1-Pentene isomerization over zeolites studied by *in situ* IR spectroscopy

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The skeletal isomerization of 1-pentene at 1.2 bar total pressure and 30 mbar 1-pentene partial pressure was investigated by *in situ* IR measurements over FER and BEA zeolites. If the reaction was carried out isothermally a small loss of Brønsted acid sites due to coke formation, a constant conversion and a high selectivity to isopentenes was found over FER. A loss of acid sites and a decrease in conversion was found over BEA, but the selectivity to isomerization increased remarkably. The pore size of FER favored the monomolecular reaction of 1-pentene and suppressed bimolecular reactions. In the bigger pores of BEA initially dimerization–cracking and hydrogen transfer reactions leading to a coke layer took place then the skeletal isomerization of 1-pentene prevailed.

KEY WORDS: skeletal isomerization; 1-pentene; FER; BEA; coke.

1. Introduction

Acid-catalyzed reactions of alkenes on zeolites are usually explained by a number of elementary reactions including skeletal isomerization, β-scissions, addition of carbenium ions to alkenes, hydrogen transfer to form alkanes, etc. [1]. Carbenium ions that were well characterized in superacids [2] have been considered to be the active intermediates in these transformations. However, due to high reactivity and transient existence, alkyl carbenium ions on zeolites usually fail to be detected by various techniques, while oligomers [3,4] or alkoxy species [5,6] were observed.

It is discussed that skeletal isomerization of *n*-butene proceeds via a monomolecular and/or bimolecular (dimerization–cracking), or via a pseudo-monomolecular mechanism [7,8]. In the latter mechanism an aromatic molecule, part of coke deposition, is described as the selective catalytic site [9]. *n*-Pentene and higher alkenes can isomerize on zeolites via a monomolecular pathway, which includes a protonated cyclopropane ring as intermediate [1]. The initial step is probably a covalently bonded alkoxy group, which can transform into transition states representing carbenium ion-like alkyl fragments. Then a cyclopropane ring is formed, a proton being donated to the zeolite. Reopening of the cyclopropane ring by protonation of another bond of the cycle results in skeletal isomerization [10].

Skeletal isomerization of alkenes is mainly controlled by catalyst pore topology, acid strength, acid site density and location of acid sites. The relation between these parameters and the activity and selectivity is still imperfectly known or a matter of debate [11].

An *in situ* IR investigation of 1-pentene isomerization over FER has been carried out to correlate the surface chemistry of the zeolites with their catalytic performance and to identify aliphatic and aromatic reaction intermediates. For comparison, BEA, a large-pore-size zeolite, was investigated as catalyst for pentene isomerization in order to discuss the influence of the pore size on isomerization selectivity.

2. Experimental

The zeolites studied consisted of Ferrierite (NH_4-FER, 0.45 mmol acid sites/g) provided by Zeolyst and zeolite Beta (BEA, 0.61 mmol acid sites/g) obtained from Degussa.

The *in situ* FTIR experiments were carried out in a reaction cell similar to that described by Mirth *et al.* [12] approximating a continuously stirred tank reactor with gas inlets and outlets and a volume of 1.5 cm^3. The samples were prepared as self-supporting wafers and placed inside a ring-shaped furnace. Measurements were carried out up to 300 °C under a helium flow of 40 ml/min, a total pressure of 1.2 bar and a pentene partial pressure of 30 mbar. The active sites and the adsorbed species were investigated by FTIR spectroscopy (Bruker IFS 28) and the reaction products were analyzed by gas chromatography (HP 5980 II), the instrument being equipped with a flame ionization detector.

To obtain the difference IR spectra of the *in situ* measurements, the spectra of the activated catalysts

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recorded at corresponding temperatures were subtracted from the spectra recorded during the reaction.

Additionally pyridine adsorption on fresh and coked BEA and FER was followed by IR measurements. For these measurements the fresh and coked samples were activated at 500 and 300 °C respectively, cooled to room temperature and exposed to 10^{-2} mbar pyridine at 40 °C. Finally the samples were heated to 120 °C for 60 min in order to remove the excess physisorbed pyridine and cooled to room temperature again.

Temperature-programmed desorption (TPD) of ammonia and pyridine was used to qualitatively and quantitatively characterize the acidity of BEA, FER and the coked samples. A MFI with a known number of acid sites was used as reference material. The measurements were carried out in vacuum with a heating rate of 10 °C/min.

