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The Shape Selectivity in the Skeletal Isomerisation of *n*-Butene to Isobutene

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This study explores several microporous materials to identify the most suitable structures for a skeletal isomerisation of *n*-butene to isobutene. The 8-membered ring zeolites are not suitable for skeletal isomerisation of *n*-butene to isobutene because their pore diameter does not allow diffusion of isobutene. The 12-membered ring zeolites do not suppress the formation of carbonaceous deposits and their pores are quickly blocked. The most suitable materials are the catalysts with a pore diameter between 4 and 5.5 Å. This is the range as met in the 10-membered ring molecular sieves. These materials allow an isobutene diffusion but they suppress the formation of dimers (and oligomers) which are intermediates leading to by-products.

I. INTRODUCTION

In the recent years, world demand for isobutene has increased continually. This is because there are various applications of isobutene e.g., in the production of methyl tertiary-butyl ether (MTBE). Isobutene can be conveniently produced by skeletal isomerisation of *n*-butene, a reaction which is the subject of this study. The isobutene yield on the best contemporary catalysts is only about 40% as a result of thermodynamical limit at high reaction temperature. This low yield stimulates a further search for novel catalysts.

A test of a broad range of oxidic materials revealed that only alumina and WO_3 (1, 2) were suitable materials. The other oxides possessed only a low activity. Activity of aluminas can be enhanced by treatment with halogens, preferentially by chlorination or bromination (3). Such materials reached satisfactory selectivity but they deactivated quickly. Problems appeared also when phosphoric acid on silica (H_3PO_4/SiO_2) was used. Although this catalyst was very selective it deactivated even faster than halogenated aluminas (4).

The use of microporous materials with proper acidity and channel dimensions and structure has lead to a breakthrough in skeletal isomerisation of *n*-butene. The stability and the selectivity of these catalysts appeared to be very high; the yield of isobutene reached was about 40% in the temperature range 620–770 K. Actually, all really successful catalysts used for this reaction so far were the 10-membered ring molecular sieves. Ferrierite (5), consisting of a 10 × 8-membered ring channel system, showed the best stability and activity. The unidimensional channel materials like SAPO 11 (4), MnAPO 11 (6), ZSM-22 (7), theta-1, and ZSM-23 (8) showed similar properties. Selected examples from the patent literature offer the same picture (9).

All above-mentioned materials, which appeared to be efficient, stable catalysts, contain moderate or strong Brønsted acid sites. These sites have been clearly identified as active sites for skeletal isomerisation of *n*-butene (4). While there is a wide consensus now about the character of the active site, general agreement about the mechanism of reaction has not been reached yet. High selectivity and stability of ferrierite were explained by its unique structure (10). It was argued that *n*-butene dimerised to octene which was sitting trapped in the place of intersection of 10- and 8-membered ring channels. Cracking of this “immobilised” octene was assumed to proceed selectively to isobutene (5, 10).

Since the other selective zeolites do not contain any cavities or intersections and they are still as active and selective as ferrierite, other mechanisms had to be suggested. Strong arguments exist that skeletal isomerisation of *n*-butene to isobutene runs via a monomolecular mechanism, probably via an alkoxyintermediate (11). This idea was supported by the fact that cracking of all primary dimers, the assumed intermediates in the above-mentioned mechanism of skeletal isomerisation, was found to be very unselective (12). The results indicated that the “bimolecular” mechanism via octenes was responsible mainly for undesired by-products.

High selectivity and catalytic stability of 10-membered ring zeolites can be explained by “shape selectivity” of these materials. While isobutene formation via monomolecular

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mechanism can still proceed in the 10-membered ring channels, dimerisation to dimethylhexenes, and especially to trimethylpentenes, is restricted—if not completely inhibited—in the confined space. Catalysts are selective, since intermediates leading to by-products cannot be formed freely (12). Polymerisation of *n*-butene starting via dimers leads to a blockage of pores and deactivation of catalysts. Since polymerisation inside channels is also restricted, the catalyst deactivation is slow.

