

Effect of the binder content on the catalytic performance of beta-based catalysts

Paula Sánchez, Fernando Dorado, Antonia Fúnez, Vicente Jiménez, María Jesús Ramos*, José Luis Valverde

Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avd. Camilo José Cela s/n, 13071 Ciudad Real, Spain

Received 19 February 2007; received in revised form 28 March 2007; accepted 31 March 2007
Available online 6 April 2007

Abstract

The influence of the amount of a clay binder (sodium bentonite) on the properties and performance of beta zeolite based catalysts for the hydroisomerization of *n*-octane was studied. The contribution of the bentonite to the total acidity of agglomerated catalysts was very low, although its presence could affect to the acidic properties. Experimental acidity values for the agglomerated catalysts did not match with those theoretically expected due to a solid-state ion exchange between protons of the zeolite and sodium of the clay during the calcination following the ion-exchange step. Metal dispersion values were in agreement with the specific surface area of the zeolite in the agglomerated catalysts, suggesting that the metal were mainly located into the zeolite.

Catalysts were tested in the hydroisomerization of *n*-octane. Concerning the agglomerated catalysts, the higher the strong acid site density per gram of zeolite was, the higher the *n*-octane conversion was observed. Non-agglomerated catalysts, even showing a higher strong acid site density per gram of zeolite, exhibited the lowest *n*-octane conversion. EFAL species were present on the agglomerated catalysts enhancing their acid strength through a synergetic effect that allowed them to be much more active for the hydroisomerization of *n*-octane.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Binder; Zeolite; Hydroisomerization; *n*-Octane; EFAL

1. Introduction

Compared to other types of catalysts, zeolites exhibit exceptional properties with respect to both activity and selectivity because of their ability to adsorb and transform molecules in their inner pore volume. An important class of reactions performed by zeolites is the acid-catalyzed reactions. For that, the zeolite framework needs to contain protons which give rise to a high Brønsted acidity. This is exploited in many organic reactions, including oil cracking, isomerization and fuel synthesis.

Isomerization of long-chain alkanes appears to be an interesting alternative since provides branched molecules which possess higher octane number than linear ones [1]. Isomerization of alkanes is carried out over bifunctional catalysts consisting of an acid function, provided by solid acids; i.e., zeolites, and a metallic

function (noble metals). Isomerization takes place on the acid sites of the bifunctional catalyst whereas the metal provides hydrogenation–dehydrogenation capability [2].

In order to provide necessary mechanical strength and/or resistance towards attrition loss, most of industrial zeolite catalysts are prepared by embedding the zeolite crystallites in a matrix, using a binder: synthetic material, such as silica and alumina or natural clay, such as kaolin, bentonite, etc. [3]. The process of pellet formation of zeolite powders creates meso and macropores, thus modifying the diffusion characteristics of the molecules [4].

Also, the interaction between binder and zeolite can have a strong influence on the activity, selectivity and stability of the zeolite [3]. It has been demonstrated that the binder is not active as a catalyst but could change the acid properties of a zeolite as a result of changes in the proton-exchange efficiency, trapping by the binder of coke precursors, and/or blocking of zeolite channels during the pelletization process [5,6]. Information regarding the influence of the binder on the acidity and

* Corresponding author. Tel.: +34 926 29 53 00; fax: +34 926 29 52 42.
E-mail address: MaríaJesus.Ramos@uclm.es (M.J. Ramos).

catalytic performance of zeolite is, therefore, very important for the development of industrial catalysts.

Choudhary et al. [3] reported the influence of the addition of alumina or kaolin, as a binder, to H-Gallosilicate zeolite in propane aromatization. The catalyst deactivation and coke deposition on the zeolite were increased due to the alumina binder, but when kaolin binder was used, the coke deposition was not changed significantly. The role of sodium montmorillonite on bounded zeolite catalysts was studied by Cañizares et al. [7]. The binder gave the required resistance to the final catalyst, but influenced strong sites density due to partial solid state ion-exchange. Dorado et al. [5] reported the influence of the agglomeration with a clay binder on the activity of ZSM-5 and beta zeolite for the hydroisomerization of *n*-butane. A lower *n*-butane conversion was always obtained for the bounded catalysts, due to neutralization of some zeolite acid sites.

