Investigations on the reaction mechanism of the skeletal isomerization of \( n \)-butenes to isobutene 
Part I. Reaction mechanism on H-ZSM-5 zeolites

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Abstract

A series of H-ZSM-5 zeolites with Si/Al ratios between 17 and 170 were tested in the skeletal isomerization of \( n \)-butenes to isobutene in the temperature range of 573–773 K. A selectivity to isobutene of ca. 20% was obtained with all zeolites at 573 K independent of the conversion of \( n \)-butenes. With increasing temperature the conversion of \( n \)-butenes increased on the zeolites with Si/Al ratios up to 70 (high number of acid sites), whereas the yield of isobutene and the selectivity to isobutene decreased. On the zeolites with higher Si/Al ratios (160 and 170) an opposite behaviour was observed; the conversion of \( n \)-butenes decreased while the yield of isobutene and the selectivity to isobutene increased with increasing temperature. A selectivity to isobutene of nearly 90% could be obtained with the latter zeolites at 773 K. These observations are interpreted in such a way that on H-ZSM-5 zeolites with a high number of acid sites, isobutene is formed via the bimolecular mechanism independent of the reaction temperature. On H-ZSM-5 zeolites with a low number of acid sites, a change from the bimolecular to the monomolecular mechanism takes place with increasing temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Skeletal isomerization; Isobutene; ZSM-5; Reaction mechanism

1. Introduction

Stringent limits for air pollutants enacted in many countries have led to an increased demand for isobutene, since this compound is used for the production of methyl tert-butyl ether (MTBE), an oxygenate with a high octane number. Since the high demand cannot be supplied by the traditional cracking processes, the catalytic isomerization of the surplus \( n \)-butene fractions to isobutene has been the subject of recent investigations. Especially a number of 10-membered ring molecular sieves like ferrierite \([1–19]\), ZSM-22 \([8,10,17,20–24]\) and the iso-structural Theta-1 \([1]\), ZSM-23 \([25]\), MeAPO-11 \([13,18,26–28]\), and SAPO-11 \([8,10,13,26,28–30]\) have been proven to be efficient catalysts for this reaction. A high selectivity to isobutene and yields of isobutene close to the thermodynamic equilibrium have been obtained with them. H-ZSM-5 zeolites, on the other hand, have been described as non-selective catalysts for the isomerization of \( n \)-butenes to isobutene \([1,2,4,7,8,10,11,13,14,29,31,32]\). Even after isomorphous substitution of framework aluminium by iron, leading to a reduced acid strength, the selectivity to isobutene was lower than the selectivity obtained with

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other 10-membered ring molecular sieves [33–35]. This difference in the selectivity has been attributed to different reaction mechanisms for the formation of isobutene. ZSM-5 zeolites have cavities with a diameter of ca. 0.9 nm [33] at the intersections of the channels so that the dimerization [4,8,11,33,43] or even trimerization [10] of \( n \)-butenes followed by non-selective cracking of the dimers or trimers is easily possible. Molecular sieves of the structure types FER, AEL, TON, and MTT show a higher shape selectivity. Thus these non-selective reactions are sterically more limited. An intramolecular isomerization \([3,4,6,8,9,11,14,17,18,24,25,27,29,36–43]\), the so-called monomolecular mechanism, and a pseudomonomolecular mechanism with carbenium ions as active sites \([10,12,16,44–46]\) have been proposed to explain the high selectivity to isobutene obtained with these molecular sieves.

In this paper are presented the results of a thorough investigation of the possible reaction mechanism for the isomerization of \( n \)-butenes to isobutene on H-ZSM-5 zeolites with a wide span of Si/Al ratio and at varying reaction temperature.

