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# Low-temperature test reaction for hydride transfer on solid acid catalysts

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A new model test reaction is proposed for the estimation of low-temperature hydride transfer (HT) activity of solid acids. The reaction of cyclohexene with isobutane on zeolite Beta, ZSM-5 and sulfated zirconia distinguished between disproportionation/hydrogen transfer and HT. The effects of acid site density, catalyst structure and interaction with isobutane are discussed.

**KEY WORDS:** hydride transfer; hydrogen transfer; isobutane; alkylation; cyclohexene; solid acid catalyst; zeolite Beta; sulfated zirconia; ZSM-5.

## 1. Introduction

Hydride transfer is a significant process that accompanies most solid-acid-catalyzed reactions of hydrocarbons. During low temperature reactions at which cracking becomes slower than oligomerization, hydride transfer has been found to be responsible for limiting the buildup of carbonaceous deposits that block catalyst active sites [1,2], as well as for determining the catalyst lifetime and product distribution in the solid-acid catalyzed alkylation of isobutane with light olefins (see for e.g. [3–5]). The process employs the bimolecular transfer of a hydride ion from a donor species to an acceptor species. On acid active sites, acceptors are carbenium-type carbocations and, following the hydride ion transfer, they desorb as neutral hydrocarbons, while a new carbocation is formed from the donor (reaction 1).

$$R^{(+)} + R' - H \rightarrow R - H + R'^{(+)} \qquad (1)$$

If both the acceptor and the donor are found in a chemisorbed state before the transfer occurs, similar to a Langmuir–Hinshelwood surface reaction model, a net transfer of hydrogen from the donor to one or more acceptors can occur, along with a buildup of the remaining carbon-rich deposits on the catalyst. This particular case is usually termed hydrogen transfer [6]. Situations also exist when a transfer between identical chemisorbed species results in a simple disproportionation. Disproportionation, however, can also be an initial step in the hydrogen transfer process when the resulting carbenium product undergoes oligomerization and dehydrogenation faster than it desorbs. Therefore, these two cases will be referred together to as disproportionation and/or hydrogen transfer (DHGT).

A contrasting case is that of hydride ion transfer from a physisorbed donor to a chemisorbed acceptor as described by the Rideal surface reaction model. This process can be viewed as a chain transfer reaction where the resulting carbocation can continue a series of reactions such as olefin addition, isomerization and cracking. It is this latter particular hydride transfer (HT) case that this work will focus on.

Few methods have been reported to date for the evaluation of the HT activity of solid acids, and these methods are based on the knowledge gained from the study of hydrocarbon cracking reactions on solid acids. Thus, the method devised by Lukyanov [7] is based on the interpretation of the product distribution obtained from the decomposition of *n*-hexane at 400 °C in the presence of the catalyst of interest. The particular HT product that is monitored is isobutane, produced via a process depicted in reaction 2:

$$n - C_6 + iC_4{}^{(+)} \rightarrow C_6{}^{(+)} + iC_4 \qquad (2)$$

However, there are a number of issues that affect the applicability of this model reaction to lower temperature conditions such as the alkylation process [8].

During alkylation of isobutane with light olefins, HT is directly responsible for the formation of the desired gasoline-range isoalkanes. For example, in the alkylation of isobutane with butene the occurrence of HT from feed isobutane to a chemisorbed isooctyl carbenium ion results in the formation of the desired isooctane product while the isobutyl carbenium ion produced undergoes olefin addition to recover the $C_8$ carbocation (Reactions 3 and 4):

$$iC_4 + C_8{}^{(+)} \rightarrow iC_4{}^{(+)} + C_8 \qquad (3)$$

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$$iC_4^{(+)} + C_4^{=} \rightarrow C_8^{(+)} \quad (4)$$

The hydride transfer from isobutane in Reaction 3 is the key step that controls the alkylation process, and therefore it is opposite of reaction 2 where isobutane is a reaction product. Moreover, the extrapolation of measured HT activities from 400 °C to the much lower temperatures typical of alkylation could prove ineffective in describing the behavior of the catalyst of interest when activation energies of the simultaneous elementary processes are very different.

It was therefore found necessary to devise a test method capable of more accurate measurements of HT activity at low temperatures that are meaningful for the study of processes such as the solid-acid catalyzed isobutane/olefin alkylation. In addition to its ability to quantitatively measure HT, further considerations of utility as a model test reaction included simplicity and unsophisticated reaction product analysis.

