detected and quantitatively characterized by XPS in certain systems [16]. However, with these limitations in mind, the data displayed in figure 1 seem to support the idea of a decoration of the Pd active species. Probably, the layers decorating Pd crystallites are thick enough to block hydrogen and carbon monoxide chemisorption, but not thick enough to completely block the Pd XPS signal. Consequently, in the following considerations, the catalytic activity is presented as the kinetic constant (k), assuming a zero-order kinetics [17], as turnover frequency could not be calculated.

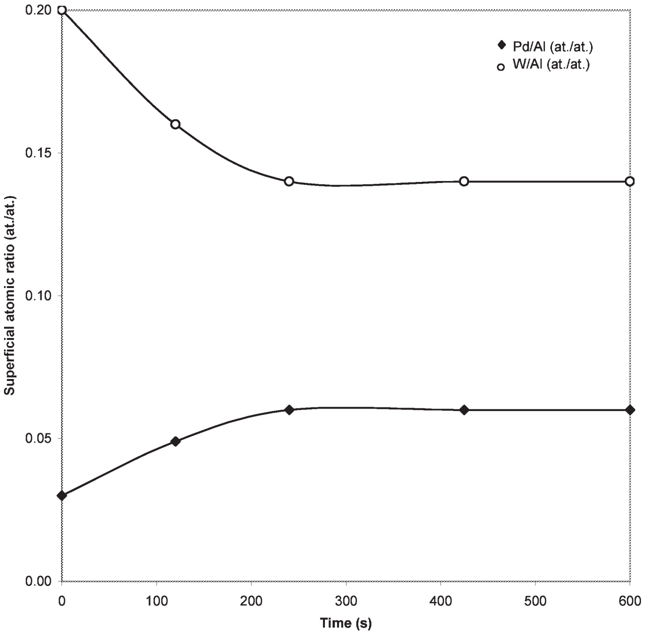
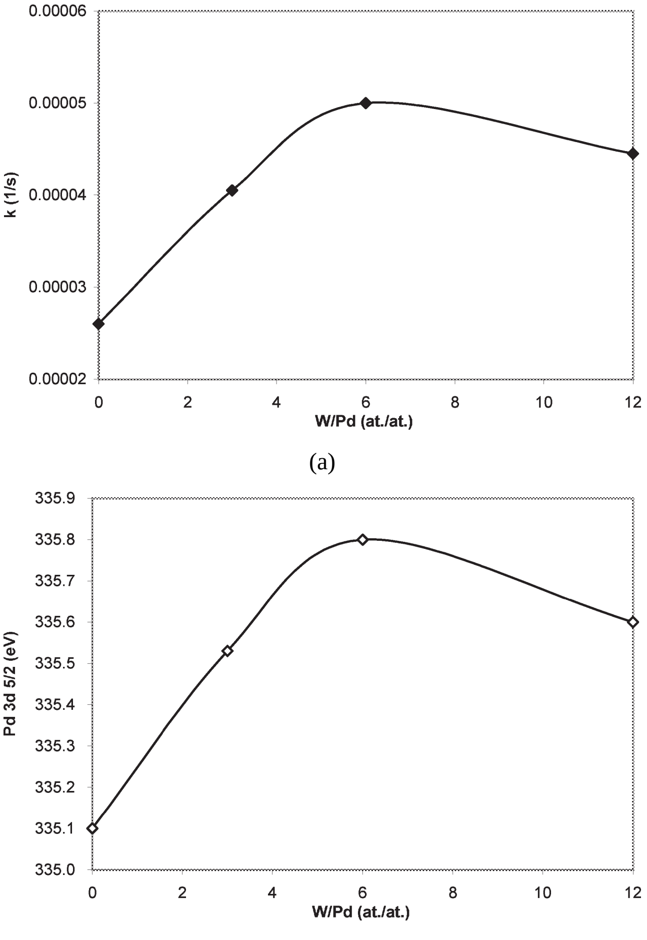


Figure 1. Superficial Pd/Al and W/Al atomic ratios (at/at) as a function of time obtained during Ar^+ sputtering over WPd-6.

