# Influence of the exchanged cation in coke deposition during *n*-hexane reactions on Pt / M$\beta$ zeolite catalysts

F.J. Maldonado-Hódar [a], J.M. Silva [b], F.R. Ribeiro [a] and M.F. Ribeiro [a]

[a] *Depto. de Eng. Química, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon Codex, Portugal*
[b] *Depto. de Eng. Química, Inst. Sup. Eng. Lisboa, Av. Cons. Emídio Navarro, 1900 Lisbon, Portugal*

Received 29 April 1997; accepted 22 July 1997

The performances of platinum $\beta$ zeolite exchanged with alkali (Na, K, Cs) and alkali-earth (Mg, Ba) cations have been examined for *n*-hexane reactions. The nature of coke deposited on the catalysts is slightly influenced by alkali cations because coke is deposited on metallic sites. In Pt / alkali-earth catalysts the coke depends on the support acidity.

**Keywords:** beta zeolite, platinum, alkali and alkali-earth cations, *n*-hexane reactions, coke deposition

## 1. Introduction

Catalytic reforming is an important process for the production of high octane gasoline and aromatics from naphtas [1]. Mainly Pt supported catalysts are used in these reactions. Zeolites have been successfully employed in the reforming of hydrocarbons. Catalysts are deactivated mainly due to the coke deposition. This process is strongly influenced by different zeolite characteristics as acidity or porous texture [2]. The coking rate is greater with increasing zeolite acidity and when the space available for its formation is larger or the intermediates to coke formation diffuse more slowly into the gas phase [2]. Pt supported on acidic $\beta$ zeolite enhances the extent of bimolecular alkylation reactions that lead to aromatics with carbon numbers different from that of the feed hydrocarbon [3,4], but shows the disadvantage of excessive coke formation and high hydrocracking. Smirniotis et al. [5] found that the control of the $\beta$ zeolite acidity via dealumination minimizes coke formation and hydrocracking and results in the preservation of the catalyst activity in the reforming of alkylcyclopentanes.

When a zeolite is exchanged with cations, two simultaneous effects that strongly affect coke deposition take place. As the exchanged cation size increases a greater porous blockage is produced and the zeolite acidity also decreases [6–8]. In this sense, ion exchange of $\beta$ zeolite with different cations permits to modify the acidic and porous characteristics of this support and consequently the catalytic behaviour of the catalysts prepared from them. Although many papers about the deactivation of acid catalysts [2,9,10] are available, there is a lack of information about the influence of the exchanged cation on coke formation. The aim of this work was to study the coke deposition on Pt supported on alkali or alkali-earth exchanged $\beta$ zeolite, during *n*-hexane transformation.

## 2. Experimental

The $\beta$ zeolite with a $SiO_2/Al_2O_3$ molar ratio of 15 was provided by EXXON in a partially protonic form, HNa$\beta$. This parent zeolite was exchanged twice with a 0.5 M $NaNO_3$ solution. The ion exchange process was carried out at 80°C under vigorous stirring for 2 h, using a ratio volume of solution (ml) / zeolite weight (g) of 70. The dispersion was centrifuged and the solid washed and dried overnight at 110°C. Further, portions of this zeolite form were exchanged twice with $KNO_3$, $MgNO_3$, $CsCH_3COO$ or $BaCH_3COO$ respectively, using the same procedure. All the samples were calcined in air flow ($3\ \ell\ h^{-1}\ g^{-1}$) at 500°C for 2 h. The obtained samples were denominated Na$\beta$, K$\beta$, Cs$\beta$, Mg$\beta$ and Ba$\beta$ respectively.

Platinum was loaded into the support materials by ion exchange using $Pt(NH_3)_4(NO_3)_2$. The procedure was carried out for 4 h at room temperature and under stirring. The programmed platinum loading was 0.5 wt% using a $Pt(NH_3)_4(NO_3)_2$ solution of 400 ppm. After centrifuging and washing, the catalyst was dried for 12 h at 110°C and calcined at 300°C in air flow ($3\ \ell\ h^{-1}\ g^{-1}$) for 2 h by increasing the temperature at a rate of 2°C / min.

KL zeolite provided by UOP was used as reference due to its well known aromatization power.

