Hydrothermal deactivation of Ce-ZSM-5, Ce-beta, Ce-mordenite and Ce-Y zeolite deNOx catalysts

W.E.J. van Kooten, J. Kaptein, C.M. van den Bleek and H.P.A. Calis

Faculty of Applied Sciences, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
E-mail: H.P.Calis@tnw.tudelft.nl

Received 21 June 1999; accepted 5 October 1999

The hydrothermal stability of Ce^{3+} zeolite catalysts used for selective catalytic reduction of NO_x was investigated. Aging of Ce-ZSM-5, Ce-beta, Ce-mordenite and Ce-Y catalysts consisted of steaming in 10 or 12 vol% water at 600 °C for 3–99 h. Ce-ZSM-5 (Si/Al ratios: Si/Al = 17.1, 22.6 and 146.6) and Ce-mordenite (Si/Al = 6.4, IE = 77.2%) showed fast deactivation. Ce-beta (Si/Al = 12, IE = 68.4%) and Ce-Y (Si/Al = 2.8, IE = 122%) are significantly more stable zeolite catalysts, Ce-beta being the most active of these two. Ce-beta and Ce-ZSM-5 catalysts – both having high initial activities – were characterized with ^{29}Si-NMR and ^{27}Al-NMR. Especially Ce-ZSM-5 showed an increase of non-framework Al, meaning that the zeolite suffered from dealumination.

Keywords: dealumination, deactivation, cerium, SCR, deNOx, ZSM-5, beta, Y, mordenite, NH_3

1. Introduction

Many zeolites have been studied as catalysts for selective catalytic reduction (SCR) of NO_x. Some zeolite-based catalysts show high initial activities with hydrocarbons as reducing agents. Even better results are obtained with ammonia as reducing agent. So far, however, the hydrothermal stability of zeolite catalysts appears to be limited. As the stability is of major importance for application, improvement of zeolite catalysts should be aimed at stability too rather than initial activity only. Hydrothermal deactivation can have several causes, the most important of which are dealumination, structural collapse, agglomeration of active cations to small oxide islands and migration of the cations to inaccessible sites.

Several studies have been reported concerning the hydrothermal stability of zeolite deNOx catalysts. Several papers deal with deactivation of Cu-ZSM-5, e.g., [1–3]. A number of authors suggest to stabilize the catalyst by co-exchanging lanthanum or cerium [4–9]. Some catalysts were claimed to be very stable, such as Co-ZSM-5 [10] and Fe-ZSM-5. The latter catalyst, however, did not have reproducible stability so far [11].

Zeolites exchanged with the Ce^{3+} cation are either active with hydrocarbons [12–15] or with ammonia [16–19] as reducing agent. This study compares the hydrothermal stability of Ce-ZSM-5, Ce-Y, Ce-mordenite and Ce-beta. Furthermore, the influence of the Si/Al ratio on the stability of Ce-ZSM-5 is investigated. Ammonia is used as reducing agent, but the results are anticipated to be representative for HC-SCR as well, because the reducing agent is believed not to interfere with the dealumination process.

2. Experimental

2.1. Catalyst preparation

The stability of a zeolite catalyst depends very much on the preparation, and thus knowledge about the starting materials is essential. For this particular reason, the study was performed with commercially available zeolites as the starting materials. Na-beta (Si/Al = 12.0, Chemie Uetikon) and Na-ZSM-5 (Si/Al = 17.1, PQ corporation), Na-ZSM-5 (Si/Al = 22.6, Si/Al = 146.6, Chemie Uetikon), Ce-mordenite (Si/Al = 6.4, PQ corporation) and Ce-Y (Si/Al = 2.8, Akzo-Nobel) were used. The starting materials were characterized with XRD, NMR and BET, the results of which were in agreement with literature data. Ion exchange of the zeolites with Ce^{3+} was performed by aqueous ion exchange for 24 h at 80–100 °C using cerium acetate. The ion-exchanged zeolites were filtered and washed and afterwards dried at 120 °C for 24 h. Further details on preparation can be found in [16].

2.2. Catalyst characterization

The elemental composition of the catalyst was determined with AAS (Perkin–Elmer 1100) and ICP-AES (Perkin–Elmer Optima 3000DV). XRD (Philips PW 1840 diffractometer) was used to examine the crystallinity of the zeolite and to examine the presence of cerium oxide in the catalyst.

