Catalysis Letters 25 (1994) 351–359

Maximum and time stable aromatic yield in the reforming of alkylcyclopentanes over Pt / β zeolites

Panagiotis G. Smirniotis and Eli Ruckenstein [1]

Department of Chemical Engineering, State University of New York at Buffalo,
Buffalo, NY 14260, USA

Received 12 November 1993; accepted 20 January 1994

The reforming of alkylcyclopentanes is performed at 100 psig over various dealuminated zeolite β catalysts supporting various amounts of Pt. As a result of the proper balance between the Brønsted acidity and the metal loading, a maximum aromatic yield was found for a dealuminated catalyst with a SiO_2/Al_2O_3 molar ratio of 130 and 0.5 wt% Pt. The activity of this catalyst remained unchanged with time on stream, and the amount of coke deposited on the catalyst was very low. The aromatic selectivity increased slightly in the initial few hours and then reached a constant value. It appears that the aromatic selectivity is enhanced by the deposition of a small amount of coke. The balancing of the acidic and metallic functions of Pt/β zeolite via dealumination and Pt loading provides a useful reforming catalyst.

Keywords: reforming; β zeolite; dealumination; balancing of the metallic and acidic functions; alkylcyclopentanes; coke

1. Introduction

Reforming has been one of the most important industrial processes for the upgrading of naphthas over the years, with the chlorided Al_2O_3 supported Pt or Pt–Ir as catalysts. Mills et al. [1] suggested that the reforming catalysts have two functions, an acidic and a metallic one. Weisz and Swegler [2] have demonstrated the synergistic role of the two functions, by employing composites of Pt/SiO_2 and SiO_2–Al_2O_3. More recently, a number of researchers have studied the reforming capabilities of zeolites as possible substitutes for the traditional chlorided Pt/Al_2O_3. The reforming of *n*-heptane over Pt or Pt/Re-Y faujasite [3], as well as the aromatization of *n*-hexane over BaK/L zeolite supported Pt are some examples [4]. It has been also found [5] that a composite containing equal amounts of Pt/γ-Al_2O_3 and Pt/β zeolite maximized the yield of aromatics when methylcyclopentane was used as feed. That behavior is a result of the balancing of the dehydrogena-

---

[1] To whom correspondence should be addressed.

tion capability due mainly to the Pt/γ-Al_2O_3 in which the dispersion of Pt is high, with the isomerization capability of the acidic β zeolite over which the Pt dispersion is lower. Another finding [6,7] was that with naphthenes as feeds, suitable pore sizes and acidities of the zeolites can enhance bimolecular alkylation reactions that lead to aromatics with higher carbon atom numbers than the feed hydrocarbon.

In the present study we examine the performance of various samples of Pt/β zeolite in the transformation of methylcyclopentane or ethylcyclopentane, via the enlargement of the C_5-cyclic ring, to aromatics. The prepared catalysts differed in the strengths of their metallic and acidic functions, the increase in the amount of Pt being associated with a decrease in their acidity. The metallic function was controlled by the Pt loading, and the acidity by the extent of dealumination of the zeolite. It was found that with both alkylcyclopentanes a pronounced maximum in the aromatic yield occurred as a result of the balancing of the two functions of the catalyst via suitable dealumination and Pt loading. The dealuminated Pt/β zeolite with a SiO_2/Al_2O_3 molar ratio of 130 and 0.5 wt% Pt exhibited an exceptional performance concerning its behavior with the time on stream, since it preserved its initial activity after three days on stream and the aromatic selectivity increased to a constant value after a few hours.

2. Experimental

The synthesis of zeolite β employed in the present study was described previously [6]. The aluminosilicate gel prepared from individual solutions had a nominal molar composition of 30 SiO_2 : Al_2O_3 : 0.9 Na_2O : 3 TEAOH : 250 H_2O, where TEAOH stands for the tetraethylammonium hydroxide. At the end of the crystallization period (10 days at 160°C and autogenous pressure), the zeolite β had a SiO_2/Al_2O_3 molar ratio of 28. The burning of the template occluded was carried out by calcination at 510°C in high purity O_2 for 5 h. The dealumination of β zeolite was achieved by heating at 95°C for 4 h in various aqueous solutions of HCl. The SiO_2/Al_2O_3 molar ratios of various dealuminated zeolite β samples, determined by atomic absorption, as well as the preparation conditions are listed in table 1. The degree of crystallinity of the dealuminated samples with respect to the non-dealuminated one was determined by X-ray diffraction (XRD). All the samples were cation exchanged with 4 M NH_4Cl (Fisher) at 95°C for 4 h. A final calcination for 1 h, at 450°C in O_2 brought the catalysts to their acidic form. For comparison purposes, SiO_2 (Aldrich grade 951) was also employed as support. Catalysts with different Pt loadings were prepared by impregnating the supports with the appropriate amounts of aqueous solutions of H_2PtCl_6 (Aldrich 8 wt% sol.). After impregnation, the catalysts were dried overnight at 130°C, and finely ground. The catalysts employed in the present study as well as the oxidation and reduction conditions to which they were subjected for activation are listed in table 1. Both the oxidation and the reduction steps were carried out in situ in the reactor and