M$\beta$ supports (where M = Na, K, Cs, Mg, Ba) were analyzed by AA and characterized by XRD and FTIR. XRD experiments were performed in a Rigaku apparatus using Cu K$\alpha$ radiation (Ni filter) at 2° / min. FTIR spectra were collected with a Perkin Elmer 1600 spectrometer using KBr pellets, in order to study the structural bands of the solids.

Acidic properties of exchanged zeolites were determined by ammonia temperature programmed desorption. The experiments were carried out in a fixed bed flow type apparatus equipped with a TCD. The calcined samples were saturated at 150°C, for 4 h using a mixture of He/$NH_3$ (0.2% $NH_3$). After purging 30 min with He, $NH_3$ was desorbed by heating at 10°C/min under He flow.

Textural characteristics of M$\beta$ supports were studied by $N_2$ adsorption and dynamic cyclohexane adsorption. The $N_2$ adsorption was carried out in an "area meter" of Strölhein Instruments. The samples were outgassed for 4 h at 200°C and $10^{-2}$ Torr and $N_2$ was adsorbed at 77 K (liquid $N_2$ temperature). The dynamic adsorption of cyclohexane was carried out at 90°C using a Setaram TG-DSC92 thermobalance. After pre-treatment under $N_2$ at 500°C for 10 min the samples were cooled to 90°C, and after stabilizing the sample weight, the $N_2$ flow was changed by the $N_2$–cyclohexane flow obtained bubbling $N_2$ (50 ml/min) in a cyclohexane saturator at 14.6°C.

Platinum contents were determined by EDX RF and platinum dispersion was studied by CO chemisorption. CO chemisorption isotherms were measured between 0 and 200 Torr, using a conventional volumetric system at room temperature (25°C). The catalysts were also previously reduced for 2 h at 500°C in $H_2$ flow and then evacuated at this temperature to less than $10^{-5}$ Torr for 2 h. After the first isotherm was measured, the sample was evacuated at $10^{-5}$ Torr for 30 min and a second isotherm was measured. Following the second isotherm, the sample was again evacuated at $10^{-5}$ Torr and the volume of the reactor determined with He. The amount of chemisorbed CO was calculated by extrapolating the isotherms to zero pressure, and taking the difference between the first and second isotherm.

*n*-hexane reactions were performed in a continuous flow reactor, using (150 mg) both the support (M$\beta$) and the Pt loaded (Pt/M$\beta$) catalysts. Pt/M$\beta$ catalysts were previously reduced in situ at 500°C for 5 h. The experiments were carried out at 450°C, molar ratio $H_2/C_6 = 6$ and space velocity (WHSV) of 15 $h^{-1}$. Only $H_2$ acts as carrier gas and *n*-hexane was mixed with the $H_2$ flow in a pre-reactor camera heated at 80°C. The reaction products were analyzed by on line gas chromatography with a FID detector and PONA column. Results are reported as conversions calculated as the mole-percent of *n*-hexane reacted, products yields and selectivities. Coke deposited on supports and catalyst was analyzed by thermogravimetry using a Setaram TG-DSC92 thermobalance which permits to obtain simultaneously the TG and DSC curves during the coke burning (air flow 60 ml/min, heating rate 20°C/min).

## 3. Results and discussion

Table 1
Composition and BET surface area of the different catalysts

| Catalyst | Unit-cell composition | Pt (wt%) | $d$[a] (nm) | $S_{BET}$ ($m^2 g^{-1}$) |
|---|---|---|---|---|
| Pt/Na$\beta$ | $Na_{2.79}H_{1.06}(Al_{3.85}Si_{60.05}O_{128})$ | 0.52 | 3.8 | 540 |
| Pt/Na$\beta$-0.2 | $Na_{2.79}H_{1.06}(Al_{3.85}Si_{60.05}O_{128})$ | 0.20 | 1.6 | 540 |
| Pt/K$\beta$ | $K_{3.08}H_{0.77}(Al_{3.85}Si_{60.05}O_{128})$ | 0.38 | 1.8 | 470 |
| Pt/Cs$\beta$ | $Cs_{3.54}H_{0.31}(Al_{3.85}Si_{60.05}O_{128})$ | 0.21 | 1.2 | 313 |
| Pt/Mg$\beta$ | $Mg_{1.55}H_{0.70}(Al_{3.85}Si_{60.05}O_{128})$ | 0.50 | 2.1 | 492 |
| Pt/Ba$\beta$ | $Ba_{1.93}(Al_{3.85}Si_{60.05}O_{128})$ | 0.24 | 1.2 | 335 |

[a] Pt particle size estimated by CO chemisorption.

