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Producing a high-quality synthetic steamcracker feedstock from different aromatic model components of pyrolysis gasoline on bifunctional zeolite catalysts

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Abstract

Aromatics with 6–9 carbon atoms, i.e., model components of pyrolysis gasoline, are hydroconverted on bifunctional Pd/H-ZSM-5 zeolites into a high-quality synthetic steamcracker feedstock (consisting mainly of ethane, propane and *n*-butane). The yield of these desired *n*-alkanes with two or more carbon atoms depends strongly on the nature of the aromatic feed: at 400 °C and 6 MPa in an excess of hydrogen, a yield of 72.8% is observed with toluene, but yields higher than 90% can be achieved with benzene or ethylbenzene as feed. These pronounced differences are rationalized in terms of varying types of classical β-scission and different contributions of non-classical Haag–Dessau cracking. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aromatics hydroconversion; Pyrolysis gasoline; Ring opening; Steamcracker feed (synthetic); Zeolites (bifunctional)

1. Introduction

Steamcrackers are widely employed for the production of ethylene and propylene from naphtha. One of the by-products of naphtha steamcracking is pyrolysis gasoline, which is rich in aromatics. Given the forecasted annual growth rate in the worldwide demand of ethylene [1] and propylene [2] for the next 10 years of 4.5 and 4.7%, respectively, the production of pyrolysis gasoline will necessarily increase as well. Until now, pyrolysis gasoline has been used as an aromatic-rich and hence high-octane gasoline component. However, to abate pollution from motor vehicles by 70% from 1990 to 2010, the European Union launched the so-called Auto Oil Programme. In this context, the aromatics content of motor gasoline will have to be reduced drastically from about 45 vol.% in 1999 to less than 35 vol.% in 2005 [3]. Therefore, new outlets for BTX aromatics have to be found, and the conversion of aromatics from pyrolysis gasoline into a high-quality steamcracker feed consisting mainly of ethane, propane and *n*-butane, i.e., its recycling into the steamcracker from which it originates may become an environmentally friendly and economically attractive process option. Its implementation into a naphtha steamcracker complex will not only provide a benign outlet for surplus aromatics but also bring about a significant enhancement of the overall olefin yield on the fresh naphtha feed. To achieve high yields of ethene and propene in steamcrackers, *n*-alkanes are the preferred feedstock type; *iso*-alkanes and cycloalkanes are less suitable; aromatics and methane are inert in the steamcracker and thus very undesired [4].

We have recently shown [5] that the conversion of aromatics into ethane, propane and *n*-butane can be achieved via hydrogenation to cycloalkanes by conventional technology and subsequent ring opening and hydrocracking on acidic zeolites. During

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conversion of the model hydrocarbon methylcyclohexane on acidic zeolites, increasing selectivity to the desired *n*-alkanes with two or more carbon atoms ($S_{\mathrm{C}_{2+}\text{-}n\text{-alkanes}}$), but decreasing conversion ($X_{\mathrm{M\text{–}CH}x}$) are observed with increasing geometrical constraints (i.e., decreasing pore dimensions) in the order H-Y, H-ZSM-5 and H-ZSM-35. Therefore, the highest yield of C_{2+}-*n*-alkanes ($Y_{\mathrm{C}_{2+}\text{-}n\text{-alkanes}}$) of 70.6% is obtained at 400 °C and 6 MPa hydrogen on the medium-pore zeolite H-ZSM-5. In addition, no deactivation is observed on this zeolite, whereas the activity of H-Y decreases with time-on-stream (TOS) [6]. Recent studies from Süd-Chemie AG revealed that comparable results can be achieved during conversion of a commercial hydrogenated pyrolysis gasoline on a commercial extruded H-ZSM-5 catalyst [7]. In another communication [8], we demonstrated that the same synthetic steamcracker feed can alternatively be produced in a single catalytic reactor by direct conversion of aromatics on a bifunctional zeolite catalyst like Pd/H-ZSM-5. In the present contribution, the conversion of different aromatics (benzene, toluene, *o*- and *p*-xylene, ethylbenzene and 1,2,4-trimethylbenzene), which occur in pyrolysis gasoline, is discussed in more detail.