Since cyclic hydrocarbons are relatively reluctant to cracking when compared to normal- or isoalkanes, Cheng and Rajagopalan [9] and Suarez *et al.* [10] have employed cyclohexene to estimate the relative reaction rates of hydrogen transfer, isomerization and other elementary processes. They found that cracking was insignificant at 250 °C on various zeolite catalysts. Chemisorbed cyclohexene (i.e. the cyclohexyl carbenium ion) is comparable in terms of molecular size to the isooctyl intermediate found in alkylation. Moreover, the oligomerization of a bulky cycloolefin such as cyclohexene should be sterically inhibited to a certain degree, especially in the narrow pores of a zeolite.

It was therefore hypothesized in this study that the reaction of cyclohexene in the presence of isobutane, a hydride donor, could prove itself useful in estimating the low temperature hydride transfer activity of solid acids. For the purpose of testing this proposed model reaction, three types of catalysts were considered: zeolites Beta and ZSM-5, and sulfated zirconia. Zeolite Beta and sulfated zirconia are reported to be active for isobutane alkylation with olefins, which, as stated earlier, is a HT-demanding process [11,12]. At the same time, zeolite ZSM-5 is a narrow-pore cracking catalyst that is known to sterically limit hydride transfer to a greater extent than zeolite Beta [13]. The presumption was made, and tested, that differences in the HT activities of these materials would result in measurable changes in the product distribution from the reaction of cyclohexene and isobutane.

## 2. Experimental

Samples of zeolite Beta with $SiO_2/Al_2O_3$ ratio values (SAR) of 25 (25BEA) and 75 (75BEA), as well as zeolite ZSM-5 with an SAR value of 80 (80ZSM5), were purchased from Zeolyst (CP814E, lot no. 1822–92; CP811E-75, lot no. 1822–74; CVB8014, lot no. 1822–80, respectively) in a very fine powder form. The 25BEA and the 80ZSM5 zeolites were supplied in the $NH_4$-exchanged form, while the 75BEA was in the acidic form. Sulfated zirconia (SZ) was previously synthesized in our laboratory, as described in an earlier publication [14].

The zeolite powders were converted into their corresponding larger particle size materials by dispersion in colloidal silica (Ludox LS 30 wt%, $d = 1.210$) to yield a zeolite concentration of approximately 65 ± 1 wt% in the resulting dry material. The dry material was crushed and sieved, and the particle size cut of 0.59–1.651 mm was retained for the subsequent measurements. The corresponding materials were coded 25BEA65, 75BEA65 and 80SZM565, respectively.

Surface area measurements were performed using a Coulter SA-3100 automated characterization machine using the BET method. The catalyst dry weights were determined by heating catalyst samples in a Netzsch STA 409PC/Balzers Quadstar 422 TGA/MS analyzer under a flow of ultra-pure argon (Air Liquide) up to 1000 °C and then holding at the maximum temperature for 1 h. The weight loss for SZ was calculated only up to 650 °C, since above about 700 °C major sulfate loss occurred. Catalyst activation temperature profiles were also identified in the TGA/MS analyzer. For the zeolite samples in their ammonium form, complete decomposition into the acidic form was achieved by holding the temperature at 500 °C for 2 h. Under a heating ramp of 10 °C/min, all zeolites showed a major water loss peak between 90 and 250 °C and a secondary one centered at about 450–500 °C, and therefore activation was considered complete after holding these materials for 2 h at 500 °C. The sulfated zirconia samples showed complete activation (as indicated by water evolution) as well as undetectable sulfur loss at 350 °C.

Total acidity measurements were carried out in an ASDI RXM-100 catalyst characterization apparatus. Catalyst samples were loaded into a quartz tube, evacuated for at least 1 h at room temperature, and then heated under continuous vacuum up to 130 °C at a rate of 2 °C/min, then up to the activation temperature at a rate of 10 °C/min, whereupon the activation temperature was held constant for 2 h. The total and physical adsorption isotherms of ammonia were measured volumetrically at 80 °C for several samples from each catalyst. An overnight evacuation of the sample was performed after every total adsorption isotherm measurement in order to allow physisorbed ammonia to desorb from the catalysts. The chemisorption amounts were calculated for each sample as the difference between the two isotherms in their flat and parallel monolayer regions, normalized to the dry catalyst weight. Total isobutane adsorption capacities were determined using the same apparatus, conditions and activation method, from the total adsorption isotherm of isobutane in contact with samples from each material, by extrapolating the linear monolayer region of each isotherm to a zero equilibrium pressure. Isobutane chemisorption could not be detected at 80 °C.