To investigate the dealumination of cerium-exchanged zeolite catalysts, ^{29}Si- and ^{27}Al-MAS-NMR (magic angle spinning nuclear magnetic resonance) spectra were acquired at 9.4 T using a VARIAN VXR-400S spectrometer at a scan frequency of 74.499 and 104.209 MHz for ^{29}Si- and ^{27}Al-NMR measurements, respectively.

2.3. Catalyst testing and steaming

The catalyst testing was done in a quartz tubular reactor containing a fixed bed of catalyst particles (0.5–1.0 mm), operated under plug flow conditions. NO_x conversions were determined under steady-state conditions, at various temperatures in the range 200–600 °C with at least 1 h dwell at each temperature. A NO_x conversion measurement series always consisted of an ascending followed by a descending temperature sequence, with a total length of about 24 h and an average temperature of about 400 °C. NO_x concentrations were measured using a NO_x analyzer (Signal 4000), based on the chemiluminescence principle. Measurement conditions used: 0.45 g of catalyst, 496 $ml_{NTP}\,min^{-1}$, 900 ppmv NO_x, 900 ppmv NH_3, 5 vol% O_2, 10 vol% H_2O and balance N_2. The catalyst bed volume was approximately 0.6 ml for all catalysts used.

Steaming of the catalysts was performed at 600 °C under typical deNOx conditions (0.45 g of catalyst, 496 $ml_{NTP}\,min^{-1}$, 900 ppmv NO_x, 900 ppmv NH_3, 5 vol% O_2, 10 or 12 vol% H_2O and balance N_2) for 3–99 h (as indicated in the text).

3. Results and discussion

In this study six different catalysts have been prepared and investigated. Table 1 lists specifications of these catalysts. Figure 1 shows a comparison between Ce-ZSM-5 (catalyst 1), Ce-mordenite (catalyst 2) and Ce-Y (catalyst 3) concerning initial activity and activity after 48 h of steaming. The catalysts show quite different initial activities (represented by the solid lines). Ce-mordenite appeared to be the most active catalyst. In this respect it should be noticed that the Si/Al ratios differ largely between catalysts 1, 2 and 3 making a good comparison between the zeolite types rather difficult. After steaming for 48 h at 600 °C in 12 vol% H_2O all three catalysts have significantly lost activity. The main loss of activity for all three catalysts lies in the region 250–500 °C. Especially Ce-mordenite and Ce-ZSM-5 deactivated enormously. In contrast, the catalyst activity at 600 °C was only slightly affected by the steaming treatment.

To estimate the deactivation rate as a function of time, steaming experiments were performed in intervals with NO_x conversion measurements in between. Figure 2 shows the NO_x conversion of Ce-ZSM-5 (catalyst 4) after incremental steaming periods of 24 h each. Before steaming, the catalyst activity is similar to the activity of catalyst 1 in figure 1. Steaming affects mainly the NO_x conversion in the low-temperature region. Figure 2 clearly shows that the effect of steaming is the most pronounced during the first 24 h of steaming and becomes less as a function of steaming time. A stable NO_x conversion is, however, still not reached after 96 h of steaming.

Figure 3 contains data on NO_x conversion measurements of Ce-beta (catalyst 5) during a similar steaming experiment. Again, steaming resulted in a clear decrease of NO_x conversion. The decrease was, however, not as dramatic as for Ce-ZSM-5. After 99 h of steaming the NO_x conver-

Table 1
Specifications of the catalysts used.

Catalyst No.	Zeolite type	Si/Al ratio	Ce^{3+} ion exchange percentage (IE%)
1	CeNa-ZSM-5	22.6	77.8
2	CeNa-mordenite	6.4	77.2
3	Ce-Y	2.8	122.1
4	Ce-ZSM-5	17.1	114.9
5	CeNa-beta	12.0	68.4
6	Ce-ZSM-5	146.6	275.0