2. Experimental section

Zeolite ZSM-5 ($n_{\mathrm{Si}}/n_{\mathrm{Al}} = 20$) was hydrothermally synthesized as described earlier [9], ion-exchanged with aqueous solutions of $\mathrm{NH_4NO_3}$ and $\mathrm{Pd(NH_3)_4Cl_2}$ and pre-treated successively in flows of air (12 h), nitrogen (1 h) and hydrogen (7 h) at 400 °C to yield bifunctional catalysts with $m_{\mathrm{Pd}}/m_{\text{dry zeolite}} = 0.01$, 0.2, 0.5 or 1.0%, respectively. The catalytic experiments were performed in a flow-type apparatus from stainless steel with a fixed-bed reactor at a total pressure of 6 MPa in an excess of hydrogen at various temperatures between 200 and 400 °C. The mass of the dry catalyst (particle size between 0.20 and 0.32 mm), the partial pressure of the aromatic hydrocarbon at the reactor inlet and the weight hourly space velocity (WHSV) amounted to 500 mg, 65 kPa and $0.68\,\mathrm{h}^{-1}$, respectively. The conversions and yields given were obtained after about 150 min TOS. Product analysis was achieved by capillary gas chromatography with an HP PONA column. Identification of the different components was accomplished by GC/MS and co-injection of the most important products.

3. Results and discussion

3.1. Principle reactions during the conversion of ethylbenzene

The conversion of ethylbenzene on the bifunctional Pd/H-ZSM-5 zeolite with 0.2 wt.% palladium is 100% throughout the temperature range studied, but the types of reactions vary drastically (cf. Fig. 1): at 250 °C, hydrogenation to ethylcyclohexane and further isomerization to other $\mathrm{C_8}$-cycloalkanes are the dominant reactions. Due to the well known reluctance of alicyclic carbenium ions to undergo classical β-scission inside the naphthenic ring [10], only very low yields of ring opening products are observed at 250 °C. With increasing temperature, more and more ring opening occurs and is accompanied by secondary cracking (mainly into propane, *iso*- and *n*-butane). While the yield of *iso*-alkanes passes through a maximum (34.1% at 300 °C), a continuous increase of the yield of *n*-alkanes is observed, possibly due to an increase in tertiary cracking reactions forming light *n*-alkanes. Between 350 and 400 °C, the yield of ethane increases strongly from 5.6 to 30.6%. This effect, leading to a yield of C_{2+}-*n*-alkanes as high as 90.2% at 40 °C, is neither observed with the other aromatics nor during hydroconversion of ethylcyclohexane on acidic zeolite H-ZSM-5 [11]. Therefore, it is attributed to de-ethylation of the aromatic ring. While tertiary cracking is ascribed only to non-classical Haag–Dessau cracking [12,13] because classical cracking into ethane or methane would require the formation of extremely unstable primary or methyl carbenium ions, both classical cracking and Haag–Dessau cracking (see Section 3.2 and Fig. 2) can contribute to ring opening and secondary cracking.

3.2. Influence of the nature of the aromatic feed

To rationalize the different product compositions observed during cracking of aromatics with 6–9 carbon atoms (see Fig. 3 and Table 1), the different possibilities of cracking reactions have to be considered. On the one hand, cracking of cycloalkanes

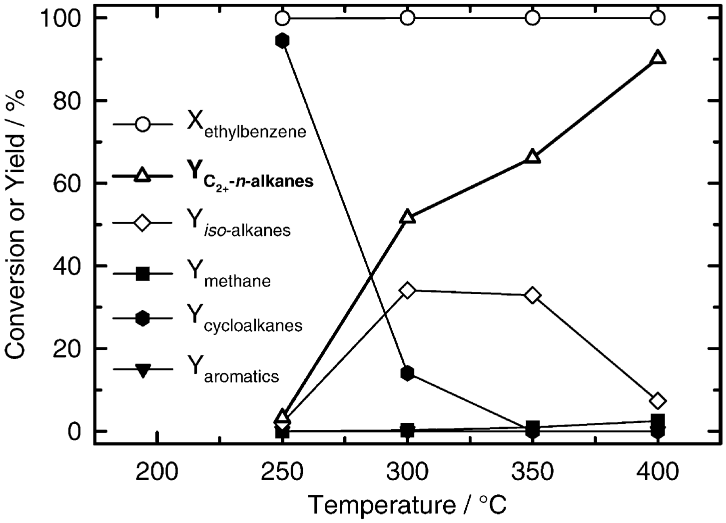

Fig. 1. Conversion of ethylbenzene on zeolite Pd/H-ZSM-5 with 0.2 wt.% Pd.

