

Comparative Study of the Catalytic Properties of ZSM-22 and ZSM-35/ Ferrierite Zeolites in the Skeletal Isomerization of 1-Butene

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The catalytic activities of the two catalysts ZSM-22 and ZSM-35 were compared in the skeletal isomerization of 1-butene. ZSM-22 demonstrated higher activity in 1-butene transformation, compared to that of ZSM-35. ZSM-35 was not selective to isobutene until non-selective acid sites had been poisoned by coke deposits, while ZSM-22 was selective already from the beginning. Information about the extent of coke formation was obtained by FTIR experiments and surface area measurements. ZSM-22 was more resistant towards coke formation, compared to that of ZSM-35. In order to obtain information about the reaction mechanism, 2,4,4-trimethyl-2-pentene and 1-octene were cracked over the catalysts. The selective mechanism for isobutene formation in the skeletal isomerization of 1-butene was most likely monomolecular. The bimolecular mechanism is not selective to isobutene, although it can contribute to the overall isobutene production. © 1998 Academic Press

1. INTRODUCTION

There has been an ever increasing interest in the skeletal isomerization of *n*-butenes over zeolites: from the industrial point of view, since isobutene can be used in the reaction with methanol to produce MTBE (methyl *tert*-butyl ether), and from the academic point of view as an intensive discussion has been going on whether the reaction proceeds through a monomolecular or a bimolecular reaction mechanism (1–5). The main problem with the monomolecular reaction mechanism is that this mechanism would require the formation of a highly energetically unfavourable primary carbenium ion intermediate. Despite this, there have recently been several papers regarding the reaction mechanism where the authors have been in favor of the monomolecular mechanism (3–5).

Although different types of zeolites have been investigated in the skeletal isomerization of 1-butene (6–13), there is still room for improvement, both in the activity of the catalysts, as well as in the selectivity to isobutene. The most promising catalysts for selective skeletal isomerization of 1-butene are 10-membered-ring molecular sieves (14).

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Production of isobutene is thermodynamically favored at low temperatures, as can be concluded from the thermodynamic equilibrium calculations presented in Fig. 1. These calculations were made using thermodynamic data from Ref. (15). In order to be able to use lower reaction temperatures, improvements in the shape selectivity of the catalysts are needed since dimerization of *n*-butene is also favored at lower temperatures.

In this paper we compare ZSM-22 and ZSM-35, two of the most promising catalysts for skeletal isomerization of 1-butene according to patents (16–18) and articles (1–2, 5–7, 19–26). Although both ZSM-22 and ZSM-35 have been thoroughly explored for skeletal isomerization it is difficult to directly compare the catalytic properties of ZSM-22 and ZSM-35 from previous publications, since different reaction conditions have been used.

ZSM-35 has a one-dimensional channel system of 10-membered-rings ($4.2 \times 5.4 \text{ \AA}$) and a one-dimensional channel system of eight-membered-rings ($3.5 \times 4.8 \text{ \AA}$). The two kinds of channel systems are perpendicularly intersected and therefore ZSM-35 contains spherical cavities with a size of about 6–7 Å (27). ZSM-22 consists of a one-dimensional, 10-membered-ring pore system with channel diameters of $4.5 \times 5.5 \text{ \AA}$ (28). Although the zeolite structures of ZSM-22 and ZSM-35 are rather different, the difference in the shape-selective properties might not be very large since it is difficult for butene molecules to enter the eight-membering channel system in ZSM-35 and its spherical cavities can be modified by the coke deposits. In fact, similar selectivity to isobutene was obtained in the isomerization experiments over deactivated ZSM-22 and ZSM-35.

2. EXPERIMENTAL

2.1. Preparation of the Catalysts

The ZSM-22 zeolite was synthesized using 1,6-diaminohexane (Fluka) as the organic template, Ludox AS-40 (Aldrich) as the silica source, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (Merck) as the aluminum source, and KOH (Merck) as the mineralizing agent according to the method used in Ref. (29). The ZSM-35 zeolite was synthesized using Pyrrolidine (Fluka)

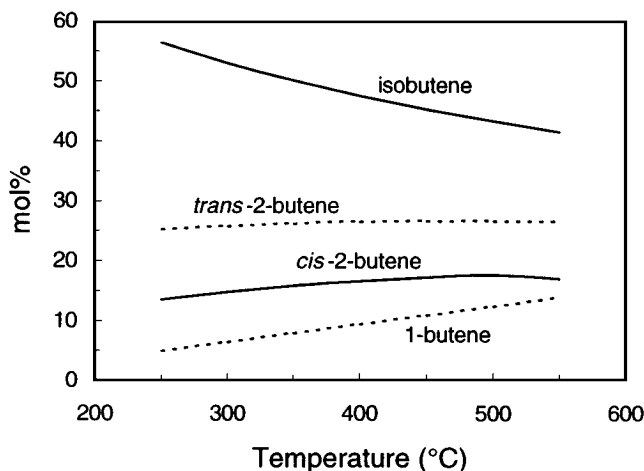


FIG. 1. The calculated thermodynamic distribution of butene isomers as a function of temperature at equilibrium.

as the organic template, Ludox AS-30 (Aldrich) as the silica source, NaAlO_2 (Riedel-de Haën) as the aluminum source, and NaOH (Merck) as the mineralizing agent using the method described in Ref. (30) with some modification.

Before calcination the zeolite powder was washed, dried, pressed, crushed, and finally sieved to 0.125–0.250 mm particle size. Calcination in order to remove the organic template was performed at 550°C in a flow of nitrogen for 6 h, followed by air for an additional 10 h. ZSM-22 and ZSM-35 zeolites were ion-exchanged for 48 h in a 1 M NH_4Cl solution in order to remove any potassium or sodium remaining from the synthesis. The ion-exchanged zeolites were washed free of chloride ions and dried for 12 h at 80°C. The proton forms of ZSM-22 and ZSM-35 were obtained after NH_4^+ ions had been decomposed in a calcination step performed in the same conditions as the removal of the organic template. The calcination steps were performed in high flows (200 ml/min per gram of catalyst) in order to prevent dealumination of the zeolite structures, since ZSM-22 zeolites calcined under limited heat and mass transfer conditions have been found to exhibit low selectivity to isobutene (26).

