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Isomerization of Linear Butenes to iso-Butene over Medium Pore Zeolites

I. Kinetic Aspects of the Reaction over H-FER

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Transformation of linear butenes and iso-butene was carried out over H-FER (Si/Al ratio of 8) in a wide temperature and pressure range and with varying contact times. Catalyst lifetime over 100 h could be achieved by eliminating small traces of contamination, which accelerate deactivation, from the feed. The kinetic analysis revealed a close connection between iso-butene and octene formation and suggested a different pathway for propene and pentenes than for iso-butene. Low-pressure experiments showed very high initial selectivity to iso-butene at 40 mol% conversion, suggesting that coke does not play a significant role in the selective skeletal isomerization leading to iso-butene. Strong desorption limitations seem to exist, which are gradually reduced at higher temperatures. A new approach of the operational mechanism is introduced, where the regain of intrinsic selectivity of FER is proposed to occur by deactivation of the coke deposited in the pores. © 2001 Academic Press

Key Words: **butene isomerization; Ferrierite; kinetics; coking; mechanism.**

INTRODUCTION

The skeletal isomerization of *n*-olefins is an important reaction in upgrading refinery and petrochemical feed streams. While for most of the larger olefins shape-selective solid acid catalysts are successfully utilized, the skeletal isomerization of *n*-butene was seen for a long time as too difficult to be achieved by conventional acid catalysts (1, 2). A joint development by Shell and Lyondell, however, succeeded to tailor Ferrierite (FER)-based catalysts (3–6) to be successful and stable catalysts. Yields close to the thermodynamic limitations (50 mol% iso-butene at 350°C at 1 bar *n*-butene pressure) have been reported. Remarkably, the selectivity to iso-butene improved continuously during time on stream, even up to 600 h (3). Despite this impressive performance, the results seen in the literature were partly conflicting and seemed to depend critically upon the origin of the Ferrierite. Most notably, consensus about the mechanism by which *n*-butene is converted is not achieved to date.

Based on kinetic experiments and molecular modeling, Mooiweer *et al.* (3), among others (2, 7), proposed a bimolecular mechanism for skeletal isomerization involving *n*-butene dimerization, isomerization, and cracking. The reaction is claimed to proceed increasingly selectively by growing steric constraints around the active site in the H-FER pores. These constraints are imposed by deposited coke, which allows dimerization but not further oligomerization of butene.

Using isotopic labeling, Meriaudeau *et al.* (8) showed that with a feed of ^{13}C-enriched 1-butene (^{13}C–C–C–C), ^{13}C was distributed intramolecularly in the resulting iso-butene, especially once the reaction became selective, an observation that was later confirmed by de Jong *et al.* (4). This was used as a strong indication that skeletal isomerization occurred monomolecularly, in accordance with previous suggestions over aluminophosphates (9).

In accordance with the results of Xu *et al.* (10) that up to 99% of the H-FER pore volume is filled with coke, it was first proposed by Guisnet *et al.* (11) that not the Brønsted acid sites, but coke is catalytically active in selective isomerization. Using the increasing selectivity as a key argument, it was claimed that the selective skeletal isomerization proceeds on aromatic carbonaceous species via C_4 olefin addition, isomerization, and subsequent cracking. Although this involves two molecules, i.e., the chemisorbed aromatic (coke) alkoxy group and *n*-butene, the carbon skeleton transformation is confined to *n*-butene and, hence, the four carbon atoms of *n*-butene will stay intact. In accordance to this latter observation, the proposed route was called a pseudo-monomolecular mechanism. Qualitatively, this mechanism allowed us to relate the slow increase in iso-butene selectivity to the coke formation.

However, it has been shown by Xu *et al.* (10) and by Guisnet *et al.* (12) that most coke is deposited on the catalyst

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in the first 2 h, even though the increase in selectivity continued for a much longer time. Andy *et al.* reported also that the coke formed at short times on stream is already aromatic in nature (13). Note that this is in contrast with the claim of de Jong *et al.* (4) that a paraffinic nature of coke is essential for selective *n*-butene conversion. Note that these authors also claimed that aromatization of the initially paraffinic coke is slow and leads to deactivation by pore blocking. Underlying this discussion is the question of whether coke directly influences the skeletal isomerization or whether it acts as indicated above as a means to constrain the catalyst pores.

Further, Houzvicka *et al.* (14) proposed the monomolecular isomerization route over a large number of medium-pore zeolites, claiming that the bimolecular reactions also lead to formation of the unwanted by-products propene and pentene. Their conclusion was based on subtle variations in the operating conditions pointing to better selectivity as the concentration of acid sites decreases, the butene pressure decreases, and the reaction temperature increases. In addition, the unselective cracking of octene isomers (possible dimerization products) was used (15, 16) as an argument against a bimolecular mechanism for the major pathway from *n*-butene to iso-butene.

Mechanistic aspects of butene isomerization discussed so far are based mainly on kinetic and to a lesser extent on *in situ* spectroscopic studies. Considering that different views exist on the mechanism of the reaction, it is important to critically revisit the kinetic behavior.

The present paper takes a closer look at how the experimental conditions, i.e., the reaction temperature and the *n*-butene partial pressure, influence the activity and selectivity of a particular H-FER catalyst. Detailed information on kinetic measurements will demonstrate how sensitive the reaction is to subtle changes in the reaction parameters. A possible mechanism operating under a wide range of conditions will be discussed briefly.

METHODS

Catalyst

The FER sample was obtained from Tosoh Co. with a nominal Si/Al ratio of 8 in Na/K form. The Si/Al ratio of 8.1 was reconfirmed by SEM-EDX. The catalyst was transformed into ammonium form by successive ion exchange with 1 M NH_4NO_3 solution at room temperature. XRF analysis did not show traces of alkali ions in the ion-exchanged sample. Platelet-like particles with a diameter of 1 μm and a cross section of 0.05 μm were observed by scanning electron microscopy. The BET surface area of the sample was 202 m^2/g with an estimated micropore surface area of 165 m^2/g.

The total acid site concentration of 2.05 mmol/g was found by temperature-programmed desorption using NH_4^+ exchanges samples (liquid ion exchange). A single desorption peak of ammonia was obtained between 250 and 450°C. ^{27}Al MAS NMR did not show the presence of extra framework aluminum in the parent sample. After *ex situ* activation at 400°C for 1 h in Ar, approximately 4% amorphous aluminum was revealed.

Catalytic Testing

Catalytic testing was carried out in a conventional plug-flow reactor under atmospheric pressure. The catalyst in its ammonium form was placed into a quartz reactor, held at the isothermal part of the reactor by quartz wool plugs. The temperature was measured at both ends of the catalyst bed. The catalyst was used without a binder present to eliminate its contribution to the catalytic performance. Preliminary experiments showed that using solid diluents, such as silica or SiC, did not improve the catalytic performance, but induced side reactions, i.e., butadiene formation. Therefore, a loosely packed catalyst bed allowing low pressure drop was used. The catalyst was activated *in situ* by increasing the temperature with 2 K/min up to 400°C and kept there for 1 h in large excess of Ar (Praxair, 5.0) flow. The sample was subsequently cooled down to the reaction temperature. Then the pure Ar flow was switched to a reactant mixture.

Depending on the type of experiments, different partial pressures of 1-butene (Scott Specialty Gases, 99%) or iso-butene (Scott Specialty Gases, 99%) in Ar were used in the range of 5–1000 mbar. The diolefin content of the hydrocarbons was below 10 ppm and was fed into the system prior to the reactor in liquid form by high-precision piston pumps (ISCO, 500D). Weight hourly space velocities (WHSV) were varied (between 2 and 160 h^{-1}) in order to obtain a wide range of conversion and yields at desired pressures. The effluent stream was analyzed on-line by gas chromatography using a 50-m HP-PLOT/Al2O3 column ("S" deactivated). Data were analyzed by Chromatography Station for Windows (DataApex version 1.7). The carbon balance was tied up to 98% from initial time on stream.

