

# Skeletal Isomerization of *n*-Butenes

## I. Mechanism of *n*-Butene Transformation on a Nondeactivated H-Ferrierite Catalyst

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The transformation of *n*-butenes and of isobutene was carried out at 350°C on a fresh H-FER zeolite (Si/Al = 13.8) with various contact times so as to obtain a large range of conversion (from 5 to 65%). With both reactants the skeletal isomerization was accompanied by the formation of various products. The skeletal isomer, propene, pentenes, octenes (traces), and *n*-butane (from *n*-butenes) or isobutane (traces from isobutene) appeared as primary products. The simultaneous formation of the skeletal isomer and of propene and pentenes proved that we were in the presence of a dimerization-cracking process. Moreover, the low amount of octenes in the products showed that dimerization was the limiting step of the process. The dimerization step involved two secondary carbenium ions, which explained its slow rate. The dimer was rapidly isomerized through Type A (alkyl shift) or Type B (via protonated cyclopropanes) isomerization into the other octenes. Lastly octenes with a trimethylpentane or a dimethylhexane skeleton were rapidly cracked into isobutene, propene, and pentenes through Type A (involving two tertiary carbenium ions) and Type B (involving one tertiary and one secondary carbenium ions) mechanisms. The transformation of *n*-pentenes and of *n*-octenes confirmed the high rate of the Type A and B isomerization and cracking steps. The slow rate of octene formation from butenes was also due to an inhibition of the diffusion of branched octenes in the narrow pores of H-FER. The shape selectivity of H-FER was also responsible for the very slow formation of isobutane by hydrogen transfer from coke precursors to isobutene and for the unexpected slow formation of propene and of pentenes from isobutene. © 1996 Academic Press, Inc.

### INTRODUCTION

Due to its use in the synthesis of methyltertiobutylether (MTBE), an oxygenated gasoline additive having a high octane number (1, 2), there is an increasing interest in the production of isobutene from *n*-butenes. A large variety

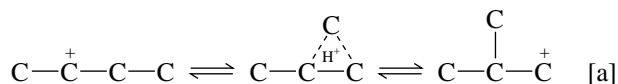
of acidic catalysts have been reported as being active in the isomerization of *n*-butenes into isobutene (3):

halogenated aluminas and particularly fluorinated aluminas (4–13),

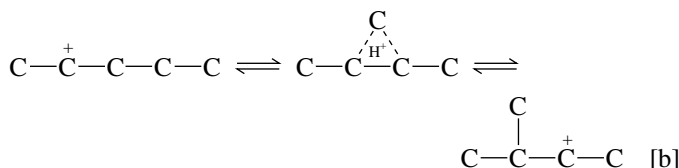
nonhalogenated doped aluminas (14–16), e.g., silicated aluminas, boron, or tin phosphate (17, 18),

10-membered ring zeolites such as MFI, MEL, FER, Theta-1 (19–25), boroaluminosilicate molecular sieves (26), MCM-22 (27), and silicoaluminophosphate (28–30).

The skeletal isomerization of C<sub>4</sub> hydrocarbons (butanes or butenes) through acid catalysis compared to that of larger hydrocarbons presents important particularities (31–33). Indeed the monomolecular mechanism of C<sub>4</sub> isomerization involves necessarily a very unstable primary carbenium ion intermediate even if, as generally admitted, a protonated cyclopropane intermediate is also involved,



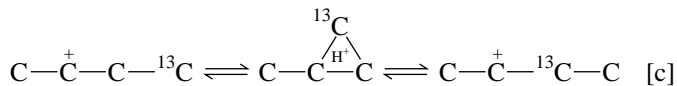
which it is not the case for the isomerization of larger hydrocarbons,



The consequence, demonstrated by Chevalier *et al.* (33) in the case of a very low pressure of butenes is that reaction [a] is much slower than reaction [b] or than the scrambling

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of  $^{13}\text{C}$  in  $\text{C}_4$  molecules which involves the same intermediates as reaction [b]



In spite of this, the monomolecular mechanism has been proposed by various authors to explain the skeletal isomerization of butanes (34) and of butenes (4, 12, 21).

According to other authors (24, 35–38) a bimolecular mechanism is responsible for the relatively rapid skeletal isomerization of *n*-butanes or of *n*-butenes when a relatively high reactant pressure is used. With *n*-butenes as a reactant this mechanism involves three successive steps: dimerization of butenes, skeletal isomerization of the dimers, and cracking of the octene isomers. When the various steps are considered, propene + pentenes and isobutene are formed simultaneously. Therefore the simultaneous formation of these alkenes (or in the case of *n*-butane transformation, that of propane, pentanes, and isobutane) constitutes a strong argument in favor of this “bimolecular” mechanism as shown in this paper. However, it has sometimes been considered that the formation of propene and pentenes was a process completely independent of the skeletal isomerization of *n*-butenes (12, 26). The participation of the bimolecular process has been demonstrated for the isomerization of *n*-butane into isobutane over mordenites (37) or over Fe, Mn-promoted sulfated  $\text{ZrO}_2$  catalyst by using  $^{13}\text{C}$ -labeled molecules (38).

We show here that this bimolecular mechanism explains the transformation of *n*-butenes and isobutene over a non-deactivated H-FER catalyst. A process for the skeletal isomerization of *n*-butenes, using this catalyst, has been developed by Lyondel Petrochemicals. This new process would “produce isobutene at potentially half the capital cost of alternative technologies” (25, 39).

## EXPERIMENTAL

Ferrierite (FER) was prepared in fluoride medium at the Laboratoire des Matériaux Minéraux in Mulhouse (France). Its H-form was prepared by  $\text{NH}_4^+$  ion exchange which was performed three times with an excess of 10 *N* ammonium nitrate solution during 4 h at 373 K; its Na, K content was less than 50 ppm and its Si/Al ratio was equal to 13.8. Prior to use, it was calcined *in situ* under dry air flow at 773 K.

The transformations of 1-butene (99.4% pure), isobutene (99.5% pure), propene (99.4% pure), 1-pentene (97% pure), and 1-octene (98% pure) were carried out in a flow reactor in the presence of nitrogen at 623 K under atmospheric pressure; the reactant and nitrogen partial pressures were equal to 0.1 and 0.9 bar, respectively. In every

case, the weight hourly space velocity (WHSV) was varied (from 2 to 70  $\text{h}^{-1}$ ) to obtain a large range of reactant conversion (from 5 to 65%). Reaction products from all these reactants were analyzed on-line by gas chromatography using a 50-mChrompack PLOT  $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$  capillary column.