formed by aromatics hydrogenation on the metal sites and further cracking of the ring opening products on the acidic sites can occur via Haag–Dessau cracking by a direct protonation forming non-classical carbonium ions with three-center, two-electron bonds in the transition state (cf. Fig. 2, part A). Because of its relatively high activation energy, Haag–Dessau cracking, leading predominantly to light *n*-alkanes, is favoured at high temperatures [12]. On the other hand, cracking can occur via classical bifunctional cracking: cycloalkenes or alkenes are formed on the metal sites and then adsorbed and protonated to carbenium ions on the acidic sites. After the usually occurring skeletal isomerization into highly branched isomers, classical β-scission can proceed. Finally, the two alkenes (or the diene) formed are hydrogenated on metal sites (cf. Fig. 2, part B) [10,16]. The classical β-scission is classified into different types according to the degree of branching of the carbenium ions involved (type A to type E, see Fig. 2, part B). Due to the decreasing stability of carbenium ions in the order tertiary, secondary, primary and methyl, the rate constants strongly

Table 1
Conversion of different aromatics on zeolite Pd/H-ZSM-5 with 0.2 wt.% Pd at 250 and 400 °C (1,2,4-TM-Bz: 1,2,4-trimethylbenzene)

	250 °C				400 °C			
	Benzene	Toluene	Ethylbenzene	1,2,4-TM-Bz	Benzene	Toluene	Ethylbenzene	1,2,4-TM-Bz
X (%)	100	100	99.9	58.5	100	100	100	100
Y_{methane} (%)	–	–	–	–	3.7	3.3	2.5	2.9
Y_{ethane} (%)	–	0.1	0.2	–	14.4	7.9	30.6	13.6
Y_{propane} (%)	–	4.0	0.8	1.0	62.8	48.6	49.0	49.4
$Y_{n\text{-butane}}$ (%)	–	0.7	0.9	0.6	11.9	15.9	9.5	15.1
$Y_{C_{5+}\text{-}n\text{-alkanes}}$ (%)	0.3 (C_6)	1.2	1.5	0.6	1.2	0.4	1.1	2.7
$Y_{C_{2+}\text{-}n\text{-alkanes}}$ (%)	0.3 (C_6)	6.0	3.3	2.2	90.3	72.8	90.2	80.8
$Y_{iso\text{-alkanes}}$ (%)	0.3 (C_6)	7.3	2.1	1.7	6.0	23.9	7.3	16.1
$Y_{\text{cycloalkanes}}$ (%)	99.5 (C_6)	86.6	94.5	48.9	–	–	–	0.2
$Y_{\text{aromatics}}$ (%)	–	–	–	5.7	–	–	–	–
$Y_{n\text{-butane}}/Y_{\text{butanes}}$	–	0.14	0.60	0.53	0.77	0.41	0.63	0.60