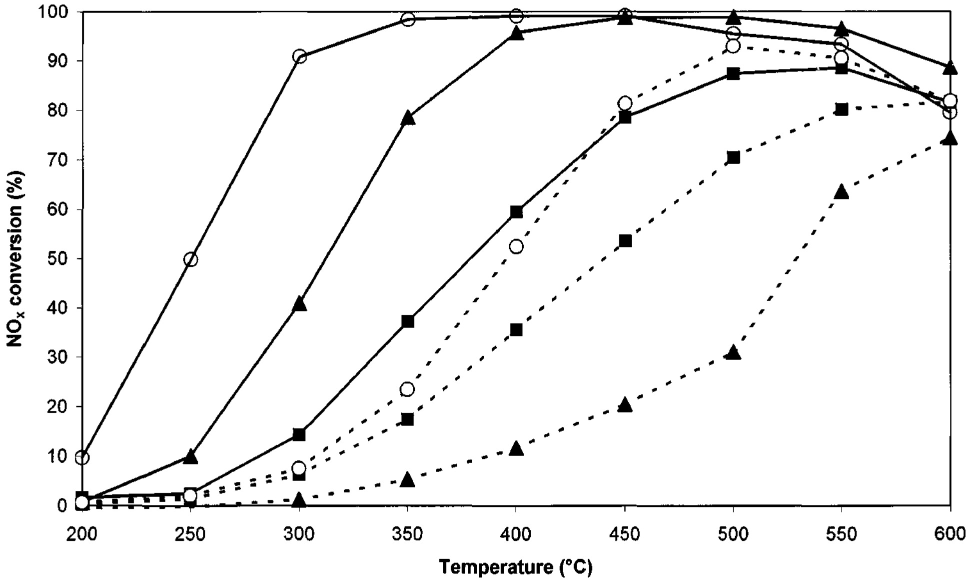


Figure 1. NO_x conversion versus temperature for Ce-ZSM-5 (catalyst 1) (▲), Ce-mordenite (catalyst 2) (○) and Ce-Y (catalyst 3) (■). Solid lines correspond to NO_x conversion before steaming, dashed lines correspond to NO_x conversion after 48 h of steaming in 12 vol% H_2O at 600 °C.

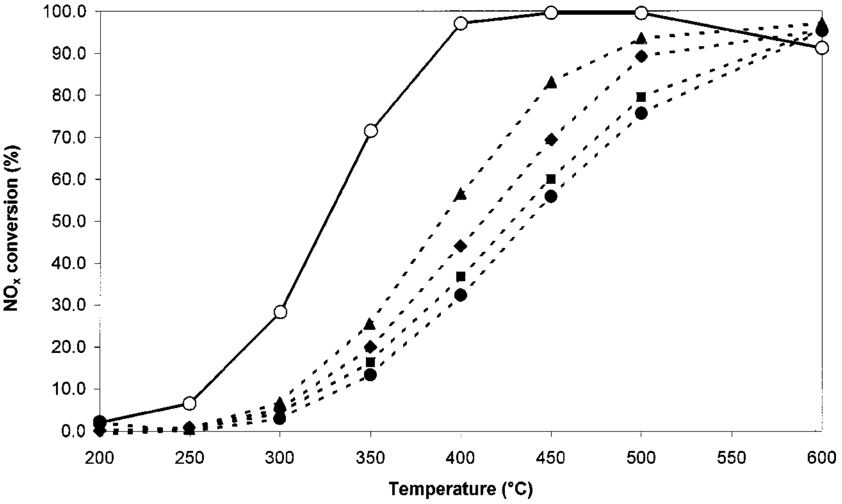


Figure 2. NO_x conversion versus temperature for Ce-ZSM-5 (catalyst 4) before steaming (○), after 24 h steaming (▲), after 48 h steaming (◆), after 72 h steaming (■) and after 96 h steaming (●) in 10 vol% H_2O at 600 °C.