## RESULTS

### 1. Preliminary Study of 1-Butene and Isobutene Transformations

A preliminary study of 1-butene and isobutene transformations was carried out under the following conditions:  $T = 623 \text{ K}$ ,  $p_{\text{alkene}} = 0.1 \text{ bar}$ ,  $p_{\text{N}_2} = 0.9 \text{ bar}$ , 0.05 g of catalyst, alkene flow rate = 18.4  $\text{mmol h}^{-1}$  (i.e.,  $\text{WHSV} = 20.6 \text{ g of alkene introduced per gram of catalyst and per hour}$ ).

From *n*-butenes the main reaction products are isobutene, propene, pentenes (iso- and *n*-), and *n*-butane. Ethylene, ethane, propane, hexenes, heptenes, and octenes are observed in low amounts. From isobutene the main products are *n*-butenes, propene, pentenes, and octenes; ethylene, propane, *n*-butane, isobutane, and hexenes are also observed. Table 1 gives the product distribution (wt%) obtained after a 5-min reaction.

Whatever the reactant, the distribution of linear butenes is close to that of thermodynamic equilibrium, which means that the double bond shift is very fast. Therefore the conversion is calculated by grouping *n*-butene isomers together. Figure 1 shows the change with time-on-stream (TOS) in the total conversion of *n*-butenes and in their conversion into the main products. The conversion into isobutene increases slightly during the first 3 h then decreases. A quasi-identical curve is obtained for the conversion into octenes. On the other hand there is a rapid initial decrease in the conversion into the other products: ethylene, propene, propane, *n*-butane, pentenes, hexenes, and heptenes. Therefore the selectivity to isobutene increases from 57 wt% at TOS = 5 min to about 92 wt% at TOS > 200 min. This selectivity increase is probably due to the formation of carbonaceous deposits (coke) (40). The same phenomenon is observed for isobutene transformation, the catalyst deactivation, however, being less pronounced. The selectivity to *n*-butenes increases from 91.5 wt% at TOS = 5 min to 97.5 wt% at TOS = 450 min. It can be remarked that this selectivity to the skeletal isomers is much higher than that observed in *n*-butene transformation.

### 2. Kinetic Study of 1-Butene and of Isobutene Transformations

To limit the effect of deactivation on the activity and selectivity, the kinetic study of 1-butene and of isobutene

TABLE 1

Distribution (wt%) of the Products of *n*-Butene and of Isobutene Transformations after 5-min Reaction for a WHSV Value of 20.6 h<sup>-1</sup>

	$X^a$	C <sub>2</sub> <sup>-</sup>	C <sub>3</sub> <sup>-</sup>	C <sub>3</sub>	<i>n</i> -C <sub>4</sub> <sup>-</sup>	<i>i</i> -C <sub>4</sub> <sup>-</sup>	<i>n</i> -C <sub>4</sub>	<i>i</i> -C <sub>4</sub>	C <sub>5</sub> <sup>-</sup>	C <sub>6</sub> <sup>-</sup>	C <sub>7</sub> <sup>-</sup>	C <sub>8</sub> <sup>-</sup>	Σ
<i>n</i> -Butenes	14.6	1	19.4	0.5	0	61.2	4.5	0	10.7	1.35	0.85	0.5	100
Isobutene	17.3	0.25	3.6	0.1	91.5	0	0.65	0.1	2.25	0.15	0	1.4	100

<sup>a</sup> Conversion.

transformations was carried out at low TOS values. A rectangular pulse technique was used for determining the effect of the operating parameters: injecting the reactant for 3 min (a constant value of the reactant concentration was obtained after about 2 min), analyzing the products by on-line gas chromatography (50 min), and the catalyst being kept during this time under a nitrogen flow of 4000 ml h<sup>-1</sup>

**2.1. Effect of contact time: Reaction scheme.** Figure 2 shows as an example the effect of contact time (actually the reverse of WHSV, i.e., a value proportional to contact

time) on the conversion of *n*-butenes into isobutene, propene, pentenes, and *n*-butane. From this type of figure the kinetic nature of the products (primary, secondary, etc., according to the classification of Abbot and Wojciechowski (41)) can be deduced. Moreover, the rates of transformation of the reactant into the primary products can be determined from the initial slope of the curves. The curves giving the yields as a function of the conversion (Fig. 3) confirm the kinetic nature of the products.

In *n*-butene transformation, isobutene, propene, pentenes, *n*-butane, ethylene, and octenes appear as primary products while ethane, propane, isobutane, hexenes, and