Some papers (4–8) and broad patent literature (9) already contain information which indicates that some microporous materials can be active, selective, and stable catalysts, but only when they posses a certain structure. This study explores several microporous materials to identify the most suitable structures for a skeletal isomerisation of *n*-butene to isobutene.

II. EXPERIMENTAL

Zeolites Omega (Si/Al = 30) and TMA-E (Si/Al = 30) were synthesised according to Ref. (13), and ferrierite (Si/Al = 9) was synthesised according to Ref. (14). Other materials used were zeolite Y (kindly supplied by TU Eindhoven), SAPO-11 (Si/Al = 0.05, kindly supplied by TU Eindhoven), SAPO 34 (kindly supplied by TU Eindhoven), mordenite (kindly supplied by TU Twente, Si/Al = 20), ZSM-5 (Si/Al = 25 and 600, kindly supplied by UFCH Prague), ZK-5 (Si/Al = 16, laboratory sample kindly supplied by Exxon), ZSM-22 (Si/Al = 140, laboratory sample kindly supplied by Exxon), erionite (Si/Al = 12, VEB Bitterfeld), zeolite L (Union Carbide), SAPO 5 (kindly supplied by TU Delft), and natural zeolite clinoptilolite (natural form, Nižný Hrabovec, Slovakia). All materials were prepared in the H-form by an exchange reaction of the original form with 1 *M* NH_4NO_3 solution (three times, 100 ml of solution per 1 g of zeolite). The ammonia form was decomposed at 713 K under oxygen flow. The only deviation from the standard preparation was with the TMA-E zeolite that was exchanged three times with 1 *M* KNO_3 before detemplation to increase its thermal stability (14). This material was exposed to a maximum temperature of only 623 K. The structure of all materials was checked by XRD. X-ray diffractograms were recorded by a Philips PW 1730.

Skeletal isomerisation of *n*-butene was performed under the conditions identical with those described in (4). The reaction was followed in continuous flow, with a fixed-bed reactor, at the total pressure of one bar. Under standard reaction conditions, 1-butene (99.5%, AGA GAS BV) was diluted by nitrogen and the mixture with 5% of *n*-butene was used as the feed. Total flow was 20 ml/min. The standard amount of catalyst used in an experiment was 0.5 g. Products were analysed by a gas chromatograph (HP 5890) equipped with a flame ion detector and a column filled with KCl-treated alumina.

The measured GC signals (N_i) are taken as proportional to the number of carbon atoms in particular molecules, that is, as being essentially proportional to the molecular weight of these hydrocarbons. The relative concentration in the effluent (some authors call it yield, in the case of isobutene) is defined as earlier (4). The sum in the denominator comprises all gases detected by GC:

$$C_i = \left[N_i \Big/ \sum N_i\right] * 100\%. \qquad [1]$$

Conversion is defined by (Ref. (4))

$$X = \left[\sum N_{i\,(i \neq \text{linear butenes})} \Big/ \sum N_i\right] * 100\%. \qquad [2]$$

The sum in the denominator comprises all compounds detected; that in the numerator is over all products except linear butenes. Selectivity is defined below, expressing that isobutene formation is related to the formation of all products:

$$S = \left[N_{\text{isobutene}} \Big/ \sum N_{i_{(i \neq \text{linear butenes})}}\right] * 100\%. \qquad [3]$$

In Eqs. [2] and [3], the linear butenes are excluded from the indicated sums ($i \neq$ linear butenes). This is because 1-butene and *cis,trans*-2-butene are in equilibrium, and thus, all these three butenes can be considered as feed.