3. Results and discussion

3.1. *TOS behavior of 1-pentene over FER and BEA*

The time on stream (TOS) behavior of 1-pentene over FER was measured at 250 °C. In the IR spectrum of activated FER two OH stretching vibration bands were detected, at 3740 $\mathrm{cm^{-1}}$ corresponding to terminal Si–OH bands and at 3590 $\mathrm{cm^{-1}}$ assigned to bridged SiOHAl bands, the Brønsted acid groups. The IR spectra obtained by subtraction of the activated spectrum during 1-pentene isomerization are shown in figure 1. With increasing TOS the intensity of both OH– bands decreased and new bands built up. The broad band between 3500 and 3300 $\mathrm{cm^{-1}}$, which appeared after some TOS could correspond to a shift of a part of the OH band at 3590 $\mathrm{cm^{-1}}$ to lower wavenumbers due to hydrogen bonding with the aliphatic part of pentene (or with oligomerized species) or with coke precursors [13]. Also Andy *et al.* [9] assigned this band, which was observed after the reaction with 1-butene over HFER, to coke in contact with OH groups.

In the region of CH stretching vibrations bands at 3078, 2965, 2935 and 2877 $\mathrm{cm^{-1}}$ were noticed. The band at 2965 $\mathrm{cm^{-1}}$ is assigned to the asymmetric stretching vibration (ν_{as}) of C–H in CH_3, that at 2935 $\mathrm{cm^{-1}}$ corresponds to ν_{as} of C–H in CH_2 and that at 2877 $\mathrm{cm^{-1}}$ stems from the non-resolved symmetric stretching vibrations of C–H in $–CH_3$ and $–CH_2$. The band at 3078 $\mathrm{cm^{-1}}$ corresponds to the stretching vibration of C–H in $–CH{=}CH_2$. The band at 1650 $\mathrm{cm^{-1}}$ is characteristic for C=C stretching vibration.

The bands at 1380 and 1460 $\mathrm{cm^{-1}}$ are assigned to C–H deformation vibrations. After adsorption of butene on different zeolites Seo *et al.* [14] attributed bands at 1470 and 1382 $\mathrm{cm^{-1}}$ to asymmetric and symmetric deformation vibrations respectively. The band near 1500 $\mathrm{cm^{-1}}$ is characteristic for ring vibrations of non-condensed aromatics or conjugated alkenes. Pazé *et al.* [13] assigned the band at 1500 $\mathrm{cm^{-1}}$ to neutral and/or cationic polyenes resulting from butene oligomerization followed by partial dehydrogenation. Dehydrogenation can occur via hydride transfer between a carbenium ion and an alkene with formation of an alkane and a surface-bound alkadiene [11]. The band near 1590 $\mathrm{cm^{-1}}$ is assigned to coke precursor or coke [15,16].

Analysis of the gas-phase composition indicated that coke formation had a small influence on the conversion and selectivities over the investigated period. Selectivities to cracking and dimerization were rather small whereas selectivity to hydrogen transfer (about 10%) was rather high. This means that hydrogen transfer took place with parallel formation of coke, which is in agreement with the IR measurements.

In figure 2 the intensities of the decreasing silanol and bridged OH bands, the increasing coke band at 1590 $\mathrm{cm^{-1}}$ and the results of the corresponding kinetic measurements against TOS are shown. (Note that

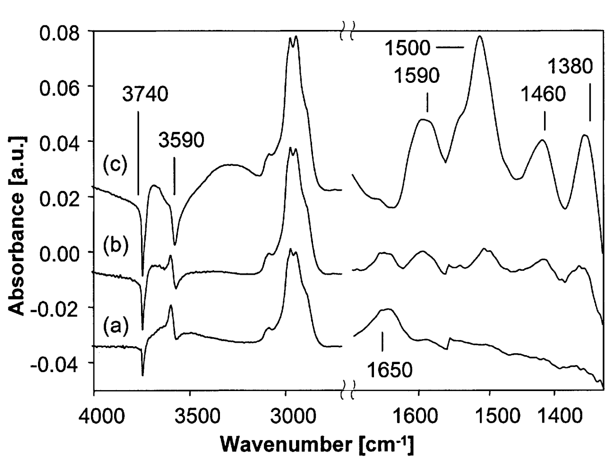

Figure 1. Difference spectra during 1-pentene isomerization over FER at 250 °C after (a) 5 min, (b) 20 min and (c) 95 min TOS.