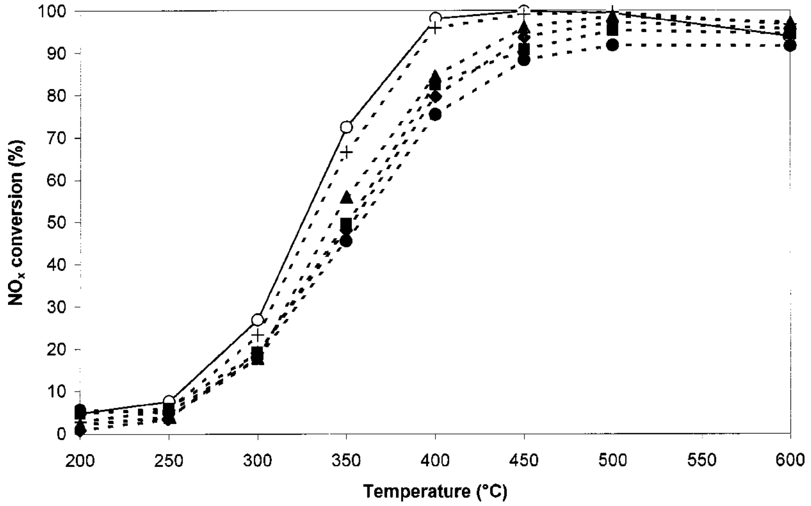


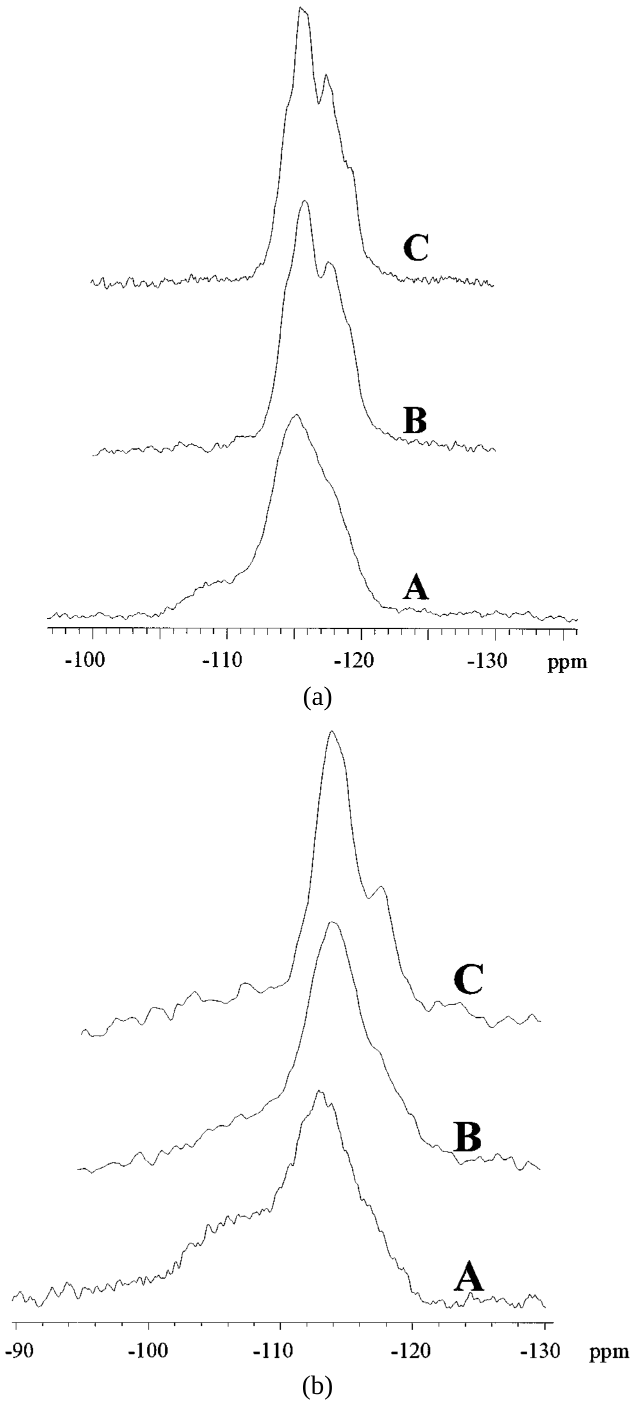
Figure 3. NO_x conversion versus temperature for Ce-beta (catalyst 5) before steaming (○), after 3 h steaming (+), after 27 h steaming (▲), after 51 h steaming (◆), after 75 h steaming (■) and after 99 h steaming (●) in 10 vol% H_2O at 600 °C.

sion at 350 °C is 45% which is high compared to Ce-ZSM-5 (catalyst 4, steamed for 96 h) having NO_x conversions of about 15%.

In figure 4 ^{29}Si-MAS-NMR spectra of fresh and deactivated Ce-ZSM-5 (catalyst 4) and Ce-beta (catalyst 5) are presented. In figure 5 ^{27}Al-MAS-NMR spectra of the same catalysts are given. The ^{29}Si-NMR spectra suffer from peak broadening due to the presence of paramagnetic cerium cations, as a result of which deconvolution of the peaks into separate contributions of Si(0Al), Si(1Al), Si(2Al), Si(3Al) and Si(4Al) peaks appeared not to be possible. What can be seen, however, is that upon steaming of Ce-ZSM-5 (figure 4(a)), the peak at -109 ppm, attributed to Si(1Al), disappears. In return, the remaining peaks at about -117.5 and -119 ppm, attributed to Si(0Al), gain resolution. This indicates dealumination. The same trend is observed for Ce-beta in figure 4(b).