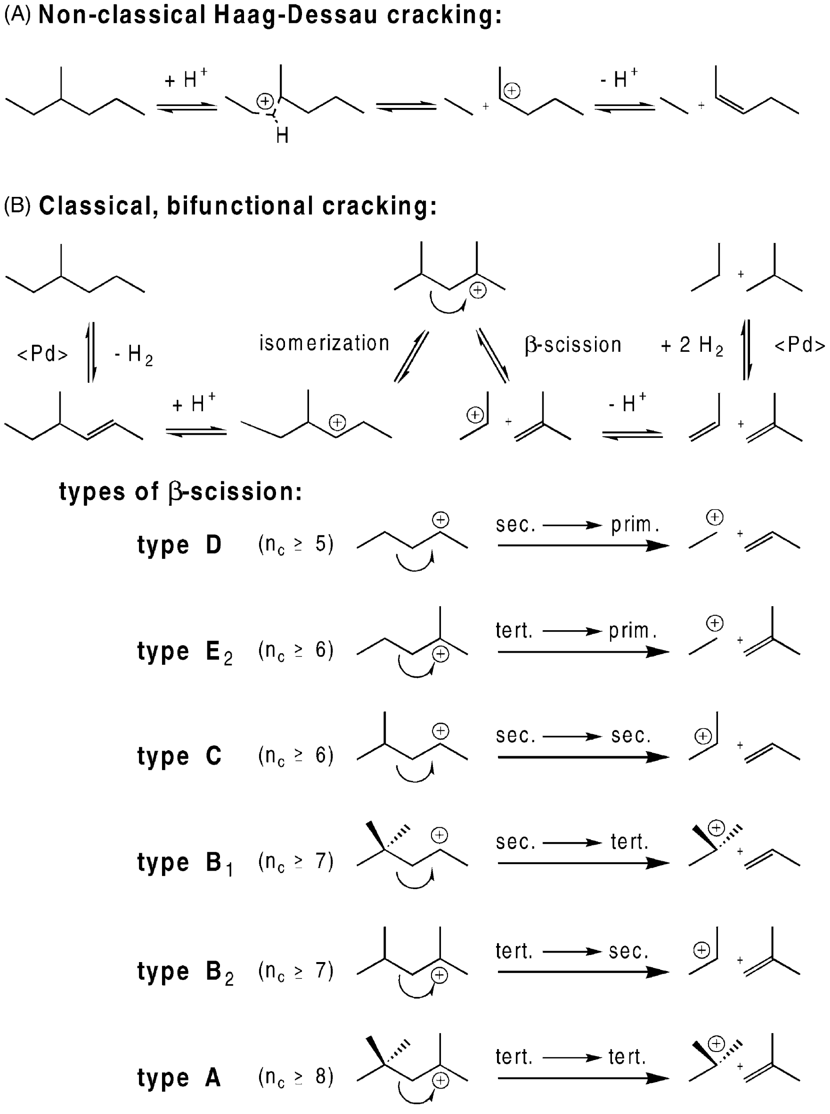

Fig. 2. Principal mechanisms of secondary cracking reactions (the mechanisms of ring opening are analogous) and classification of β-scissions according to the degree of branching of the carbenium ions involved [14,15]. The minimum number of carbon atoms (n_c) necessary for each type of β-scission is given in parentheses.

decrease from type A to type D β-scissions [14] and therefore *iso*-alkanes will normally be formed, if this is structurally possible. However, due to the geometrical constraints in zeolite ZSM-5, a contribution of type A β-scissions is very unlikely [14].

On the basis of these mechanistic concepts, an attempt will be made to interpret the product compositions found for different aromatic feeds: during the conversion of benzene at 250 °C, besides C_6-cycloalkanes only a small amount of ring opening products, but no secondary cracking products are detected (cf. Table 1), whereas with toluene 10.5% secondary cracking products are formed at the same temperature. This may be readily understood, because with C_6-hydrocarbons only the relatively slow type C or the even slower type D or type E_2 β-scissions can proceed

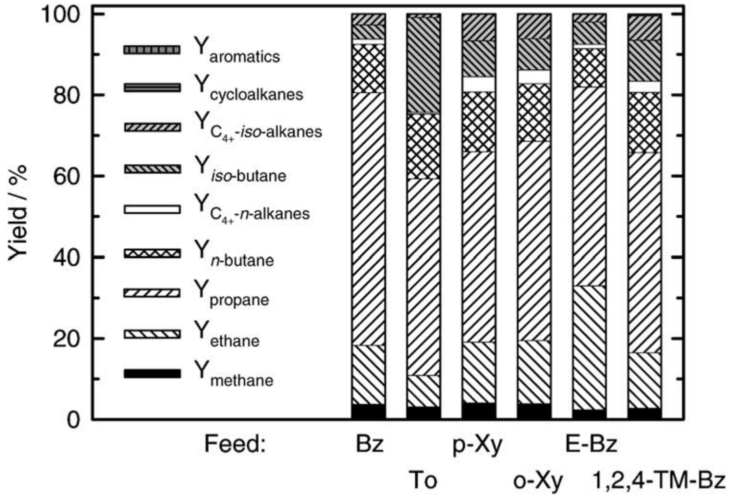

Fig. 3. Yields during the conversion of different aromatic model compounds on zeolite Pd/H-ZSM-5 with 0.2 wt.% Pd at 400 °C (Bz: benzene, To: toluene, Xy: xylene, E: ethyl, TM: trimethyl).