Table 1
Catalysts employed in the present study, activation conditions, Pt amount (wt% of the catalyst), Pt dispersion D ($=$ H/Pt, %) and Pt amount dispersed (wt% of the catalyst). *Note*: Both the oxidation and the reduction steps lasted 1 h each. After oxidation a purging of the catalyst with He for 15 min followed

Sample	Catalyst	SiO_2/Al_2O_3	Crystallinity	T_O [c] (°C)	T_R [c] (°C)	Pt (wt%)	D (%)	Pt dispersed (wt%)
B1	zeolite β	28	100	550	550	0.1	22	0.022
B2	zeolite β	28	100	550	550	0.5	6	0.030
B3 [a]	zeolite β	130	90	300	300	0.5	29	0.143
B4 [b]	zeolite β	270	83	300	300	1.0	nd [d]	–
Si	SiO_2	–	–	300	300	1.0	25	0.290

[a] The dealumination was carried out with 2 N HCl for 4 h.
[b] The dealumination was carried out with 3.5 N HCl for 4 h.
[c] T_O = oxidation temperature, T_R = reduction temperature.
[d] nd: not determined.

lasted 1 h each. A He purging of the catalyst for 15 min after oxidation was performed. Details regarding the characterization of the catalysts by H_2-chemisorption, acidity measurements, transmission electron microscopy (TEM), Cl^- concentration, and the characterization of the deposited coke by ^1H NMR, GC/MS, thermogravimetric analysis (TGA) and HPLC will be published elsewhere.

The catalytic experiments were performed at 400–450°C in the presence of high purity H_2. In each experiment, 100 ± 2 mg of fresh catalyst particles with sizes below 100 μm (150 mesh) were loaded in the middle of the reactor. The reactor was a stainless steel tube of 0.318 cm o.d. and 40 cm length, located vertically in a temperature programmable furnace. The pressure regulation was achieved with a backpressure regulator, while the H_2 flow was controlled with a flow controller. The reactants, methylcyclopentane (Aldrich, 99 + %) or ethylcyclopentane (DWR Research Co., 99.7%) were introduced into the reactor with a liquid infusion pump, through a heated line, at a predetermined flow rate. High resolution gas chromatography has been employed for the on-line identification of the products. The analysis was performed with a gas chromatograph (HP 5890 series II) equipped with a mass spectrometer (HP 5971 series). The GC was loaded in series with a high performance capillary column (HP-1), a molecular sieve packed column (5A), and a PoraPLOT wide bore capillary column. A PC was attached to the GC/MS unit for storage and data manipulations.

3. Results and discussion

The Pt dispersion of the samples employed, determined by H_2-chemisorption, is given in table 1. In the five catalysts employed, denoted B1, B2, B3, B4, Si in table 1, the Pt loading was increased as the molar ratio of SiO_2/Al_2O_3 was increased. The acidity and the acid strength distribution of the catalysts have been determined by *n*-butylamine titration, using suitable indicators [9]. It was found, as expected, that the total acidity decreases as the molar ratio of SiO_2/Al_2O_3 increases, being 4.08 mmol/g catalyst for B1 and 2.80 mmol/g catalyst for B4, for indicators with $pK_a \leq 6.8$. No change in color for B1 occurred for $pK_a < -10.1$ and B4 for $pK_a < -3.0$.