2.2. Characterization of the Zeolites

The structure and phase purity of the synthesized zeolites were determined by X-ray powder diffraction (XRD) using $\text{Cu K}\alpha$ radiation. The XRD patterns of the synthesized zeolites were similar to those previously reported in the literature for ZSM-22 (6) and ZSM-35 (11). The bulk Si/Al ratio of the zeolites was measured by X-ray fluorescence (XRF) and found to be 53 for the ZSM-22 zeolite and 12 for the ZSM-35 zeolite. The crystal size of the zeolites was determined using scanning electron microscopy (SEM). The average width of the needle shaped ZSM-22 crystals was found to be 0.4 μm and the length was 2.9 μm . The corresponding size of the rod shaped ZSM-35 crystals was approximately 1.6 μm and 5.2 μm .

Acid sites of the zeolites were characterized by a FTIR spectrometer (ATI Mattson infinity spectrometer) equipped with a Mercury Cadmium Telluride (MCT) detector. The *in situ* diffusion reflectance infrared Fourier transformed (DRIFT) measurements of adsorbed pyridine on a 1/1 (weight ratio) mixture of zeolite and KBr powder were performed in a diffuse reflectance accessory equipped with a standard controlled environmental chamber (Spectra-Tech, model 0030-103). The zeolites were evacuated in vacuum (10^{-5} atm) at 500°C for 2 h before pyridine adsorption at 100°C for 30 min. The zeolite samples were kept at 100°C in a flow of helium for 1 h to allow the pyridine to penetrate the samples. The zeolites were evacuated at 200°C for 2 h before the FTIR spectra were recorded at ambient temperature. Acid sites in the fresh and deactivated as well as the ion-exchanged (proton form) zeolites were characterized by means of FTIR spectroscopy.

Surface areas of the zeolites were determined by nitrogen adsorption (Carlo Erba Instruments). Zeolite samples of 0.2 g were evacuated at 300°C for 3 h before the surface area measurements. The Dubinin method was used in the calculation of the surface areas. Surface areas of fresh and deactivated catalysts were measured in order to obtain information about the extent of pore blocking by the coke deposits.

2.3. Catalyst Testing

The catalytic activities of the synthesized zeolites in the isomerization of 1-butene (99.0% purity, AGA) to isobutene were studied in a micro fixed-bed reactor system at near atmospheric pressure (1.1 atm). The amount of catalyst was varied between 0.05 and 0.5 g and the flow of 1-butene between 21 and 55 ml/min in order to obtain the different weight hourly space velocities (WHSV) used in the experiments. The reactant was diluted with a 0–55 ml/min flow of nitrogen (99.999% purity, AGA) to obtain different partial pressures of 1-butene. The products from the reactor were analyzed by a gas chromatograph (Varian 3700) equipped with a flame-ionization detector (FID). A capillary column (50 m \times 0.32 mm ID fused-silica PLOT Al_2O_3 -KCL) was used for product separation.

In the calculations the three *n*-butene isomers 1-butene, *cis*-2-butene, and *trans*-2-butene were considered reactants, thus conversion, yield, and selectivity were defined as follows:

$$\text{Conversion} = \frac{(\text{1-butene})_{\text{feed}} - (n\text{-butene})_{\text{effluent}}}{(\text{1-butene})_{\text{feed}}}$$

$$\text{Yield} = \frac{(\text{isobutene})_{\text{effluent}}}{(\text{1-butene})_{\text{feed}}}$$

$$\text{Selectivity} = \frac{(\text{isobutene})_{\text{effluent}}}{(\text{1-butene})_{\text{feed}} - (n\text{-butene})_{\text{effluent}}}$$

3. RESULTS AND DISCUSSION

3.1. Effect of Ion-Exchange on the Catalytic Properties of the Zeolites

Acid sites were characterized using FTIR of adsorbed pyridine. Spectra recorded over the as-synthesized and proton ion-exchanged zeolites are compared in Fig. 2. The band at 1548 cm^{-1} which is characteristic for pyridine adsorbed on Brønsted acid sites and the band at 1453 cm^{-1} associated with pyridine adsorbed on Lewis acid sites were present in the ion-exchanged zeolites as well as in the as-synthesized zeolites. The band at 1491 cm^{-1} is usually associated with pyridine adsorbed on both Lewis and Brønsted acid sites. These experiments demonstrated that Brønsted acid sites were present in the as-synthesized zeolites even before any ion-exchange procedures had been performed.

The as-synthesized and proton ion-exchanged zeolites were compared in the transformation of 1-butene. The results from these experiments are presented in Table 1. These experiments indicate that there was no improvement in the activity of the catalysts in 1-butene isomerization after ion-exchanging the zeolites with NH_4^+ and subsequent calcination. The reason for this might be that the reaction was diffusion limited since 1-butene is a very reactive molecule and the pores in the zeolites are of molecular size. Even though the number of acid sites increased after ion-exchanging the zeolites, the activity was unchanged since the rate limiting step was the transportation of the molecules to the active sites. Internal pore diffusion was most likely the reason for the diffusion resistance since the external film diffusion was negligible because of the high flows used in the exper-

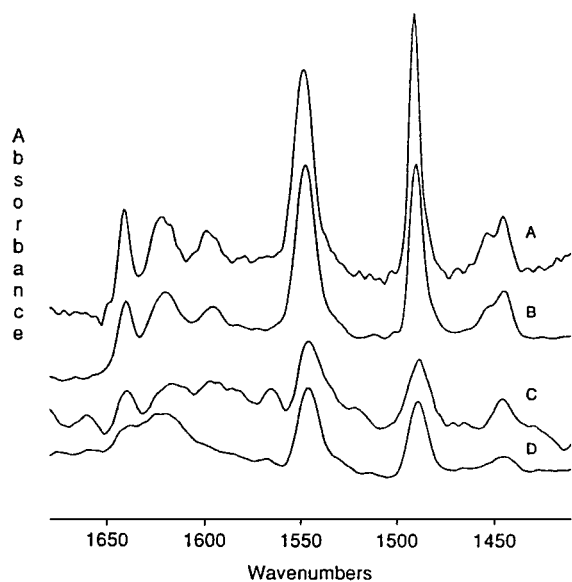


FIG. 2. FTIR spectra of adsorbed pyridine on (A) as synthesized ZSM-22, (B) ion-exchanged ZSM-22, (C) as-synthesized ZSM-35, and (D) ion-exchanged ZSM-35.