III. RESULTS

Materials tested can be divided in three main groups: small pore zeolites—erionite, ZK-5, TMA-E, SAPO 34, and clinoptilolite (cliniptilolite is the 10-membered ring zeolite, but with a very small pore diameter (see Table 1)); the 10-membered ring zeolites—SAPO-11, ferrierite, ZSM-22, and ZSM-5; and the 12-membered ring zeolites—omega, zeolites L and Y, mordenite, and SAPO-5. The structure, selectivity, and activity of these materials are presented in Table 1.

Small pore zeolites are not selective. Moreover, these catalysts deactivate in a few hours. The highest relative concentration of isobutene was obtained over clinoptilolite—12% at 623 K and 16% at 713 K after 10 min on stream (Fig. 1). Deactivation of the last-mentioned catalyst is slower than that of the other zeolites. The main by-products of *n*-butene reaction are propene, pentenes, and butane. Only a small amount of isobutane is detected. Concentration of aromates is below the detection limit. Since by-product formation decreases with a higher deactivation more than isobutene formation, the relative concentration of isobutene seems to be stable. The total conversion decreases rapidly.

The group of the 10-membered ring molecular sieves includes ferrierite, ZSM-22, SAPO-11, and ZSM-5. All these catalysts are very stable (Fig. 2); for example, SAPO 11

TABLE 1

Materials Tested for Skeletal Isomerisation of *n*-Butene under Standard Reaction Conditions

Catalyst	Type	Structure	Isobutene (%)	Butanes (%)	$C_3^= + C_5^=$ (%)	Isobutane/ butane	Stability
SAPO 34	CHA	2-dim. ø 3.8 Å	8.3	11.4	33.3	0.096	Low
ZK-5	KFI	3-dim. ø 3.9 Å	1.5	33.0	51.6	0.003	Very low
Erionite	ERI	3-dim. 5.1 × 3.6 Å	3.5	14.6	20.9	0.016	Very low
TMA-E	EAB	2-dim. 5.1 × 3.7 Å	7.3	10.4	22.2	1.17 0.30[a]	Low
Clinoptilolite	HEU	7.6 × 3.0 Å and 4.7 × 2.6 Å	12.6	1.15	15.8	0.10	Low
Ferrierite	FER	5.4 × 4.2 Å and 4.8 × 3.7 Å	33.1	3.9	17.5	0.70	Very high
ZSM-22	TON	5.5 × 4.4 Å	23.7	4.5	26.4	0.45	High
SAPO 11	AEL	6.3 × 3.9 Å	31.3	0.7	3.0	2.85	Very high
ZSM-5	MFI	5.6 × 5.3 Å and 5.5 × 5.1 Å	12.5	5.9	29.8	2.93	Very high
Mordenite	MOR	7.0 × 6.5 Å	2.8	46.3	39.0	2.24	Low
L	LTL	ø 7.1 Å	0.6	67.4	4.2	2.33	Low
SAPO 5	AFI	ø 7.3 Å	9.1[b]	2.2[b]	4.6[b]	1.75[b]	Very low
Omega	MAZ	ø 7.4 and 5.6 × 3.4 Å	8.1	6.1	13.0	1.54	Low
Y	FAU	3-dim. ø 7.4 Å	0.5	68.6	2.6	4.91	Very low

Note. 10 min on stream. $T = 623$ K.
[a] 90 min on stream.
[b] $T = 713$ K.

is active for more than 95 h (the relative concentration of isobutene after 95 h on stream is still 27.7%), and ferrierite is even more stable. Grandvallet *et al.* (14) claim that the relative concentration of isobutene is 41.2% after 336 h on stream. In the first stage of reaction on this group of zeolites, a significant amount of by-product is produced. The main by-products observed with 10-membered ring molecular sieves are propene, pentenes, isobutane, and butane. Relative concentration of aromates on ferrierite is 0.85% after 10 min on stream. The selectivity increases after the initial stage of reaction, but after several hours on stream, the product pattern changes further only slightly.