In the kinetic measurements used in the determination of apparent orders and activation energies, the following testing method was applied. The catalyst was kept in the desired hydrocarbon feed for 3 min. After that, a sample was taken and analyzed. Subsequently, the reactor was switched back to a pure argon stream and flushed for an hour. Then the parameters (temperature, pressure, and space velocity of gases) were set again, and the reactor was switched from pure Ar to the hydrocarbon-containing feed. This way, four to five times the initial TOS data could be obtained over a "fresh" catalyst without having more than 2% deviation in reproducibility in terms of rates. Then the catalyst was replaced with a new batch and activated.

Conversion of 1-butene and yield of any product were calculated as usual and can be formulated as

$$X_{(1\text{-butene})} = \left[\sum N_{i\,(i \neq \text{linear butenes})} \Big/ \sum N_i\right] \times 100\%$$

$$\mathrm{Y}_i = \left[N_i \Big/ \sum N_i\right] \times 100\%,$$

where N_i is calculated from the GC response signal using the response factors for individual components (i) and converted into moles.

Since linear butenes are expected to be in equilibrium at temperatures at which skeletal isomerization occurs, in all calculations they are summed up as linear butenes and not counted as converted molecules. In the following, therefore, we use "conversion of 1-butene" and "conversion of linear butenes" as synonyms. In yields the denominator indicates the signal of all compounds. In this way, conversion and yield are expressed in terms of mol%.

Selectivity was calculated from yield and conversion according to the conventions

$$\mathrm{S}_i = \mathrm{Y}_i / X_{(1\text{-butene})}.$$

TABLE 1

Selectivities of Various Components at Different Partial Pressures of 1-Butene in Butene Isomerization at 350°C over H-FER

	Selectivity (mol%)				
	$p_{(\mathrm{C4})} = 100$ mbar (h)			$p_{(\mathrm{C4})} = 5$ mbar (h)	
Component	0	50	120	0	50
C1	0.2	0.0	0.0	0.0	0.0
C2	4.1	0.1	0.1	0.0	0.0
$\mathrm{C3}^{=}$	32.4	5.5	2.0	3.3	3.0
$i\text{-C4}^{=}$	30.2	84.5	92.6	93.4	93.9
$\mathrm{C5}^{=}$	17.3	4.9	1.8	2.6	2.5
$\mathrm{C5}^{+}$	10.9	4.0	2.8	0.3	0.1
Yield of $i\text{-C4}^{=}$	22.1	37.8	33.3	32.3	27.1
Conversion	73.1	44.7	35.9	34.5	28.9

Note. WHSV of 1-butene was set to 2 h^{-1}. Yield of isobutene and conversion of linear butenes are also included for comparison (represented in mol%).

RESULTS

Time on Stream Profile

Catalytic testing of H-FER revealed a complex time on stream (TOS) profile during the butene isomerization reaction at 100 mbar 1-butene pressure, 350°C, and weight hourly space velocity of 2 h^{-1}. Selectivities to various components, the yield of iso-butene, and conversion of 1-butene are compiled into Table 1 and Fig. 1. As is shown in Fig. 1, three different regions in the time on stream profile can be observed.

In the first period, between 0 and 8 h time on stream, rapid deactivation occurred and the conversion decreased from 73 to 46 mol%. A similar decrease was also observed in heavy products ranging from pentenes up to C_{12} compounds, except C_8 molecules. The yield of pentenes, hexenes, and heptenes decreased during the initial period of 8 h TOS. The iso-butene yield was constant in the first 2 h and then slightly improved from the initial value of 22 to 25 mol% at 8 h TOS. The production of octenes was stable with a slightly improving yield after 10 h TOS (Fig. 1). Butane formation and the overall level of hydride transfer products (alkanes) decayed quickly in the first few hours. The latter can be used as an indication for coke formation, since the starting olefins molecules can obtain a hydride only by leaving a hydrogen-poor residue on the surface. Strictly speaking, hydride transfer products can be formed with parallel production of butadiene on the surface. As was shown earlier, butadiene would then irreversibly adsorb on H-FER (15).

In the second phase (from 8 to 75 h TOS) n-butene conversion stayed nearly the same (decreasing only from 46 to 42 mol% at times on stream of 8 and 75 h, respectively) while the iso-butene yield increased significantly from 25 to 37 mol%. The selectivity to iso-butene therefore increased to 89 mol%. A steady decrease in heavy products (from 10 to 3 mol%) was observed except in octene production. Steady low amounts of hydride transfer products (below 1 mol%) were obtained in this region.

An overall decay in catalytic performance was observed after 75 h TOS (last period). Conversion of n-butenes slowly decreased from 42 to 35 mol% and the iso-butene yield from 37 to 33 mol%. Selectivity to iso-butene increased up to 93 mol%. Hydride transfer products were reduced to the detection limit. The carbon content of the spent catalyst was 8.25 wt% after 150 h TOS. The BET surface area of the used sample was considerably lower than that of the parent sample (7 m^2/g). Micropore volume decreased approximately by a factor of 10, from 0.076 ml/g for fresh catalyst to 0.0062 ml/g for used catalyst.

Effect of Contact Time

Changing the weight hourly space velocity of 1-butene or iso-butene at 100 mbar pressure and temperature of 350°C (TOS = 3 min) allowed us to gain more information about the reaction network occurring during forward and backward skeletal isomerization. By increasing the average residence time during n-butene isomerization (Fig. 2), the initial ratio of iso-butene/propene yield decreased from 3.3 to approximately 1.7. The iso-butene/pentene ratio also changed similarly; it decreased from 5.7 to 1.7 with increasing residence time. It is important to note that the ratio of propene to pentene yield remained between 1.7 and 1.8 in the range considered above. Except butane, the rest of the yield of the light by-products was proportional to the residence time.

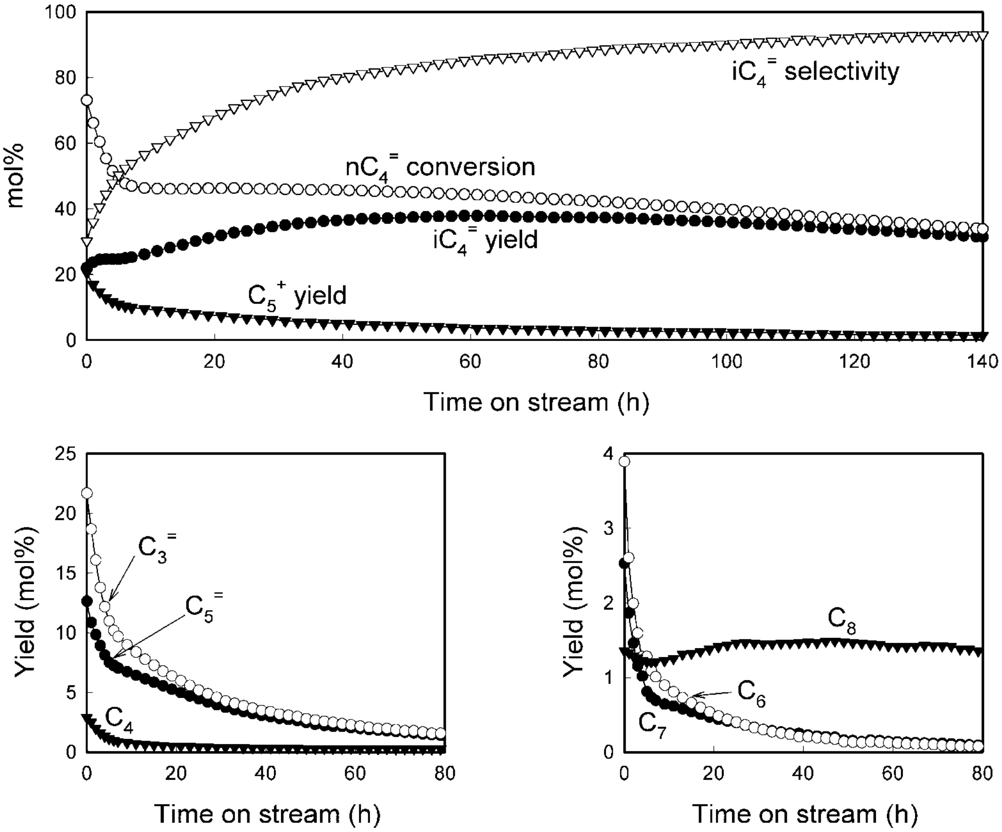

FIG. 1. Time on stream profile obtained during *n*-butene isomerization at 350°C and 100 mbar of 1-butene over H-FER. Weight hourly space velocity of 1-butene was set to 2 h^{-1}.