TABLE 1

Differences between Proton and As-Synthesized ZSM-22 and ZSM-35 Zeolites

Catalyst	Ion-exchange	WHSV (h^{-1})	Conversion (mol%)	Yield of isobutene (mol%)	Selectivity to isobutene (mol%)
ZSM-22	No	150	41.8	33.0	79.0
ZSM-22	Yes	150	40.4	31.7	78.3
ZSM-35	No	10	55.8	28.5	51.0
ZSM-35	Yes	10	53.5	25.6	49.7

Note. Reaction conditions: temperature = 400°C ; partial pressure of 1-butene = 0.5 atm; TOS = 10 min.

iments. An indication that the external diffusion was negligible was obtained from the double-bond isomerization, which is faster than the skeletal isomerization, dimerization, or cracking reactions. The ratios between 1-butene, *cis*-2-butene, and *trans*-2-butene were approximately the same in all the experiments and fairly close to the calculated equilibrium values, although the ratio between *trans*-2-butene and *cis*-2-butene exceeded the value expected from the thermodynamic equilibrium calculations.

The reason for the lower activity of ZSM-35, compared to that of ZSM-22 in 1-butene isomerization could also be because of internal pore diffusion limitations. According to the Si/Al ratio ZSM-35 could be expected to have higher activity. If the internal pore diffusion is slow the crystal size might have a profound effect on the catalytic activity since most of the 1-butene transformation would occur close to the external surface. If internal pore diffusion is the rate-limiting step the activity would improve with decreasing crystal size. This might explain why in our investigation ZSM-22 was more active in skeletal isomerization of 1-butene, since the average crystal size of ZSM-22 was smaller, compared to that of ZSM-35. For comparison we also made some experiments with the less reactive molecule *n*-butane. In these experiments there was in fact an improvement in the catalytic activity after ion-exchanging the zeolites, and ZSM-35 was more active, compared to that of ZSM-22.

Since there was no improvement in the activity in skeletal isomerization of 1-butene after ion-exchanging the zeolites, the as-synthesized zeolites were used in all of the following experiments.

3.2. Effect of Time on Stream (TOS) on the Activity and Selectivity of ZSM-22 and ZSM-35

In the 1-butene skeletal isomerization experiments the catalysts are modified by coke deposits. The surface areas of fresh catalysts and catalysts deactivated at 400°C for 20 h were measured in order to obtain information about the extent of pore blocking by the coke deposits. These

TABLE 2

Differences between Fresh and Deactivated Catalysts

Catalyst	TOS (min)	Surface area (m ² /g)	Conversion (mol%)	Yield of isobutene (mol%)	Selectivity to isobutene (mol%)
ZSM-22	1	255.7	49.4	36.9	74.7
ZSM-22	1200	92.2	29.4	25.7	87.3
ZSM-35	1	400.6	16.7	8.8	52.6
ZSM-35	1200	39.6	0.0	0.0	—

Note. Reaction conditions: temperature = 400°C; WHSV = 150 h⁻¹; partial pressure of 1-butene = 0.5 atm.

surface area measurements demonstrated that there was a substantial decrease in the surface area between fresh and deactivated catalysts. The results from the surface area experiments are presented in Table 2, together with conversion, yield of isobutene, and selectivity to isobutene for both fresh and deactivated catalysts. Deactivated ZSM-35 catalysts did not show any activity at all when the WHSV of 1-butene was 150 h⁻¹, but it was active at lower WHSV. The decrease in the surface area was higher for ZSM-35, compared to ZSM-22. The reason for this might be that coke deposits are formed more easily inside the spherical cavities of ZSM-35 than in the one-dimensional channel system of ZSM-22.

FTIR spectra of adsorbed pyridine over the fresh and deactivated are compared in Fig. 3. As can be seen the number of acid sites accessible for pyridine decreased substantially for the deactivated catalysts, compared to the fresh catalysts. The activity of the deactivated catalysts was found to be restored after burning off the coke deposits.

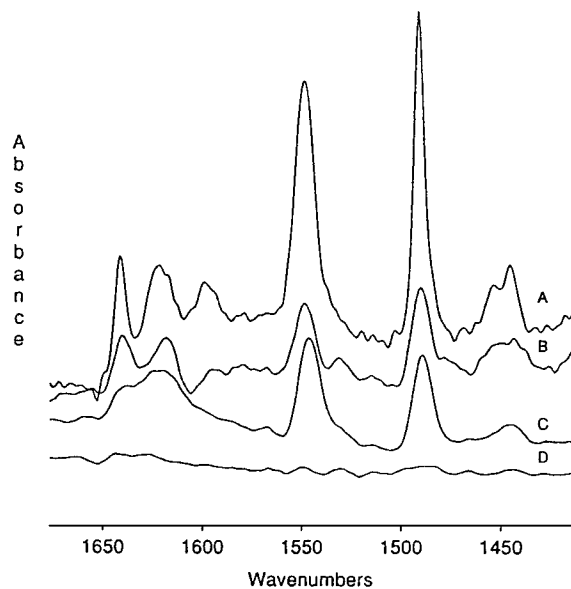


FIG. 3. FTIR spectra of adsorbed pyridine on (A) fresh ZSM-22, (B) deactivated ZSM-22, (C) fresh ZSM-35, and (D) deactivated ZSM-35.