3.1. METHYLCYCLOPENTANE

The performance of various catalysts with methylcyclopentane is presented in fig. 1. Two main reactions can occur, namely hydrocracking and aromatization to benzene. The latter reaction involves as a first step the generation of methylcyclopentenes on the Pt sites of the catalyst, the isomerization-enlargement of the C_5-ring of the latter intermediates to a C_6-ring, followed by the dehydrogenation to benzene [10]. For a reaction of this type, which involves both the metallic and the acidic functions, the balancing of the two can ensure the maximization of the aromatic yield. Indeed, the benzene yield (benzene is the main product, but small amounts of $C_{>6}$ aromatics are also formed by benzene alkylation [11]) exhibited a pronounced maximum for the B3 catalyst. Among the catalysts employed, this catalyst provides the optimum combination of the two functions.

From the product distribution presented in table 2, one can observe that the B1 sample provides high C_3–C_5 paraffinic selectivities and a low $C_{\geq 6}$ aromatic selectivity. In contrast, the dealuminated sample B3 exhibits a dramatic decrease in the C_1–C_6 paraffinic and olefinic selectivities as a result of reduced hydrocracking,

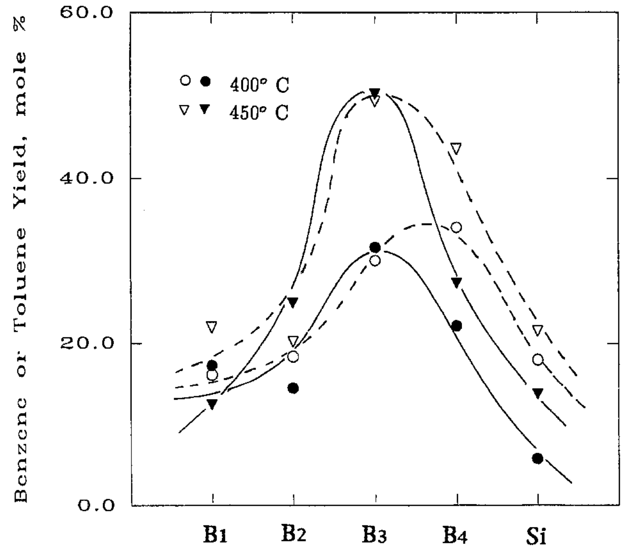

Fig. 1. Benzene yield (filled symbols) and toluene yields (open symbols) for various Pt zeolite β catalysts and for methylcyclopentane and ethylcyclopentane, respectively (100 psig, 2 h on stream, WHSV = 2.0 h^{-1}, H_2/oil = 12.0).

Table 2
Product distribution and conversion over B1, B2, B3, B4 and Si catalysts at $T = 450°C$ and 100 psig total pressure (2 h on stream, WHSV = 2.0 h^{-1}, H_2/oil = 12.0 for both naphthenes)

Products (mol%)	Methylcyclopentane					Ethylcyclopentane				
	B1	B2	B3	B4	Si	B1	B2	B3	B4	Si
methane	–	–	0.1	2.1	–	3.5	1.6	0.7	1.3	1.2
ethane	0.8	1.5	1.3	3.9	0.4	2.8	8.1	1.4	2.2	1.8
propane	21.9	17.0	16.4	23.9	2.2	21.5	29.6	11.4	13.9	2.1
i-butane	10.7	12.3	–	5.5	1.0	13.9	13.2	10.0	10.1	1.1
2-butene	2.4	0.3	–	–	–	–	–	–	–	–
n-butane	10.0	16.2	9.9	8.3	2.0	13.8	15.4	8.1	9.5	2.7
i-pentane	7.1	8.5	6.6	5.3	2.7	4.5	1.8	2.0	2.3	1.4
n-pentane	4.8	5.3	4.1	3.5	4.2	3.0	1.1	1.2	1.5	2.6
2-pentene	2.9	1.0	0.7	–	0.8	–	–	–	–	0.5
2-methylpentane	6.8	1.5	1.1	6.1	28.1	–	–	–	0.5	2.2
3-methylpentane	2.9	0.9	0.7	4.0	24.0	–	–	–	0.3	2.0
n-hexane	–	–	–	2.2	17.8	–	–	0.1	0.8	1.9
benzene	16.6	25.8	52.4	28.0	14.8	5.0	4.4	9.4	10.9	2.1
cyclohexane	1.3	–	–	–	–	–	–	–	–	–
2-methylhexane	–	–	–	–	–	–	–	–	–	8.8
3-methylhexane	–	–	–	–	–	–	–	–	–	26.0
heptane	–	–	–	–	–	–	–	–	–	20.0
toluene	6.9	7.9	3.8	5.8	0.9	21.9	12.5	50.4	43.5	21.5
ethylbenzene	1.3	0.4	0.4	0.2	–	–	1.9	0.6	0.7	–
m-xylene	0.4	0.3	0.5	0.3	–	1.8	1.4	0.4	0.2	–
o-xylene	1.0	0.2	0.3	0.2	–	2.1	2.7	0.9	0.3	–
p-xylene	2.0	1.0	0.9	0.9	–	5.9	6.1	2.7	2.1	–
conversion (mol%)	74.5	93.1	97.2	96.9	93.0	100.0	100.0	100.0	100.0	100.0