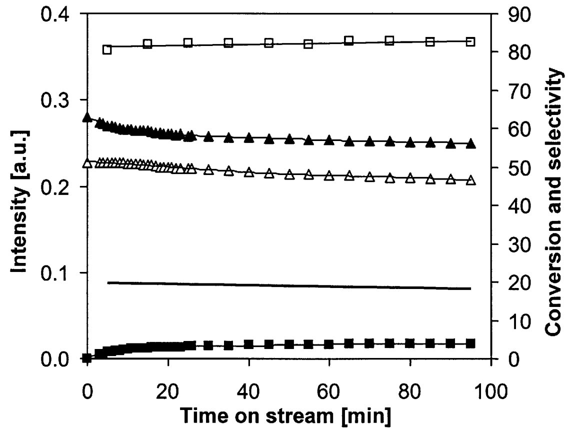

Figure 2. Reaction of 1-pentene over FER at 250 °C: intensities of OH and coke bands versus TOS compared to the conversion and isomerization selectivity: (▲ 3740 $\mathrm{cm^{-1}}$, △ 3590 $\mathrm{cm^{-1}}$, ■ 1590 $\mathrm{cm^{-1}}$, — conversion, □ skeletal isomerization).

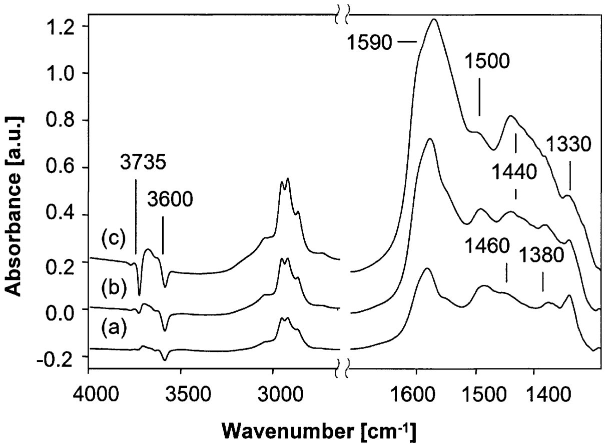

Figure 3. Difference spectra during 1-pentene isomerization over BEA at 250 °C after (a) 3 min, (b) 10 min and (c) 95 min TOS.

absorbance values for the two OH bands are absolute values.) Both OH groups, Brønsted acid sites and silanols, are involved in the reaction. The reaction of alkenes with silanol groups on the external surfaces of zeolites was observed earlier [6,17]. The coverage of the OH groups, partly with coke, after 95 min TOS was small, i.e. only 9% was found for the Brønsted acid sites and 11% for the terminal silanol groups. Therefore, the effect on the activity due to the loss of active sites is negligible.

In the IR spectrum of activated BEA terminal SiOH groups are found at 3735 cm^{-1}, Brønsted acid sites at 3600 cm^{-1} and OH groups on extra-framework alumina at 3668 cm^{-1}. In figure 3 the IR spectra obtained by subtraction of the activated spectrum during 1-pentene isomerization after different TOS are shown. The coverage of the bridged OH groups increased with TOS and was constant after 20 min, whereas an increase in coverage of the silanol groups was detected over the whole time with the main rise within the first 20 min. The C–H stretching and deformation bands increased in intensity and were approximately constant after 20 min TOS. In contrast to FER, BEA exhibited significantly more coke formation. (Note the different scale for the absorbance in figures 1 and 3.) No frequency-shifted band to Brønsted acid sites and no band near 1650 cm^{-1} corresponding to C=C stretching vibration were found.

Figure 4 shows the intensities of OH and coke bands and the corresponding 1-pentene conversion and isopentene selectivity analyzed by GC versus TOS. The OH bands decreased while the CH and coke precursor (coke) bands increased. After 3 min TOS 37% and after 40 min 97% of the Brønsted OH groups are covered with coke precursor species, whereas the coverage of the silanol groups amounted to 28% after 95 min TOS. The increase of the intensity of the CH and coke precursor bands proceeds in parallel with the decrease of the Brønsted OH bands.