The chemical and porous nature of the different exchanged $\beta$ zeolite samples are shown in table 1. Similar transformations are observed exchanging $\beta$ zeolite with alkali or alkali-earth cations. The determination of the BET surface area (table 1) or the dynamic cyclohexane adsorption (figure 1) shows that in both series a greater porous blockage occurs as the size of the exchanged cation increases. From $NH_3$ TPD spectra (figure 2) it was observed that the zeolite acidity also decreases in the order Mg$\beta$ > Ba$\beta$ > Na$\beta$ > K$\beta$ > Cs$\beta$ ≈ KL. In both series for cations of similar size (i.e. Na–Mg or Cs–Ba), the alkali-earth exchanged zeolites show greater acidity and mainly stronger acid sites than the corresponding alkali exchanged zeolites. Porous and acidic characteristics of exchanged $\beta$ zeolites tend to the corresponding KL ones as the cation size increases.

Despite the programmed Pt loading of 0.5 wt% for all the samples, the data of table 1 show that the Pt content obtained in both series of catalysts decreases as the cation size increases, and particle size shows a similar trend. To compare the effect of the different Pt loading, Na$\beta$ support was also prepared with the same Pt content found for Cs$\beta$ and Ba$\beta$ supports (0.2 wt% Pt). CO chemisorption data (table 1) show that Pt dispersion increases when Pt loading decreases and in the case of the samples exchanged with larger cations (Ba, Cs) the dispersion is better than for Na$\beta$ with similar Pt loading. Some authors [11,12] have already reported that the characteristics of Pt particles (dispersion, special location and electronic state of the Pt in the zeolite) can be influenced by the exchanged cation, namely due to its basicity.

The catalytic activity of the different supports M$\beta$ was determined under the same experimental conditions that were used for Pt/M$\beta$ catalysts (450°C, $H_2/C_6 = 6$

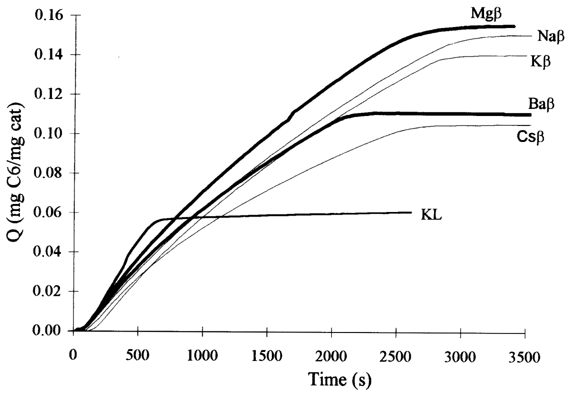

Figure 1. Dynamic cyclohexane adsorption on the different M$\beta$ supports and KL zeolite.

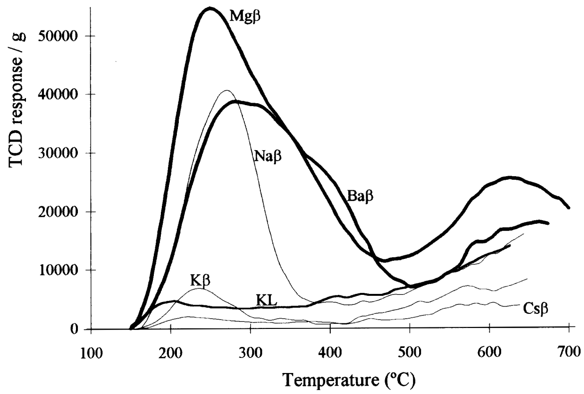

Figure 2. $NH_3$ temperature programmed desorption profiles of different Mβ supports and KL zeolite.

and WHSV = 15 $h^{-1}$). The different acidity of the exchanged support leads to different reactivity. Alkali exchanged supports, even in the case of Naβ which is the more acid of this series, do not present significant catalytic activity in *n*-hexane reactions. However, alkali-earth exchanged zeolites show an important catalytic activity. Mgβ shows an initial hexane conversion (at $t = 7$ min) about 40%, while for Baβ conversion it is 18%, decreasing quickly with the time on stream. Propane was obtained as the main cracking product, and no aromatics products were observed, the amount of isomerization processes being also depreciable. Pt alkali catalyst will be considered as monofunctional (Pt function) and the Pt alkali-earth ones as bifunctional catalysts.