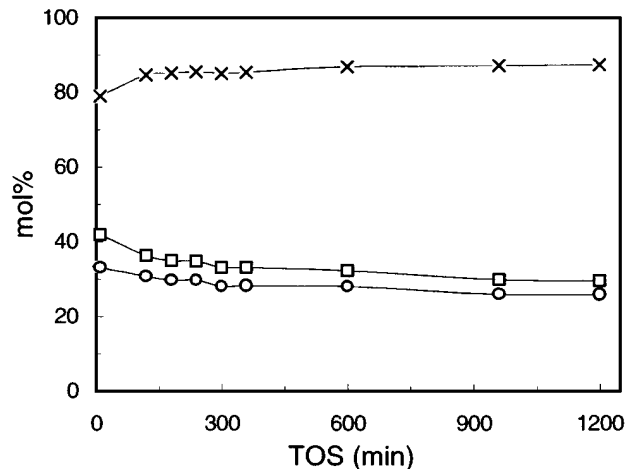


FIG. 4. Conversion (□), yield of isobutene (o), and selectivity to isobutene (x) over ZSM-22 as a function of TOS. Reaction conditions: temperature = 400°C; partial pressure of 1-butene = 0.5 atm; WHSV = 150 h⁻¹.

The main difference between ZSM-22 and ZSM-35 in the 1-butene isomerization experiments was observed in the selectivity to isobutene as a function of time on stream (TOS). Results from deactivation experiments over ZSM-22 and ZSM-35 zeolites are presented in Figs. 4 and 5, respectively. ZSM-35 demonstrated high selectivity to isobutene after the nonselective acid sites had been poisoned by coke deposits, while ZSM-22 showed high selectivity already from the beginning. It can be concluded from the figures that the selectivity to isobutene over deactivated ZSM-22 and ZSM-35 obtained the same value, but ZSM-22 was more active, compared to ZSM-35 since the contact time needed in order to acquire the same level of conversion and yield of

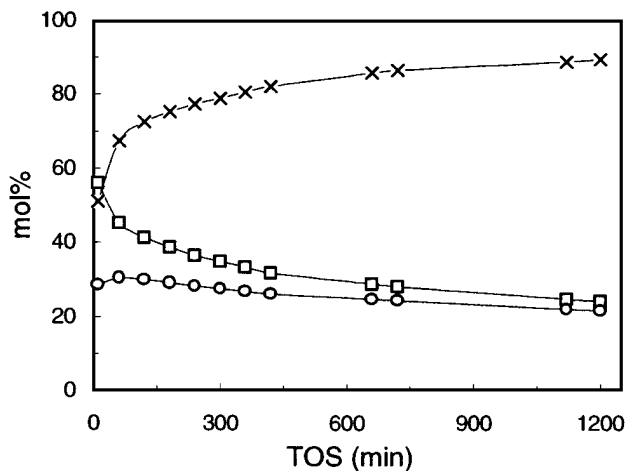


FIG. 5. Conversion (□), yield of isobutene (o), and selectivity to isobutene (x) over ZSM-35 as a function of TOS. Reaction conditions: temperature = 400°C; partial pressure of 1-butene = 0.5 atm; WHSV = 10 h⁻¹.

TABLE 3
Effect of TOS on the Product Selectivity over ZSM-22
and ZSM-35 Zeolites

Catalyst	ZSM-22		ZSM-35	
	TOS (min)	10	660	10
WHSV (h^{-1})	150	60	20	3
Selectivity (mol%)				
Ethene	0.5	0.2	3.3	0.3
Propane	0.2	0.1	1.2	0.1
Propene	9.0	6.9	22.2	7.6
Isobutane	0.3	0.2	0.6	0.5
<i>n</i> -Butane	2.6	2.6	3.3	0.8
Isobutene	79.0	80.1	53.2	79.1
Pentenes	5.2	4.5	10.2	6.7
Hexenes	0.4	0.5	1.3	0.4
Heptenes	0.3	0.5	1.3	0.4
Octenes	2.5	4.3	3.0	4.1
Yield of isobutene	33.0	34.4	21.6	33.4
Conversion	41.8	43.0	40.6	42.2

Note. Reaction conditions: temperature = 400°C; partial pressure of 1-butene = 0.5 atm.

isobutene was only 1/15 of that needed for ZSM-35. Several papers have been published about the positive effect of coke on the selectivity to isobutene over ZSM-35 (2, 20–22). When the effect of deactivation is evaluated, similar conversion should be used since the selectivity to isobutene also improved when the WHSV of 1-butene was increased and conversion decreased. Even if fresh and deactivated ZSM-35 catalysts are evaluated at similar conversions, as in Table 3, it is evident that there is a substantial increase in the selectivity to isobutene because of changes in the shape-selective properties of the zeolite caused by the

coke deposits. It was found that the selectivity to isobutene increased mainly during the first hours of TOS. The selectivity increased from 53 to 73% over ZSM-35 during the first 2 h when the conversion was kept constant by changing the WHSV, but only by 7% during the next 14 h. There was also an improvement in the selectivity to isobutene over ZSM-22 because of coke deposits, but the selectivity increased only by 2% during 20 h of TOS. Active sites on the outer surface of the zeolite might be poisoned, making the zeolite more shape-selective. Carbon deposits might poison preferentially stronger Brønsted acid sites known to induce dimerization reactions. Carbonaceous deposits can fill irregularities in the zeolite lattice, modifying the space inside the zeolite pores. In fact, coke deposits inside the cavities of ZSM-35 were most likely needed in order to receive high selectivity to isobutene. On the other hand, since ZSM-22 does not contain any cavities because of the one-dimensional channel system, the modifications by the coke deposits were not as dramatic as for ZSM-35. The difference in selectivity between ZSM-22 and ZSM-35 has previously been compared by Mooiweer *et al.* (19) and, according to their results, ZSM-35 demonstrated a much higher selectivity to isobutene than ZSM-22. The discrepancies between this paper and Ref. (19) might be in the quality of the ZSM-22 catalyst sample and the reaction conditions used. Since shape-selectivity is required in order to obtain high selectivity to isobutene in skeletal isomerization of 1-butene the quality of the zeolite sample is of great importance. The quality of the zeolite sample depends upon synthesis parameters, type and purity of reactants, and postsynthesis treatments.