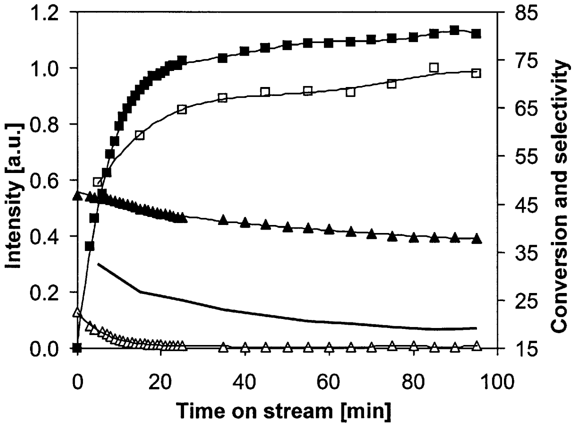

Figure 4. Reaction of 1-pentene over BEA at 250 °C: intensities of OH and coke bands versus TOS compared to the conversion and isomerization selectivity: (▲ 3735 cm^{-1}, △ 3600 cm^{-1}, ■ 1590 cm^{-1}, — conversion, □ skeletal isomerization).

The conversion and the selectivity to dimerization decreased, skeletal isomerization increased from 49 to 72%, hydrogen transfer remained constant (12%) and the selectivity to cracking was negligible.

BEA showed good activity and increasing isomerization selectivity after an initial period in which a coke layer was built up. Therefore it can be assumed that coke has a positive influence on the isomerization reaction over BEA. Over FER only a minor part of the active sites was covered with coke under the reaction conditions and all take part in the reaction reaching a steady-state conversion and constant high isomerization selectivity.

Zholobenko and Stevens [18] studied 1-butene conversion over MOR and found a rapid decrease in activity with TOS, which can be explained by the extensive coke formation and blockage of the unidimensional pore system. At the same time the selectivity for isobutene increased to 60%, which is attributed to the significant decrease in the concentration of acid sites and the space limitation around the active sites imposed by coke. The same is found for FER, the selectivity to isobutene significantly increased whereas the conversion decreased with TOS [19].

Such catalytic performance has previously been attributed to the pore narrowing by coke deposits formed during reaction and to the increasing role of the monomolecular mechanism [20]. Donk *et al.* [21] reported that aliphatic carbonaceous deposits largely fill the pore system of FER after some time on stream of 1-butene, with isomerization primarily occurring at the pore mouths of the channels. Since 1-pentene can react via a monomolecular pathway, no coke formation over FER is necessary to obtain high isomerization selectivity. In the bigger pores of BEA side reactions leading to coke deposits, which fill the channels, took place. Therefore it is very likely that the reaction occurred near the pore mouth. Kleestorfer [22]

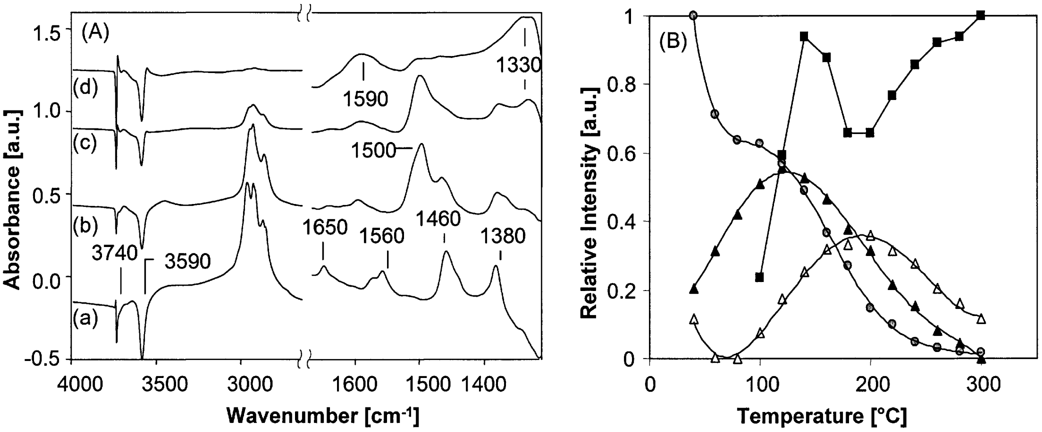

Figure 5. (A) Difference spectra of 1-pentene over FER at (a) 60 °C, (b) 140 °C, (c) 200 °C and (d) 300 °C. (B) Change of relative intensities of OH, CH and coke bands with temperature during the reaction of 1-pentene over FER (▲ 3740 cm^{-1}, △ 3590 cm^{-1}, ● 2935 cm^{-1}, ■ 1590 cm^{-1}).

calculated that the OH groups in the pore mouths of BEA are very flexible and he showed that they have high stabilization energy in contrast to MFI and MCM-22.