The conversion and products selectivity of *n*-hexane obtained for Pt/Mβ catalysts are presented in table 2. The Cs form has the lowest activity and the highest aromatic selectivity, comparable to Pt/KL zeolite. The better Pt dispersion for Pt/Naβ-0.2% catalyst can be responsible for the similar catalytic behaviour observed for both Pt/Naβ catalysts during the first 3 h of reaction. Pt/alkali-earth exchanged catalysts are more active but less selective to aromatic products than alkali exchanged ones, mainly favouring the development of cracking processes, which correspond to the acidity evolution discussed above.

During the *n*-hexane transformation coke deposition takes place. The amounts of coke deposited on supports and catalysts after 3 h on stream were determined by TG. The coke content deposited on supports or Pt catalysts decreases as the cation size increases (table 2). The most acidic and active support (Mgβ) presents a coke content of 3.1% while in Baβ the amount of coke is lower than 1%. No coke was found on alkali exchanged supports, because, as mentioned above, they do not present significant catalytic activity. Figure 3 compares DTG profiles corresponding to the burning of coke deposited on Mgβ support and Pt/Mgβ catalyst. Similar profiles are presented in both DTG curves, showing a minimum about 500°C, although slightly displaced to higher temperatures for coke deposited on the Pt catalyst. The greater maximum burning rate observed for coke deposited on the catalyst ($1.15 \times 10^{-3}$ vs. $8.70 \times 10^{-4}$ mg/(s mg)) can also indicate the formation of a more dehydrogenated coke on the Pt particles or that Pt catalyses the coke burning.

DSC curves associated to coke burning are also appropriated to compare the coke stability (when coke DTG profiles show a minimum and the heat flow a maximum) and can provide additional information about its nature, because, unfortunately, in this work we did not analyze the coke composition by conventional techniques. The coke reactivity and its calorific power increases as the H/C ratio (less aromatic coke) increases [2]. DSC profiles obtained for Pt/Mgβ and Pt/Baβ are shown in figure 4. Both curves show similar profiles, but the coke deposited on Pt/Baβ catalyst burned at lower temperatures and produced a greater heat flow, i.e. less polymerized or aromatic coke was obtained as the catalyst acidity decreases.

As in the case of Pt/alkali-earth β catalysts, the amount of coke deposited on Pt/alkali β catalysts decreases from Na to K forms and no coke was found on Pt/Csβ and on Pt/KL catalysts (table 2). As described previously, chemical and porous texture of KL and Csβ supports present significant similarities. Iglesia et al.

Table 2

Catalytic behaviour observed at 7 min time on stream, and amount of coke deposited (after 3 h of reaction) on the different catalysts during *n*-hexane reactions (450°C, $H_2/C_6 = 6$, WHSV = 15 $h^{-1}$)

| Catalyst | Conversion (%) | Selectivity (%) | | | Coke (wt%) |
|---|---|---|---|---|---|
| | | cracking | isomerization | aromatization | |
| Pt/Naβ | 90 | 41 | 36 | 23 | 8.5 |
| Pt/Naβ-0.2 | 85 | 33 | 41 | 26 | 8.3 |
| Pt/Kβ | 68 | 23 | 52 | 25 | 4.6 |
| Pt/Csβ | 42 | 21 | 44 | 35 | 0.0 |
| Pt/Mgβ | 100 | 80 | 4 | 16 | 9.6 |
| Pt/Baβ | 80 | 53 | 28 | 19 | 5.7 |
| Pt/KL | 51 | 20 | 34 | 46 | 0.0 |

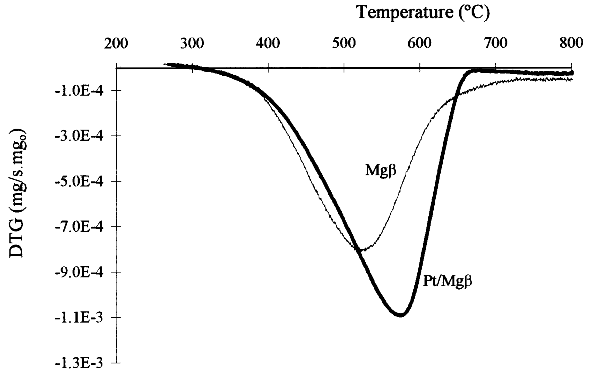

Figure 3. DTG profiles of coke deposited on Mg$\beta$ support and Pt/Mg$\beta$ catalyst.