The ^{27}Al-NMR spectra of Ce-ZSM-5 in figure 5(a) show a large peak at 55 ppm which is attributed to framework Al. A small peak at about 0 ppm can be caused by a spinning side band or to a small amount of octahedral non-framework aluminium. Furthermore, figure 5(a) shows that after 48 h of steaming two new peaks are present, viz. at about 0 and about 30 ppm. The peak at 0 ppm can be ascribed to octahedral non-framework aluminium and the peak at 30 ppm arises from tetrahedral or a second type of octahedral non-framework aluminium (30 ppm is rather low for tetrahedral aluminium). After 96 h of steaming the peak of octahedral non-framework aluminium has increased even further. Figure 5(b) shows the ^{27}Al-NMR spectra for Ce-beta. After steaming, peaks appear at 0 and 30 ppm. Like for Ce-ZSM-5 these peaks are attributed to non-framework aluminium. The peak areas are, however, much smaller, indicating that the degree of dealumination is much lower than in the case of Ce-ZSM-5.

The catalytic activity before steaming of Ce-ZSM-5 with a high Si/Al ratio of 146.6 (catalyst 6) was relatively low

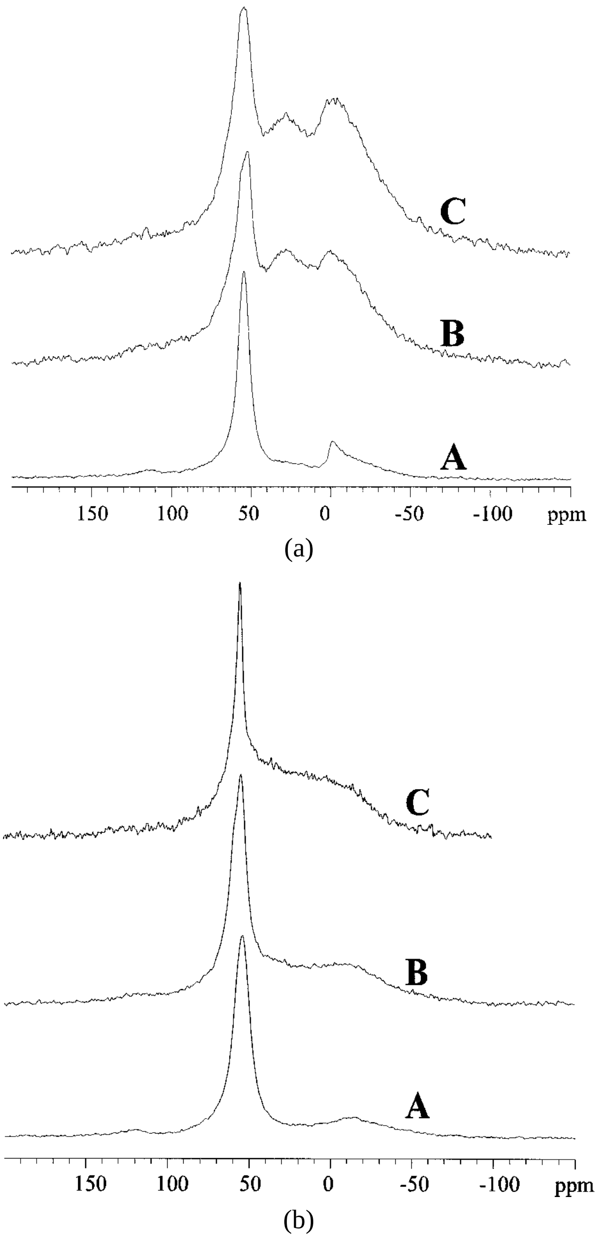


(a)

(b)