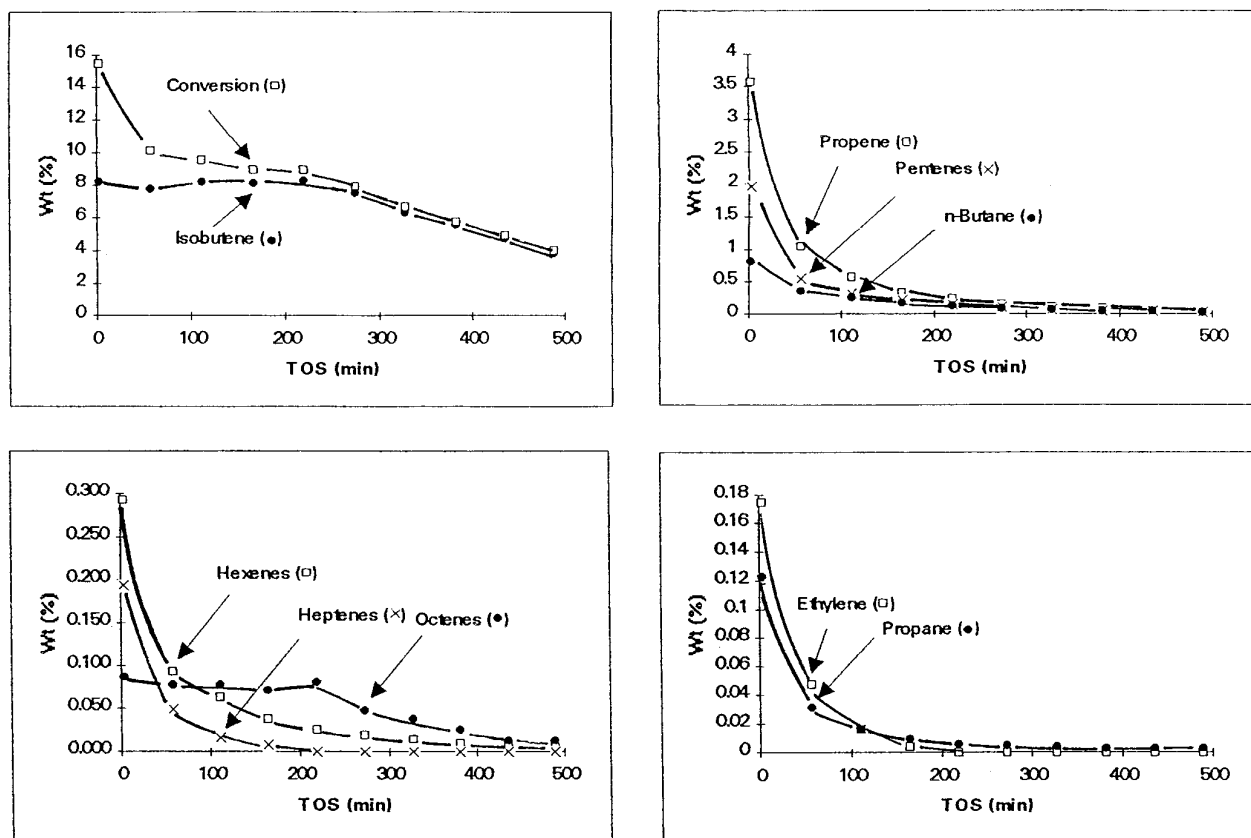


FIG. 1. Influence of time-on-stream (TOS) on the conversion of *n*-butenes into various products. Operating conditions:  $P_{n\text{-butene}} = 0.1$  bar; WHSV = 20.6 h<sup>-1</sup>.

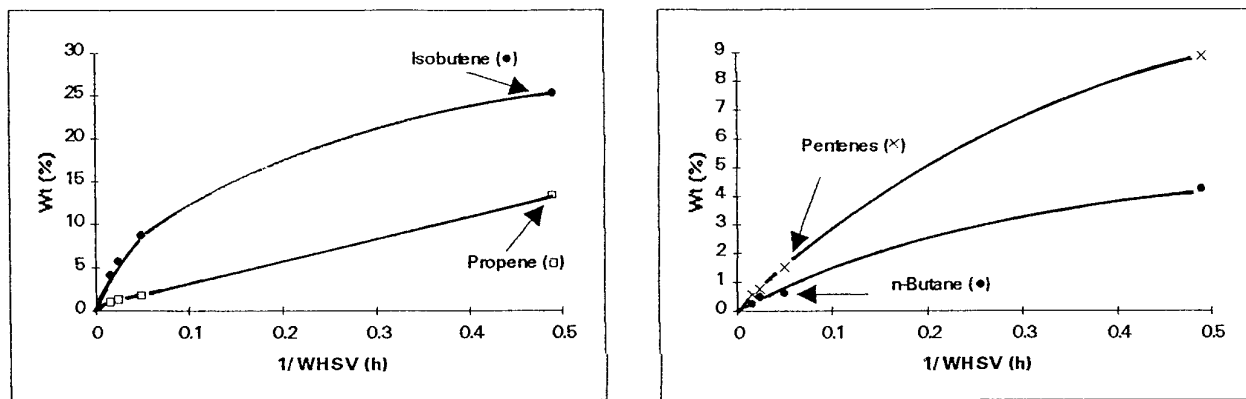


FIG. 2. Transformation of *n*-butenes on a nondeactivated H-FER sample. Effect of contact time on the yields of the main reaction products.

heptenes are secondary. It must be emphasized that the molar ratios between propene and pentenes and between ethylene and hexenes are always greater than 1. Thus the molar ratio between propene and pentenes passes from about 2 at zero conversion to about 3 at 60% conversion. In isobutene transformation, *n*-butenes, pro-

pane, pentenes, isobutane (only traces), and octenes appear as primary products while ethylene, propane, *n*-butane, and hexenes are secondary products. Moreover, there is also a secondary mode of formation of propene and pentenes. Like for *n*-butene transformation the propene/pentenes molar ratio is between 2 and 3 and