When iso-butene was isomerized over H-FER, the linear butenes were also counted as products. The ratio between the linear isomers was constant at sufficiently large space times (Fig. 3). Concerning the major hydride transfer products, the ratio of isobutane to butane was above 1, while in the case of butene isomerization the same ratio stayed below 0.2. Among the heavier products, C_6 and C_7 isomers showed a similar variation as propene with increasing space time, while the variation in octenes resembled the variation of linear butenes.

Rates of *n*-butene and iso-butene isomerization at 350°C, 7% conversion, and 100 mbar partial pressure are compiled in Table 2 (data collected at 3 min TOS). Generally, the corresponding rates are lower in the case of iso-butene feed than with *n*-butenes. The ratio of propene to pentenes is lower for the reaction of iso-butene. Note that, in contrast, octene formation is more pronounced with iso-butene. *n*-Butene showed lower rates in octene formation, but it is converted approximately two to three times faster into propene and pentene than iso-butene.

The rate of isobutane formation (hydride transfer product originating from iso-butene) is comparable with both reactants, while *n*-butane formation is much less pronounced in iso-butene transformation due to the lower concentration of linear butenes present. Comparing the abundance of these hydride transfer products reveals, however, that the iso-butene to iso-butane hydrogenation is eight times slower than the corresponding *n*-butene to *n*-butane

TABLE 2

Rates of Formation of Various Components at 350°C and 100 mbar Reactant Pressure

	Rate of formation (mmol h^{-1} g^{-1})							
Reactant	Ethene	Propene	Isobutane	Butane	Isobutene	*n*-Butenes	Pentenes	Octenes
n-Butenes	1.1	23	0.6	4.0	64		12	2.2
Isobutene	0.13	7.4	0.5	0.2		197	5.5	3.1

Note. Conversion is kept at 7 mol%; data were collected at time on stream of 3 min.

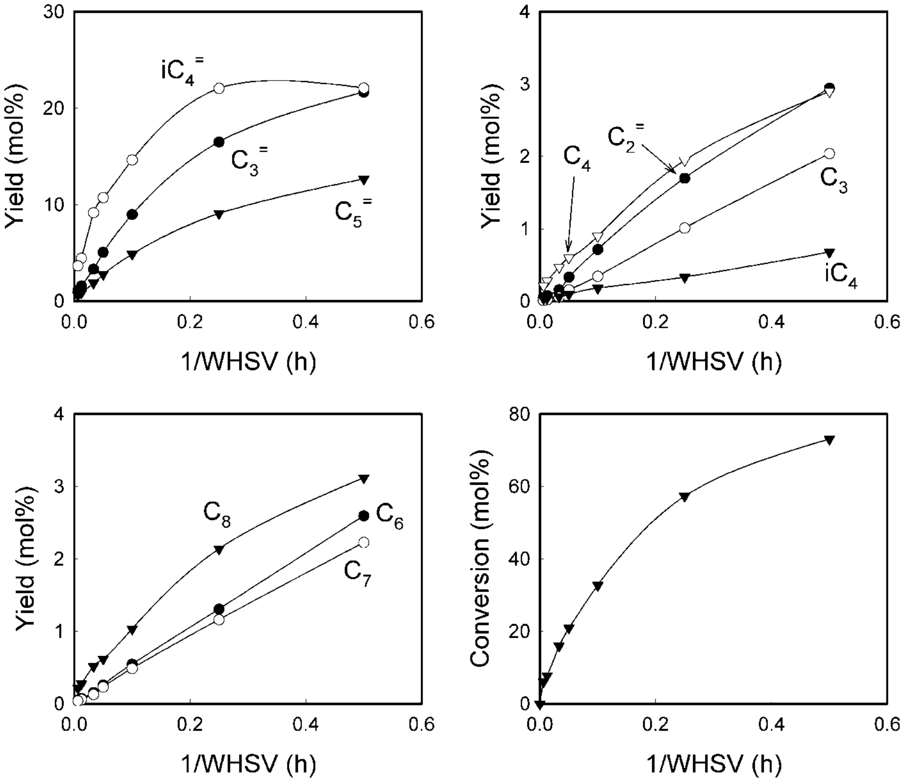

FIG. 2. Yield of various components and conversion on *n*-butene against 1/WHSV for H-FER in *n*-butene isomerization. Data were collected at 350°C, at 100 mbar 1-butene pressure over fresh catalyst. TOS = 3 min.

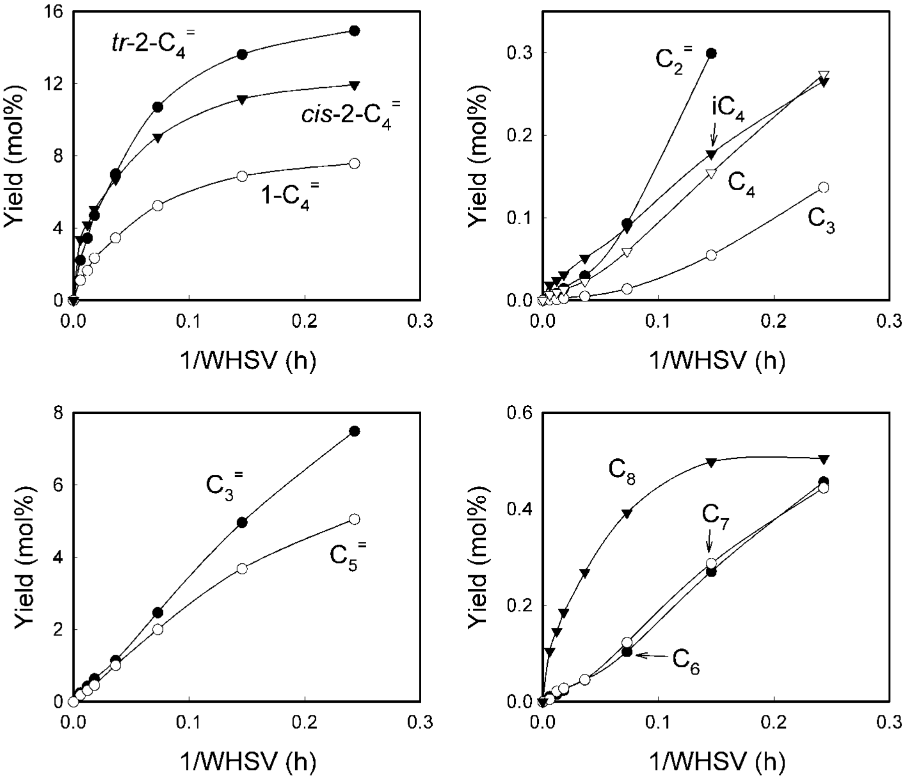

FIG. 3. Yield of various components against 1/WHSV for H-FER in isobutene transformation. Data were collected at 350°C, at 100 mbar isobutene pressure over fresh catalyst. TOS = 3 min.

reaction, implying that the narrow pores hinder the transition state in the hydride transfer reaction.