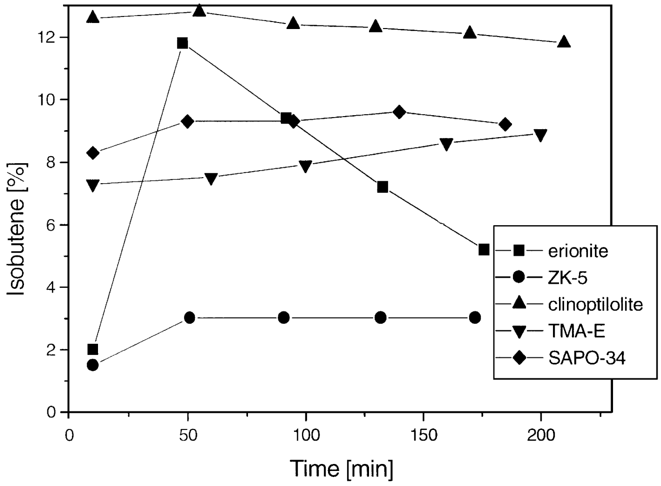

FIG. 1. Isobutene formation over small-pore zeolites at 623 K, as a function of time on stream. Standard reaction conditions.

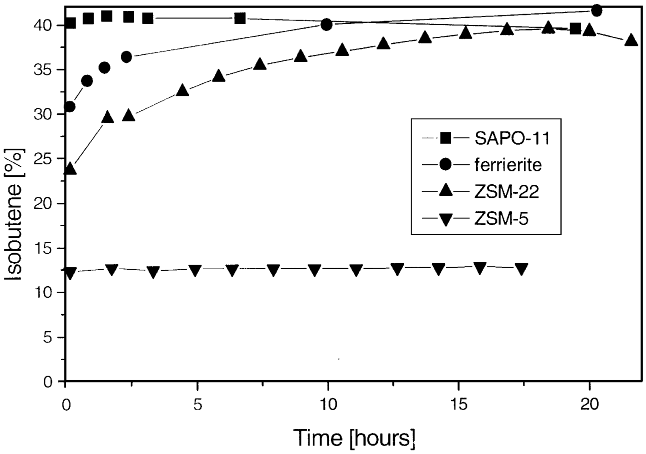

FIG. 2. Isobutene formation over 10-membered ring molecular sieves as a function of time on stream. Temperature, 623 K (only less acidic SAPO 11— $T = 753$ K). Standard reaction conditions.

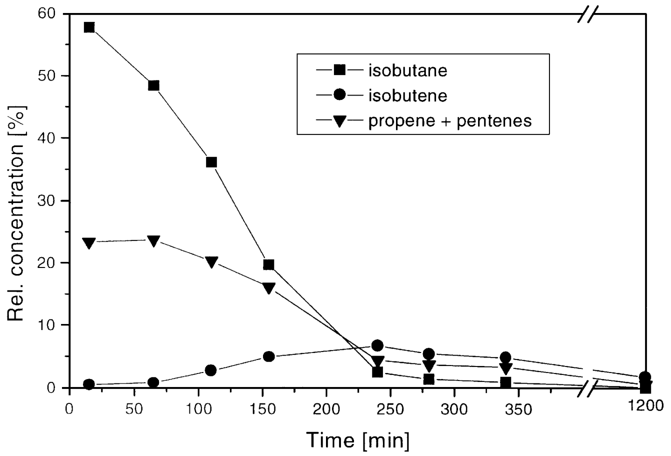

FIG. 3. Formation of main products of *n*-butene reaction as a function of time on stream, with the zeolite Y, at 623 K. Standard reaction conditions.

The highest selectivity has been obtained on SAPO 11 at 753 K—98%, at a conversion of 42%.

ZSM-5 is the only exception among the 10-membered ring zeolites studied here. Although the channel diameter is similar to that of the rest of the group, ZSM-5 is not selective. Hydrogen transfer (alkanes and aromates) is a prevailing reaction under the standard reaction conditions on ZSM-5 with Si/Al ratio = 25. Prevailing products on *n*-butene reaction over ZSM-5 with Si/Al = 600 are propene and pentenes. Although the selectivity of the ZSM-5 is low, this catalyst is very stable.