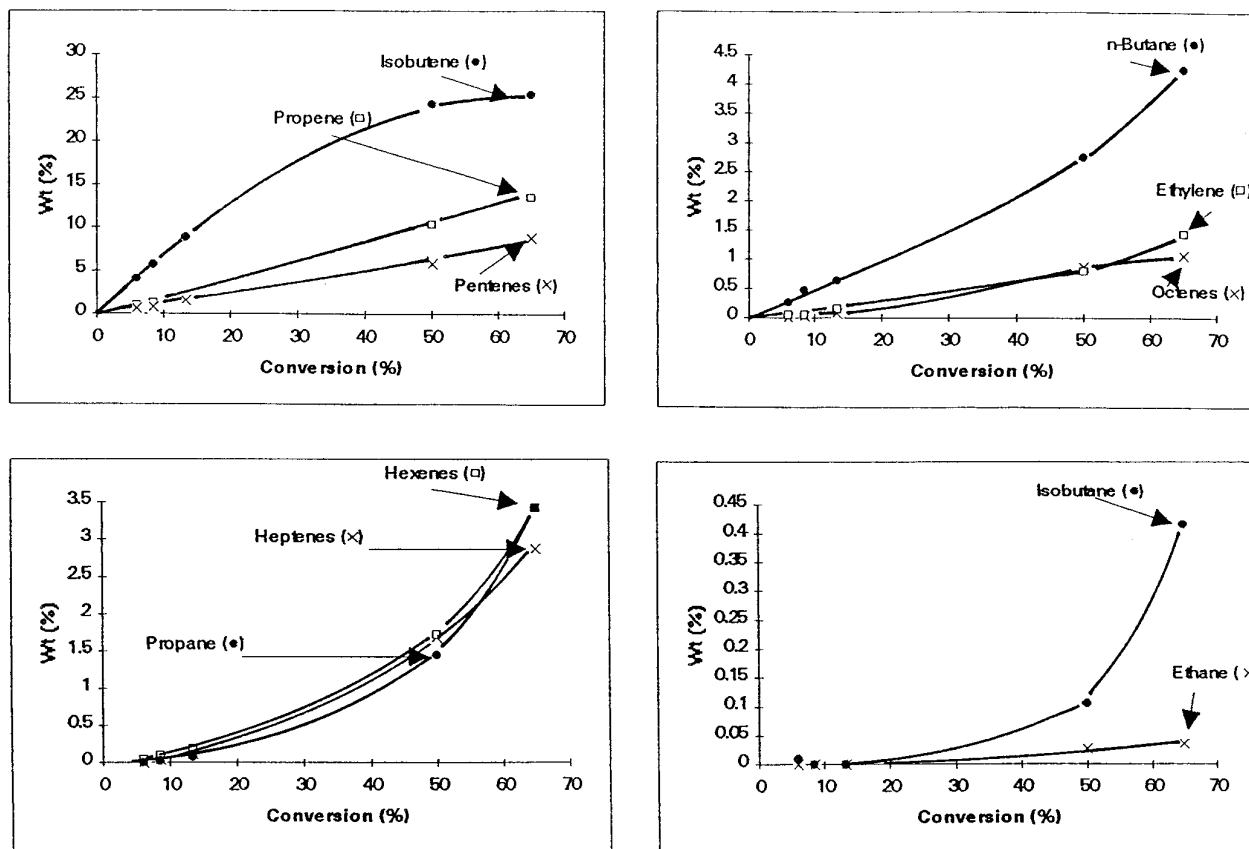


FIG. 3. Transformation of *n*-butenes on a nondeactivated H-FER sample. Yields of products versus conversion of *n*-butenes.

TABLE 2  
Rates of Transformation of Alkenes into Apparent Primary Products on the  
Nondeactivated Ferrierite

Product: Reactant	Rate (mmol h <sup>-1</sup> g <sup>-1</sup> )						
	Propene	Isobutene	<i>n</i> -Butenes	Pentenes	Butane	Hexenes	Octenes
<i>n</i> -Butenes	9	68		7 ( <i>n</i> + <i>i</i> )	4 ( <i>n</i> )	1-2	0.7 ( <i>n</i> + <i>i</i> )
Isobutene	1.2		141	1 ( <i>n</i> + <i>i</i> )	0.2 ( <i>i</i> )		3.4 ( <i>n</i> + <i>i</i> )
Propene						100	
<i>n</i> -Pentenes				1300 ( <i>i</i> )			
1-Octenes	33	6	40	50 ( <i>n</i> + <i>i</i> )			4500 ( <i>i</i> )

the distribution of pentenes is slightly different from that at thermodynamic equilibrium.

The rates of *n*-butene and of isobutene transformations into the apparent primary reaction products are reported in Table 2. Curiously the ratio between the skeletal isomerization rates of isobutene and of *n*-butenes is greater than the ratio expected from the thermodynamic equilibrium (2 instead of 1.3). This greater value cannot be due to deactivation phenomena because the initial deactivation of *n*-butene isomerization (Fig. 1) or of isobutene isomerization is slow. Furthermore, *n*-butenes are transformed more rapidly into propene and pentenes than isobutene (about 7 times) and more slowly into octenes (about 5 times). Moreover the rate of transformation of *n*-butenes into *n*-butane is at least 20 times greater than that of isobutene into isobutane.

**2.2. Influence of the operating parameters.** The effect of the operating parameters is as follows: partial pressure of the reactant, temperature, on the initial rates of formation of the main primary products was determined either by using various samples of catalysts under different conditions or by varying the operating conditions on one sample. In the range of pressure under consideration (0.05 to 0.3 bar) the reaction order with respect to *n*-butenes is close to 1 for the formation of propene and pentenes while it is smaller than 1 (about 0.5) for the skeletal isomerization of *n*-butenes. On the other hand, the order with respect to isobutene for its isomerization into *n*-butenes is close to 1. The activation energy for *n*-butene isomerization is equal to  $14 \pm 1$  kcal mol<sup>-1</sup> and that for isobutene isomerization is equal to  $10 \pm 1$  kcal mol<sup>-1</sup>. The values for the formation of propene and of pentenes from *n*-butenes are lower, but rapid deactivation makes it impossible to determine them with precision.

### 3. Transformation of Side Products of Butene Conversion

The transformation of propene, 1-pentene, and 1-octene was carried out under the standard conditions of butene

conversion, the pressure of reactant being equal to 0.1 bar. The following main products were obtained:

- from propene: hexenes, butenes, pentenes, ethene, propane
- from 1-pentene: the thermodynamic equilibrium mixture of *n*-pentenes, isopentenes, propene, ethene, butenes, hexenes
- from 1-octene: *n*-octenes and most of the isoctenes (more than 20 GC peaks), butenes, pentenes, propene.

From the effect of the contact time (carried out with the rectangular pulse technique) it is possible to classify these products into primary and secondary ones. From propene, only hexenes appear as primary products, from *n*-pentenes, only isopentenes, and from *n*-octenes, isoctenes, butenes, pentenes, and propene. Table 2 compares the rates of transformation of the reactants into these primary products with those of *n*-butenes and isobutene transformations.

## DISCUSSION

The preliminary study of *n*-butene and isobutene transformations on H-FER confirms the significant positive effect deactivation by coke deposit has on the selectivity of the skeletal isomerization (29, 40). This curious positive effect of coke was recently attributed to the development of a new reaction mechanism involving as active sites carbocations blocked in the zeolite pores (40). The present article is limited to the establishment of reaction schemes and mechanisms on nondeactivated catalyst samples.