Influence of Operating Parameters

The influence of the temperature between 250 and 450°C and the pressure (5–1000 mbar) was determined on a fresh catalyst using initial TOS data of 3 min. Kinetic parameters were measured at sufficiently high space velocities (WHSV above 100 h^{-1}) of 1-butene in order to obtain conversions below 5 mol%.

Experiments in a large fraction of the contributions presented earlier were adjusted to lower partial pressures of *n*-butene, since below 250 mbar and preferably below 100 mbar oligomerization is sufficiently suppressed that at 350°C high iso-butene yields and selectivities were obtained. Therefore, pressure variation of 1-butene in the range of 5–50 mbar was carried out at WHSV of 2 h^{-1} in order to compare the rates of formation of different components at 350°C (Fig. 4). The yield of iso-butene showed negligible variation in this pressure range. The rate of propene and pentene formation was, however, proportional to the increasing pressure, indicating a different reaction pathway for the latter products.

By lowering the partial pressure of 1-butene to 5 mbar, while keeping the space velocity at 2 h^{-1}, it was possible to obtain very high initial selectivities to iso-butene also at short times on stream (Fig. 5). Although the iso-butene yield was slightly lower than that at 100 mbar (Fig. 1), the selectivity to iso-butene was above 90 mol%. The absence of hydride transfer products (aliphatic compounds) indicated a low amount of coke formation, in line with the low carbon contents of the spent sample (1.2 wt% after 50 h TOS).

Between butene pressures of 5 and 50 mbar (Table 3), the apparent order of iso-butene formation with respect to *n*-butenes was zero, while the order of propene and pentene was approximately 1 (1.1 and 1.0, respectively).

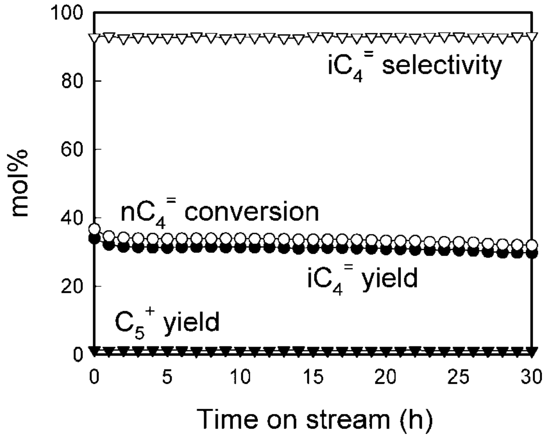

FIG. 5. Time on stream profile obtained during *n*-butene isomerization at 350°C and 5 mbar of 1-butene over H-FER. Weight hourly space velocity of 1-butene was set to 2 h^{-1}.

The order for octene formation was around 1.2. At higher *n*-butene pressures (between 100 and 500 mbar) the order of iso-butene increased slightly to 0.2, while the order of propene and pentene decreased to 0.8 and 0.9, respectively. The order of octene formation also decreased to 0.8 (Table 3).

Increasing the pressure of *n*-butene up to 1000 mbar generally decreased the apparent reaction orders. The order of iso-butene formation, however, increased to 0.5 while the order of octene formation stayed at 1.0. This indicates that possibly two separate pathways exist, one for octene formation and another for a dimerization and subsequent cracking, resulting in propene and pentene.

With respect to iso-butene pressure between 100 and 500 mbar, the orders of propene and pentene were found to be 0.7 and 0.6, respectively. Note that the order for octene formation was 1.0. The order of linear butenes was lower than 1; in the case of *cis*-2-butene, it was negative.

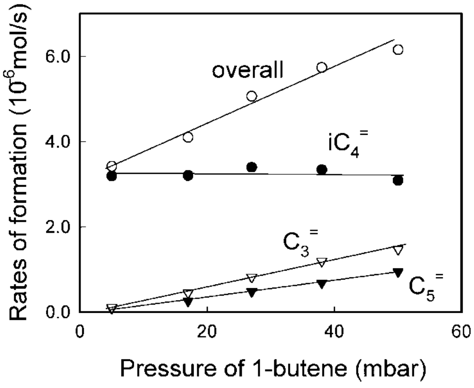

FIG. 4. Initial rates of formation of isobutene, propene, and pentene and overall rate of *n*-butene conversion vs 1-butene partial pressure in butene isomerization at 350°C and 2 h^{-1} space velocity. Data were collected at 3 min TOS.

TABLE 3

Apparent Order of Various Components at 350°C over Fresh H-FER

	1-Butene (mbar)			iso-Butene (mbar)	
Component	5–50	100–500	above 500	100–500	above 500
$C2^=$	1.2	0.9	−0.2	0.6	0.4
$C3^=$	1.1	0.8	−0.1	0.7	−0.1
i-C4	0.9	0.2	0.0	0.4	0.0
n-C4	1.0	0.7	0.2	1.0	1.0
tr-2-$C4^=$		0.0	0.8	0.4	0.1
i-$C4^=$	0.0	0.2	0.5		
cis-2-$C4^=$		0.2	0.1	−0.4	−1.0
$C5^=$	1.0	0.9	0.1	0.6	−0.2
$C8^=$	1.2	0.8	1.0	1.0	0.9

Note. Conversion of reactant is kept below 6 mol%; data were collected at time on stream of 3 min.

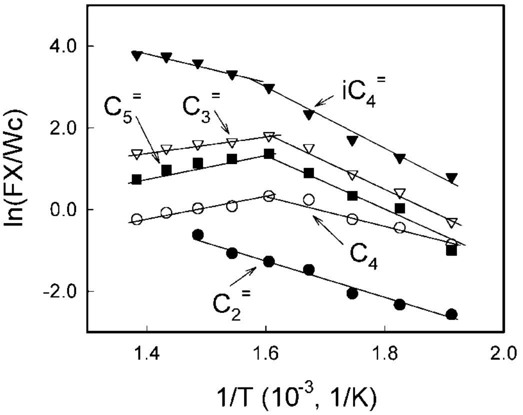

FIG. 6. Initial rate constants of formation of various components vs 1/temperature. Rates are measured at TOS = 3 min. Rate constants are calculated as $F \cdot X/W \cdot c$, where F is flow in [mol/s], X is conversion, W is the volume of the catalyst bed in [m^3], and c is the average concentration of 1-butene over the bed in [mol/m^3].

TABLE 4

Apparent Activation Energies of Various Components in the Range of 250–350°C and 100 mbar *n*-Butene Pressure

Component	Activation energy (kJ/mol)
$C2^=$	42.8
$C3^=$	56.9
i-C4	28.1
n-C4	33.2
i-$C4^=$	58.8
$C5^=$	60.0

Note. Conversion is kept below 5 mol%; data were collected at time on stream of 3 min.

Raising the iso-butene pressure up to 1000 mbar caused the apparent order of propene and pentene production to decrease below zero, while the order of octene formation remained close to 1. Note that the order of butane formation had an order of 1 in both pressure ranges while isobutane formation decreased to zero from 0.4. The order of *cis*-2-butene was found to decrease to −1.0, indicating its special role in skeletal isomerization.

Apparent activation energies of various products obtained under differential conditions are presented in Table 4. Although the corresponding rates of formation were obtained from data in the temperature region of 250–450°C, a consistent bending in the Arrhenius plot (Fig. 6) above 350°C allowed only the use of the lower temperature region. Note that lower weight molecules such as ethene or methane (not shown) did not show this phenomenon throughout the whole temperature region. Consistent with the values reported earlier (11), approximately a 60 kJ/mol activation energy was found for iso-butene formation. Similar values were obtained for propene and pentene formation. Hydride transfer products, such butane and iso-butene, showed lower activation energy (around 30 kJ/mol).