3.2. *Influence of temperature on coke formation*

The *in situ* IR spectra obtained over FER at various temperatures are shown in figure 5(A). At lower temperatures CH bands in the deformation vibration region at 1650, 1460 and 1380 cm^{-1} are detected. With increasing temperature bands at 1590, 1500 and 1330 cm^{-1}, assigned to polymeric species, coke precursor and coke, appeared.

Figure 5(B) shows the variation of relative intensities of OH, CH and coke bands with temperature. The relative intensity of terminal silanol groups first increased from 40 to 120 °C than decreased upon further heating. The Brønsted OH band showed the same behavior with the minimum coverage at 200 °C.

The intensity of the CH bands decreased with temperature whereas the intensity of the coke bands increased, the latter showed a minimum at 200 °C. Up to 100 °C the OH groups are only covered with hydrocarbon molecules corresponding to a shift of the Brønsted OH band of about 120 cm^{-1}. With increasing temperature the coverage with hydrocarbons became smaller while that with coke bigger. Oligomers and coke precursors, such as condensed polyenes or other non-condensed aromatic structures, can be built up. The formation of more bulky structures such as cycloparaffins (coke precursors) is sterically hindered by the restrictive pore system of FER. Domokos *et al.* [23] showed by molecular simulation that condensed ring structures are unlikely to be formed inside the channels of FER.

The difference spectra of 1-pentene over BEA at different temperatures are shown in figure 6(A). The spectrum obtained at 60 °C shows CH_2 and CH_3 deformation bands at 1380 and 1460 cm^{-1} and three CH bands in the stretching vibration region. With increasing temperature a small band at 3050 cm^{-1} was observed which would be indicative of aromatic compounds [24]. The formation of polymeric species was identified by bands at 1590, 1490, 1440 and 1330 cm^{-1}, increasing with temperature.

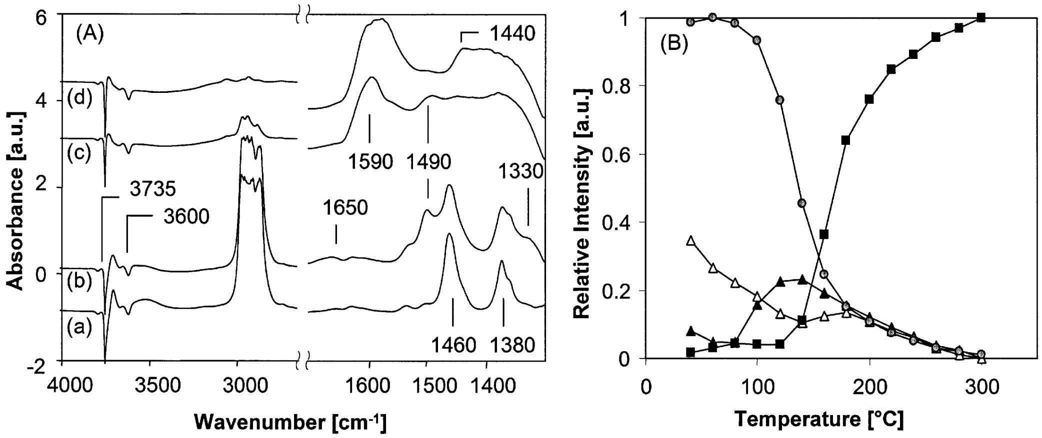

Figure 6. (A) Difference spectra of 1-pentene over BEA at (a) 60 °C, (b) 100 °C, (c) 200 °C and (d) 300 °C. (B) Change of relative intensities of OH, CH and coke bands with temperature during the reaction of 1-pentene over BEA (▲ 3735 cm^{-1}, △ 3600 cm^{-1}, ● 2860 cm^{-1}, ■ 1590 cm^{-1}).

The change in the relative intensities of different bands in the OH, CH and coke regions with temperature is shown in figure 6(B). The intensity of the silanol groups increased to 140 °C and then decreased at higher temperature. The intensity of Brønsted acid groups decreased over the whole temperature range studied. Above 120 °C, bands assigned to coke and coke precursors increased strongly.