### 1. Generalities

On the nondeactivated H-FER catalysts the transformation of *n*-butenes and of isobutene is very complex. Indeed the skeletal isomerization is accompanied by the formation of various products. This formation involves one or several of the following reactions: dimerization of alkenes (or al-

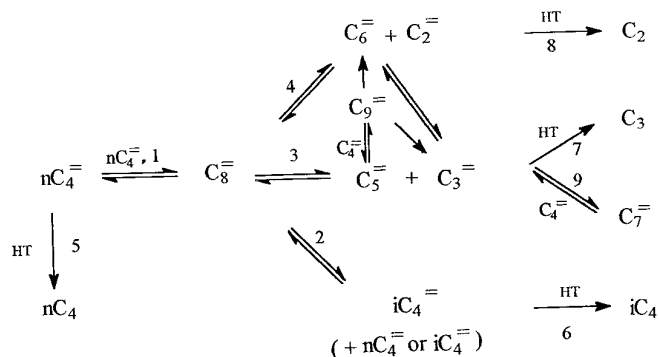


FIG. 4. Scheme of *n*-butene transformation on a nondeactivated H-FER sample.

kylation of one alkene by another), cracking, and hydride transfer from coke precursors to alkenes. Moreover, if the same reversible steps are involved in *n*-butene and isobutene isomerizations, certain results cannot be easily explained, namely the following.

i. The ratio between the initial rates of skeletal isomerization of isobutene and of *n*-butenes is greater than the

value deduced from the thermodynamic equilibrium data (2 instead of 1.3).

ii. The activation energy for isobutene isomerization is lower than that found for *n*-butene isomerization although the reverse is expected from the exothermicity of *n*-butene isomerization.

iii. The reaction order with respect to *n*-butenes is equal to 0.5 while the one with respect to isobutene is equal to 1. If it is supposed that the reversible *n*-butene–isobutene isomerization occurs through a monomolecular mechanism this would mean that isobutene is weakly adsorbed, *n*-butene adsorption being relatively strong although the contrary is expected from the stability of the corresponding carbocations.

Therefore it can be concluded that *n*-butene and isobutene isomerization reactions do not involve the same steps and hence do not occur through the same mechanisms. Since isobutene isomerization occurs with only the slow formation of propene and pentenes (which requires necessarily a dimerization-cracking mechanism with an intermediate isomerization of the C<sub>8</sub> dimer), it could be supposed that this reaction occurs mainly through a monomolecular

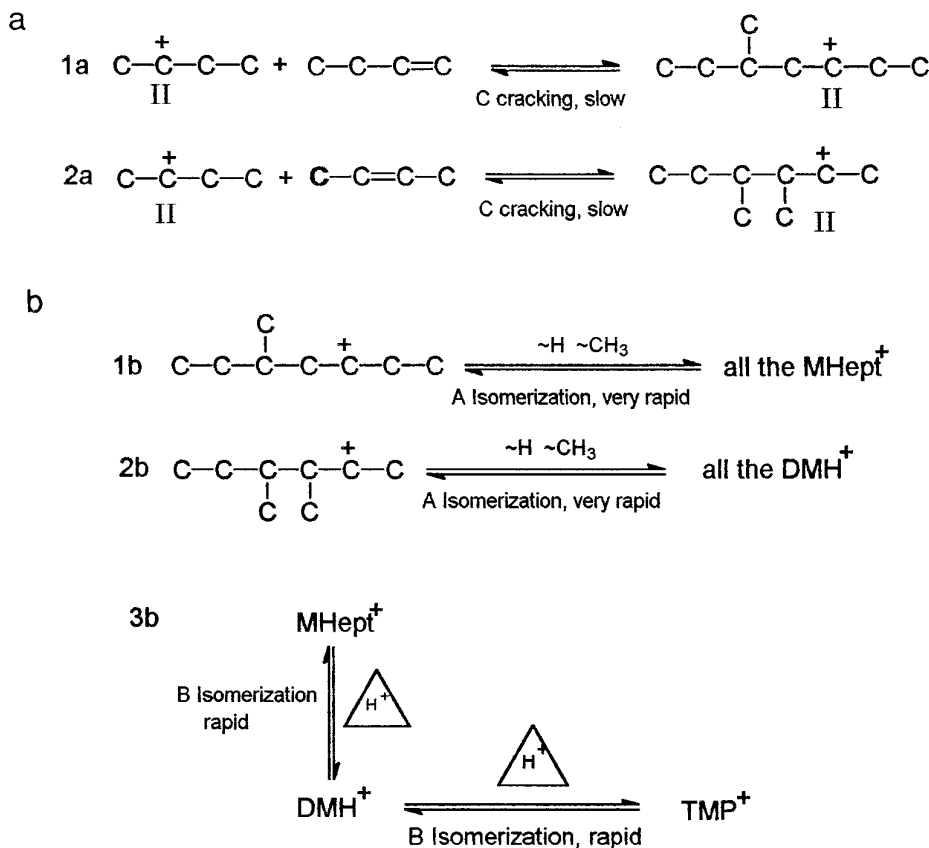


FIG. 5. Transformation of *n*-butenes through the dimerization-cracking mechanism: (a) Dimerization steps, (b) isomerization of the dimers, and (c) cracking steps. MHept, methylheptyl; DMH, dimethylhexyl; TMP, trimethylpentyl.