Influence of Traces in the Feed

When isomerization was carried out at 350°C with a WHSV of 2 h^{-1} in the presence of 50 ppm of oxygen in the feed (50 mbar of 1-butene), a completely new TOS profile was observed (Fig. 7, left). The lifetime of the catalyst was much shorter, and although slightly higher iso-butene yields were obtained at short times on stream, the catalyst lost its activity in 24 h. Butadiene yield of 0.7 mol% was found in the effluent stream after total deactivation, suggesting that oxygen caused the formation of butadiene in the absence of impurities. This could be compared to the reaction represented in Fig. 7, right (identical to Fig. 1,

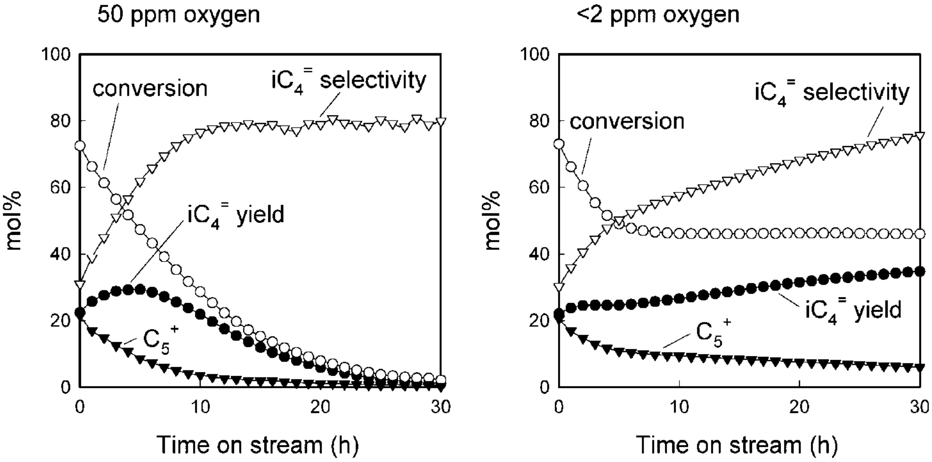

FIG. 7. Effect of oxygen contamination in *n*-butene isomerization over H-FER at 350°C with WHSV set to 2 h^{-1}. Left: Reaction performed in the presence of 50 ppm oxygen; right: oxygen level is below 2 ppm.

TOS = 0–40 h), where oxygen traces were absent, and in which case butadiene formation was marginal.

DISCUSSION

General

Over a fresh H-FER catalyst the overall pattern of the reaction pathways is very complex. The desired skeletal isomerization leading to iso-butene is accompanied by several other reactions. Typically, these are oligomerization (addition of an olefin molecule to an olefin molecule), alkylation (olefin addition to a paraffinic molecule), cracking (directly or subsequently after oligomerization), and hydride transfer taking simultaneously place over the catalyst.

During reaction at short times on stream, oligomerization and cracking reactions leading mainly to propene and pentenes dominated over skeletal isomerization. The level of higher isomers (C_5^+) decreased after the first period of 10 h. The yield of octenes did not decrease with TOS, but varied in parallel to the iso-butene yield. This suggests that there is a closer connection between the octenes and iso-butene.

As the selectivity to iso-butene increased with time on stream, one might argue that the reaction pattern is shifting, and a new, more selective pathway is opened for iso-butene production. According to the pseudo-monomolecular mechanism proposed by Guisnet *et al.* (11), this is achieved by the appearance of a new type of catalytically active carbonaceous species, engaging in iso-butene production without by-product formation. This, however, would also imply that a different catalytic chemistry should start upon the development of active carbonaceous species.

Even though the yield of by-products decreased with time on stream, the ratio between the propene and pentene did not change (see Fig. 8). The distribution of propene, iso-butene, pentene, hexene, heptene, and octene yields is plotted against time on stream in Fig. 8A. When comparing the overall product distribution (Fig. 8A), the large increase in iso-butene selectivity at approximately constant overall rates implies indeed that a shift in the reaction mechanism might occur. In contrast, when iso-butene and octenes are excluded (Fig. 8B), the product distribution does not change significantly with TOS, as would be expected for a drastic change in mechanism. It should be emphasized that the ratio between octene and iso-butene yield stayed constant (see Fig. 1) as the selectivity to iso-butene increased up to 93 mol% at 100 h TOS. This indicates that the intrinsic route leading to the by-products produced by oligomerization and subsequent cracking is unchanged, although the rate of iso-butene formation increases with TOS. Interestingly, the order for octene formation stays close to 1 in the butene pressure range of 0.1–1 bar, while the order for propene and pentene decreases with increasing *n*-butene pressure, probably suggesting a parallel pathway for octene formation (possibly on weak acid sites).

During butene isomerization at 350°C, the three dominating products, iso-butene, propene, and pentenes, are primary products (Fig. 9). At higher conversion, the yield of propene and pentenes is increased further while the iso-butene yield declined. It should be noted that at this point thermodynamics (18) influence on iso-butene production, up to 25 mol% iso-butene yield is allowed at 75 mol% *n*-butene conversion at 350°C. Propane and isobutane are secondary products (Fig. 9). All other products seemed to have formed in a primary reaction, but are also produced at higher conversions in a secondary pathway from iso-butene.

In the reverse reaction, in iso-butene isomerization, all linear butenes and octenes are primary products (Fig. 10), while ethene, propane, and butane are secondary products. Propene, isobutane, pentenes, hexenes, and heptenes show

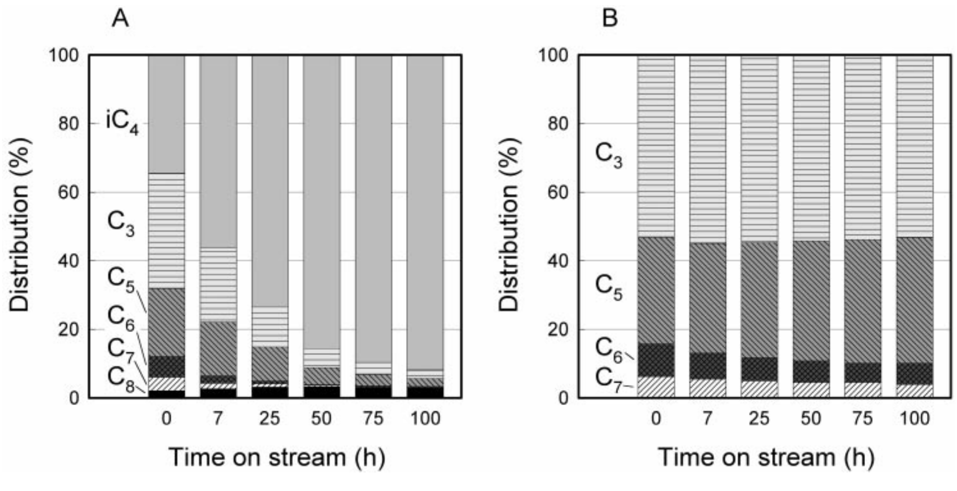

FIG. 8. Distribution of various products at 350°C, 2 h^{-1}, and 100 mbar of butene pressure over H-FER. Data are taken from Fig. 1.