The reaction scheme in Fig. 6 is proposed in order to explain the product distribution in Table 3. Since the ratio

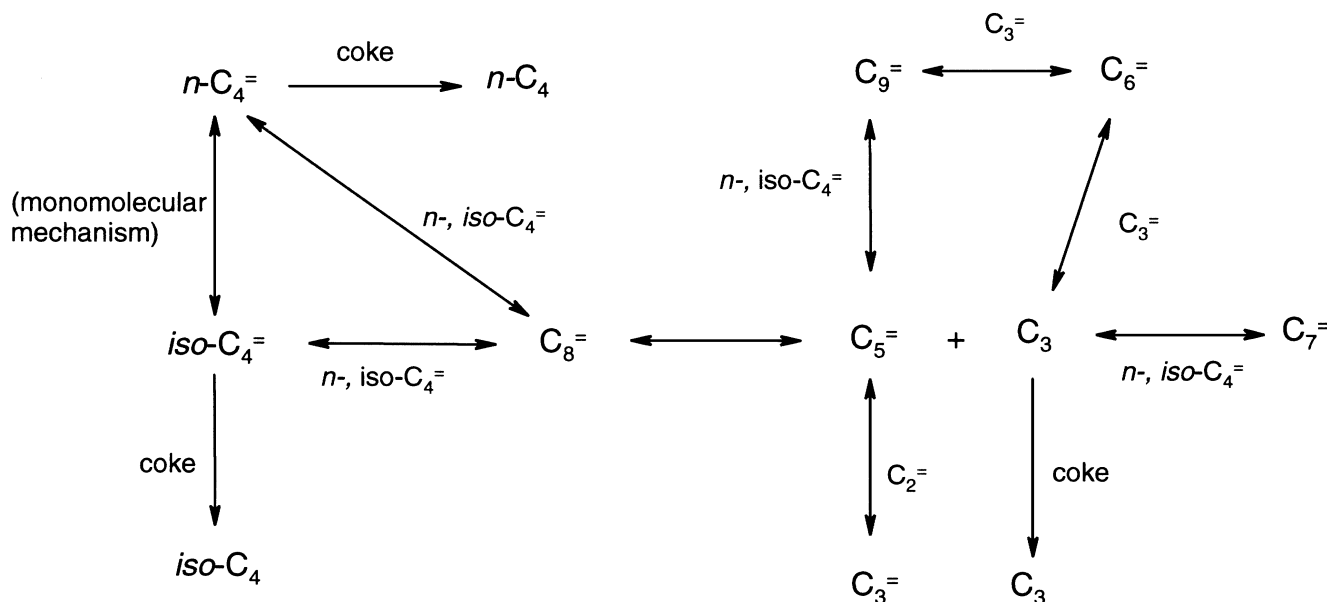


FIG. 6. Proposed reaction scheme to explain the obtained products.

between propene and pentene was not one, as expected from the direct cracking of octenes, the formation of nonenes (C_9^-) are included in Fig. 6 in order to explain the excess formation of propene. Another explanation could be that propene was less reactive in the coke formation. As the catalysts became deactivated the ratio between propene and pentene became closer to one because of the improvements in the shape-selective properties of the zeolites. Saturated hydrocarbons were produced mainly because of the hydrogen transfer reactions in coke formation. Because the rate of coke formation over ZSM-35 was lower for the deactivated catalyst, compared to the fresh catalyst, the selectivity to propane, isobutane, and *n*-butane reduced with TOS. Since the rate of coke formation was higher on fresh catalysts, deactivated catalysts were used in all of the following experiments.

3.3. Cracking of 2,4,4-Trimethyl-2-Pentene (TMP) and 1-Octene over ZSM-22 and ZSM-35

Two different mechanisms, a monomolecular and a bimolecular, have been proposed in the literature for the formation of isobutene (1–5). The different steps in the monomolecular mechanism are given in Fig. 7. This mechanism requires a highly energetically and thermodynamically unfavourable ring opening to form a primary carbenium ion as an intermediate and has therefore been considered to be too slow in order to explain the high rate of isobutene formation in skeletal isomerization of *n*-butene. On the other hand, the monomolecular reaction mechanism could explain the high selectivity to isobutene, if bimolecular reactions were inhibited by the shape-selective properties of the zeolites. A “pseudo-monomolecular” mechanism has also been proposed in the literature (2). According to this mechanism the active sites would be the coke, instead of the Brønsted acid sites and would not therefore require a primary carbenium ion. The problem with “pseudo-monomolecular” mechanism is to explain the

high selectivity to isobutene received after the very short TOS over zeolites with one-dimensional channels systems such as ZSM-22.

The other proposed reaction mechanisms are bimolecular. The dimerization, isomerization, and cracking scheme for the butene isomers is given in Fig. 8. The rate of A isomerization (methyl shift) is faster than B isomerization (chain branching), while the rate of the dimerization/cracking steps is decreasing as follows: A cracking (tertiary carbenium ions) > B cracking (secondary and tertiary carbenium ions) > C cracking (secondary carbenium ions). If isobutene was only produced through a bimolecular reaction mechanism, the problem would be to explain the high isobutene selectivity observed in the skeletal isomerization of 1-butene since the main by-products propene and pentene are also produced through bimolecular reactions.

In order to discriminate between the monomolecular and bimolecular mechanism, an attempt was made to obtain information about the selectivity of the bimolecular mechanisms through cracking of 2,4,4-trimethyl-2-pentene (TMP) and 1-octene. Results from these experiments are presented in Table 4.