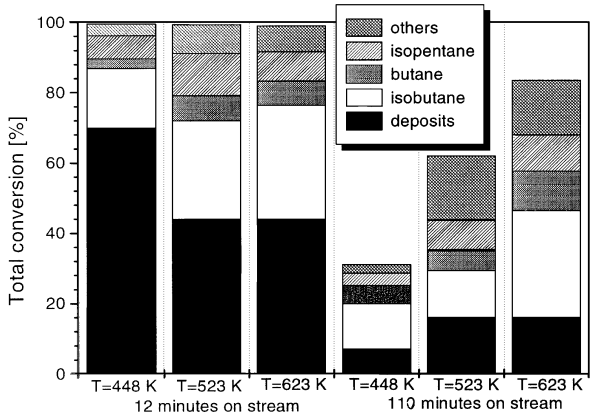

FIG. 4. Butene reaction on zeolite Y at different temperatures. 0.5 g catalyst; standard reaction conditions.

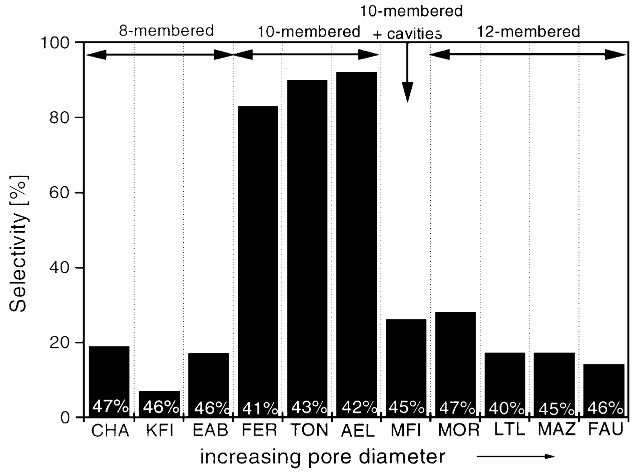

FIG. 5. A comparison of the selectivity to isobutene, on different catalysts, at the conversion level in the range 40–47%. Temperature, 623 K (SAPO 11 at 713 K). Standard reaction conditions (ferrierite, 0.3 g catalyst). Conversion is indicated within the bars. See Table 1 for codes.

The group of the 12-membered ring molecular sieves includes the zeolites Y, L, omega, mordenite, and SAPO-5. All these materials are unselective. Butene reaction leads to a large amount of alkanes and carbonaceous deposits in the first stage of reaction. The catalysts deactivate quickly. The product pattern of *n*-butene reaction on zeolite Y, which is shown in Fig. 3, is typical for this group. Initially, the main geseous product of self-hydrogenation is isobutane. Butane production is much slower. The isobutane/butane ratio is clearly above the thermodynamical value which is 0.79 at 623 K (16). Polymerisation and hydrogen transfer are very extensive, especially at low temperature. After 7 min on stream at 398 K, and under standard flow conditions, 96% of *n*-butene remains bound to the surface of Y zeolite (or in the form of carbonaceous deposits or as oligomers with a high boiling point). A total of 73.8% of the gaseous products is isobutane, and isopentane concentration is 18%, while butane concentration is only 5.6%. Carbonaceous deposits poison the catalyst very quickly. At elevated temperatures cracking of carbonaceous deposits formed on the surface becomes a competing reaction to polymerisation so that the catalyst is more stable (Fig. 4). The amount of carbon in the deposits was estimated from the difference in the total number of counts (the total FID current) obtained with or without catalyst in the catalytic bed, under the standard reaction conditions.