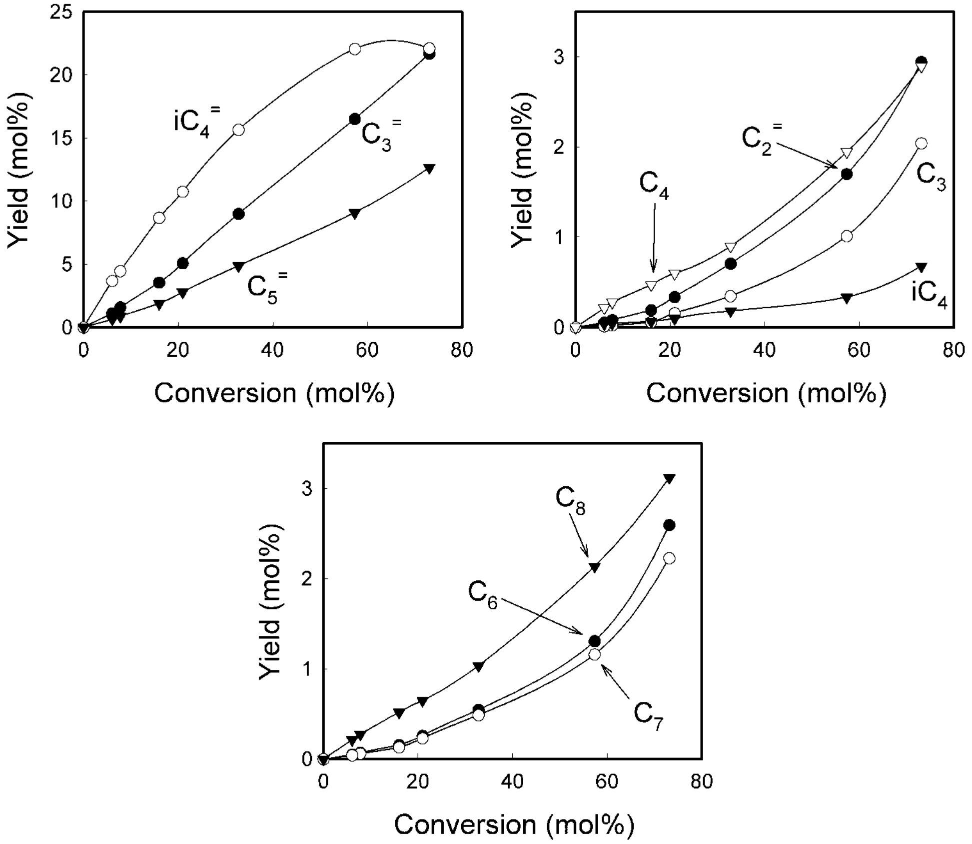

FIG. 9. Yield of various components against conversion of *n*-butenes over H-FER in *n*-butene isomerization. Data were collected at 350°C, at 100 mbar 1-butene pressure over fresh catalyst at 3 min TOS.

primary character with strong secondary increase at higher conversions. The strong primary nature of octene formation indicates that octenes are formed via a parallel route to other major reactions (probably on weak acid sites). Interestingly, the ratio between the linear butenes is beyond the thermodynamic equilibrium at low conversions (short contact times) in favor of *cis*-2-butene, probably due to steric confinements caused by the zeolite pores.

It is important to note that propene and pentene are primary products from *n*-butenes. If they were produced from the octenes observed in the products, one would expect a stronger contribution of a secondary pathway at lower conversions (via bimolecular mechanism). However, there seemed to be a closer connection between the desorbing octenes and iso-butene, as well as among *n*-butenes, propene, and pentene. This let us speculate that there is a separate pathway for the production of a pair of propene and pentene and for octene formation.

During the first 3 h time on stream (Fig. 1), the iso-butene yield is limited by thermodynamics (18). After 3 h, however, the further decrease in *n*-butene conversion (from 62 to 48 mol%) would allow much higher yields of iso-butene (up to 40 mol%) than observed. However, during the first period of 10 h TOS the iso-butene yield did not increase and slowly increased during the next phase.

Iso-butene yield is lowered by two factors at short times on stream, i.e., (i) extensive formation of carbonaceous deposits, which might consume part of the adsorbed iso-butene, and (ii) molecular transport limitation in *n*-butene or iso-butene in the pores of H-FER.

Role of Coke Formation

It is important to note that over H-FER in almost every case extensive coke formation was reported, with the presence of highly unsaturated products from short times on steam (13). Formation of such species is related to Brønsted acid sites. By definition, then, a higher concentration of acid sites would favor hydride transfer and result in a higher rate of coke formation. The H-FER reported here has a relatively high concentration of acid sites, due to its lower Si/Al ratio, and, therefore, its lifetime is limited. As was reported earlier by de Jong *et al.* (4), Wichterlova *et al.* (19), and Asensi *et al.* (20), a zeolite with higher Si/Al ratio can suppress the unfavored side reactions and increase the lifetime of the catalyst. However, in our case using a

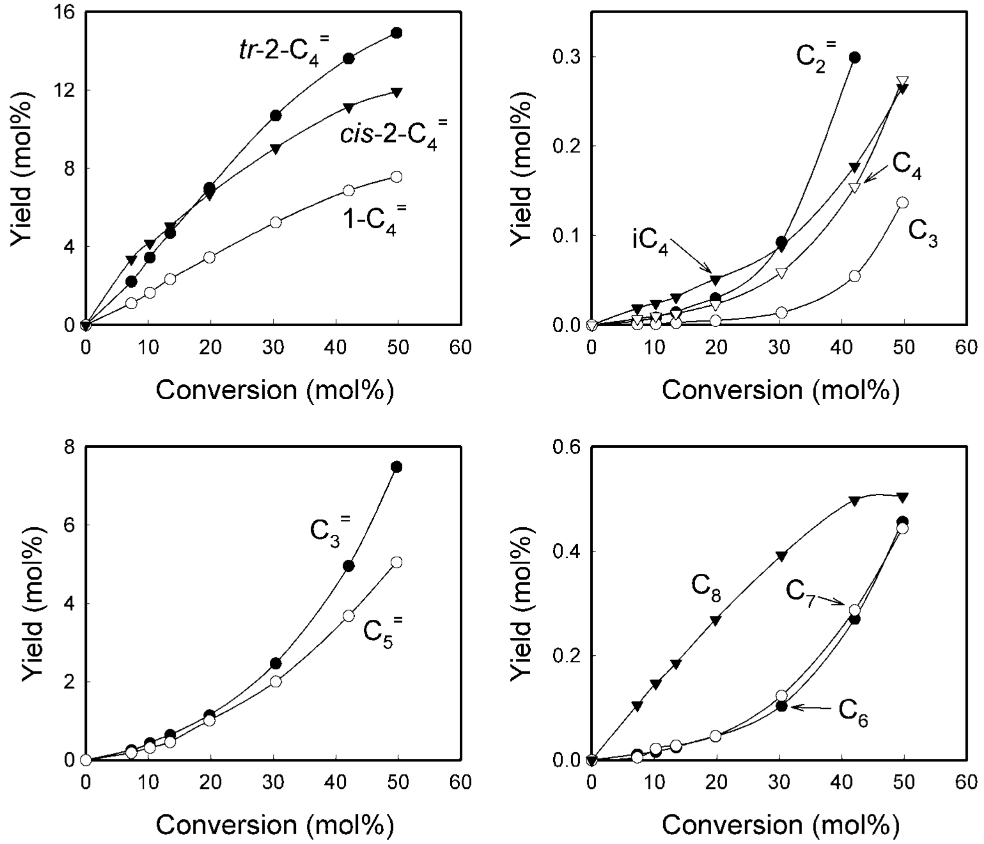

FIG. 10. Yield of various components against conversion of isobutene over H-FER in isobutene transformation. Data were collected at 350°C, at 100 mbar isobutene pressure over fresh catalyst at 3 min TOS.

zeolite with a Si/Al ratio of 8, it was possible to achieve a long lifetime compared to other reports (1, 13). This indeed emphasizes that the influence of parameters others than hydride transfer is also important, e.g., levels of contaminations.

It was shown earlier by Pirngruber *et al.* (17) that butadiene has a large effect on the catalytic performance of H-FER. When traces of oxygen were allowed in the feed (Fig. 7), the catalytic performance was significantly altered. The striking decrease in catalyst lifetime can be attributed to the faster pore/site blocking initiated by the larger concentration of butadiene formed, which is irreversibly adsorbed in the pores. Note that this raises the issue of possible feed contaminations in the reported literature.