Karge [25] studied reactions of alkenes over acidic mordenite between 78 and 103 °C and observed instantaneous polymerization upon contact of the alkenes with the zeolite surface. In the IR spectrum he found bands of saturated hydrocarbons and after successive heating to higher temperatures in high vacuum a coke band around 1585 cm^{-1} appeared.

A decrease of Brønsted acid groups due to coke formation was discussed by Andy *et al.* [26] and Wichterlóva *et al.* [27]; however, also the complete disappearance of that band by coke deposition has also been reported [28]. Karge and Boldingh [29] found via *in situ* IR and conversion measurements using dealkylation/disproportionation of ethylbenzene as a test reaction that the number of acidic OH groups in MOR and MFI remained essentially unaffected in spite of severe coking and loss of activity. This was explained by deactivation through blocking rather than consumption of sites. The intensity of the Brønsted OH band was constant. This means that the active sites were not poisoned or consumed even though the activity decreased and consequently the band at 1600 cm^{-1} increased. Deactivation during isomerization of 1-pentene over SAPO-5 and CoAPO-5 was explained in the same way, i.e. by pore blocking rather than by deactivation of the active sites [15].

In the case of FER and BEA, coke molecules caused a decrease in intensity of all hydroxyl bands. Upon successive heating in the presence of 1-pentene to 300 °C, 84% of the silanol and 76% of the Brønsted acid sites of FER are covered with coke, whereas after 95 min isothermally at 300 °C only 11% silanol and 9% Brønsted acid sites were affected. Over BEA the coverage of the acid sites with coke was much higher corresponding to a decrease in conversion from 33 to 19% and an increase in isomerization selectivity. Therefore one of the main factors governing the isomerization selectivity is believed to be the restricted transition state selectivity and/or the restricted space around the active sites.

3.3. *Desorption of ammonia and pyridine on fresh and coked catalysts*

Ammonia TPD over coked FER indicated that 90% of the sites corresponding to the high-temperature desorption peak are accessible. This result corresponds very well with that from IR measurements (9% of the Brønsted acid sites are covered at 250 °C after 95 min TOS). The IR spectra after adsorption of pyridine on fresh (figure 7(a)) and on coked FER (figure 7(b)) show that the (remaining) Brønsted acid sites and silanol groups are accessible for pyridine.

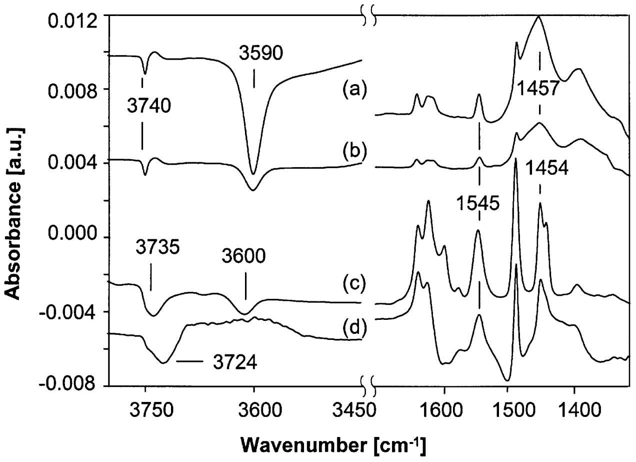

Figure 7. Difference spectra of pyridine adsorption on (a) HFER, (b) coked FER, (c) HBEA and (d) coked BEA.

Desorption of ammonia from coked BEA indicated that only 64% of the acid sites are available. Adsorption of pyridine on fresh BEA (figure 7(c)) led to a decrease of the silanol and the bridged OH groups and to the formation of bands of pyridinium ions (1545 cm^{-1}) and coordinated pyridine (1454 cm^{-1}). Coked BEA (figure 7(d)) did not show a decrease of the remaining bridged OH groups after adsorption of pyridine. Under the same conditions, the band assigned to silanol groups decreased in intensity and was shifted to lower wavenumber indicating that internal silanol groups are involved [30]. However, the bands of pyridinium ions and of coordinated pyridine were present.

Furthermore, pyridine adsorption caused a decrease in the intensity of the corresponding coke bands. It was therefore concluded that pyridine could displace a part of the coke.

The presence of the pyridinium ions can result from (i) the interaction with Brønsted acid sites where coke molecules are removed by pyridine, (ii) the interaction with internal silanol groups which are more acidic than the terminal ones, or (iii) the interaction with coke molecules.