but enhances significantly the benzene generation. Hence, this catalyst ensures the isomerization of the cycloolefinic intermediates and simultaneously minimizes both the hydrocracking of the feed and the bimolecular alkylation reactions of benzene. It appears that 0.5 wt% Pt of the B3 catalyst provides sufficient dehydrogenation capability, even though the dispersion of Pt on this catalyst (see table 1) is relatively low.

Catalyst B1, which has a higher Brønsted acidity, has also a higher $C_{\geqslant 7}$ aromatic selectivity than B3. This is because, in addition to a suitable pore size which is needed to increase the proximity of hydrocarbon molecules, a relatively high Brønsted acidity is required for bimolecular alkylation reactions (reactions which lead to the enlargement of the primary aromatics) to occur [5,12,13].

Sample B4, which has a higher SiO_2/Al_2O_3 molar ratio and a larger Pt loading than B3, provides a lower aromatization than B3, but slightly higher C_1–C_6 paraffinic and olefinic selectivities because of increased hydrogenolysis.

Pt/SiO_2 with a metal loading of 1.0 wt% (sample Si), which represents a catalyst without acidity and relatively high Pt loading, was also employed. The absence of acidity is responsible for the low aromatic and C_1–C_5 paraffinic and olefinic selectivities (table 2). In contrast, the selectivity for the C_6 isomers is very high because of the ring opening of methylcyclopentane over the metal sites. One can observe that the isomers do not obey the statistical distribution *n*-hex : 2-MP : 3-MP = 2 : 2 : 1, the equilibrium among the isomers being shifted towards the 2-methylpentane. The 3-MP to *n*-hex ratio determined in the present study is larger than unity (table 2), indicating, as suggested by Gault [14], that hydrogenolysis occurs. The observation [14] that hydrogenolysis occurs when the size of the Pt crystallites is above the critical value of 25 Å was confirmed by our TEM investigations, which indicated that the size of the crystallites was greater than the above value.

3.2. ETHYLCYCLOPENTANE

The performance of ethylcyclopentane is presented in fig. 1 as well. The trends are similar to those of the previous feed naphthene, and are also a result of the actions of the two functions of the catalysts. Toluene is, however, the dominant aromatic generated via the dehydroisomerization of ethylcyclopentane followed by dehydrogenation. The selectivities for other aromatics are higher over B1, due to the bimolecular alkylation reactions which are enhanced by its higher Brønsted acidity, and to the partial transalkylation of toluene to benzene and xylenes. The maximum yield of toluene is somewhat shifted towards the B4 catalyst (for methylcyclopentane the maximum is not as broad and occurs for the B3 catalyst). This indicates that the proper balancing of the two catalytic functions depends to some extent on the number of carbons of the feed naphthene. With methylcyclopentane this balancing occurred for the B3 catalyst (0.5 wt% Pt), while for ethylcyclopentane the optimum conditions seem to occur to a somewhat higher metal loading and smaller acidity.

If the metal loading is too high, hydrogenolysis becomes dominant for any bifunctional catalyst. In addition, high metal loadings generate larger amounts of olefins which can polymerize to coke. Indeed, this occurs with catalysts B4 and Si for which the hydrogenolysis is more pronounced (see table 2), and the amounts of coke formed are higher than those for B3 (table 3).

An increase in temperature favors the dehydroisomerization of both naphthenes leading to higher aromatic yields, but has an opposite effect on the yields of C_1–C_6 linear and branched hydrocarbons (fig. 1).