Figure 4. ^{29}Si-MAS-NMR spectra of fresh and steamed catalysts. (a) Ce-ZSM-5 (catalyst 4). Untreated catalyst (A), catalyst after 48 h of steaming (and NO_x conversion measurements before steaming and after 48 h of steaming) (B), catalyst after 96 h of steaming (and NO_x conversion measurements before steaming and after 24, 48, 72 and 96 h of steaming) (C). (b) Ce-beta (catalyst 5). Untreated catalyst (A), catalyst after 48 h of steaming (and NO_x conversion measurements before steaming and after 48 h of steaming) (B), catalyst after 99 h of steaming (and NO_x conversion measurements before steaming and after 3, 27, 51, 75 and 99 h of steaming) (C).

compared to other catalysts, due to the low ion exchange capacity of this zeolite. A maximum conversion of about 35% at 550 °C was observed. After steaming at 600 °C for 48 h, the activity had decreased by 55 to 70% over the entire temperature range. The idea that zeolites with higher Si/Al ratios are more stable can therefore not be confirmed, at least not for Ce-ZSM-5. The problem might be the trivalency of the cation. Using fluorescence spectroscopy, Ito [20] showed that the oxidation state of cerium in zeolites in principal is 3+. A Ce^{3+} cation has to neutralise three widely spaced negative Al^- charges. The higher the Si/Al ratio, the larger the average distance between these negative charges, complicating the role of Ce^{3+}. This might be the reason that higher Si/Al ratios in case of Ce-ZSM-5 do not result in more stable zeolites.



(a)

(b)

Figure 5. ^{27}Al-MAS-NMR spectra of fresh and steamed catalysts. (a) Ce-ZSM-5 (catalyst 4). (b) Ce-beta (catalyst 5). For legend see figure 4.

To correlate the decrease of NO_x conversion to a change in the number of catalytically active sites, the reaction rate constant k_r (s^{-1}) can be calculated using the equation for

Table 2
Ratio of reaction rate constants before and after steaming ($k_{r(\mathrm{after})}/k_{r(\mathrm{before})}$).

Catalyst	$k_{r(\mathrm{after})}/k_{r(\mathrm{before})}$				
No.	250 °C	350 °C	450 °C	500 °C	550 °C
1 (Ce-ZSM-5)	0.00	0.04	0.05	–	0.30
2 (Ce-mordenite)	0.03	0.07	0.36	–	0.87
3 (Ce-Y)	0.54	0.41	0.50	–	0.75
4 (Ce-ZSM-5)	0.13	0.18	0.22	0.42	–
5 (Ce-beta)[a]	0.45	0.51	0.48	0.72	–
6 (Ce-ZSM-5)	0.45	–	0.30	–	0.42

[a] After 51 h of steaming instead of 48 h.

the NO conversion (ξ_{NO}) in a plug flow reactor, assuming first-order kinetics:

$$\xi_{\mathrm{NO}} = 1 - \exp(-k_r V/\phi_v), \tag{1}$$

where V is the volume of the catalyst bed (ml) and ϕ_v the volume of the gas feed per time interval (ml min^{-1}).

Table 2 gives the ratio of the calculated k_r values before and after 48 h of steaming. k_r is assumed to be proportional to the number of catalytically active sites. The ratio $k_{r(\mathrm{after})}/k_{r(\mathrm{before})}$ is a measure of the loss in active sites, assuming that only the number but not the nature of the available sites changes during deactivation (E_{act}, the activation energy in kJ mol^{-1}, then stays the same). Even though reality will be much more complex than we suggest here, this approach generally provides a useful insight into changes in the number of active sites. A complicating factor is that the activity of the catalysts is probably determined by two different sites, as was found during the elucidation of the SCR mechanism for Ce-mordenite [18,21]. Ce^{3+} sites are mainly active at low temperatures and acid sites at high temperatures. In a two-site mechanism the reaction rate constant k_r is made up of two parts. As it is likely that dealumination affects the number of one type of site more than the other type, a change in the ratio $k_{r(\mathrm{after})}/k_{r(\mathrm{before})}$ is a function of temperature. This effect is visible in table 2. At higher temperatures the ratio $k_{r(\mathrm{after})}/k_{r(\mathrm{before})}$ is higher, indicating that the acid sites are less affected than the Ce^{3+} sites. Figures 1–3 show that Ce-mordenite, Ce-ZSM-5 and Ce-beta have high initial activities. Ce-Y and Ce-beta have high values for the ratio $k_{r(\mathrm{after})}/k_{r(\mathrm{before})}$ at 250–450 °C indicating that these zeolites are the most stable. About 50% of the active sites is lost after about 50 h of steaming in 10 vol% water at 600 °C. For Ce-ZSM-5 (catalyst 4) about 80% of the active low-temperature sites is lost under similar conditions. This is in accordance with the NMR results, that showed a large increase of non-framework Al for Ce-ZSM-5. A smaller increase was found for Ce-beta, indicating that Ce-ZSM-5 suffered more from dealumination than Ce-beta.