4. Conclusions

1-Pentene can react with Brønsted acid sites and with silanol groups of FER and BEA. The loss of OH groups after 95 min TOS at 250 °C, was small over FER and significant over BEA.

The increase of the intensity of the CH and coke bands proceeded in parallel with the decrease of the OH bands when the isomerization was carried out isothermally. The activity and selectivity of FER in the isomerization of 1-pentene was hardly affected by coke formation, whereas a large effect was observed over BEA. In BEA, with a 12-ring pore system, bimolecular side reactions build up a coke layer, which decrease the conversion but improve the isomerization selectivity.

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References

[1] V.B. Kazansky, Catal. Today 51 (1999) 419.

[2] G.A. Olah, G.K. Surya Praksh and J. Sommer, *Superacids* (Wiley-Interscience, 1985).

[3] F. Geobaldo, G. Spoto, S. Bordiga, C. Lambert and A. Zecchina, J. Chem. Soc. Faraday Trans. 93 (1997) 1243.

[4] J.N. Kondo, K. Domen and F. Wakabayashi, Catal. Lett. 53 (1998) 215.

[5] J.N. Kondo, F. Wakabayashi and K. Domen, J. Phys. Chem. B 102 (1998) 2259.

[6] H. Ishikawa, E. Yoda, J.N. Kondo, F. Wakabayashi and K. Domen, J. Phys. Chem. B 103 (1999) 5681.

[7] M. Guisnet, P. Andy, N.S. Gnep, C. Travers and E. Benazzi, Ind. Eng. Chem. Res. 37 (1998) 300.

[8] M. Guisnet, P. Andy, Y. Boucheffa, N.S. Gnep, C. Travers and E. Benazzi, Catal. Lett. 50 (1998) 159.

[9] P. Andy, N.S. Gnep, M. Guisnet, E. Benazzi and J. Travers, J. Catal. 173 (1998) 322.

[10] J.A. Martens and P.A. Jacobs, in: *Theoretical Aspects of Heterogeneous Catalysis* (van Nostrand Reinhold, 1990), p. 52.

[11] M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani and R.J. Willey, J. Catal. 179 (1998) 581.

[12] G. Mirth, J. Cejka and J.A. Lercher, J. Catal. 139 (1994) 24.

[13] C. Pazè, B. Sazak, A. Zecchina and J. Dwyer J. Phys. Chem. B 103 (1999) 9978.

[14] G. Seo, M. Kim and J. Kim, Catal. Lett. 67 (2000) 207.

[15] M. Höchtl, A. Jentys and H. Vinek, Appl. Catal. 207 (2001) 397.

[16] J. Datka, Z. Sarbak and R.P. Eischens, J. Catal. 145 (1994) 544.

[17] J.N. Kondo, H. Ishikawa, E. Yoda, F. Wakabayashi and K. Domen, J. Phys. Chem. B 103 (1999) 8538.

[18] V.L. Zholobenko and C.L.T. Stevens, Stud. Surf. Sci. Catal. 135 (2001) 276.

[19] R. Byggningsbacka, N. Kumar and L.-E. Lindfors, J. Catal. 178 (1998) 611.

[20] J. Houzvicka and V. Ponec, Catal. Rev. Sci. Eng. 39 (1997) 319.

[21] S. van Donk, J.H. Bitter and K.P. de Jong, Appl. Catal. A 212 (2001) 97.

[22] K. Kleestorfer, Thesis, TU Vienna, 2002.

[23] L. Domokos, L. Lefferts, K. Sheshan and J.A. Lercher, J. Catal. 203 (2001) 351.

[24] H.G. Karge, Stud. Surf. Sci. Catal. 58 (1991) 531.

[25] H.G. Karge, ACS Symp. Ser. 40 (1977) 584.

[26] P. Andy, N.S. Gnep, M. Guisnet, E. Benazzi and J. Travers, J. Catal. 173 (1998) 322.

[27] B. Wichterlová, N. Zilova, E. Uvarova, J. Cejka, P. Sarv, C. Paganini and J.A. Lercher, Appl. Catal. A 182 (1999) 297.

[28] J. Datka, Stud. Surf. Sci. Catal. 5 (1980) 121.

[29] H.G. Karge and E.P. Boldingh, Catal. Today 3 (1988) 53.

[30] Chun Yang and Qinhua Xu, Zeolites 19 (1997) 404.