In earlier works [1,6], our research group reported, for the hydroisomerization of *n*-octane, the influence of the bentonite on the catalytic performance using three zeolite-based catalysts: mordenite, beta and ZSM-5. The *n*-octane conversion decreased when zeolites mordenite and ZSM-5 were agglomerated with bentonite as compared with that of non-agglomerated ones. However, the catalytic performance of catalysts based on zeolite beta was improved because the presence of extraframework aluminium species provided by the binder.

In this work, several catalysts consisting of zeolite beta agglomerated with different proportion of sodium bentonite were prepared. This proportion was optimized for the hydroisomerization of *n*-octane. The aim of this work is to select a suitable catalyst and to study the influence that the agglomeration process with different binder amounts can induce on both the catalyst acidity and the catalytic performance.

2. Experimental

2.1. Catalyst preparation

NH₄-BETA (Si/Al = 12.5) was supplied by Zeolyst International (CP 814E). The sample was calcined at 550 °C for 15 h in order to obtain the protonic form of the zeolite. The obtained sample was named as HBETA.

Sodium bentonite was supplied by Aldrich Chemical Co. For the agglomeration process, the zeolite (protonic form) and the clay (sodium bentonite) were mixed together and suspended in water at 60 °C during 2 h. The suspension was then dried at 120 °C overnight. After grinding and sieving, particles with an average particle size of 0.75 mm were obtained. Finally, agglomerated zeolite was calcined at 550 °C for 15 h. Five samples were synthesized varying the binder amount (from 35 to 65 wt%).

After the agglomeration process, samples were ion-exchanged three times with 1 M NH₄Cl (30 ml g⁻¹), and calcined again at 550 °C for 15 h in order to obtain the acid form of the agglomerated zeolites.

The obtained samples were named as follows: first, the name of the zeolite is shown (HBETA). Then, the character B is related to the binder name (bentonite) and finally a number represents the amount of binder in the catalyst (wt%). For instance,

HBETAB35 is a catalyst based on HBETA agglomerated with bentonite, and containing a proportion of clay in the final catalyst of 35 wt%.

A known volume of an aqueous H₂PtCl₆ solution was poured over all the catalysts. The solvent was removed by evaporation under vacuum. The metal concentration of the impregnating solution was calculated to yield a final platinum content in the catalysts of 1 wt%. After the impregnation process, the catalysts were calcined at 400 °C for 4 h and reduced in situ under a hydrogen flow of 190 ml min⁻¹ g⁻¹ at 410 °C for 4 h.

Bifunctional catalysts were named as above mentioned but including the symbol of the metal (Pt).

2.2. Catalyst characterization

To quantify the sodium content of each sample, atomic absorption measurements (AA) were performed using a SpectraAA 220FS spectrophotometer. Prior to measurement, the samples were dissolved in hydrofluoric acid and diluted to the interval measurement. The atomic absorption measurements had an error of ±1%.

Surface area was determined by using N₂ as the sorbate at 77 K in a static apparatus (Micromeritics ASAP 2010 adsorptive and desorptive apparatus). The samples were evacuated under a vacuum of 5 × 10⁻³ Torr at 350 °C for 15 h. Specific total surface areas were calculated using the BET equation. Surface area measurements had an error of ±3%.

The total acid site density and the acid strength distribution of the catalysts were measured by temperature-programmed desorption of ammonia (TPDA), using a Micromeritics TPD/TPR 2900 analyzer. The method was described in earlier works [1,6]. The average relative error in the acidity determination was lower than 3%.

The chemisorption measurements were carried out using a dynamic pulse technique described in previous works [1,6]. The dispersion measurements with H₂ pulses had an error of ±5%.

Solid-state ²⁷Al NMR spectra were collected in a BRUKER Avance WB 400 spectrometer. The ²⁷Al NMR spectra were obtained at 12.5 kHz using 15° pulses and 1 s delay, a total of 5000 pulses being accumulated.