Figure 2(a) shows the kinetic constant using the poison-free feed as a function of the W/Pd atomic ratio. All catalytic tests were run in duplicate and the kinetic constants are accurate within ±4%. A maximum in activity is observed for WPd-6. We have previously found that the addition of tungsten increases the activity of a palladium catalyst [13], but according to these results, there also exists an optimum W/Pd ratio in order to obtain the best results. The increase in activity cannot be ascribed to the independent effect of W, because $\mathrm{W/Al_2O_3}$ is not active for styrene selective hydrogenation, as previously reported [13]. Figure 2(b) presents the Pd $3d_{5/2}$ BE for the different catalysts, also showing a maximum for WPd-6.

Pd in $\mathrm{Pd/Al_2O_3}$ is present as Pd^0 after reduction at 120 °C. For the other catalysts, an increase in the Pd binding energy (BE) is observed, which can be attributed, considering the preparation conditions, to an electron transfer from Pd to W rather than to the formation of a Pd–W bond. It can be observed in figure 2(b) that the Pd $\leftrightarrow$ W interaction depends upon the W concentration, with a maximum at a



(a)

(b)

Figure 2. (a) Kinetic constant for styrene selective hydrogenation as a function of the W/Pd atomic ratio for unpoisoned catalysts. (b) Pd $3d_{5/2}$ BE as a function of the W/Pd atomic ratio for unpoisoned catalysts.

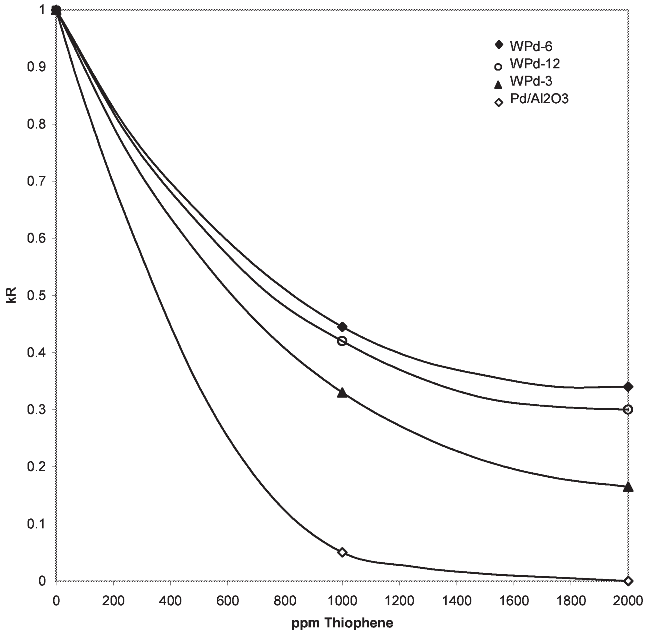


Figure 3. Relative activity (k_R) as a function of the thiophene concentration in the feed for catalysts having different W/Pd atomic ratios.