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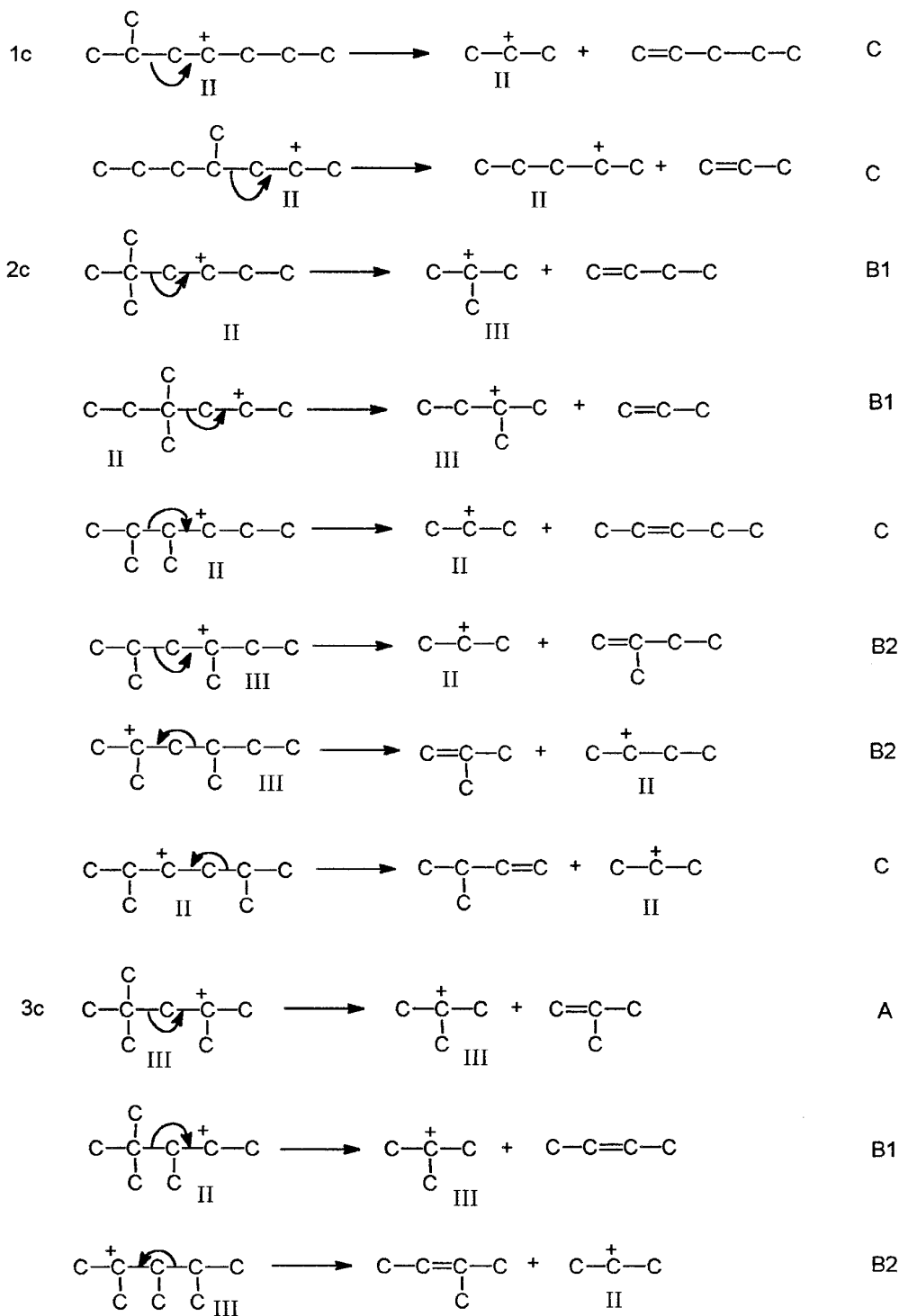


FIG. 5—Continued

mechanism. On the other hand the skeletal isomerization of *n*-butenes which is accompanied by the formation of a large amount of propene and pentenes would occur preferentially through the dimerization-cracking mechanism. However, the monomolecular mechanism which requires the formation of a very unstable primary carbenium ion (reaction [a]) is most unlikely. Also, in disfavor of this monomolecular mechanism the activation energy for isobutene isomerization is lower than that for *n*-butene isomerization whose intermediates are more stable. A more realistic proposal is that *n*-butene and isobutene skeletal isomerizations occur through the dimerization-cracking mechanism but that these isomerization reactions do not involve the same C<sub>8</sub> intermediates.

## 2. *n*-Butene Transformation: Reaction Scheme and Mechanisms

The scheme in Fig. 4 could be proposed to explain the primary or secondary apparent formations of the products. It must be underlined that most likely the C<sub>8</sub> carbenium ions (rather than the octenes desorbed from the zeolite) are the real intermediates in the production of C<sub>2</sub><sup>2-</sup>, C<sub>3</sub><sup>2-</sup>, *i*-C<sub>4</sub><sup>2-</sup>, C<sub>5</sub><sup>2-</sup>, C<sub>6</sub><sup>2-</sup>. Because these products appear as primary ones, steps 2, 3, and 4 are necessarily faster than step 1. Furthermore line 1 in Table 2 shows that step 2 is faster than step 3 (about 4 times) and much faster than step 4 (20–50 times). Hydride transfer to *n*-C<sub>4</sub><sup>2-</sup> (step 5) is about 15 times slower than butene isomerization (through steps 1 and 2). Hydride transfer to isobutene (step 6) is very slow, which could be due to the bulk of the reaction intermediate while hydride transfer to propene (step 7) and to ethylene (step 8) appears to occur at rates similar to those in step 5. Hydrogen transfer reactions can be considered as irreversible while dimerization, alkylation, and cracking are reversible (Fig. 4).

The main steps involved in the dimerization-cracking mechanism of *n*-butene transformation are described in Fig. 5. For the sake of simplification the steps involving primary carbenium ions as intermediates which are very slow are not included. Three types of steps can be distinguished: (a) the dimerization steps, (b) the isomerization of the dimers, and (c) the cracking of the C<sub>8</sub> carbenium ions.

Dimerization (steps 1a and 2a) leads to carbenium ions with a 3-methylheptane and with a 3,4-dimethylhexane skeleton, respectively, the second one being certainly favored because of the larger amount of 2-butenes. Indeed, even at very low contact times, a thermodynamic equilibrium mixture of *n*-butenes (22.5% 1-butene, 77.5% 2-butenes) is formed. It must be emphasized that steps 1a and 2a are the reverse steps of Type C cracking reactions (i.e., involving two secondary carbenium ions (42)).

The carbenium ions formed through steps 1a and 2a can be transformed through hydride transfer and alkyl shift

(Type A isomerization) into all the carbenium ions with methylheptane or dimethylhexane skeletons (steps 1b and 2b). Isomerization with supplementary branching (Type B isomerization, i.e., through protonated cyclopropanes) can also occur with formation of carbenium ions with a trimethylpentane skeleton (step 3b).

The cracking of carbenium ions with a monobranched skeleton involves two secondary carbenium ions as intermediates (Type C cracking), while the cracking of di-branched carbenium ions can occur through Types B1 and B2 (one secondary + one tertiary carbenium ions involved) or through Type C steps. Lastly scission of carbenium ions with a tribranched skeleton can occur through Type A (two tertiary carbenium ions involved) or through Type B steps (see Fig. 5).

According to Brouwer (32), the rates of the various cracking and isomerization steps decrease as follows:

Hydride shift > A isomerization > A cracking  
> B isomerization > B1, B2 cracking  
> C cracking.

However, Martens *et al.* (43) report that Type A cracking is faster than Type A isomerization. Therefore the slowest step of the dimerization-cracking mechanism would be the dimerization steps (steps 1a and 2a), which are the reverse steps of C cracking reactions and even more that at the reaction temperature, dimerization compared to cracking is highly unfavored.