2. Experimental

2.1. Synthesis

In Table 1, the H-ZSM-5 zeolites investigated are listed. The crystallization of the samples synthesized at the University Halle–Wittenberg was carried out at 448 K in a 2 l stainless-steel autoclave under moderate stirring for 12 h. After cooling the autoclaves, the samples were taken out, filtered, washed with de-ionized water, and dried at 393 K in air. To remove the template in case of the zeolites with Si/Al ratios from 28 to 160, the samples were calcined at 823 K in a furnace under a flowing air stream for 4 h. The protonic form of the resulting sodium form was prepared by heating the ammonium form, obtained by ion exchange three times with a 1 M \( \text{NH}_4\text{NO}_3 \) solution at 323 K for 16 h, at 823 K in a continuous nitrogen flow for 2 h. The protonic form of the samples with Si/Al ratios of 17 and 170 was prepared in the same way from the silicon form. The samples supplied by Süd-Chemie and VAW were delivered in the protonic form.

2.2. Characterization

All samples were characterized by X-ray diffraction (XRD) performed with Cu K\( \alpha \) radiation using a Siemens D 5000 spectrometer. The diffraction patterns indicated a high crystallinity and showed only the characteristic peaks of MFI type zeolites.

\(^{27}\text{Al} \text{MAS NMR} \) measurements for the determination of the framework Si/Al ratio were performed on hydrated samples using a Bruker MSL 500 spectrometer with a sample rotation frequency of 10 kHz. Hydration was performed by keeping the samples in a desiccator for more than 48 h over aqueous \( \text{NH}_4\text{Cl} \). The framework aluminium atoms in ZSM-5 zeolites cause a narrow \(^{27}\text{Al} \text{MAS NMR} \) signal at ca. 55 ppm. Its intensity expressed in number of \(^{27}\text{Al} \) atoms per unit cell, \( \text{Al}_F \), was determined by comparing the area of the signal with that of a well characterized ZSM-5 sample with \( \text{Al}_F=5.3 \). The weight of the samples in the rotor was taken into account for calculation. The framework Si/Al ratio is \((96/\text{Al}_F)–1\). The Si/Al ratio determined by \(^{27}\text{Al} \text{MAS NMR} \) was confirmed by \(^{29}\text{Si} \text{MAS NMR} \) for the sample with the Si/Al ratio of 28. The signal intensity of extraneous aluminium species at 0 ppm and ca. 50 ppm was less than 5% compared to the intensity of the signal of framework aluminium for all samples.

2.3. Catalysis

Catalytic experiments were performed at temperatures from 573 to 773 K in a continuous flow reactor at atmospheric pressure. A mixture of 5% butene

<table>
<thead>
<tr>
<th>Table 1</th>
<th>H-ZSM-5 zeolites used for investigation</th>
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<tbody>
<tr>
<td>Si/Al ratio</td>
<td>Template</td>
</tr>
<tr>
<td>17</td>
<td>Template-free</td>
</tr>
<tr>
<td>20</td>
<td>Template-free</td>
</tr>
<tr>
<td>22</td>
<td>Template-free</td>
</tr>
<tr>
<td>24</td>
<td>Template-free</td>
</tr>
<tr>
<td>28</td>
<td>TPABr*</td>
</tr>
<tr>
<td>40</td>
<td>TPABr</td>
</tr>
<tr>
<td>60</td>
<td>TPABr</td>
</tr>
<tr>
<td>70</td>
<td>TPABr</td>
</tr>
<tr>
<td>160</td>
<td>TPABr</td>
</tr>
<tr>
<td>170</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

* TPABr: Tetrapropylammonium bromide.
(99.0%, AGA) in nitrogen was used as feed. The weight hourly space velocity (WHSV) was varied from 4 to 64 h\(^{-1}\) by changing the catalyst mass from 100 to 13 mg at a total flow of 60 ml/min except for the experiments at WHSV=64 h\(^{-1}\), where the total flow was adjusted to 120 ml/min. Prior to the experiments, the catalysts were heated in situ to 723 K in a nitrogen flow of 120 ml/min at a temperature ramp rate of 10 K/min. A Varian 3300 gas chromatograph (GC) equipped with a flame ionization detector (FID) and a capillary column (HP-PLOT/Al\(_2\)O\(_3\), 50 m × 0.53 mm × 0.15 μm) was used for product analysis. For calculation purposes, the three \(n\)-butene isomers were grouped together, since it was established that under experimental conditions the isomerization between 1-butene and the two 2-butene isomers is much faster than the skeletal isomerization, and the 2-butenes are also converted to isobutene via the same intermediate. The product distribution was calculated from the GC peak areas divided by the number of carbon atoms for the respective compound, since for hydrocarbons the signal of a FID is proportional to the number of carbon atoms [47]. The selectivity to isobutene was determined by division of the yield of \(n\)-butenes, with the conversion defined as the percentage of the linear butenes consumed.