A rough comparison of selectivity at about the same conversion with different catalysts can be made for most of the materials (Fig. 5). Since it is difficult to vary the conversion sufficiently by only the variation of the total flow, catalysts at different stages of deactivation are also included in the comparison, mostly after about 2 h on stream. Conversion between 40 and 47% could not be obtained with some catalysts, so these are not included in the comparison.

IV. DISCUSSION

All 8-membered ring zeolites deactivate quickly and their selectivity is low. The small-pore 10-membered ring zeolite clinoptilolite is a similar case, but the relative concentration of isobutene in the effluent is slightly higher and deactivation of this material is slower. The main by-products occurring amongst the products are, next to propene and pentenes, butane and isobutane. They are a result of hydrogen transfer. If self-hydrogenation is controlled thermodynamically, the isobutane/butane ratio should be 0.79 at 623 K (16). On all small-pore zeolites this ratio is clearly below the thermodynamical value.

All facts indicate that *n*-butene reacts to by-products on the outer surface or in the cavities formed at intersections of channels. Diffusion of branched products out of the channels is the rate determining step of isomerisation. The outer surface is quickly poisoned by carbonaceous deposits. The higher stability of clinoptilolite, and—in particular—the higher relative concentration of isobutene observed, show that this material represents the limiting case, in which the diffusion of isobutene out of pores is possible to only a certain extent.

The large, 12-membered ring zeolites also deactivate quickly. Compared to the 8-membered ring zeolite, isobutane is here the prevailing by-product, under standard reaction conditions. In this case, the isobutane/butane ratio is clearly above the thermodynamical value. Isobutene self-hydrogenation is faster than hydrogenation of butenes. This indicates that hydrogen transfer involves a carbenium ion. A reaction via the tertiary carbenium ion is known to be much faster than a reaction via the secondary (or even the primary) ion (12, 17). At low temperatures, the reaction step from *n*-butene to isobutene is slow. In contrast, a large amount of carbonaceous deposits is formed under these conditions. A high isobutane and isopentane (and no propane) formation from *n*-butene can be explained by the direct cracking of deposits, via a tertiary carbenium ion.

Only a very small amount of aromates was found among the products, on both the 8-membered and the 12-membered ring zeolites. Hydrogen transfer leads to alkanes and carbonaceous deposits; the latter block pores and the catalyst deactivates quickly. At high temperatures, cracking of carbonaceous deposits becomes a competing reaction to polymerisation and the same catalyst becomes more stable (Fig. 4).

The ZSM-5 zeolite is an intermediate case between the selective and stable 10-membered ring zeolites (which are all "unidimensional" as far as isobutene is concerned) and the unstable and unselective 12-membered ring catalysts. In ZSM-5, large cavities exist in place of intersection of channels and they offer enough space for dimerisation of *n*-butene or isobutene and for other consecutive reactions. Therefore, selectivity to isobutene is as low as on large-pore materials. However, in contrast to large-pore materials, aromates are produced with ZSM-5 in large concentrations. The ZSM-5 zeolite shows an excellent stability in time. Hydrogen transfer leads in this case to alkanes and aromates, but the formation of carbonaceous deposits is limited. Pore diameter and the form of intersection obviously allow a single cycle formation, but no further polymerisation is possible. The selectivity of ZSM-5 increases, when temperature is increased; a higher temperature suppresses oligomerisation (20).

Ferrierite, SAPO-11, and ZSM-22 are very stable in time. Once the outer surface is poisoned by deactivation, hydrogen transfer no longer plays a role. Formation of carbonaceous deposits in pores is slow. Gielgens *et al.* (6) compared the activity of two molecular sieves, MnAPO 11 and MnAPO 5. The 10-membered ring MnAPO 11 was stable for a long time, and its pores remained open, while the 12-membered ring MnAPO 5 deactivated, and its channels became blocked. This finding can be seen as an additional support for the suggestions in the foregoing paragraph.