(cf. Fig. 2, part B, no Haag–Dessau cracking occurs at this low temperature). At 400 °C, very large amounts of propane ($Y_{\text{propane}} = 62.8\%$, see Fig. 3 and Table 1) leading to the very high yield of C_{2+}-*n*-alkanes of 90.3% are formed, which can be rationalized by type C β-scissions, which are much more favoured at this high temperature. The formation of the other two main products ethane (14.4%) and *n*-butane (11.9%) and of methane (3.7%) is attributed mainly to Haag–Dessau cracking. The occurrence of type D β-scissions is unlikely because, if it occurred, more *iso*-butane would be expected to form by the faster type E_2 β-scission than *n*-butane by the type D variant. This is in good agreement with earlier results [14].

At 250 °C, the conversion and yield of cracked products decrease with increasing carbon number from 7 to 9. It is well known from adsorption experiments that at 150 °C benzene, toluene and *p*-xylene have free access to the pore system of zeolite ZSM-5, whereas *m*- and *o*-xylene are adsorbed partially only [17]. Therefore, this decrease is tentatively attributed to diffusion limitations for the larger molecules at this moderate temperature. During conversion of xylenes or 1,2,4-trimethylbenzene at 400 °C, less *iso*-alkanes (ca. 15%, cf. Table 1 and Fig. 3) are formed compared to toluene (23.9%, mainly *iso*-butane). Therefore, significantly higher yields of C_{2+}-*n*-alkanes (ca. 80%) are achieved with these aromatics than with toluene (72.8%). This effect is even more pronounced, if the proportion of *n*-butane in the butane fraction ($Y_{n\text{-butane}}/(Y_{iso\text{-butane}} + Y_{n\text{-butane}})$) is considered. This ratio is about 0.6 for the conversion of C_8- or C_9-aromatics (almost independent of the temperature and in the range of the thermodynamic equilibrium ratio: 0.48 at 250 °C and 0.59 at 400 °C), but 0.4 for the conversion of toluene at 400 °C and only 0.14 at 250 °C (see Table 1; the higher ratio at 400 °C is ascribed to a higher contribution of Haag–Dessau cracking, discernible by the much higher yields of methane and ethane). These pronounced differences can be accounted for by the different possibilities of *n*-butane formation by classical cracking: via the most favoured type B β-scissions of C_7-hydrocarbons, only propane and *iso*-butane are formed (cf. Fig. 2, part B; the formation of propane and *n*-butane by type C β-scissions is significantly slower). During cracking of C_8- or C_9-hydrocarbons, *n*-butane is also a product of smoothly proceeding type B β-scissions.

At 400 °C, similar product patterns (cf. Fig. 3) are obtained from *p*-xylene (which has easy access to the pores of ZSM-5 even at 150 °C [17]) and *o*-xylene, and even from 1,2,4-trimethylbenzene. Therefore, diffusion control of the reaction seems very unlikely at this elevated temperature.

3.3. Time-on-stream behavior

Regardless of the hydrocarbon fed, no significant change in the product yields is observed during 10 h TOS at 400 °C. However, at low temperatures (200–275 °C), a slight decrease of the yields of light cracking products is observed. If the temperature is raised again to 400 °C after toluene conversion at such low temperatures for about 50 h, significantly higher yields of the desired C_{2+}-*n*-alkanes (80.4% instead of 72.8%) can be achieved [8]. Because hydrogenated dimers of toluene (e.g., 1-(cyclohexylmethyl)-4-methylcyclohexane) are found during its conversion at 200 °C, this selectivity gain is interpreted in terms of a so-called coke selectivation, i.e., coke build-up by aromatics dimerization and alkylation at low temperatures which brings about a subtle narrowing of the pores.

3.4. Influence of the palladium content of the catalyst

With an increase of the palladium content of the catalyst from 0.2 to 0.5 and 1.0 wt.%, the yields during toluene conversion at 400 °C do not change significantly. Therefore, the formation of methane is attributed to Haag–Dessau cracking, rather than to hydrogenolysis on the noble metal [8]. It is only upon reducing the Pd content to as little as 100 wt. ppm that the catalytic behavior changes in a pronounced manner; the conversion of toluene drops from 100 to 38.2% at 400 °C, and other aromatics become the dominant products, in much the same way as if aromatics had been converted on metal-free, acidic zeolites [18].