2.3. Catalytic experiments

Hydroisomerization of *n*-octane reactions were carried out in an Autoclave Engineers (BTRS-Jr) micro reactor that consisted of a tubular stainless steel reactor with vertical placing and downward flow. The liquid feed (*n*-octane) was performed by a HPLC pump. A backpressure regulator valve allowed high-pressure experiments. Experimental conditions were as follows: weight of catalyst, 1.5 g; temperature, 270–370 °C; total pressure, 10 bar; WHSV = 10 g_{*n*-C₈} h⁻¹ g_{zeolite}⁻¹; and H₂/*n*-C₈ molar ratio, 14. All data were collected at 1 h on stream. Reaction products were analyzed with a HP 5890 Series II gas chromatograph equipped with a flame ionization detector and automatic valve for continuous analysis. The reactor effluent stream was sent for analysis through a heated line (about 180 °C) to the automatic valve. The gas chromatograph was equipped with a

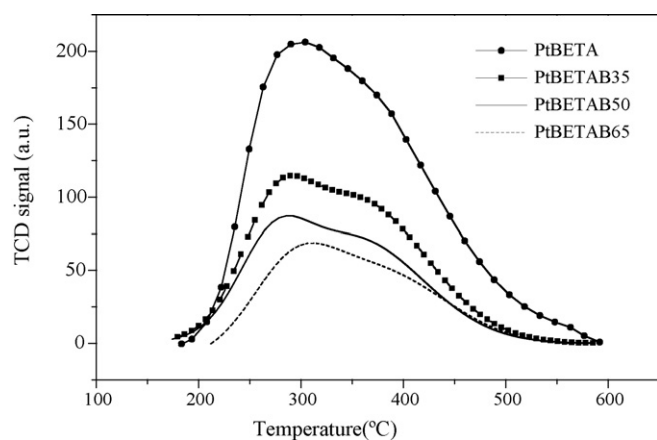


Fig. 1. TPDA curves for the non-agglomerated and agglomerated catalysts.

capillary column SUPELCO Petrocol DH 50.2, 0.2 mm i.d. and 50 m length. Results from a reproduced experiment showed that conversion and isomer selectivity had an error of $\pm 4\%$.

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 shows the TPDA profiles for all the catalysts here prepared (non-agglomerated and agglomerated catalysts). Total acidity was defined as the total acid site density, which was obtained by integration of the area under the curve. To obtain the strength distribution, desorption profiles were fitted using two peaks, the maxima and widths of these peaks being held as constant as possible. Values of the corresponding total, weak and strong acidity for all the catalysts are given in Table 1. Total acidity of the bentonite was clearly lower than that obtained for sample PtBETA. Strong acidity was not observed for the parent bentonite. Thus, the contribution of bentonite to the acidity

of agglomerated catalysts should be very small [1,6], although its presence could affect acidic properties as will be discussed further. The neglected contribution of the metal to zeolite acid properties has been previously reported [1,6,8,9].

Table 1 also lists the acidity of the agglomerated catalysts. The predicted acidity values calculated from the proportional contribution of the raw materials (zeolite and binder) are also included. It can be seen that there were differences between the experimentally measured acidity and the predicted one: the weak acidity of the agglomerated catalysts, but that with the lowest bentonite content, was higher than the predicted values. The opposite effect was observed for the strong acidity, the deviation being higher with increasing binder content.

According to previous works [1,6], the possible blocking of zeolite channels by the binder was excluded. In this sense, the deviation of the experimental weak acidity values for the agglomerated catalysts with respect to the predicted ones must be explained as an interference of sodium cations in acidity measurements. It should be taken into account that sodium cations are also weak acid sites [10].

According to other studies [3,11], the decrease in the number of strong acid sites can be attributed to solid-state ion exchange between protons of the zeolite and sodium of the clay during the calcination following the ion-exchange step.

To sum it up, experimental acidity values for agglomerated catalysts did not match with those theoretically expected due to solid-state ion exchange of sodium cations.

These effects can be roughly related to the initial sodium content of the clay. Thus, the higher the sodium content introduced by the clay was, the larger the differences between experimental and predicted values were observed (Table 1).

Table 2 shows the measurements of metal dispersion, surface area and pore volume for the different samples. Since our catalysts were shaped with bentonite, the surface area, the pore volume and the metal dispersion measurements of the agglomerated catalysts differed from those of the non-agglomerated

Table 1
Characterization data for the different samples

Sample	Na content (wt%)	Total acidity (mmol NH ₃ g _{cat} ⁻¹)	Weak acidity (mmol NH ₃ g _{cat} ⁻¹) ^a	Strong acidity (mmol NH ₃ g _{cat} ⁻¹) ^b
Bentonite	0.48	0.038	0.038	n.d. ^c
PtBETA	0.25	0.694	0.154	0.540
PtBETAB35	0.30	0.446 ^d 0.420 ^e	0.097 ^d 0.097 ^e (+0%) ^f	0.349 ^d 0.351 ^e (-0.6%) ^f
PtBETAB50	0.37	0.364 ^d 0.332 ^e	0.106 ^d 0.096 ^e (+10%) ^f	0.258 ^d 0.270 ^e (-8%) ^f
PtBETAB65	0.40	0.264 ^d 0.244 ^e	0.093 ^d 0.079 ^e (+18%) ^f	0.171 ^d 0.189 ^e (-10%) ^f

^a Desorption temperature of 280 °C.