1-Octene is not directly produced in dimerization of *n*-butene since this would require a primary carbenium ion and therefore be substantially slower than the A, B, and C dimerization steps in Fig. 8. Since direct cracking of 1-octene also would require a primary carbenium ion, most of the cracking occurred after the skeletal isomerization of 1-octene. Consequently only small amounts of ethene and hexene were observed in the 1-octene cracking experiments. Because of the skeletal isomerization, most of the different octene isomers were detected in the product stream, in addition to butene, propene, and pentene from the cracking reactions. Cracking of 1-octene was not very selective to isobutene. Less than half the products from the cracking reactions were butene isomers. The received product distribution is close to that expected from the cracking

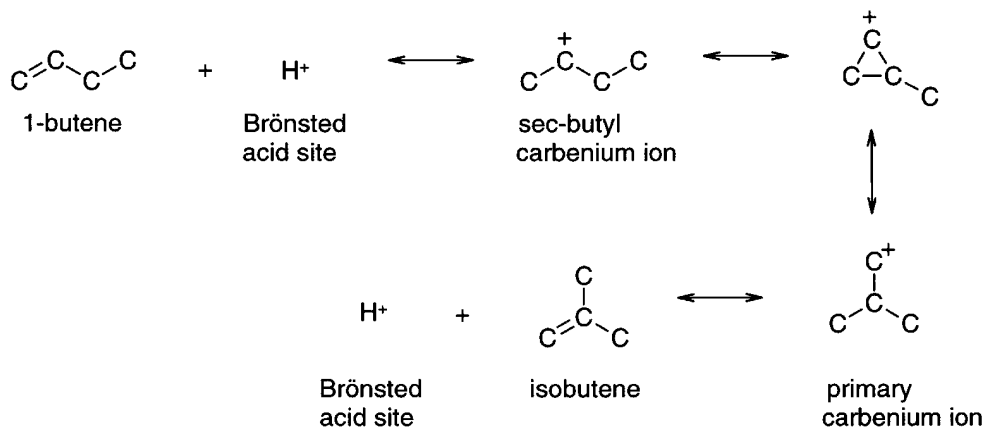


FIG. 7. The monomolecular reaction scheme in skeletal isomerization of 1-butene.

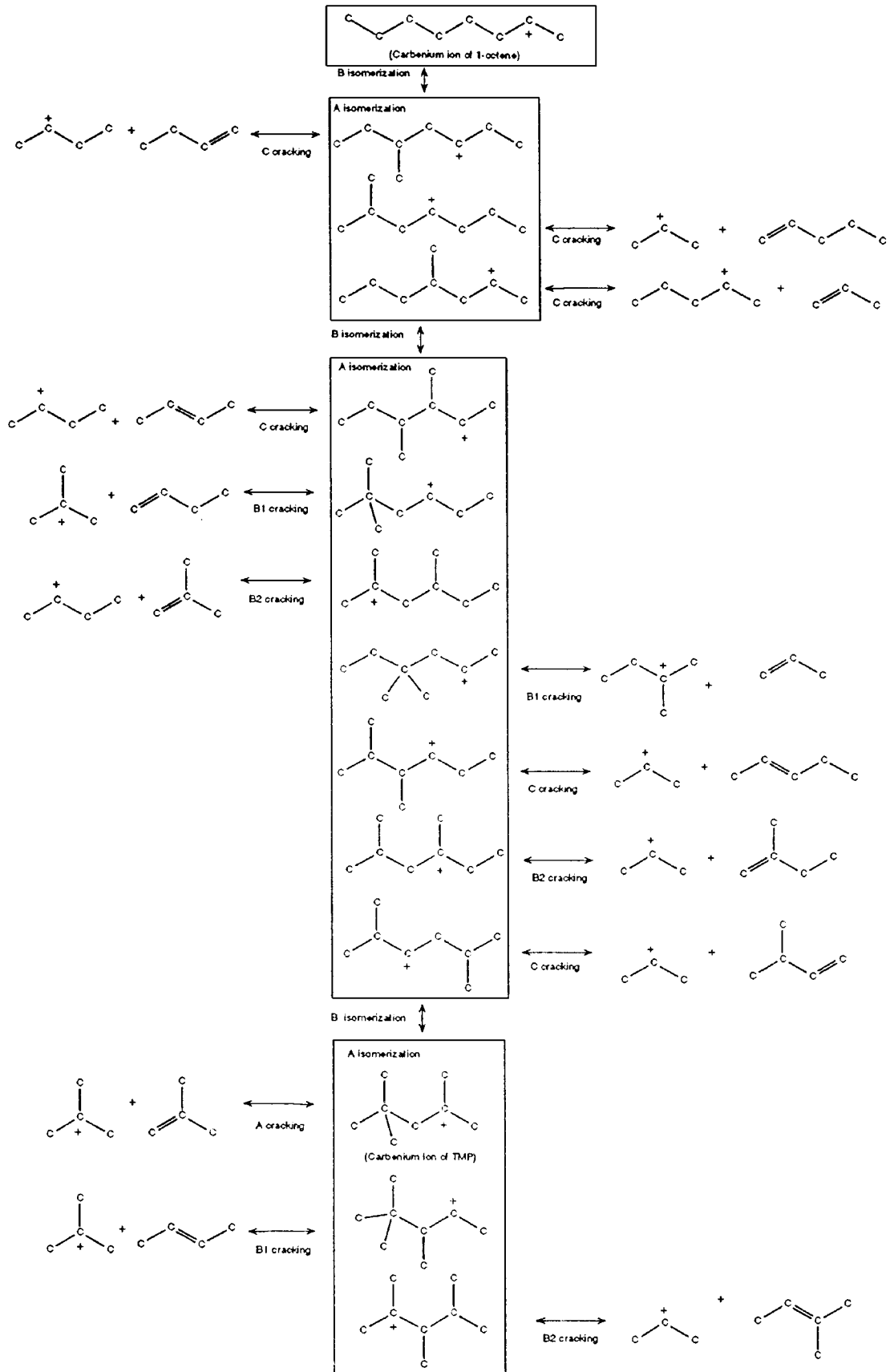


FIG. 8. The dimerization, isomerization, and cracking scheme for the butene isomers.