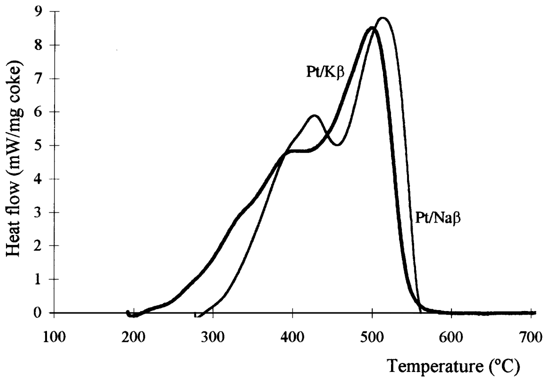

Figure 5. DSC profiles of coke deposited on Pt/M$\beta$ monofunctional catalysts.

[13] found that no coke was formed on Pt/KL catalyst during heptane reforming, concluding that L zeolite pores inhibit coke formation so that Pt inside the pores remains free of carbon residues.

In the case of our Pt/M$\beta$ catalysts the porous transformations undergone by the supports as consequence of the ion exchange depends on the size of the exchanged cation, producing the blockage of pores or the reduction of the channel dimension. In this sense, as the cation size increases, the diffusion of reactants, intermediates or products becomes more difficult, and the formation of a small amount of coke could deactivate the catalyst by blockage of the zeolite channels. It is noteworthy that similar effects are produced by cations of similar size. Comparing the effects of the larger cations, similar BET surface areas and cyclohexane adsorption capacity were observed for Cs$\beta$ and Ba$\beta$. The kinetics of cyclohexane adsorption is slower on alkali exchanged zeolites (figure 1), which can favour the coke formation on these catalysts. However, it was observed coke deposited on Ba$\beta$ support and on Pt/Ba$\beta$ catalyst and no coke was found on Cs$\beta$ samples. In such a basis, the different behaviour of these samples must be due to different support acidity or Pt/support interactions.

Comparing the heat flow profiles shown in figures 4 and 5 it is notorious that while in the case of bifunctional Pt/Mg–Ba$\beta$ catalysts the curve only presents one peak as exposed above, for monofunctional Pt/Na–K$\beta$ catalysts two maxima (about 420 and 520°C) are observed. Moreover, while for bifunctional catalysts the maximum is displaced about 100°C between Pt/Mg$\beta$ and Pt/Ba$\beta$ catalysts, for monofunctional catalysts the position of the maxima is only slightly influenced by the presence of Na or K cations. The heat flow profiles are also very similar in both cases. These results point out the greater similarity of the coke nature deposited on monofunctional catalysts.

On the other hand, (as their catalytic behaviour) similar amount of coke was deposited on Pt/Na$\beta$ catalysts independently of the Pt loading. However, the DSC profiles of figure 6 show that for lower Pt content, the formed coke must contain lighter compounds in its composition. The coke burning began at lower temperatures and two new peaks appeared below 300°C. These results are in agreement with those of Marecot et al. [14] who found a loss of the TPO peaks intensity as the Pd dispersion decreases, leading even to the disappearance of some peaks.

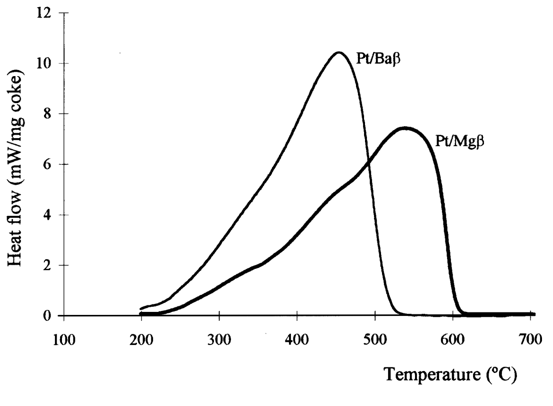

Figure 4. DSC profiles of coke deposited on Pt/M$\beta$ bifunctional catalysts.