The 10-membered ring molecular sieves are very selective. Selectivity increases shortly after the start of reaction, and after several hours on stream, changes in selectivity are small. Open-surface catalysts, and the 12- or 8-membered ring zeolites, all deactivate in a few hours, because their surface becomes strongly poisoned by carbonaceous deposits. It is reasonable to expect that the same happens with the outer surface of the 10-membered ring zeolites. The selectivity to isobutene of the steady-state catalysts, when the reaction still can run, but only in pores, is higher than that in the initial stages of the reaction, on the same fresh catalysts.

The positive effect of coke deposits can have, in our opinion, several reasons. First, the outer surface of zeolite is poisoned and thus the catalyst becomes more shape selective. Second, carbonaceous deposits poison preferentially the strongest acid sites (18), and the strong Brønsted acid sites are known to induce dimerisation and in this way, also the formation of by-products (12). Third, the carbonaceous deposits can fill all irregularities in zeolite lattice and they can also alter the space in channels available for the reaction. Consequently, the formation of large molecules, like octenes, is then slowed down. Finally, there is the fourth possibility: a deactivated catalyst has a lower activity and achieves a lower conversion, and consequently a higher selectivity, due to suppression of consecutive reactions of isobutene.

A rough comparison of selectivity was performed for all catalysts tested, and it can be seen in Fig. 5. Catalysts of different Si/Al ratio and of different stage of deactivation have been compared. A varying Si/Al ratio does not influence the selectivity pattern significantly. The *n*-butene reactions obviously occur on single active sites so that the selectivity does not depend on the aerial density of the active sites (19). The acid strength also plays a limited role in the selectivity of a catalyst (20, 21). The comparison presented above shows that the optimal pore diameter is between 4 and 5.5 Å. The pore diameter of the 10-membered ring zeolites allows the formation of isobutene and its diffusion, but it suppresses (although not completely) the formation of intermediates leading to by-products and to carbonaceous deposits. Analyses of dimers formed on the 10-membered ring molecular sieve SAPO 11 (12) showed the formation of dimethylhexenes is slowed down here, compared to an open-surface catalyst (H_3PO_4/SiO_2), while under the same test trimethylpentenes cannot be formed at all in the 10-membered ring channels.

It is interesting to note the large difference in selectivities of ZSM-5 on one side and ferrierite on the other side. Both catalysts contain cavities, but those in ZSM-5 are slightly larger than those in ferrierite. This information can be also found in Ref. (21), the authors of which stress that the mentioned difference in selectivity must be ascribed to the shape selectivity, because the acidity of the materials being compared is almost identical.

It is necessary to note that even open-surface materials, like the H_3PO_4/SiO_2 catalyst (4) or chlorinated alumina (3), are able to reach a high selectivity. The H_3PO_4/SiO_2 catalyst contains active sites identical to those of MnAPO 5, and very similar centres are also SAPO 5. So when these catalysts are compared all differences in the catalytic stability can be ascribed to the difference in the structure. The high selectivity of the H_3PO_4/SiO_2 catalyst (90%, at a conversion of 46.9%) compared to that of the 12-membered ring molecular sieves MnAPO-5 and SAPO-5 can be explained as follows. Isobutene formed in the pore must escape out of the pore into the gas phase. However, the highly reactive isobutene molecule undergoes a random collision path, which increases the extent of consecutive reaction leading to the by-products (19, 22).

V. CONCLUSION

The 8-membered ring zeolites are not suitable for skeletal isomerisation of *n*-butene to isobutene because their pore diameter does not allow diffusion of isobutene. The 12-membered ring zeolites do not suppress the formation of carbonaceous deposits and their pores are quickly blocked. The most suitable materials are the catalysts with a pore diameter between 4 and 5.5 Å. This is the range as found in the 10-membered ring molecular sieves. Isobutene can diffuse through these pores but the formation of its dimers, leading mainly to the by-products and carbonaceous deposits, is suppressed here. The 10-membered ring sieves can, however, sustain any monomolecular reaction. These catalysts are thus active, selective, and stable.

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