The participation of Type B isomerization steps in *n*-butene transformation (step 3b) is confirmed by experiments with *n*-pentenes and *n*-octenes. Indeed the skeletal isomerization of *n*-pentenes which occurs through protonated cyclopropane intermediates (Type B isomerization) is much faster than the transformation of *n*-butenes into isobutene (20 times), into propene (150 times), and into pentenes (200 times). Moreover, this is demonstrated by the apparent direct formation of isobutene and isopentenes from 1-octene: the formation of these products requires two or three successive Type B isomerization steps (for the formation of carbenium ions with a di- or tribranched skeletons) followed by Type A or B cracking steps.

Figure 5 shows that isobutene, propene, and pentenes can be formed from *n*-butenes through various pathways. Isobutene can result from A and B1 cracking of carbenium ions with trimethylpentane skeleton (TMP<sup>+</sup>) and from B1 and B2 cracking of carbenium ions with a dimethylhexane skeleton (DMH<sup>+</sup>). The formation of TMP<sup>+</sup> requires at least one Type B isomerization of the carbenium ions resulting from *n*-butene dimerization while that of DMH<sup>+</sup> can occur through a Type A isomerization. Propene and pentenes can result from Type B2 cracking of TMP<sup>+</sup>; from B1, B2, and C cracking (two possibilities) of DMH<sup>+</sup>; and from C cracking of carbenium ions with a methylheptane

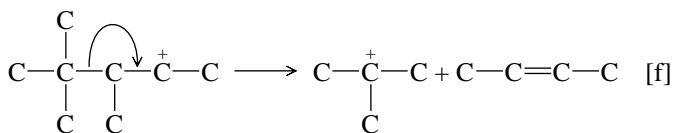
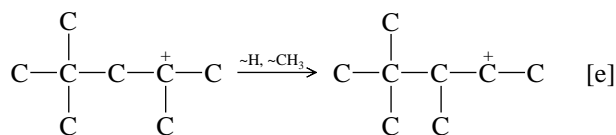
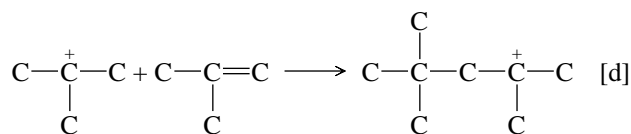


skeleton. C cracking steps, being very slow compared to B cracking, can probably be neglected. From this figure it can be concluded that the dimerization-cracking mechanism must lead not only from *n*-butenes to propene and pentenes but also to isobutene. However, as observed, isobutene formation is faster than propene + pentenes formation for it involves a very rapid A cracking step.

### 3. Isobutene Transformation: Reaction Scheme and Mechanisms

The formation of *n*-butenes, propene, and pentenes as primary products shows that the cracking steps of the dimerization-cracking mechanism are, as is the case for *n*-butene transformation, faster than the dimerization steps. However, a larger amount of octenes is found. This shows that the difference between the rates of dimerization and cracking steps is less pronounced than in the case of *n*-butene transformation. In agreement with this proposal, ethylene appears as a secondary product, whereas it is an apparent primary product of *n*-butene transformation. Moreover, to the primary mode of propene + pentenes formation is added another mode of formation (probably via secondary transformation of *n*-butenes). Furthermore hydrogen transfer from coke precursors to isobutene is 20 times slower than that to *n*-butenes. This is probably due to steric constraints in the formation of the transition state of hydrogen transfer to isobutene.

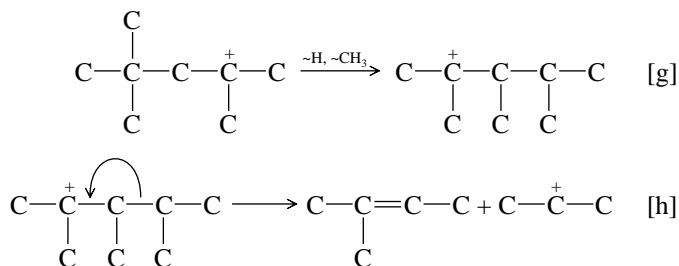
As suggested previously, isobutene isomerization does not occur through the reverse steps of *n*-butene isomerization. Indeed the most likely pathway of isobutene isomerization is as follows:



All these steps are rapid. Indeed step [d] is the reverse step of Type A cracking, step [e] is an A type isomerization, and step [f] a B2 type cracking. This explains why the rate of isobutene isomerization is twice as fast as the rate of *n*-butene isomerization (instead of the 1.3 value expected from a reversible process) and also why the activation

energy is lower for isobutene than for *n*-butene isomerization.

The propene + pentenes formation is much slower than isobutene isomerization, which was not expected from the dimerization-cracking mechanism. Indeed the formation of these products involves practically the same steps as isobutene isomerization:



This means most likely that either the formation of the 2,3,4-TMP<sup>+</sup> carbenium ion (reaction [g]) or its cracking (reaction [h]) are strongly inhibited in the H-FER pores.

Another effect of the H-FER shape selectivity is the slow formation of octenes. Indeed step [f] (B cracking) being slower than step [e] (A isomerization) and slower than the reverse of step [d] (A cracking), a large amount of octenes should be observed in the products of isobutene transformation. This is not the case even if the formation of octenes from isobutene is faster than from *n*-butenes (Table 2). This can be attributed to limitations in the diffusion of branched dimers in the narrow pores of H-FER (24), hence in the desorption of these dimers from the zeolite crystallites.

## CONCLUSION

The reaction schemes of *n*-butene and of isobutene transformations on a nondeactivated H-FER sample were established. The formation of the main products, skeletal isomer(s), propene, and pentenes, involves dimerization steps followed by isomerization of the dimers and their cracking. The dimerization step is much slower than the isomerization and cracking steps because the latter involve more stable carbenium ions and because the diffusion of branched dimers in the narrow pores of H-FER is inhibited. The shape selectivity of H-FER limits also the formation of propene, pentenes, and isobutane from isobutene. There is no need to involve a monomolecular mechanism to explain the skeletal isomerization of butenes on the nondeactivated H-FER catalyst.