Table 3
Coke deposited (g coke/100 g catalyst) over B1, B3 and Si catalysts at 450°C and 100 psig total pressure (WHSV = 2.0 h^{-1}, for both naphthenes H_2/oil = 12.0)

Duration (h)	Methylcyclopentane			Ethylcyclopentane		
	B1	B3	Si	B1	B3	Si
3	10.8	0.5	1.0	2.6	0.2	1.1
72	13.4	5.6	1.3	5.5	0.6	1.2

Table 4
Benzene and toluene selectivities and yields for methylcyclopentane and ethylcyclopentane, respectively over B1, B3, Si catalysts at 450°C and 100 psig total pressure (WHSV = 16.6 h^{-1}, 2 h on stream and H_2/oil = 12.0)

Catalyst	Methylcyclopentane			Ethylcyclopentane		
	conversion	benzene selectivity	benzene yield	conversion	toluene selectivity	toluene yield
B1	32.4	28.6	9.3	36.7	30.3	11.1
B3	35.1	68.7	24.1	41.3	59.2	24.4
Si	29.8	23.4	6.9	37.9	27.1	24.7

Reforming at lower conversions (table 4) than those presented in table 2, shows pronounced maxima for benzene and toluene selectivities and yields. Consequently, the balancing of the two functions of the β zeolite which results in the above maxima does not depend on the conversion level.

3.3. TIME ON STREAM BEHAVIOR

The activity of the catalysts as a function of time on stream for both naphthenes is presented in figs. 2 and 3 for methylcyclopentane and ethylcyclopentane, respectively. For the dealuminated catalyst B3 the conversion remains unchanged for 3 days for both feed hydrocarbons, and the aromatic selectivity increases initially attaining after a few hours a constant value. The small amount of coke deposited on catalyst B3 appears to enhance the aromatic selectivity (fig. 2). This behavior may be a result of the selective coking of some residual acid sites in the initial stages of

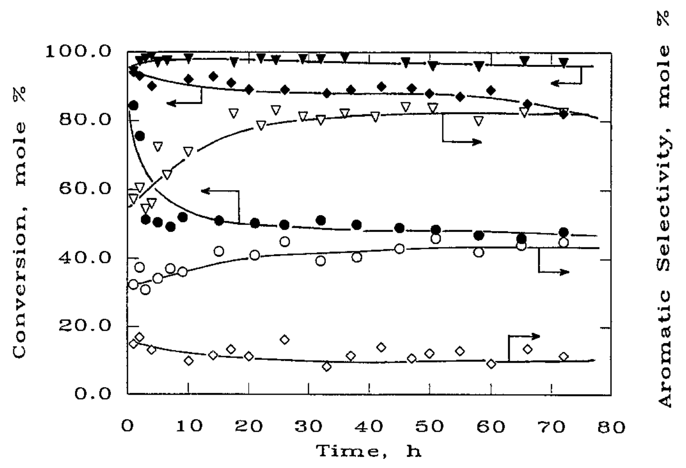

Fig. 2. Conversion over B1 (●), B3 (▼) and Si (◆) and aromatic selectivity over B1 (○), B2 (▽) and Si (◇) as a function of time on stream for methylcyclopentane at 450°C and 100 psig total pressure (WHSV = 2.0 h^{-1}, H_2/oil = 12.0).

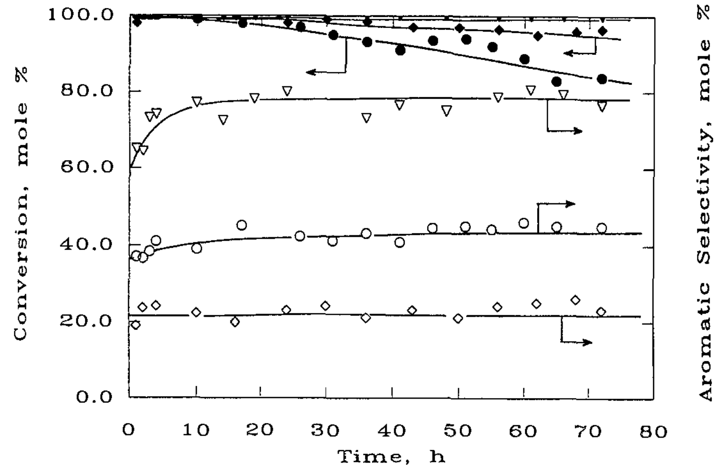

Fig. 3. Conversion over B1 (●), B3 (▼) and Si (◆) and aromatic selectivity over B1 (○), B2 (▽) and Si (◇) as a function of time on stream for ethylcyclopentane at 450°C and 100 psig total pressure (WHSV = 2.0 h^{-1}, H_2/oil = 12.0).

reaction, which eliminates potential cracking sites and preserves aromatic precursors. The moderate acidity of B3 provides, however, the necessary isomerization capability without enhancing the hydrocracking favored by the relatively high H_2 pressure employed. In contrast, the non-dealuminated β zeolite catalyst loses its activity after a few hours on stream due to severe coke deposition. In addition to the extensive coke buildup on the acidic sites, the hydrocracking constitutes another negative feature of the non-dealuminated zeolite B1. The balancing of the two functions of the bifunctional zeolites by suitable dealumination and Pt loading can lead to a very good time on stream behavior and high aromatization yield.