There is, however, also another way of suppressing the side reactions. When isomerization was carried out at low partial pressures of *n*-butene (Fig. 5), very high initial selectivities to iso-butene could be obtained from 3 min time on stream, when the coke formation has hardly started. This strongly suggests that coke formation does not improve iso-butene production, in agreement with Asensi *et al.* (20).

Furthermore, it implies that H-FER itself is intrinsically very selective, and its pore geometry is the key for the selective isomerization reaction, although successive reactions might take place internally or externally over the catalyst. More importantly, it demonstrates that coke formation is not essential per se to achieve high selectivity to iso-butene over H-FER, although at higher pressures it cannot be avoided.

Role of Molecular Transport

The size of the iso-butene molecule is close to the size of the pores in FER. With a kinetic diameter of 5.0 Å, iso-butene is slightly larger than the pore entrance of the 8-member ring channels (3.5 × 4.8 Å) and matches closely with the 10-member ring channels (4.2 × 5.4 Å) (21). Indeed, as was shown earlier (22, 23), the diffusion of iso-butene is hindered in 8-member ring channels with a high activation barrier of 160 kJ/mol. Note that in the 10-member ring channels this barrier is still approximately 40 kJ/mol. In addition, the size of the iso-butene molecule does not allow other molecules to pass by or counterdiffuse in the pores of H-FER, inducing single-file-type diffusion in the pores.

The apparent activation energies of the reaction pathways to the three main components, propene, iso-butene, and pentenes, are approximately 60 kJ/mol over fresh

H-FER catalyst. These relatively low activation energies are in the range of the estimated adsorption enthalpy of iso-butene. Although direct information is not available, a close estimation can be obtained, taking the olefinic character of iso-butene into account. From the adsorption enthalpy of *n*-butane and isobutane over H-FER reported by Eder (24) we estimate an approximately 60 kJ/mol adsorption enthalpy for iso-butene and 70 kJ/mol for *n*-butene. This clearly suggests that desorption may be the rate-determining step in iso-butene formation. This is in good agreement with the zero order of iso-butene formation with respect to butene pressure.

As described above, a deviation from the straight line in the Arrhenius plot of iso-butene was observed (Fig. 6). This can be explained in several ways (25). The deviation might be a result of a change in the rate-determining step or a change in coverage of the intermediate over the surface with increasing temperature, result of intracrystalline diffusion, or single-file diffusion in one-dimensional zeolite channels.

Although the concept of single-file diffusion is very appealing, in our case the loosely packed bed provides other diffusion pathways than a single file across the particles. In other words, molecules do not have to pass through the whole particle (like in the case of a membrane); the transport is mainly governed by adsorption and desorption at the edge of the particle. This suggests that single-file type diffusion may be present, but it is restricted to the outer shell of the catalyst particles.

While there are no indications for intracrystalline diffusion limitations (the linear butenes were in thermodynamic equilibrium under all reaction conditions), the existing limitation in iso-butene formation is tentatively attributed to (i) a change in the rate-determining step or (ii) a change in the coverage of the intermediate with increasing temperature.

Let us examine these two possibilities in more detail. In a hypothetical monomolecular reaction, where a reversible reaction occurs between reactant (A) and product (B), the rate-limiting step and implicitly the coverage can be derived from the adsorption enthalpies of A and B. If the reactant (A) has a much higher adsorption enthalpy, then its coverage will be high, causing zero-order dependence of B in A. If the adsorption enthalpy of the product (B) is dominant, the coverage of B will be high, causing desorption limitation. If their adsorption enthalpies are comparable, like in the case of butene isomerization, where the adsorption enthalpy of *n*-butenes is approximately 15 kJ/mol higher than that of iso-butene, no significant change in coverage can be expected.

The pore structure of Ferrierite inherently modifies this situation. Since the pore size is close to the size of the product (iso-butene), the free movement of different molecules is hindered. From the gas phase or an external physisorbed site, the linear butenes cannot reach the nearest acid site close to the pore entrance until physisorbed iso-butene, already desorbed from the acid site, leaves the pore, freeing up the inward pathway, that is to say, even though iso-butene is apparently desorption limited at certain temperatures, the real limitation in the reaction is the frequency, at which the next linear butene reaches the acid site. *n*-Butene transport, therefore, is not governed by its own diffusion in the pore; it is regulated by the restrictive desorption/transport of the iso-butene molecule.

In other words, the free accessibility of the nearest active site is governed by molecular flow in the pore. This invokes three important implications concerning the skeletal isomerization reaction. First, it supports the experimental finding of zero order of iso-butene formation in butene pressure. It also implies that, by increasing temperature, the reaction should move into a first-order dependence as desorption limitation will change into a limitation in adsorption or surface reaction.

Apparent orders of iso-butene, propene, pentene, and octene formation in 1-butene pressure in the temperature range of 350–450°C are compiled Table 5. As can be clearly seen, no significant change was observed in the apparent order of propene, pentenes, and octenes. In contrast, the apparent order of iso-butene increased from 0.2 to 0.5 as temperature increased from 350 to 450°C, showing a gradual change in the rate-limiting step and diminishing desorption limitation.

Second, the constrained molecular flow inherently verifies the need for a specific pore structure with a size close to the size of iso-butene. This only would allow the depletion of the acid sites and, therefore, indirectly increase the selectivity to iso-butene by prohibiting any bimolecular or successive reactions. By using the same argument, one would argue that increasing the Si/Al ratio, and by this increasing the average distance of Brønsted acid sites, is beneficial to the reaction rate because of the same reasoning.

TABLE 5

Apparent Order of Various Components in 1-Butene at 350, 400, and 450°C over Fresh H-FER

	Apparent order in 1-butene (°C)		
Component	350	400	450
C1	1.0	1.0	0.9
$C2^=$	0.9	1.0	1.0
$C3^=$	0.8	1.0	1.1
i-C4	0.2	0.6	0.7
n-C4	0.7	1.0	1.0
tr-2-$C4^=$	0.0	−0.1	−0.2
i-$C4^=$	0.2	0.4	0.5
cis-2-$C4^=$	0.2	0.1	0.1
$C5^=$	0.8	0.9	0.9
$C8^=$	0.8	0.9	1.1

Note. Conversion of 1-butene was kept below 10 mol%; data were collected at time on stream of 3 min in the pressure range of 100–500 mbar.

Large-pore zeolites allow transport in a counter direction leading to consecutive reactions, and therefore a decrease in the selectivity to iso-butene. In small-pore zeolites, for geometric reasons iso-butene could not be either produced in the pores or desorbed from the channels depending on the size of the channels.

The third implication of the model is that the crystallinity of the zeolite indeed plays a major role in skeletal isomerization. The more crystalline the sample the fewer defects present at the pore entrance, and therefore the more pronounced the beneficial effect of the directed molecular flow can be.

Reaction Mechanism

Since there is a clear indication about the strong relation between the structure of H-FER and its catalytic performance, as the size of the iso-butene molecule fits the pores well (23), we must examine the reasons behind the initial lower level of iso-butene production over H-FER under the reported conditions.

The iso-butene molecule is considered readily activated, since it is transformed to a tertiary carbenium ion after adsorption over an acidic surface. The rates of reaction obtained from iso-butene transformation, however, were generally lower compared to *n*-butene isomerization. Thus, on an intrinsically selective catalyst the isobutene formed reacts further only at relatively high conversions (approaching the thermodynamic equilibrium).

Based on the kinetic data, it is most plausible to propose a monomolecular mechanism for iso-butene formation, which is controlled by desorption under the present operating conditions. Propene and pentanes are produced via a common intermediate (having similar activation energy), which is different from that for iso-butene formation. Although it is reasonable to assume that they are formed by a cracking of octenes, a clear difference between the kinetics of octenes in the educt stream compared to propene and pentenes is noted.