TABLE 4

Selectivity to Different Products when 1-Octene and 2,4,4-Trimethyl-2-Pentene Were Cracked over Deactivated ZSM-22 and ZSM-35

Reactant	TMP		1-Octene	
	ZSM-22	ZSM-35	ZSM-22	ZSM-35
Selectivity (mol%)				
Propene	2.9	1.3	27.3	27.6
<i>trans</i> -2-Butene	9.4	4.3	11.1	10.2
1-Butene	5.2	2.4	6.6	6.1
Isobutene	72.5	87.2	18.2	21.4
<i>cis</i> -2-Butene	8.0	3.7	8.1	7.0
Pentenes	2.0	1.1	27.2	27.0

Note. Temperature = 400°C.

scheme in Fig. 8, if cracking takes place before isomerization to TMP molecules. The number of cracking reactions producing propene and pentene would then be higher than the cracking reactions producing butene isomers. From the cracking of 1-octene it is possible to exclude that the selective mechanism in skeletal isomerization of 1-butene to isobutene would be: n -butene + n -butene \rightarrow octenes \rightarrow isobutene + n -butene. According to the 1-octene cracking experiments, the highest expected selectivity to isobutene for this bimolecular reaction mechanism would be approximately 27%, while on the other hand, over 90% selectivity was observed in the skeletal isomerization of 1-butene. The cracking rate of 1-octene was also too slow to explain the high production rate of isobutene in skeletal isomerization of 1-butene.

Cracking of TMP produced mostly isobutene, since A cracking was faster than both B2 cracking and B isomerization. Isobutene exceeds the value predicted by the thermodynamic calculations because isobutene (A cracking) was kinetically favored over the other butene isomers (B and C cracking) and the equilibrium was approached from the opposite side, compared to monomolecular skele-

tal isomerization of 1-butene. In dimerization of n -butene, TMP would most likely be produced in a reaction between isobutene and *trans*-2-butene or *cis*-2-butene as described in Fig. 9.

Because the double-bond isomerization is fast, the equilibrium between 1-butene, *trans*-2-butene, and *cis*-2-butene is established rapidly and at 400°C only 30% of n -butene is left as 1-butene. Consequently, the majority of the dimerization reactions between isobutene (as a tertiary carbenium ion) and n -butene would proceed according to the mechanism in Fig. 9. In order to receive high selectivity to TMP, the B1 dimerization in Fig. 8 would also have to be faster than B2 dimerization. If this were the case, isobutene would be produced mainly through cracking of TMP while the by-products, propene and pentenes, would be produced in dimerization between isobutene and 1-butene and subsequent cracking of the dimers. TMP molecules have been considered to be too large to be formed inside channels of 10-membered-ring zeolites (4). On the other hand, the cracking rate of TMP was much higher, compared to 1-octene. This indicates that TMP can reach the active sites in the zeolites.

Although it might be difficult to explain a selectivity of over 90% with a bimolecular mechanism, this mechanism could still contribute to the overall isobutene production.

3.4. Effect of Temperature, WHSV of 1-Butene, and Partial Pressure of 1-Butene

The relative reaction rate between a monomolecular and a bimolecular mechanism should also depend on the reaction conditions. The changes in the product selectivity over ZSM-35 as a function of WHSV, partial pressures of 1-butene, and temperature are presented in Table 5. The changes in the product distribution over ZSM-22 as a result of WHSV, partial pressure of 1-butene, and temperature were similar to those of ZSM-35.

Results from 1-butene isomerization experiments over ZSM-35 using different WHSV are presented in Fig. 10.

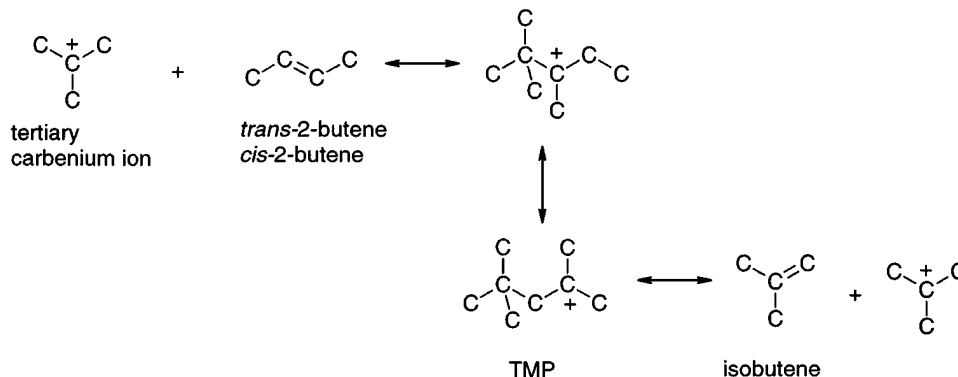


FIG. 9. Reaction mechanism for TMP formation and subsequent cracking to isobutene.

TABLE 5

Effect of WHSV, Partial Pressure of 1-Butene, and Temperature on the Product Distribution over Deactivated ZSM-35

	WHSV		Partial pressure		Temperature	
	3	30	5	10	3	10
WHSV (h^{-1})	3	30	5	10	3	10
Pressure (atm)	0.5	0.5	0.5	1.0	0.5	0.5
Temperature ($^{\circ}\text{C}$)	400	400	400	400	350	500
<i>Selectivity (mol%)</i>						
Ethene	0.3	0.0	0.2	0.3	0.1	0.4
Propane	0.1	0.1	0.1	0.1	0.1	0.1
Propene	7.6	2.3	6.0	8.8	5.8	2.8
Isobutane	0.5	0.2	0.4	0.6	0.5	0.4
<i>n</i> -Butane	0.8	0.4	0.7	1.3	1.2	0.3
Isobutene	79.1	94.5	83.7	72.3	75.5	93.7
Pentenenes	6.7	1.6	5.0	7.5	5.3	2.0
Hexenes	0.4	0.0	0.2	0.8	0.6	0.3
Heptenes	0.4	0.0	0.1	1.0	0.5	0.0
Octenes	4.1	0.9	3.6	7.3	10.4	0.0
Yield of isobutene	33.4	11.1	31.6	28.1	24.1	26.1
Conversion	42.2	11.7	37.7	38.8	32.0	28.0

Isobutene is a very reactive molecule since it is reacting according to the A or B mechanisms in the dimerization reactions. Therefore it easily reacts in consecutive reactions, reducing the selectivity to isobutene, especially at low WHSV. This was evident when the thermodynamic equilibrium between the butene isomers was established, since then the main reactions were dimerization and subsequent cracking of the dimers, increasing the selectivity to the by-products propene and pentenes.