The reaction tests were performed at atmospheric pressure in a simple quartz plug-flow reactor situated inside a furnace at a controlled temperature. Empty spaces in the reactor were filled with inert material (pyrex wool and glass beads) in order to minimize axial dispersion and mixing transients. Gas flows were controlled using Matheson 8272 mass-flow controllers. Catalyst samples were activated in situ under a constant flow of 20 $\mathrm{STDcm^3/min}$ (sccm) of UHP helium (Air Liquide). The activation temperature profiles were identical to those used for the total acidity measurements. Following activation, the temperature was lowered to 80 °C and a flow of 20 sccm of isobutane (99%, Matheson) was added to the helium feed for at least 30 min. Cyclohexene (≥99.0%, Aldrich) was then added to the feed stream at a rate of 0.371 equivalent sccm, by passing 10 sccm of UHP helium through a saturator containing liquid at 0 °C. The catalyst loadings in the reactor were calculated to yield a constant cyclohexene molar space velocity of 0.208 $\mathrm{min^{-1}}$ with respect to the number of catalyst acid sites as determined from the total acidity measurements. The effluent composition was measured by means of a mass spectrometer-coupled gas chromatograph (GC/MS, Hewlett-Packard model GCD G1800A) equipped with a Supelco Supel-Q-Plot capillary column. For each experiment, samples were injected every 3.2 min using an in-line sampling valve during a continuous, isothermal GC analysis at 150 °C. GC peak separation was enhanced by extracting the corresponding characteristic ion fragments for cyclohexane (M/z = 80), cyclohexene (M/z = 67), methylcyclopentane (M/z = 56) and methylcyclopentene (M/z = 67) from the total ion current recorded in the MS. Isobutane concentrations were not quantified; no other products were detected during the experiments.

Control experiments were run for each material with the purpose of testing the cyclohexene DHGT activity when isobutane was absent. Cyclohexene feed concentrations and molar space velocities were maintained identical to the test employing isobutane, by balancing the feed with supplemental helium. Experimental uncertainties, although not evaluated for these controls, were considered similar to those observed for each material during the hydride transfer tests.

## 3. Results and discussion

Table 1 summarizes all the measured characteristics for the four materials tested. Aside from the quantities measured directly, surface acid site density and adsorbed isobutane/acid site ratios have been calculated in order to help in the interpretation of the reaction results.

The observed product distribution from the reaction of cyclohexene (CHXE) with isobutane (IBU) included cyclohexane (CHX), methylcyclopentane (MCP) and 1-methylcyclopentene (MCPE). No other $C_4$ hydrocarbons were detected in the product stream. Small traces of bicyclohexyl were detected at the end of the whole experiment series upon reconditioning the GC column at an elevated temperature. The proposed reaction mechanism is represented in figure 1. It is assumed that CHX is a product of HT, MCPE a product of isomerization (ISO), while MCP is a product of ISO followed by HT (similar to Ref. [9]).

Typical experimental data from the test reaction on 25BEA65 at 80 °C is presented in figure 2. During all experiments, CHX, MCP and MCPE concentrations have peaked within the first 40 min on stream, while CHXE conversions dropped to values lower than the observed noise level in experimental data. Since no $C_4$ hydrocarbon products were detected, it was concluded that once one HT turnover was complete on an active site, the formed $t\mathrm{C}_4^+$ carbenium ion completely blocks the active site from participating in any subsequent reaction cycle. While this situation is not suitable for a practical reactor due to the almost instantaneous deactivation of the catalyst, it is however ideal for the purpose of titrating the acid sites active for hydride transfer.