As mentioned earlier, the relative abundance of hydride transfer products (alkanes) at short times on stream (Fig. 1) indicates the initial formation of carbonaceous species. Hydride transfer from *n*-butene molecules would lead to significant butadiene formation, which is known to adsorb irreversibly on H-FER and to induce the formation of hydrogen-poor oligomers. Alternatively, a reacting butene molecule can attach to the carbonaceous species resulting from the extensive oligomerization. Subsequent cracking of this carbenium ion can produce a wide variety of olefinic molecules ranging from C_1 up to C_{6-7} including propene and pentenes. Cyclization and further dehydrogenation of the surface species converting the more active aliphatic oligomer to a less active aromatic compound is speculated to reduce the chance for unselective cracking by shortening the length of the paraffinic side chains on the aromatic rings.

The possible consumption of the already produced iso-butene is, therefore, decreased when the oligomers in the pore lose activity. This concept mirrors the previously proposed pseudo-monomolecular mechanism. It suggests that the increase in the iso-butene yield is not a coke-aided gain in production, but a regained intrinsic selectivity by the loss in the reactivity of carbon deposited, which would otherwise allow *n*- and iso-butene addition.

The proposed model is compatible with all experimental observations. At low pressures, when the oligomerization does not take place to a significant extent, the isomerization reaction can be very selective (the rate of coke formation is low). At higher butene pressures, the formed oligomer is involved in the reaction leading to different products. As the oligomer loses hydrogen, it becomes less active, reducing the probability of forming compounds other than C_4 molecules. This implies that the selectivity to iso-butene will increase, while conversion remains the same.

The present model also justifies the observed differences in propene, pentene, and octene formation. While the latter can be produced from two *n*- or iso-butenes on very weak acid sites, most probably at the external surface of the particle, the propene and pentene are formed via cracking of carbenium ions from the carbonaceous deposit inside of the pores. It also explains that the ratio of propene to pentene (Fig. 8) does not vary with TOS because the reaction pathway to propene or pentene formation is not altered when the concentration of active sites is reduced with time on stream.

CONCLUSIONS

The present contribution compares kinetic data presented here with experimental conditions reported in several articles (1, 11, 15) and demonstrates that substantial differences in level of traces, e.g., oxygen contamination, could fundamentally alter the reaction mixture *in situ* and cause dramatic changes in catalytic performances. Therefore, by eliminating these hindering components, it was possible to extend the lifetime of a low Si/Al ratio H-FER catalyst (Si/Al ratio of 8) to beyond 150 h at 350°C and 1-butene weight hourly space velocity of 2 h^{-1}, showing excellent catalytic performance. According to the literature, the low Si/Al ratio in general makes it very difficult to maintain the reaction for such a long period. This shows that oxygen induces/enhances dehydrogenation of *n*-butene to butadiene to an unexpected high level, although the concentration of Fe and other transition metal oxides was lower than 50 ppm (XRF).

Detailed analysis of kinetic data revealed that separate pathways for propene and pentene formation and octene formation over H-FER exist. It is concluded that transport of reactants and products constrains *n*-butene isomerization to the outer shell of the zeolite particle. At typical reaction temperatures (at around 350°C) iso-butene production is limited by desorption. After a few hours time on stream at 350°C, due to diffusion constrains and extensive pore filling by coke deposition, the isomerization reaction is in all cases confined to the pore entrance of the channels. The desorbing iso-butene molecules, however, restrict the free access of *n*-butenes to the active sites.

Our results demonstrate, in perfect agreement, what was said above, that coke does not play a vital role in selective skeletal isomerization leading to iso-butene. A mechanism is described in which the selective isomerization is related to the Brønsted acid sites of the zeolite. Coke, resulting from oligomerization and gradual dehydrogenation, is involved in unselective reactions resulting in a wide range of molecules with skeleton of C_1–C_7.

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REFERENCES

1. Butler, A. C., and Nicolaides, C. P., *Catal. Today* **18**, 443–471 (1993).
2. Szabo, J., Perrotey, J., Szabo, G., Duchet, J.-C., and Cornet, D., *J. Mol. Catal.* **67**, 79–90 (1991).
3. Mooiweer, H. H., de Jong, K. P., Kraushaar-Czarnetzki, B., Stork, W. H. J., and Krutzen, B. C. H., *in* "Zeolites and Related Microporous Materials; State of the Art 1994" (J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Hölderich, Eds.). *Stud. Surf. Sci. Cat.* **84**, 2327–2334 (1994).
4. de Jong, K. P., Mooiweer, H. H., Buglass, J. G., and Maarsen, P. K., *in* "Catalyst Deactivation 1997" (C. H. Bartholomew and G. A. Fuentes, Eds.). *Stud. Surf. Sci. Cat.* **111**, 127–138 (1997).
5. EP 0 574 994 A1, EP 0 574 994 B1.
6. US 4 251 499.
7. Szabo, J., *Appl. Catal. A* **96**, 319–330 (1993).
8. Meriaudeau, P., Bacaud, R., Ngoc Hung, L., and Vu, Anh. T., *J. Mol. Catal. A* **110**, L177–L179 (1996).
9. Gielgens, L. H., Veenstra, I. H. E., Ponec, V., Haanepen, M. J., and Hooff, J. H. C., *Catal. Lett.* **32**, 195–203 (1995).
10. Xu, W.-Q., Yin, Y.-G., Suib, S. L., and O'Young, C.-L., *J. Phys. Chem.* **99**, 758–765 (1995).
11. Guisnet, M., Andy, P., Gnep, N. S., Travers, C., and Benazzi, E., *J. Chem. Soc., Chem. Commun.* 1685 (1995).
12. Guisnet, M., Andy, P., Boucheffa, Y., Gnep, N. S., Travers, C., and Benazzi, E., *Catal. Lett.* **50**, 159–164 (1998).
13. Andy, P., Gnep, N. S., Guisnet, M., Benazzi, E., and Travers, C., *J. Catal.* **173**, 322–332 (1998).
14. Houzvicka, J., Hansildaar, S., and Ponec, V., *J. Catal.* **167**, 273–278 (1997).
15. Houzvicka, J., Klik, R., Kubelkova, L., and Ponec, V., *Catal. Lett.* **43**, 7–10 (1997).
16. Houzvicka, J., Diefenbach, O., and Ponec, V., *J. Catal.* **164**, 288–300 (1996).
17. Pirngruber, G. D., Seshan, K., and Lercher, J. A., *in* "Catalyst Deactivation 1999" (B. Delmon and G. F. Froment, Eds.). *Stud. Surf. Sci. Cat.* **81**, 307–315 (1999).
18. Roine, A., "HSC Chemistry." Outokumpu Research Oy, Pori, Finland, 1994. Available at http://www.outokumpu.com/hsc/index.htm.
19. Wichterlova, B., Zilkova, N., Uvarova, E., Cejka, J., Sarv, P., Paganini, M. C., and Lercher, J. A., *Appl. Catal. A: Gen.* **182**, 297–308 (1999).
20. Asensi, M. A., and Martínez, A., *Appl. Catal. A: Gen.* **183**, 155–165 (1999).
21. Meier, W. M., Olson, D. H., and Baerlocher, Ch., "Atlas of Zeolite Structure Types," 3rd ed., 1992.
22. Millini, R., and Rossini, S., *in* "Progress in Zeolite and Microporous Materials." *Stud. Surf. Sci. Cat.* **105**, 1389–1396 (1997).
23. Jousse, F., Leherte, L., and Vercauteren, D. P., *Mol. Sim.* **17**, 175–196 (1996).
24. Eder, F., Ph.D. thesis, University of Twente, Enschede, The Netherlands, 1996.
25. van de Runstraat, A., van Grondelle, J., and van Santen, R. A., *J. Catal.* **167**, 460–463 (1997).