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## REFERENCES

- Juguin, B., Torck, B., and Martino, G., in "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), Stud. Surf. Sci. Catal., Vol. 20, p. 253. Elsevier, Amsterdam, 1985.
- Maxwell, I. E., Naber, J. E., and de Jong, K. P., *Appl. Catal., A: General* **113**, 153 (1994).
- Butler, A. C., and Nicolaidis, C. P., *Cataly. Today* **18**, 443 (1993).
- Choudhary, V. R., and Doraiswamy, L. K., *J. Catal.* **23**, 54 (1971).
- Choudhary, V. R., "Chemical Industry Developments," Vol. VIII, No. 7, p. 32. Incorporating CP & E, 1974.
- Choudhary, V. R., *Ind. Eng. Chem., Prod. Res. Dev.* **16**, 12 (1977).
- Raghavan, N. S., and Doraiswamy, L. K., *J. Catal.* **48**, 21 (1977).
- Juguin, B., and Miguel, J., EP Patent No. 66485 (1982), assigned to Institut Français du Pétrole.
- Juguin, B., and Miguel, J., U.S. Patent No. 4434315 (1984), assigned to Institut Français du Pétrole.
- Cheng, Z. X., and Ponec, V., *Appl. Catal.* **118**, 127 (1994).
- Cheng, Z. X., and Ponec, V., *J. Catal.* **148**, 607 (1994).
- Szabo, J., Perrotey, J., Szabo, G., Duchet, J. C., and Cornet, D., *J. Mol. Catal.* **67**, 76 (1991).
- Szabo, J., Szabo, G., van Gestel, J., and Cornet, D., *Appl. Catal., A: General* **96**, 319 (1993).
- Juguin, B., and Martino, G., SA Patent No. 90/2870 (1991) and FR Patent No. 2657605 (1991), assigned to Institut Français du Pétrole.
- Travers, C., Dagand, J., Burzynski, J. P., and Courty, P., EP Patent No. 588660 (1992), assigned to Institut Français du Pétrole.
- Nilsen, B. P., Omferlo, J. H., and Gates, B. C., *Ind. Eng. Chem. Fundam.* **25**, 337 (1986).
- Nilsen, B. P., Stoeker, M., and Riis, T., in "Catalysis by Acids and Bases" (B. Imelik *et al.*, Eds.), Stud. Surf. Sci. Catal., Vol. 20, p. 253. Elsevier, Amsterdam, 1985.
- La Ginestra, A., Patrono, P., Massucci, M. A., Galli, P., Ferragina, C., and Mancini, C., in "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 1, p. 449. Chem. Institute of Canada, Ottawa, 1988.
- O'Young, C. L., Xu, W. Q., Simon, M. W., and Suib, S. L., in "Zeolite and Related Microporous Materials: State of the Art 1994" (J. Weitkamp *et al.*, Eds.), Stud. Surf. Sci. Catal., Vol. 84, p. 1671. Elsevier, Amsterdam, 1994.
- Simon, M. W., Suib, S. L., and O'Young, C. L., *J. Catal.* **147**, 484 (1994).
- Xu, W. Q., Yin, Y. G., Suib, S. L., and O'Young, C. L., *J. Catal.* **150**, 34 (1994).
- Simon, M. W., Xu, W. Q., Suib, S. L., and O'Young, *Microporous Mat.* **2**, 477 (1994).
- Grandvallet, P., Mooiweer, H. H., Kortfeek, A. G., and Kraushaar-Czarnetzki, B., EP Patent No. 0501577 A1 (1992), assigned to Shell International Research Maatschappij B.V..
- Mooiweer, H. H., de Jong, K. P., Kraushaar-Czarnetzki, B., Storck, W. H. J., and Krutzen, S. C. H., in "Zeolite and Related Microporous Materials: State of the Art 1994" (J. Weitkamp *et al.*, Eds.), Stud. Surf. Sci. Catal., Vol. 84, p. 2327. Elsevier, Amsterdam, 1994.
- Powers, D. H., Murray, B. D., Winquist, B. H. C., Callender, E. M., and Varner, J. H., EP Patent No. 0523823 A2 (1992), assigned to Lyondell Petrochemical Company.
- Bianchi, D., Simon, M. W., Nam, S. S., Xu, W. Q., Suib, S. L., and O'Young, *J. Catal.* **145**, 551 (1994).
- Bundens, R. G., Keville, K. M., Huss, A., Chu, C. T. W., and Husain, A., U.S. Patent No. 5146029 (1990), assigned to Mobil Oil Corporation.
- Gaffney, A. M., and Jones, C. A., U.S. Patent No. 5107050 (1990), assigned to Ares Chemical Technology L.P..
- Gajda, G. J., U.S. Patent No. 5132484 (1991), assigned to UOP.
- Gajda, G. J., and Barger, P. T., U.S. Patent No. 5191146 (1991), assigned to UOP.
- Brouwer, D. M., *Rec. Trav. Chim., Pays-Bas* **87**, 1435 (1968).
- Brouwer, D. M., in "Nato Adv. Stud. Inst., Series E" (R. Prins and G. C. A. Schuit, Eds.), Vol. 39, p. 137. Sijthoff & Noordhoff, Alphen aan den Rijn, 1980.
- Chevalier, F., Guisnet, M., and Maurel, R. in "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, F. C. Tompkins, Eds.), Vol. 1, p. 478. The Chemical Society, London, 1976.
- Garin, F., Seyfried, L., Girard, P., Maire, G., Abdulsamad, A., and Sommer, J., *J. Catal.* **151**, 26 (1995).
- Guisnet, M., Gnep, N. S., Bearez, C., and Chevalier, F., in "Catalysis by Zeolites" (B. Imelik *et al.*, Eds.), Stud. Surf. Sci. Catal., Vol. 5, p. 77. Elsevier, Amsterdam, 1980.
- Bearez, C., Chevalier, F., and Guisnet, M., *React. Kinet. Catal. Lett.* **22**, 405 (1983).
- Bearez, C., Avendano, F., Chevalier, F., and Guisnet, M., *Bull. Soc. Chim. Fr.* **3**, 346 (1985).
- Adeeva, V., Lei, G. D., and Sachtler, W. M. H., *Appl. Catal., A: General* **118**, L11 (1994).
- Chem. Eng. News*, March 23, 7 (1992).
- Guisnet, M., Andy, P., Travers, C. and Benazzi, E., *J. Chem. Soc., Chem. Commun.*, 1685 (1995).
- Abbot, J., and Wojciechowski, B. W., *J. Catal.* **90**, 270 (1984).
- Weitkamp, J., Jacobs, P. A., and Martens, J. A., *Appl. Catal.* **8**, 123 (1983).
- Martens, J. A., Jacobs, P. A., and Weitkamp, J., *Appl. Catal.* **20**, 239 (1986).