^b Desorption temperature of 380 °C.

^c n.d.: no detected.

^d Experimental value.

^e Predicted value calculated from the proportional contribution of the zeolite and the binder present in the catalysts.

^f Deviation from the predicted value (%).

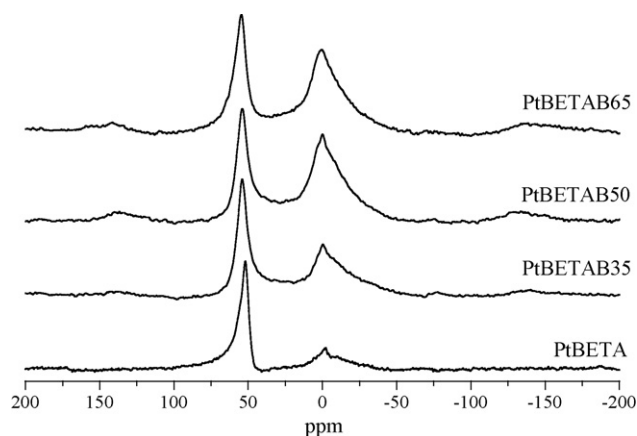


Fig. 2. ^{27}Al NMR spectra for the non-agglomerated and agglomerated catalysts.

zeolite. It can be observed an increase of the metal dispersion values with increasing the binder content. As was previously reported [1,2], platinum particles were located mainly on the external surface of the zeolite crystals. In this case, the metal dispersion values must be related to the surface area values contributed by the zeolite. The surface area per gram of zeolite, calculated from the proportional contribution of the raw materials, is shown in Table 2. It is clear that the metal dispersion values were in agreement with the surface area per gram of zeolite, suggesting that the metal were mainly located into the zeolite.

However, the surface area per gram of zeolite for the agglomerated catalysts differed from that of non-agglomerated ones, suggesting a blockage of the zeolite channels, this effect being more remarkable for the catalyst with a 35 wt% of bentonite (sample HBETAB35).

Generally, it has been clearly demonstrated that ammonium and, also, other metal cations balancing negative-framework charge prevent formation of octahedrally coordinated Al in beta zeolites [12]. In addition, ammoniac treatment of beta zeolite could lead to the transformation of octahedrally coordinated Al into regular tetrahedral framework sites [13].

It has also been reported [1,6] that the agglomeration process can cause a migration of extraframework aluminium species (EFAL) from the clay to the zeolite. This fact has been supported by different authors [4,14]. Fig. 2 shows the ^{27}Al NMR spectra for the different samples. The signal at 0 ppm was assigned to octahedral Al species (EFAL) [15]. Thus, it is possible that part of the EFAL provided by the binder could have return to

Table 3

Strong acid site density per gram of zeolite, *n*-octane conversion at 330 °C and isomer selectivity at 50 mol% of conversion

Sample	Strong acidity (mmol NH_3 $\text{g}_{\text{zeolite}}^{-1}$)	<i>n</i> -Octane conversion (330 °C)	Isomer selectivity (50% conversion)
PtBETA	0.540	52.2	93.9
PtBETAB35	0.537	90.8	92.3
PtBETAB50	0.516	87.0	90.3
PtBETAB65	0.488	81.5	90.7

the tetrahedral position of the zeolite as a consequence of the ammonium treatment. This fact could decrease the surface area of the zeolite due to a blocking of the zeolite channels (Table 2). This effect was more evident in the catalyst with 65 wt% of zeolite (HBETAB35) with a surface area of $481 \text{ m}^2 \text{ g}_{\text{zeolite}}^{-1}$ (against $636 \text{ m}^2 \text{ g}_{\text{zeolite}}^{-1}$ of the parent zeolite). Al species could be easily incorporated to the framework of the zeolite in sample HBETAB35 with the highest content of zeolite, causing a block of the zeolite channels.