3. Results

All samples that were synthesized using a template exhibited an excellent stability with time on stream (TOS). There was nearly no deactivation over the investigated reaction time of 6 h [48]. For the samples synthesized template-free an increasing conversion of \(n\)-butenes and an increasing yield of isobutene with TOS was observed at 573 K. This catalytic behaviour is yet not understood. The selectivity to isobutene, however, remained constant. At higher temperatures there was no difference in the catalytic behaviour between samples synthesized with and without template.

The conversion of \(n\)-butenes increased, whereas the yield of isobutene and the selectivity to isobutene decreased with increasing reaction temperature on the zeolites with Si/Al ratios up to 70. On the zeolites with Si/Al ratios of 160 and 170 the opposite behaviour was observed; the conversion of \(n\)-butenes decreased and the yield of and selectivity to isobutene increased with increasing reaction temperature. As an example for these contrary trends in dependence on the different Si/Al ratios, the conversion of \(n\)-butenes and the yield of isobutene is depicted in Figs. 1 and 2 as a function of the reaction temperature for the zeolites with Si/Al ratios of 28 and 170, respectively.

![Fig. 1. Conversion of \(n\)-butenes after 10 min TOS on the zeolites with Si/Al=28 and 170 as a function of the reaction temperature (WHSV=8 h\(^{-1}\)).](image-url)
Fig. 2. Yield of isobutene after 10 min TOS on the zeolites with Si/Al=28 and 170 as a function of the reaction temperature (WHSV=8 h⁻¹).

Fig. 3. Yield of the four main products at 573 K as a function of the conversion of n-butenes. The lines depict the thermodynamic limits for the yield of isobutene.

Fig. 3 shows the yield of the four main products obtained with all the different catalysts as a function of the conversion of n-butenes at 573 K. In Fig. 4, the corresponding selectivities are depicted. The straight lines in Fig. 3 represent the thermodynamic maximum for the yield of isobutene at the respective conversion of n-butenes. It can be seen in Fig. 3 that the yields increased nearly linearly with increasing conversion of n-butenes. Only at high conversions of n-butenes there was a decrease in the yield of propene. The selectivities to isobutene, pentenes, and hexenes did not change significantly with increasing conversion of n-butenes. A selectivity value for isobutene of ca. 20% was measured independent of the conversion of
$n$-butenes. Further reaction products at 573 K with an amount $>1$ wt.% were C$_7$- and C$_8$- (they were not separated by the GC column) as well as C$_9$-hydrocarbons, ethene, and different alkanes, especially isobutane and pentanes. The C$_9$-hydrocarbons, ethene, and alkanes were only detected at conversions of $n$-butenes $>80\%$.

A different catalytic behaviour was observed at higher temperatures. In Figs. 5 and 6 the yields of and selectivities to the four main products obtained at 773 K are plotted as a function of the conversion of $n$-butenes, respectively. The values up to a conversion of $n$-butenes of about 60% were obtained on the
samples with Si/Al ratios of 160 and 170, whereas the other values were obtained on the samples with Si/Al ratios up to 70. Because of experimental limitations, it was not possible to obtain the same level of conversion of n-butenes on the zeolites with high and low Si/Al ratio. It can be seen that at low conversions the selectivity to isobutene was much higher than at 573 K, whereas at high conversions a lower selectivity was observed. Extrapolated to zero conversion a selectivity value of about 90% is obtained. At 673 K, the selectivities to isobutene were between those measured at 573 and 773 K.

Regarding the by-products, it is striking that the higher the reaction temperature the higher the amount of ethene. On the other hand, the amount of hexenes and C7- and C8-hydrocarbons was the highest at 573 K. The amount of alkanes (not depicted) compared at the same conversion level also decreased with increasing reaction temperature.