Figure 11 presents results from experiments using different partial pressures of 1-butene over deactivated ZSM-35. The conversion increased with increasing partial pressures

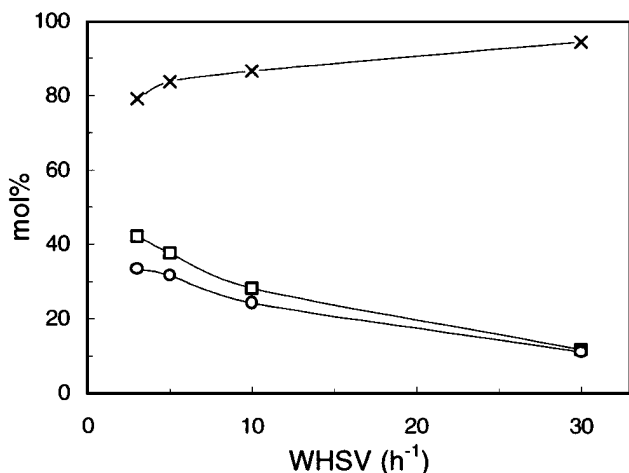


FIG. 10. Conversion (□), yield of isobutene (o), and selectivity to isobutene (x) over the deactivated ZSM-35 catalyst as a function of WHSV. Reaction conditions: temperature = 400°C ; partial pressure of 1-butene = 0.5 atm.

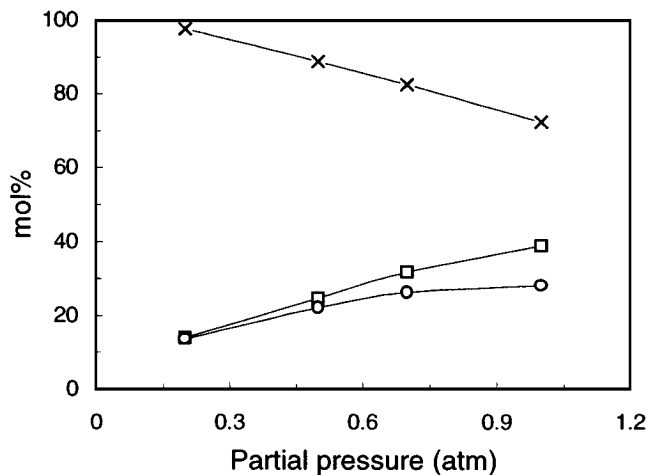


FIG. 11. Conversion (□), Yield of isobutene (o), and selectivity to isobutene (x) over the deactivated ZSM-35 catalyst as a function of partial pressure of 1-butene. Reaction conditions: temperature = 400°C ; WHSV = 10 h^{-1} .

of 1-butene because of dimerization reactions. Since dimerization reactions were favored over cracking reactions at high partial pressures of 1-butene, an increasing selectivity to hexenes, heptenes, and especially octenes was observed with increasing partial pressures of 1-butene. The selectivity to propene and pentenes increased at the expense of isobutene with increasing partial pressure of 1-butene because of increasing dimerization between butene isomers and subsequent cracking to propene and pentenes. An indication that isobutene might be partly produced through dimerization and cracking reactions can be found in Fig. 11, since the yield of isobutene increased with increasing partial pressure of 1-butene.

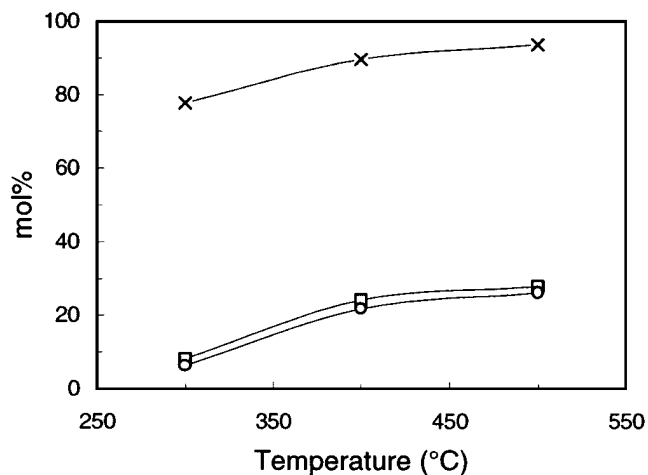


FIG. 12. Conversion (□), yield of isobutene (o), and selectivity to isobutene (x) over the deactivated ZSM-35 catalyst as a function of temperature. Reaction conditions: partial pressure of 1-butene = 0.5 atm; WHSV = 10 h^{-1} .

Results from experiments using different temperatures over ZSM-35 are presented in Fig. 12. The selectivity to isobutene increased with increasing temperature, since dimerization reactions became less favored, compared to cracking reactions. Especially, the selectivity to octene isomers was greatly reduced at high temperatures.

4. CONCLUSIONS

ZSM-22 and ZSM-35 are both promising catalysts for skeletal isomerization of 1-butene, as can be concluded from the results presented in this paper. The selective reaction mechanism producing isobutene was most likely monomolecular over both the catalysts, since cracking of 1-octene was not selective to isobutene. The selectivity to isobutene increased with increasing temperature, decreasing partial pressure of 1-butene, and increasing WHSV of 1-butene for both catalysts, which also supports the monomolecular mechanism. ZSM-22 was more selective to isobutene, compared to that of ZSM-35 during the first hours of TOS, while the deactivated catalysts demonstrated similar selectivity. Both ZSM-22 and ZSM-35 can be used as synthesized without any ion-exchanging steps, since there was no improvement in the activity in 1-butene transformation after the zeolites had been ion-exchanged in order to increase the number of Brønsted acid sites. The main advantages of using ZSM-22 would be that approximately 15 times higher WHSV can be used and the total selectivity to isobutene is higher over ZSM-22, since no deactivation is needed in order to get high selectivity to isobutene.

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