For the purpose of active site titration, HT product formation rates were expressed in terms of turnover frequency (TOF), as moles of cycloalkane products formed per mole of acid site per unit time, although this quantity loses its meaning when applied to transient data. Upon integration of the HT TOF peak with respect to time on stream, the total number of moles of HT products formed on each mole of active sites can be calculated. It was shown above that acid sites

Table 1

Measured and calculated characteristics of the catalysts used in the study

| Material | Dry weight | | BET S.A. $\mathrm{m^2/g}$ (dry) | $NH_3$ chemisorption | | | $i\mathrm{C}_4$ total adsorption | | |
|---|---|---|---|---|---|---|---|---|---|
| | wt% | ± % | | mmol/g (dry) | ± % | μmol/$\mathrm{m^2}$ | mmol/g (dry) | ± % | $i\mathrm{C}_4$:acid |
| 75BEA65 | 91.9 | 0.19 | 441 | 0.254 | 7.5 | 0.58 | 0.733 | 0.8 | 2.89 |
| 25BEA65 | 90.5 | 0.01 | 444 | 0.572 | 1.3 | 1.29 | 0.780 | 0.0 | 1.36 |
| SZ | 97.4 | 0.11 | 90 | 0.230 | 1.7 | 2.56 | 0.034 | 10.0 | 0.15 |
| 80ZSM565 | 95.7 | 0.07 | 333 | 0.336 | 5.5 | 1.01 | 0.377 | 1.8 | 1.12 |

(S.A. – surface area; $i\mathrm{C}_4$ – isobutane).

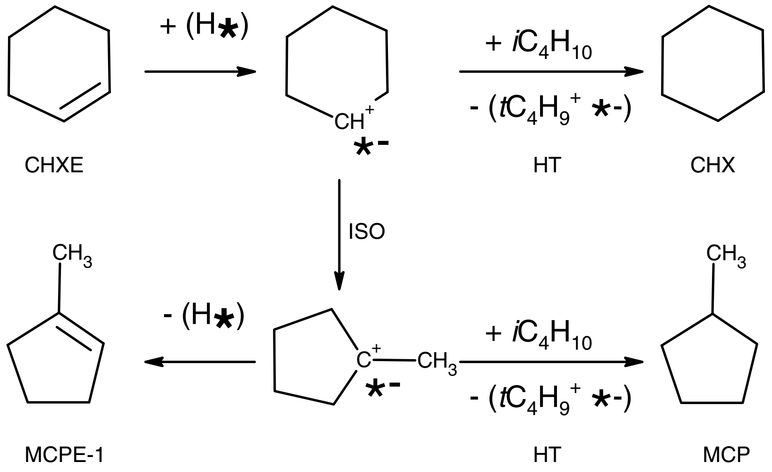

Figure 1. Proposed reaction mechanism. (*) symbolizes an active site.

undergoing hydride transfer are completely deactivated after one turnover. Indeed, this is in part validated by the fact that the above integral was always smaller than unity for all materials tested, as shown by the results in figure 3. Therefore, the above integral can be thought of as the apparent fraction of sites active for HT out of the total acid sites that are detected by ammonia chemisorption, or in other words, the acid site availability to hydride transfer (AHT). It was of interest to also estimate the activities for the Rideal-type HT decoupled from the undesired DHGT contributions. Product formation rates measured for each material during the DHGT control experiments ("no IBU" in figure 3) were subtracted from the data obtained above. Based upon this difference, 25BEA65 fared best in terms of acid site AHT (7.3%), followed closely by 75BEA65 (6.5%) and then by SZ (2.9%). 80ZSM565 seems to completely lack HT activity at 80 °C, in accord with Ref. [13], but shows a significant DHGT activity as judged by this calculation.

Peak values of HT and ISO turnover frequencies were also compared in figure 4. While the overall AHT was more elevated on 75BEA65 than on SZ, the peak HT TOF was lower on the 75BEA65. The observed maximum rates could be affected to some degree by the limited diffusion rates in the narrow pores of the zeolite structure, while the overall AHT should be more closely related to the intrinsic activity of the catalysts. The diffusion limitation effect becomes more evident when comparing the total transient time in SZ (12 min) to that of the zeolites (25–40 min) during the HT experiments. SZ as well as both BEA materials showed almost identical DHGT activities, both in terms of percent availability (figure 3) and peak rates (figure 4), indicating that the tendency to form polyunsaturated carbonaceous deposits should be similar in all three materials at 80 °C. Although the TOF values reported in figure 4 are not accurately describing the process kinetics due to the transient nature of the experiment, it is noticeable that the formation rate of HT products is comparable for SZ and the Beta zeolites, despite the significantly lower