The amounts of coke deposited over the present catalysts are listed in table 3 for both feed hydrocarbons. It is worthwhile to note the small amount of coke deposited over the dealuminated B3 catalyst even after 72 h on stream compared to that over the non-dealuminated zeolite after 3 h of operation. Under the same conditions, more coke is deposited over the catalyst when methylcyclopentane is employed as feed than ethylcyclopentane. However, the yield of the aromatization of ethylcyclopentane to toluene is higher than that of aromatization of methylcyclopentane to benzene. Aromatization and coke formation have some common intermediates and when the aromatization is higher the coke formation is lower.

4. Conclusions

In the present study it was found that the balancing of the Brønsted acidity with the metallic function of Pt/β zeolite by proper dealumination and metal loading can maximize the yield of aromatics in the reforming of alkylcyclopentanes;

this maximum yield remained unchanged with the time on stream. This beneficial behavior is attributed to the moderate acidity of the dealuminated zeolite β which keeps the catalyst surface free of coke and minimizes the hydrocracking which is stimulated by high hydrogen pressures. An optimum Pt loading, together with an optimum dealumination maximize the aromatization of the feed naphthenes.

References

[1] G.A. Mills, H. Heinemann, T.H. Milliken and A.G. Oblad, Ind. Eng. Chem. 45 (1953) 134.

[2] P.B. Weisz and E.W. Swegler, Science 126 (1957) 31.

[3] C. Dossi, C.M. Tsang, W.M.H. Sachtler, R. Psaro and R. Ugo, Energy & Fuels 3 (1989) 468.

[4] T.R. Hughes, W.C. Buss, P.W. Tamm and R.L. Jacobson, in: *New Developments in Zeolite Science and Technology*, Studies in Surface Science and Catalysis, Vol. 28, eds. Y. Murakami, A. Iijima and J.W. Ward (Kodansha/Elsevier, Tokyo/Amsterdam, 1986) p. 725.

[5] H. Schulz, J. Weitkamp and H. Eberth, in: *Proc. 5th Congr. on Catalysis*, Vol. 2 (North-Holland, Amsterdam, 1973) p. 1229.

[6] P.G. Smirniotis and E. Ruckenstein, J. Catal. 140 (1993) 526.

[7] P.G. Smirniotis and E. Ruckenstein, Chem. Eng. Sci. 48 (1993) 3263.

[8] P.B. Weisz, Adv. Catal. 13 (1962) 137.

[9] K. Tanabe, M. Misono, Y. Ono and Hattori, in: *New Solid Acids and Bases: Their Catalytic Properties*, Vol. 51, eds. B. Delmon and J.T. Yates (Elsevier, Amsterdam, 1984).

[10] A.I.M. Keulemans and H.H. Voge, J. Phys. Chem. 63 (1959) 476.

[11] J. Weitkamp, in: *Proc. Int. Symp. on Zeolite Catalysis*, Siofok 1985, p. 271.

[12] J. Weitkamp, P.A. Jacobs and S. Ernst, in: *Structure and Reactivity of Modified Zeolites*, Studies in Surface Science and Catalysis, Vol. 18, eds. P.A. Jacobs, N.I. Jaeger, P. Jiru, V.B. Kazansky and G. Schulz-Ekloff (Elsevier, Amsterdam, 1984) p. 279.

[13] E. Ruckenstein and P.G. Smirniotis, Catal. Lett. 24 (1994) 123.

[14] F.G. Gault, Adv. Catal. 30 (1981) 1.

[15] J.M. Parera, R.J. Verderone and C.A. Querini, in: *Catalyst Deactivation*, Studies in Surface Science and Catalysis, Vol. 34, eds. B. Delmon and G.F. Froment (Elsevier, Amsterdam, 1987) p. 135.