3.2. Hydroisomerization of *n*-octane

3.2.1. Reaction test

The influence of the binder amount on the catalytic performance, obtained at the same WHSV (related to the weight of zeolite), for all agglomerated and non-agglomerated catalysts was studied. Table 3 shows the *n*-octane conversion at 330 °C and the isomer selectivity at 50 mol% of *n*-octane conversion. In the same table, the strong acid site density per gram of zeolite is included. Since the presence of the binder clearly influenced the strong acid site density of the zeolite, it is expected that the catalyst performance should be related to the binder content.

As expected, the higher the strong acid site density per gram of zeolite in the agglomerated catalysts was, the higher the *n*-octane conversion was observed. As can be clearly seen in Fig. 3, the *n*-octane conversion showed the same trend when the reaction temperature was changed from 270 to 370 °C. It is often assumed that a catalyst is ideal when the metal component is present in sufficient excess, meaning that the reactions in the acid sites can be considered to be the rate-limiting step [16]. Therefore, the *n*-octane conversion would depend only on the strong acid site density. In a previous work [2], the influence of the metal content on the hydroisomerization of *n*-octane was

Table 2
Metal dispersion, surface area and pore volume

Sample	D_{H_2} (%) ^a	Surface area ($\text{m}^2 \text{ g}_{\text{zeolite}}^{-1}$)	Surface area ($\text{m}^2 \text{ g}_{\text{cat}}^{-1}$)	Pore volume ($\mu\text{l g}_{\text{cat}}^{-1}$)	
				Micropores	Meso- and macropores
Bentonite	–	–	37	4	89
HBETA	66	636	636	175	404
HBETAB35	27	481	326	85	239
HBETAB50	48	543	290	77	230
HBETAB65	73	620	241	58	198

^a Metal dispersion measured by hydrogen chemisorption of samples with 1 wt% of platinum.

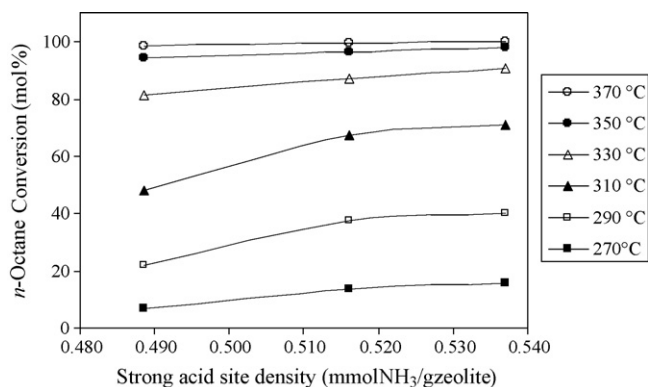


Fig. 3. Conversion of *n*-octane vs. strong acid site density at different reaction temperatures for all the agglomerated catalysts.

studied, reporting a metal content of 1 wt% as the amount to reach an ideal behaviour of the catalyst.

On the contrary, sample PtBETA, even showing the highest strong acid site density per gram of zeolite, exhibited the lowest *n*-octane conversion. Several authors have demonstrated how, apart from the number of framework aluminium atoms per unit cell, the presence of some EFAL species can increase the catalytic activity in beta zeolites [6,15,17–19].

As observed in Fig. 2, EFAL species were present in all agglomerated catalysts. Some cationic EFAL species having strong Lewis acidity could interact with the structural Brønsted acid sites, enhancing their acid strength through a synergetic effect [15] and, consequently, making them much more active for *n*-octane hydroisomerization.

Anyway, regardless the EFAL presence, the decrease of the *n*-octane conversion with increasing binder content was due to the decrease of the strong acid site density.

On the other hand, all the catalysts showed similar values of selectivity towards branched isomers (Table 3). Typical isomerization products were obtained, and no major changes in the product distribution were observed [1]. The influence of the binder concentration on the isomers selectivity was not significant.

Summarizing, it is clear that the *n*-octane conversion seems to be the decisive parameter to choose the right binder amount. Thus, the agglomerated catalyst containing 35 wt% of bentonite allowed to obtain a catalyst leading to the highest *n*-octane conversion values with suitable isomer selectivity.