W/Pd ratio 6. For other systems, such as $NiPd/Al_2O_3$ [18] and $MnPd/Al_2O_3$ [19], such increase in the Pd BE was associated to a decrease in catalytic activity. The increase in activity over WPd-x catalysts could be due to the existence of a Pd–WO_x interface more active for the styrene selective hydrogenation. WO_x patches decorating Pd particles may generate this interface, as suggested by the chemisorption and Ar^+ sputtering results. The nature of the Pd–WO_x interface is related to the W/Pd ratio, increasing its activity when the ratio increases from 3 to 6. Farbokto et al. [20], studying the Pt/Al_2O_3 system, have also found an increase in activity with the addition of tungsten, which was attributed to the generation of a very active interface. Pârvulescu et al. [21] for Pd–Fe/Al_2O_3 also reported that the interaction Pd–Fe, due to the "d" character of the nonplatinum metal, led to the formation of new centers of high electron density, which may be responsible for the higher activity of these catalysts compared with the monometallic Pd/Al_2O_3. Regalbuto and Wolf [22] also observed an increase in activity by the addition of tungsten over Pt/SiO_2, which they attributed to the existence of new sites denominated "adlineation sites". These authors stated that the increased activity is probably the result of the contributions of the Pt superficial sites and of the "adlineation sites", considering that the loss of Pt sites by decoration is more than compensated by the higher activity of the "adlineation sites". In the WPd-x system, the suggested new interface would also compensate the lower activity of electron-deficient palladium. However, we could not corroborate this statement, as it was not likely to determine the amount of the new sites, because it was impossible to differentiate their XPS signal from the corresponding palladium signal. Hence, as in the case of the Pt–WO_3/SiO_2 catalysts studied by Regalbuto and Wolf [21], the particular character of the new interface and the reason why they present higher activity than Pd sites is still obscure.

The effect of sulfur poisoning on activity (using feeds containing 1000 and 2000 ppm thiophene) over the different catalysts is presented in figure 3 as relative activity (k_R) vs. the thiophene concentration in the feed. k_R is the ratio between the kinetic constant using poison-free feed and the corresponding kinetic constant using the poisoned feed. The highest sulfur resistance is presented by WPd-6 and the lowest by Pd/Al_2O_3. This behavior can be associated with the S/Pd atomic ratio measured by XPS on the catalysts used with the poison-containing feeds, shown in figure 4, where the same trend is observed: the lowest S/Pd ratio after poisoning corresponds to WPd-6. We have attributed the higher activity of WPd-x catalysts, compared to Pd/Al_2O_3, to the existence of a Pd–WO_x interface. The possibility for the poisoning molecule adsorption at that interface may be lower than in Pd/Al_2O_3.

The S 2p peak position for the poisoned catalysts was observed at 164.4 eV, showing that the poisoning species adsorbed is mainly thiophene, as has also been found by Ramachandran and Massoth [23]. Hence, under the oper-

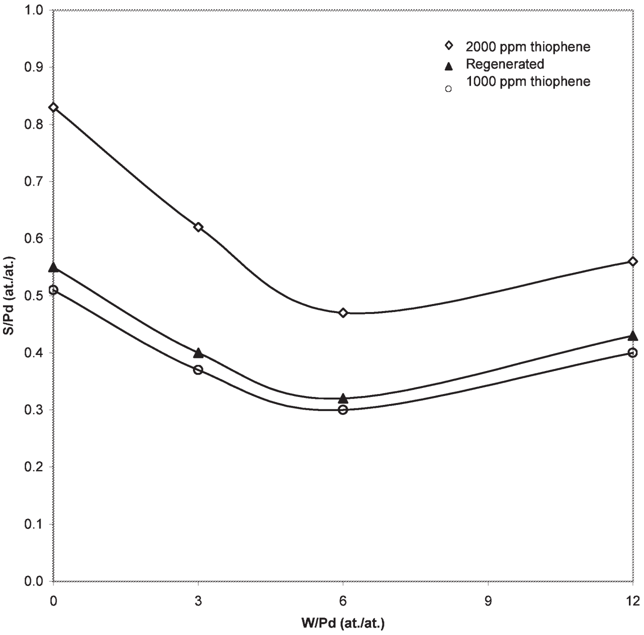


Figure 4. S/Pd superficial atomic ratios obtained from XPS results for catalysts used with the poisoned feeds and with poison-free feed after regeneration.

Table 1
Selectivity to ethylbenzene for the different catalysts using the poison-free and the poison-containing feeds.