4. Conclusions

Ce-ZSM-5 and Ce-mordenite (Si/Al = 6.4, IE = 77.2%) show fast deactivation. Ce-ZSM-5 lost 80% of the active sites during 50 h steaming at 600 °C. The deactivation of Ce-ZSM-5 was observed for three different Si/Al ratios: Si/Al = 17.3, 22.6 and 146.6. Apparently the Si/Al ratio does not play a key role in the deactivation process. Ce-ZSM-5 showed an increase of non-framework aluminium, indicating that the zeolite deactivation was caused by dealumination. Ce-beta (Si/Al = 12, IE = 68.4%) and Ce-Y (Si/Al = 2.8, IE = 122%) are the most stable zeolite catalysts. Ce-beta is the most active of these two.

Acknowledgement

The investigations were supported (in part) by the Netherlands Technology Foundation (STW) with financial aid from the Netherlands Organization for Scientific Research (NWO). This support is gratefully acknowledged.

References

[1] P. Denton, Z. Chajar, N. Bainier-Davias, M. Chevrier, C. Gauthier, H. Parliaud and M. Primet, Stud. Surf. Sci. Catal. 116 (1998) 335.
[2] K.C.C. Kharas, H.J. Robota and D.J. Liu, Appl. Catal. B 2 (1993) 225.
[3] J.Y. Yan, G.-D. Lei, W.M.H. Sachtler and H.H. Kung, J. Catal. 161 (1996) 43.
[4] P. Budi and R.F. Howe, Catal. Today 38 (1997) 175.
[5] P. Budi, E. Curry-Hyde and R.F. Howe, Catal. Lett. 41 (1996) 47.
[6] A.V. Kucherov, C.P. Hubbard, T.N. Kucherova and M. Shelef, Appl. Catal. B 7 (1996) 285.
[7] J.Y. Yan, W.M.H. Sachtler and H.H. Kung, Catal. Today 33 (1997) 279.
[8] Y. Zhang and M. Flytzani-Stephanopoulos, J. Catal. 164 (1996) 131.
[9] M. Guyon, V. Le Chanu, P. Gilot, H. Kessler and G. Prado, Stud. Surf. Sci. Catal. 116 (1998) 297.
[10] J.N. Armor and T.S. Farris, Appl. Catal. B 4 (1994) L11.
[11] W.K. Hall, X. Feng, J. Dumesic and R. Watwe, Catal. Lett. 52 (1998) 13, and references therein.
[12] M. Misono and K. Kondo, Chem. Lett. (1991) 1001.
[13] C. Yokoyama and M. Misono, Chem. Lett. (1992) 1669.
[14] C. Yokoyama and M. Misono, J. Catal. 150 (1994) 9.
[15] C. Yokoyama and M. Misono, J. Catal. 160 (1996) 95.
[16] W.E.J. van Kooten, B. Liang, H.C. Krijnsen, O.L. Oudshoorn, H.P.A. Calis and C.M. van den Bleek, Appl. Catal. B 21 (1999) 203.
[17] W.E.J. van Kooten, H.P.A. Calis and C.M. van den Bleek, Stud. Surf. Sci. Catal. 116 (1998) 357.
[18] E. Ito, Y.J. Mergler, B.E. Nieuwenhuys, H.P.A. Calis, H. van Bekkum and C.M. van den Bleek, J. Chem. Soc. Faraday Trans. 92 (1996) 1799.
[19] E. Ito, R.J. Hultermans, H.P. Calis, J.C. Jansen, H. van Bekkum and C.M. van den Bleek, Catal. Today 27 (1996) 123.
[20] E. Ito, Ph.D. thesis, Delft University of Technology, Delft, The Netherlands (1996) ch. 4, p. 122.
[21] E. Ito, Y.J. Mergler, B.E. Nieuwenhuys, H. Van Bekkum and C.M. van den Bleek, Micropor. Mater. 4 (1995) 455.