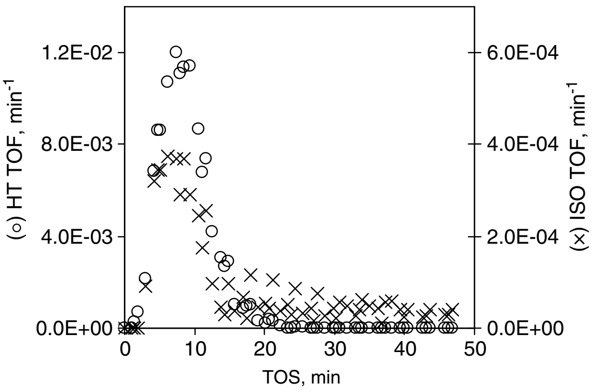

Figure 2. Cumulative data obtained on zeolite 25BEA65 at 80 °C.

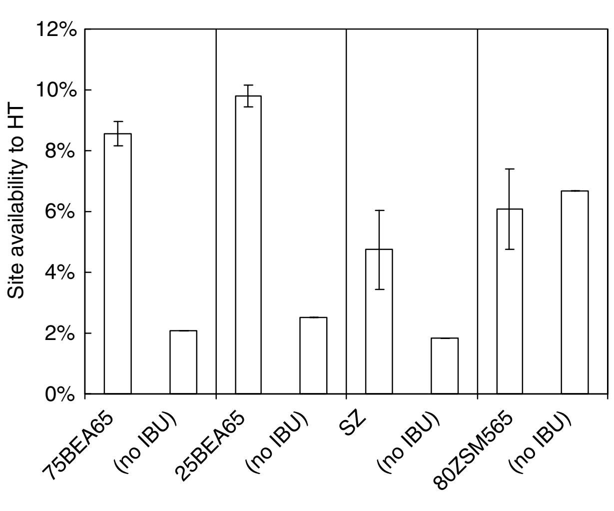

Figure 3. Integrals of HT TOF peaks can be interpreted as a measure of the fraction of the total acid sites that are available for hydride transfer.

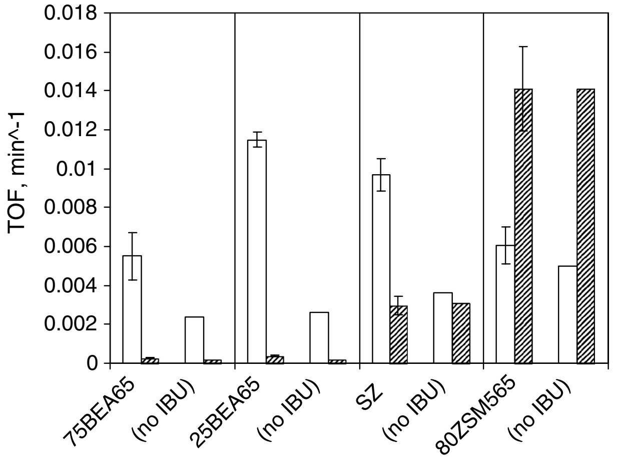

Figure 4. Maximum formation rates recorded for the HT (open bars) and ISO (filled bars) products.

isobutane adsorption capacity of SZ. Considering the amount of adsorbed isobutane per acid site (table 1) as a measure of its concentration, in a rough approximation, the apparent HT global rate constant is greater in SZ than in the zeolites. SZ also showed a significantly higher ISO peak rate than the two BEA zeolites, while the higher acid density 25BEA65 was slightly more active for ISO than 75BEA65. The peak isomerization rate was not influenced by the presence or absence of IBU on SZ and 80ZSM565, as the ISO results indicate, while on zeolites Beta, ISO is somewhat inhibited by the presence of IBU. Based on this observation, ring rearrangement isomerization in intermediates on SZ and 80ZSM565 happens much faster than any subsequent HT, DHGT or cycloolefin desorption process.

As expected from the higher aluminum content, a higher ammonia chemisorption amount was measured on 25BEA65 than on 75BEA65. The measured AHT values suggest that within the same type of structure (BEA), the higher acid site density of 25BEA65 improves hydride transfer activity in terms of the apparent number of acid sites involved in HT. This result is to a certain degree in accord with the report from Suarez *et al.* [10] who have found that the hydrogen transfer activity, measured during CHXE conversion at 250 °C on several zeolites, correlates directly with the fraction of paired aluminum sites in the zeolite structure. Following theoretical calculations of carbocations interacting with Si–O–Si and Si–O–Al zeolite-like sites, Mota *et al.* [15] concluded that the carbenium ion resulting from a HT reaction (such as $t\mathrm{C}_4^+$ in the scheme in figure 1) is better stabilized by the more acidic Si–O–Al site and therefore, the direct mutual proximity of such highly acidic sites should enhance the likelihood of HT reactions.