Catalyst	Selectivity (S_E) (%)		
	Poison-free feed	1000 ppm thiophene	2000 ppm thiophene
Pd/Al_2O_3	100	76	68
WPd-3	100	79	70
WPd-6	100	85	79
WPd-12	100	82	74

Table 2
Catalytic activity with the poison-free feed before and after regeneration and of the catalyst used with the 2000 ppm thiophene feed and percentual recovery of activity (referred to the unpoisoned catalyst) for the different catalysts.

Catalyst	Activity $\times 10^5$ (s^{-1})			
	Pd/Al_2O_3	WPd-3	WPd-6	WPd-12
Poison-free feed	2.6	3.6	5	4.4
2000 ppm thiophene	0	0.6	1.7	1.4
Poison-free feed after regeneration	0	0.9	2.2	1.7
Percentual activity recovery	0	25	44	39

ational conditions used in this work, thiophene is not hydrogenolized during poisoning.

Selectivities to ethylbenzene (S_E) are presented in table 1. All catalysts are 100% selective in the absence of thiophene. This means that the presence of WO_x species does not induce the polymerization parallel reaction. Moreover, Soled et al. [24] found that the addition of WO_3 to Al_2O_3 do not increase acidity, measured by ammonia temperature desorption. These authors observed the transformation of Lewis into Brønsted sites upon tungsten addition, but using a higher tungsten concentration. Besides the decrease in catalytic activity, thiophene induced a decrease in the selectivity for ethylbenzene formation because of the appearance of the polymerization reaction. Ethylcyclohexane was never detected in any of the tests performed. This is logical, since it is unlikely that palladium catalysts would hydrogenate the benzene ring under the operational conditions of this work. The decrease in selectivity in the presence of thiophene may be explained by considering that for reactions occurring at low temperature (80 °C) the adsorption of poison on the catalyst support may be very important [25–28]. Thiophene may be adsorbed on the acid sites of alumina, which are electrophilic. A consequence of this adsorption is the liberation of a proton from the aromatic ring of thiophene; this proton may be a catalyst for the parallel polymerization reaction. The rate of solid-acid-catalyzed reactions is greatly enhanced by the presence of H^+ in the system. The enhancement occurs only for acid-catalyzed reactions and is reversible [25].

The different catalysts were regenerated under the conditions mentioned in section 2 after being used with the feed containing 2000 ppm thiophene. After this treatment, an important recovery in activity was observed; the percentual recovery of catalytic activity after regeneration and using the poison-free feed is presented in table 2. The hydrogen treatment also produced an important decrease in the S/Pd superficial atomic ratios (figure 4), thus indicating a partial elimination of thiophene from the catalyst surface, possibly due to the hydrogenolysis of the poison favored by the high hydrogen pressure. However, under the conditions presently used for the catalyst regeneration, irreversible adsorbed sulfur still remains in the catalyst. The highest activity recovery corresponds to the lowest S/Pd ratio. The highest sulfur resistance and activity recovery after the hydrogen treatment are presented by PdW-6. The activity recovery was not produced by the contact with the poison-free feed, because when the treatment with hydrogen was omitted and the catalysts were run with the poison-free feed (after being run with the thiophene-containing feed), no activity recuperation was observed.

4. Conclusions

An optimum catalytic activity and sulfur resistance was observed for a WPd atomic ratio 6 in alumina-supported catalysts during styrene selective hydrogenation. A WO_x–Pd interface, suggested in all the bimetallic catalysts, presents a higher catalytic activity. The properties of the interface depend on the WPd atomic ratio. For W/Pd ratio 6, the sulfur resistance is the best; this can be associated to a reduced possibility of the poison adsorption. A partial regeneration can be obtained by H_2 treatments in mild conditions (200 °C and 10 $kg\,cm^{-2}$), this being an advantage of the proposed regenerating procedure.

Acknowledgement

The experimental assistance of C. Mázzaro and M. González, the financial support of CONICET and UNL (CAI+D Program) and the donation of a XPS equipment by JICA are greatly acknowledged.