4. Conclusions

In this work, several catalysts consisting of zeolite beta agglomerated with sodium bentonite in different proportion were prepared. This proportion was optimized for the hydroisomerization of *n*-octane.

It can be seen that there were differences between the experimentally measured acidity and the predicted one: the weak acidity of the agglomerated catalysts, but that with the lowest bentonite content, was always higher than the predicted values.

Experimental acidity values did not match with those theoretically expected due to solid-state ion exchange.

Since our catalysts were shaped with bentonite, the surface area, the pore volume and the metal dispersion measurements of the agglomerated catalysts differed from those of the non-agglomerated zeolite.

The presence of the binder increased the *n*-octane conversion. EFAL species were present in all the agglomerated catalysts. Some cationic EFAL species having strong Lewis acidity could interact with the structural Brønsted acid sites, enhancing their acid strength through a synergetic effect and, consequently, making them much more active for *n*-octane hydroisomerization. The influence of the binder concentration on the isomers selectivity was not significant.

Acknowledgments

Financial support from the Ministerio de Ciencia y Tecnología of Spain (Project CTQ-2004-07350-C02-O) and the Consejería de Ciencia y Tecnología de la Junta de Comunidades de Castilla-La Mancha (Project PBI-05-038) are gratefully acknowledged.

References

- [1] A. de Lucas, J.L. Valverde, P. Sánchez, F. Dorado, M.J. Ramos, *Appl. Catal. A* 282 (2005) 15–24.
- [2] A. de Lucas, P. Sánchez, F. Dorado, M.J. Ramos, J.L. Valverde, *Appl. Catal. A* 294 (2005) 215–225.
- [3] V.R. Choudhary, P. Devadas, A.K. Kinage, M. Guisnet, *Appl. Catal. A* 162 (1997) 223–233.
- [4] R.V. Jasra, B. Tyagi, Y.M. Badheka, V.N. Choudhary, T.S.G. Bhat, *Ind. Eng. Chem. Res.* 42 (2003) 3263–3272.
- [5] F. Dorado, R. Romero, P. Cañizares, *Appl. Catal. A* 236 (2002) 235–243.
- [6] A. de Lucas, J.L. Valverde, P. Sánchez, F. Dorado, M.J. Ramos, *Ind. Eng. Chem. Res.* 43 (2004) 8217–8225.
- [7] P. Cañizares, A. Durán, F. Dorado, M. Carmona, *Appl. Clay Sci.* 16 (2000) 273–287.
- [8] F. Dorado, R. Romero, P. Cañizares, *Ind. Eng. Chem. Res.* 40 (2001) 3428–3434.
- [9] A. de Lucas, M.J. Ramos, F. Dorado, P. Sánchez, J.L. Valverde, *Appl. Catal. A* 289 (2005) 205–213.
- [10] V.R. Choudhary, V.S. Nayak, *Zeolites* 5 (1985) 15–20.
- [11] M.D. Romero, J.A. Calles, A. Rodríguez, A. De Lucas, *Microporous Mesoporous Mater.* 9 (1997) 221–228.
- [12] E. Bourgeat-Lami, P. Massiani, F. Di Renzo, P. Espiau, F. Fajula, *Appl. Catal. A* 72 (1991) 139–152.
- [13] O. Bortnovsky, Z. Sobalík, B. Wichterlová, Z. Bastl, *J. Catal.* 210 (2002) 171–182.
- [14] J.M. Fougerit, N.S. Gnep, M. Guisnet, P. Amigues, *Stud. Surf. Sci. Catal.* 84 (1994) 1723–1730.
- [15] L.D. Fernandes, J.L.F. Monteiro, E.F. Sousa-Aguiar, S.A. Martínez, A. Corma, *J. Catal.* 177 (1998) 363.
- [16] J. Weitkamp, *Erdoel, Kohle-Erdgas-Petrochem* 31 (1978) 13.
- [17] P.J. Kunkeler, B.J. Zuurdeeg, J.C. van der Waal, J.A. van Bokhoven, *J. Catal.* 180 (1998) 234.
- [18] A. Berreghis, P. Ayrault, E. Fromentin, M. Guisnet, *Catal. Lett.* 68 (2000) 121.
- [19] H.K. Heinichen, W.F. Hölderich, *J. Catal.* 185 (1999) 408.