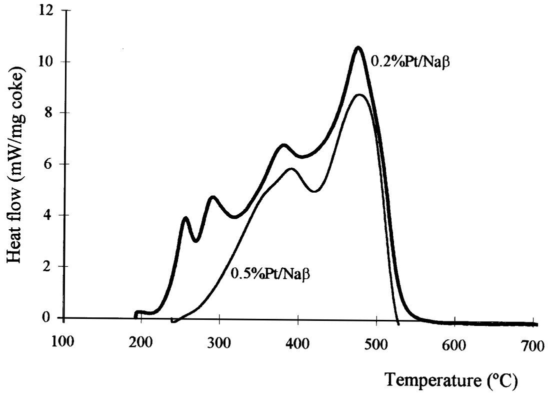

Figure 6. Effect of the Pt content on the DSC profiles of coke deposited on Pt/Na$\beta$ catalysts.

Differences in the DSC profiles observed in mono- and bifunctional catalysts are also due to the different coke localization. While in monofunctional catalysts coke must be on the Pt particles, in bifunctional catalysts a large part of the coke is deposited on the support acid sites. This fact can be explained on the basis of the results exposed above. In bifunctional catalysts the large amount of coke deposited on the acid sites of the support can mask the appearing of some peaks on the heat flow profiles. The nature of this coke deposited on the support is strongly influenced by the acid strength, in such a manner that significant differences (burning temperature and heat flow) are observed on coke deposited on Pt/Mg$\beta$ and Pt/Ba$\beta$ catalysts. In monofunctional catalysts *n*-hexane is transformed mainly on metallic sites and the catalytic behaviour depends on the strength of the Pt/support interactions which are influenced by Pt dispersion that depends on the exchanged cation. In that case coke would be only deposited on Pt particles. The amount of coke deposited decreases according to the catalytic activity decrease, but the coke nature is not strongly influenced because changes in the interactions between the active sites and reactant are not so strong as in the case of bifunctional catalysts. These results are in good agreement with those of other authors. Smirniotis et al. [5] found that the aromaticity of the soluble coke deposited on Pt/$\beta$ catalyst used for methylcyclopentane reforming decrease as the dealumination of $\beta$ zeolite increases. In the more acid catalyst (less dealuminated) coke is deposited preferably on acidic sites while as this parameter decreases, coke is located on Pt sites.

Therefore, from our results we conclude that the amount of coke deposited on the catalysts depends on the cation type, decreasing as the cation size increases. In Pt/alkali catalysts, the coke nature is only slightly influenced by the exchanged cation because coke is deposited on metallic sites. The nature of the coke deposited on Pt/alkali-earth catalysts depends on the strength of the support acid sites.

## Acknowledgement

Support of this work by EC, HCM network contract number ERB CHRX CT 940477 is gratefully acknowledged.

## References

[1] F.G. Ciapetta and D.N. Wallace, Catal. Rev. 5 (1971) 67.
[2] M. Guisnet and P. Magnoux, Appl. Catal. 54 (1989) 1.
[3] P.G. Smirniotis and E. Ruckenstein, Chem. Eng. Sci. 48 (1993) 3263.
[4] P.G. Smirniotis and E. Ruckenstein, J. Catal. 140 (1993) 526.
[5] P.G. Smirniotis and E. Ruckenstein, Appl. Catal. 117 (1994) 75.
[6] C. Besoukhanova, J. Guidot, D. Barthomeuf, M. Breysse and J. Bernard, J. Chem. Soc. Faraday Trans. II 77 (1981) 1595.
[7] M. Huang, A. Adnot and S. Kaliaguine, J. Catal. 137 (1992) 322.
[8] P.E. Hathaway and M.E. Davis, J. Catal. 116 (1989) 263.
[9] D.M. Bibby, R.H. Howe and G.D. McLellan, Appl. Catal. 93 (1992) 1.
[10] G.F. Froment, J. De Meyer and E.G. Derouane, J. Catal. 124 (1990) 391.
[11] D. Barthomeuf, Catal. Rev. 38 (1996) 521.
[12] J. Zheng, J.L. Dong, Q.H. Xu, Y. Liu and A.Z. Yan, Appl. Catal. 126 (1995) 141.
[13] E. Iglesia and J.E. Baumgartner, in: *Proc. 10th Int. Congr. on Catalysis*, Budapest 1992, Part B, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier/Akadémiai Kiadó, Amsterdam/Budapest, 1993) p. 993.
[14] P. Marecot, A. Akhachane and J. Barbier, Catal. Lett. 36 (1996) 37.