An intriguing case however is sulfated zirconia. Its surface acid site density as calculated in table 1 is twice the surface acid density on 25BEA65, yet its hydride transfer activity is 2.5 times lower. A possible explanation of the poor AHT in SZ is its lower adsorption capacity for IBU due to its lower surface area, as shown in table 1. Indeed, when compared with 25BEA65, the IBU physisorption amount detected on SZ was 23 times lower when normalized to the dry weight, or 9 times lower when normalized to the number of acid sites. It was shown that the dilution of the hydride donor IBU was detrimental to the formation of HT products during solid-acid catalyzed alkylation [2,16]. An argument can be made that a catalyst structure capable of adsorbing an increased amount of IBU in the proximity of the active sites should exhibit enhanced HT from the adsorbed hydride donor.

## 4. Conclusion

Little choice exists to date in the estimation of low-temperature activities for hydride transfer (HT) of solid acid catalysts. Methods originally developed to describe high temperature cracking reaction systems could be of little help in conjunction with reactions such as isobutane/olefin alkylation. The reaction between isobutane and cyclohexene is proposed as a test to estimate the HT activity of solid acids at low temperatures. The proposed test easily discerned between disproportionation/hydrogen transfer and isobutane/cyclohexene HT on zeolites Beta, ZSM-5 and sulfated zirconia. Out of the total number of acid sites determined by ammonia chemisorption titration, the apparent fraction available to mediate HT reactions could be estimated. The results obtained for two silica/alumina ratio values in zeolite Beta were found in perfect accord with evidence indicating that denser strong-acid sites enhance the HT process. The lower per-site HT activity measured in the even denser-acid-site sulfated zirconia could be explained by its much lower isobutane adsorption capacity per acid site. Although zeolite ZSM-5 showed significant disproportionation/hydrogen transfer activity, no measurable Rideal-type, low-temperature HT activity was detected for this otherwise successful cracking catalyst.

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## References

[1] C. Flego, G. Bellussi and I. Kiricsi, Appl. Catal. A 126 (1995) 401.
[2] D.M. Ginosar, D.N. Thompson and K.C. Burch, Appl. Catal. A 262 (2004) 223.
[3] F.W. Kirsch, J.D. Potts and D.S. Barmby, *Proceedings – American Petroleum Institute*, Division of Refining 48 (1968) 1000..
[4] G.S. Nivarthy, Y. He, K. Seshan and J.A. Lercher, J. Catal. 176 (1998) 192.

[5] A. Feller, I. Zuazo, A. Guzman, J.O. Barth and J.A. Lercher, J. Catal. 216 (2003) 313.

[6] A. Corma, P.J. Miguel and A.V. Orchillés, Appl. Catal. A 138 (1996) 57.

[7] D.B. Lukyanov, J. Catal. 145 (1994) 54.

[8] K. Yoo and P.G. Smirniotis, Appl. Catal. A 227 (2002) 171.

[9] W.-C. Cheng and K. Rajagopalan, J. Catal. 35 (1993) 483.

[10] W. Suarez, W.-C. Cheng, K. Rajagopalan and A.W. Peters, Chem. Eng. Sci. 45 (1990) 2581.

[11] K. Hatakeyama, T. Suzuka and M. Yamane, Sekiyu Gakkaishi 34 (1991) 267.

[12] A. Corma, M.I. Juan-Rajadell, J.M. Lopez-Nieto, A. Martinez and C. Martinez, Appl. Catal. A 111 (1994) 175.

[13] B.G. Anderson, R.R. Schumacher, R. Duren, A.P. Singh and R.A. Santen, J. Mol. Catal. A 181 (2002) 291.

[14] A.S. Chellappa, R.C. Miller and W.J. Thomson, Appl. Catal. A 209 (2001) 359.

[15] C.J.A. Mota, P.M. Esteves and M.B. Amorim, J. Phys. Chem. 100 (1996) 12418.

[16] D.M. Ginosar, D.N. Thompson, K. Coates and D.J. Zalewski, Ind. Eng. Chem. Res. 41 (2002) 2864.