4. Conclusions

Surplus aromatics can directly be hydroconverted into a high-quality synthetic steamcracker feed (consisting mainly of ethane, propane and *n*-butane) on bifunctional zeolite catalysts such as Pd/H-ZSM-5. At 400 °C, the yields of the desired C_{2+}-*n*-alkanes with toluene (72.8%) are comparable to those obtained during conversion of its cycloalkane analogue methylcyclohexane on the acidic zeolite H-ZSM-5 (70.6%). Yields of C_{2+}-*n*-alkanes above 90% are attained with benzene or ethylbenzene as feed. The distinct differences occurring during the conversion of various aromatics with 6–9 carbon atoms can be rationalized in terms of variable contributions of classical cracking with its different types of β-scission (type B to type E) and Haag–Dessau cracking. No evidence for the occurrence of hydrogenolysis on the metal sites has been obtained under the conditions applied in this study.

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References

[1] T. Chang, Oil Gas J. 98 (14) (2000) 56.
[2] W. Weirauch, Hydrocarb. Process. Int. Ed. 79 (6) (2000) 9.
[3] Directive 98/70/EC, Official J. Eur. Commun. (L350) (1998) 58.
[4] C. Dembny, in: G. Emig, M. Rupp, J. Weitkamp (Eds.), Tagungsbericht 9903: Proceedings of the DGMK Conference: The Future Role of Aromatics in Refining and Petrochemistry, Erlangen, Germany, October 13–15, 1999, DGMK, Hamburg, p. 115.
[5] J. Weitkamp, A. Raichle, Y. Traa, M. Rupp, F. Fuder, Chem. Commun. (2000) 403.
[6] A. Raichle, H. Scharl, Y. Traa, J. Weitkamp, in: A. Galarneau, F. Di Renzo, F. Fajula, J. Védrine (Eds.), Studies in Surface Science and Catalysis, Vol. 135, Elsevier, Amsterdam, 2001, p. 302, Proceedings of the 13th International Zeolite Conference: Zeolites and Mesoporous Materials at the Dawn of the 21st Century, Montpellier, France, July 8–13, 2001, Full Paper No. 26-P-10 on CD-ROM.
[7] C. Ringelhan, V. Kurth, G. Burgfels, J.G. Neumayr, W. Seuffert, J. Klose, in: G. Emig, H.-J. Krämer, J. Weitkamp (Eds.), Tagungsbericht 2001-4: Proceedings of the DGMK Conference: Creating Value from Light Olefins-Production and Conversion, Hamburg, Germany, October 10–12, 2001, DGMK, Hamburg, 2001, p. 57.
[8] J. Weitkamp, A. Raichle, Y. Traa, M. Rupp, F. Fuder, Chem. Commun. (2000) 1133.
[9] S. Ernst, J. Weitkamp, Chem.-Ing.-Tech. 63 (1991) 748.
[10] J. Weitkamp, S. Ernst, H.G. Karge, Erdöl, Kohle-Erdgas-Petrochem. 37 (1984) 457.

[11] A. Raichle, Y. Traa, J. Weitkamp, in: G. Emig, H.-J. Krämer, J. Weitkamp (Eds.), Tagungsbericht 2001-4: Proceedings of the DGMK Conference: Creating Value from Light Olefins-Production and Conversion, Hamburg, Germany, October 10–12, 2001, DGMK, Hamburg, 2001, p. 49.
[12] W.O. Haag, R.M. Dessau, Proceedings of the Eighth International Congress on Catalysis, Vol. 2, Berlin, Germany, July 2–6, 1984, Verlag Chemie, Weinheim, 1984, p. 305.
[13] S. Kotrel, H. Knözinger, B.C. Gates, Micropor. Mesopor. Mater. 35–36 (2000) 11.
[14] J. Weitkamp, P.A. Jacobs, J.A. Martens, Appl. Catal. 8 (1983) 123.
[15] J.S. Buchanan, J.G. Santiesteban, W.O. Haag, J. Catal. 158 (1996) 279.
[16] H.L. Coonradt, W.E. Garwood, Ind. Eng. Chem. Proc. Des. Dev. 3 (1964) 38.
[17] D. Ohayon, R.L. Van Mao, D. Ciaravino, H. Hazel, A. Cochennec, N. Rolland, Appl. Catal. A 217 (2001) 241.
[18] A. Chambellan, O. Cairon, T. Chevreau, in: M.M.J. Treacy, B.K. Marcus, M.E. Bisher, J.B. Higgins (Eds.), Proceedings of the 12th International Zeolite Conference, Vol. 2, Baltimore, MD, July 5–10, 1998, Materials Research Society, Warrendale, PA, 1999, p. 1025.