References

[1] A. Sárkáni, A.H. Weiss and L. Guczi, J. Catal. 98 (1986) 550.

[2] J. Barbier, E. Lamy-Pitara, P. Marecot, J.P. Boitiaux, J. Cosyns and F. Verna, Adv. Catal. 37 (1990) 279.

[3] P.C. L'Argentière and N.S. Fígoli, Appl. Catal. 61 (1990) 275.

[4] C.H. Bartholomew, P.K. Agrawal and J.R. Katzer, Adv. Catal. 31 (1982) 135.

[5] J.R. Rostrup-Nielsen, in: *Progress in Catalyst Deactivation,* NATO Advanced Study Institute Series, Vol. 54, ed. J.L. Figueiredo (Nijhoff, Amsterdam, 1982) p. 209.

[6] A. Aguinaga and M. Montes, Appl. Catal. A 90 (1992) 131.

[7] Y. Song, G. Seo and S. Ihm, Appl. Catal. A 83 (1992) 75.

[8] J.E. Benson, H.S. Hwang and M. Boudart, J. Catal. 30 (1973) 146.

[9] M.A. Martin, J.A. Pajares and L. Gonzalez Tejuca, J. Colloid. Int. Sci. 107 (1985) 540.

[10] N.S. Fígoli, P.C. L'Argentière, A. Arcoya and X.L. Seoane, J. Catal. 155 (1995) 95.

[11] A. Arcoya, X.L. Seoane, N.S. Fígoli and P.C. L'Argentière, Appl. Catal. 62 (1990) 35.

[12] A. Borade, A. Sayari, S. Adnot and J. Kaliaguine, J. Phys. Chem. 94 (1990) 5989.

[13] P.C. L'Argentière and N.S. Fígoli, Ind. Eng. Chem. Res. 36 (1997) 2543.

[14] J.L. Contreras and G.A. Fuentes, Stud. Surf. Sci. Catal. 101 (1996) 1145.

[15] G. Betz and G.K. Wehner, in: *Sputtering by Particle Bombardment II*, ed. R. Behrish (Springer, Berlin, 1984) chapter 2.

[16] A.R. González-Elipe, G. Munuera and J.P. Espinos, Surf. Sci. 220 (1989) 389.

[17] C. Niklasson, B. Andersson and N.-H. Schoon, Ind. Eng. Chem. Res. 26 (1987) 1459.

[18] P.C. L'Argentière, M. Cañón, N.S. Fígoli and J. Ferrón, Appl. Surf. Sci. 68 (1993) 41.

[19] P.C. L'Argentière, M. Cañón and N.S. Fígoli, Appl. Surf. Sci. 89 (1995) 63.

[20] J.M. Farbokto, F. Garin, P. Girad and G. Maire, J. Catal. 79 (1993) 185.

[21] V.I. Pârvulescu, G. Filoti, G. Parvulescu, N. Grecy, E. Angelescu and I.V. Nicolescu, J. Mol. Catal. 89 (1994) 267.

[22] J.R. Regalbuto and E.E. Wolf, J. Catal. 109 (1988) 12.

[23] R. Ramachandran and F.E. Massoth, Can. J. Chem. Eng. 60 (1982) 17.

[24] S.L. Soled, G.B. McVicker, L.L. Murrel, L.G. Sherman, N.C. Dispenziere, S.L. Hsu and D. Waldman, J. Catal. 111 (1988) 286.

[25] P. Biloen, J.N. Helle, N. Verbeek, F.M. Dautzemberg and W.H.M. Sachtler, J. Catal. 63 (1980) 112.

[26] R. Maurel and J. Barbier, J. Chim. Phys. 73 (1976) 995.

[27] R. Maurel and J. Barbier, J. Chim. Phys. 75 (1978) 995.

[28] L.L. Hegedus and R.W. McCabe, Catal. Rev. Sci. Eng. 23 (1981) 377.