4. Discussion

The low selectivity to isobutene obtained at 573 K independent of the conversion of n-butenes and of the Si/Al ratios of the samples shows that isobutene is formed via the bimolecular mechanism on H-ZSM-5 zeolites at this temperature. This is also indicated by the linearly increasing yield of the products with increasing conversion of n-butenes (Fig. 3). According to the classification of Abbot and Wojciechowski [49], such an increase is characteristic for primary products. Since on the samples with Si/Al ratios up to 70, the conversion of n-butenes increased and the yield of and the selectivity to isobutene decreased with increasing reaction temperature, the conclusion can be drawn that on H-ZSM-5 zeolites with a high number of acid sites isobutene is formed via the bimolecular mechanism independent of the reaction temperature. On the samples with Si/Al ratios of 160 and 170 a different catalytic behaviour was observed as on those with lower Si/Al ratios. Very high selectivities to isobutene could be obtained with them at 773 K. These facts indicate that there should be a change in the reaction mechanism for the formation of isobutene with increasing reaction temperature from the bimolecular to a more selective one on H-ZSM-5 zeolites with a low number of acid sites.

Two mechanisms for the selective formation of isobutene have been proposed in the literature as pointed out in Section 1, the monomolecular and the pseudomonomolecular one. The pseudomonomolecular mechanism requires carbenium ions as active sites. According to Guisnet et al., these are benzylic...
Table 2

<table>
<thead>
<tr>
<th>Si/Al ratio</th>
<th>Coke content (wt.%)</th>
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<tbody>
<tr>
<td></td>
<td>573 K</td>
</tr>
<tr>
<td>17</td>
<td>6.3</td>
</tr>
<tr>
<td>20</td>
<td>5.4</td>
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<tr>
<td>28</td>
<td>6.2</td>
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<td>70</td>
<td>3.9</td>
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<tr>
<td>160</td>
<td>2.4</td>
</tr>
<tr>
<td>170</td>
<td>2.5</td>
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</table>

*a WHSV=8 h⁻¹.

carbenium ions at long TOS when the pores of the molecular sieves are blocked by carbonaceous compounds [12,16,45,46]. In Table 2 the coke contents of the samples after 6 h TOS are listed. It can be seen that the catalysts with Si/Al ratios of 160 and 170 contained only a very low amount of coke of less than 2 wt.% after reaction at 773 K. This amount should be too low for a blockage of the pores of H-ZSM-5 zeolites, since an amount of coke of ca. 8 wt.% is already necessary for the blockage of the pores of ferrierites [12,16], which have smaller pores than H-ZSM-5 zeolites [50]. The pseudomonomolecular mechanism with benzylic carbenium ions as active sites can therefore be excluded as an explanation for the high selectivity to isobutene obtained with the H-ZSM-5 zeolites with a low number of acid sites at 773 K.

However, Guisnet et al. also proposed tert-butyl carbenium ions as active sites, formed by the adsorption of isobutene on the protonic sites of the catalysts [46]. They proposed these active sites especially for ferrierites, since in this molecular sieve type diffusion of isobutene might be slow due to steric constraints so that isobutene molecules are retained inside the pores and transformed into active sites. Because of the larger dimension of the pores of H-ZSM-5 zeolites in comparison to ferrierites, this seems unlikely for MFI type molecular sieves. Secondly, if mainly tert-butyl carbenium ions were the active sites, the selectivity to isobutene should be only slightly dependent on the temperature and the conversion of n-butenes. It should be even more likely that a pseudomonomolecular mechanism involving tert-butyl carbenium ions operates at low temperatures, since the lower the temperature the slower the diffusion. Thus, more isobutene molecules should be retained at low reaction temperature and can therefore be transformed into active sites. Nevertheless, selectivities to isobutene between ca. 20 and nearly 90% were obtained in dependence on the reaction temperature and the conversion of n-butenes (Figs. 4 and 6). Based on these considerations, a change from the bimolecular to the monomolecular mechanism with increasing temperature seems much more likely than a change to a pseudomonomolecular one.

Assuming a change from the bimolecular to the monomolecular mechanism, also the decreasing conversion of n-butenes and the increasing yield of isobutene with increasing reaction temperature observed on the samples with Si/Al ratios of 160 and 170 is explainable. In Fig. 7, the yield of isobutene obtained with the samples with Si/Al ratios of 28 and 170 at 573, 673, and 773 K after 10 min TOS, respectively, is plotted as a function of the conversion of n-butenes. Furthermore, the thermodynamic limit for the yield of isobutene at each temperature in dependence on the conversion of n-butenes is shown by straight lines. From this figure it can be seen that there has to be a decrease in the conversion of n-butenes when a change takes place from the bimolecular to the monomolecular mechanism with increasing reaction temperature. Otherwise the higher yield of isobutene formed by the monomolecular mechanism in comparison to the bimolecular one would exceed the thermodynamic equilibrium concentration for isobutene. With a pseudomonomolecular mechanism, selectively producing isobutene without or nearly without by-products, such a drastic change in the conversion of n-butenes and the yield of isobutene would not be possible.

The reason for the different catalytic behaviour of H-ZSM-5 zeolites with low and high Si/Al ratios at high temperature is obviously related to the different number of acid sites. At a low number of acid sites the adsorption sites are more separated than at a high number so that the probability of a bimolecular reaction is less. The monomolecular reaction path becomes favoured with increasing temperature because dimerization of n-butenes is thermodynamically disfavoured at high temperature.

The formation of the different reaction products obtained under conditions when the transformation of n-butenes takes place mainly via the bimolecu-
lar mechanism (low temperature, high number of acid sites) can be explained by the scheme shown in Fig. 8. First, \(n\)-butenes dimerize to \(C_8\)-units. These are mainly cracked into propene and pentenes and to a minor part into isobutene as well as hexenes and ethene. Furthermore, the \(C_8\)-units can react to \(C_{12}\)-units, oligomers, and aromatics. Oligomers and aromatics are the precursors of coke. Aromatics were observed by Houzvicka et al. [31] when they investigated the skeletal isomerization of \(n\)-butenes to isobutene on H-ZSM-5 zeolites. Unfortunately, aromatics could not be detected by the GC column we used for our work.

It is likely that a part of the products formed by cracking of the \(C_8\)-units is transformed into nonenes and heptenes in consecutive reactions. The \(C_{12}\)-units can be cracked into hexenes, pentenes and heptenes as well as propene and nonenes. Furthermore, they can also react to oligomers, aromatics, and coke like the \(C_8\)-units. The transformation of alkenes into alkanes is not depicted in Fig. 8, since otherwise the scheme would be overcrowded. The formation of alkanes can be explained by hydrogen transfer to the respective alkenes during the formation of aromatics and coke [8,51].

The scheme in Fig. 9 is proposed in order to explain the formation of the different products observed under reaction conditions when the transformation of \(n\)-butenes takes place mainly via the monomolecular mechanism (high temperature combined with a low number of acid sites). The main reaction is the monomolecular isomerization of \(n\)-butenes to isobutene. Besides, some \(n\)-butene molecules dimerize to \(C_8\)-units. At high conversions of \(n\)-butenes, co-dimerization with isobutene molecules and dimerization of the last ones also takes place. The
consecutive reactions of the C₈-units are the same as mentioned above, except that probably no C₁₂-units are involved. Since the amount of ethene and propene detected was much higher than the amount of hexenes and pentenes, respectively, the last ones are likely to be partly transformed into oligomers, aromatics, and coke, too. Another possibility would be the cracking of hexenes into propene.

5. Conclusion

On H-ZSM-5 zeolites with a high number of acid sites (low Si/Al ratio) the isomerization of n-butenes to isobutene proceeds via the bimolecular mechanism independent of the reaction temperature. On H-ZSM-5 zeolites with a low number of acid sites the reaction mechanism changes from the bimolecular to the monomolecular one with increasing temperature.

Acknowledgements

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