

Skeletal Isomerization of *n*-Butenes

II. Composition, Mode of Formation, and Influence of Coke Deposits on the Reaction Mechanism

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On a fresh HFER zeolite (Si/Al = 13.8) at 623 K, the skeletal isomerization of *n*-butenes is accompanied by various reactions: disproportionation into propene and pentenes, coking, hydrogen transfer (in the decreasing order of significance). While there is a rapid deactivation of disproportionation, coking, and hydrogen transfer reactions, owing to the blockage of the pores by carbonaceous compounds (coke), an increase in the rate of isomerization is at first observed followed by a decrease at long time-on-stream. At the maximum of isomerization only 10% of the pore volume remains accessible to nitrogen adsorbent. Moreover, IR spectroscopy shows that 75% of the OH groups are in interaction with coke molecules, the remaining 25% being inaccessible to ammonia and, hence, to the reactant. Coke was found to be composed of slightly condensed aromatics (with two to four aromatic rings) trapped at the intersections of the eight- and 10-membered-ring channels. Coke molecules result from the transformation of secondary benzenic products, slowly desorbed from the zeolite pores, through two different ways, (i) the classical route via alkylation, cyclization, and hydrogen transfer steps and (ii) dehydrogenative coupling. The large significance of this latter reaction in the formation of HFER coke molecules in comparison to the other zeolites, can be related to the proximity of adjacent channel intersections. To explain the initial increase in the rate of butene isomerization a new reaction process is proposed involving as active sites benzylic carbocations formed from coke molecules trapped in pores located near the outer surface of the crystallites (pore mouth catalysis). The deactivation of this reaction which occurs at long time-on-stream is shown to be due to the growth of the active coke molecules. © 1998 Academic Press

INTRODUCTION

Skeletal isomerization of *n*-butenes could play in the near future a significant role in the production of the isobutene intermediate in the synthesis of methyl *tert*-butylether (MTBE) (1, 2). This isomerization can be catalyzed by a large variety of acid catalysts (3, 4) in particular doped aluminas (5–7) and 10-membered-ring zeolites (7–11). The two main problems to be solved concern the secondary forma-

tion of dimers and of propene plus pentenes resulting from dimer cracking and the catalyst deactivation. It has been recently claimed that H ferrierite (HFER) was an excellent isomerization catalyst capable of operating at a relatively low temperature (623 K) (8) with a high selectivity to isobutene and a high stability. This zeolite presents two kinds of one-dimensional channels perpendicular intersected, one with small size apertures ($3.4 \times 4.7 \text{ \AA}$) the other with 10-membered ring apertures ($4.2 \times 5.4 \text{ \AA}$) (12).

On the fresh HFER catalyst, *n*-butene isomerization is accompanied by a significant formation of propene and pentenes, but of only a very small amount of octenes (smaller than with other catalysts (8)). This suggests a dimerization cracking mechanism in which the desorption of dimers is limited by the narrow pores of HFER (13). Curiously the rate of skeletal isomerization at first increases with time-on-stream while that of propene and pentenes rapidly decreases. The blockage by carbonaceous deposits (coke) of the access of the reactant to the zeolite pores is responsible for the rapid deactivation observed for propene and pentenes formation. To explain the curious increase in the rate of isobutene formation a new isomerization process involving as active sites carbocations formed from coke molecules located in pores close to the outer surface of the zeolite crystallites has been proposed (14, 15).

In this work the formation of coke during *n*-butene transformation over a HFER sample (Si/Al = 13.8) is investigated in detail. The composition of coke and its change as a function of reaction time was investigated and mechanisms are proposed for the formation of the various coke components. Moreover, the effect of coke on the acidic and catalytic properties of the zeolite was established, which allows us to understand the role played by coke on the various reactions and on their deactivation.

EXPERIMENTAL

Ferrierite (FER) was prepared in a fluoride medium at the "Laboratoire des Matériaux Minéraux" in Mulhouse (France). The H form was obtained by a threefold NH_4^+

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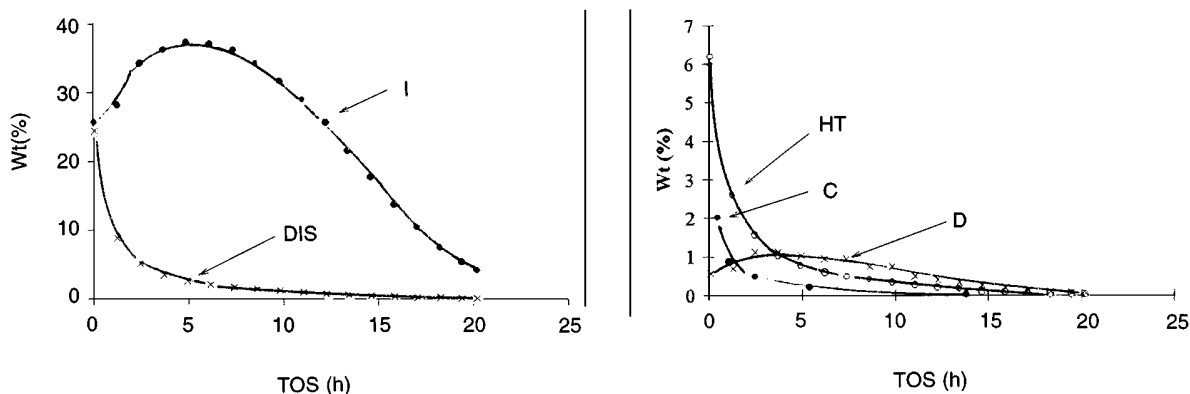


FIG. 1. Influence of time-on-stream (TOS) on the conversion of *n*-butenes into various products. Operating conditions: 623 K, $P_{n\text{-butene}} = 0.1$ bar; WHSV = 2.1. I, isomerization; DIS, disproportionation; C, coking; HT, hydrogen transfer; and D, dimerization.

ion-exchange carried out with an excess of 10 N ammonium nitrate solution for 4 h at 373 K; the Na, K content was below 50 ppm and the Si/Al ratio equal to 13.8. Prior to use the zeolite was calcined "in-situ" under dry air flow at 773 K.

The transformation of 1-butene was carried out in a flow reactor in the presence of nitrogen ($N_2/1\text{-butene}$ molar ratio = 9) at 623 K for investigating skeletal butene isomerization and coking, and at 323 K for characterizing the coked samples by their activity in butene double bond shift. At 623 K, as the distribution of linear butenes is always close to that of thermodynamic equilibrium the conversion into the various products is calculated by grouping *n*-butene isomers together. Reaction products were analyzed on-line by FID gas chromatography using a 50-m Chrompack PLOT Al_2O_3/Na_2SO_4 capillary column. The coke content was determined by the "Service Central d'Analyse—Centre National de la Recherche Scientifique" at Vernaison (France). The method for determining the coke composition has been previously described (16).

For the acidity characterization, IR spectra of the ferrierite sample were recorded with a Nicolet Magna IR 550 spectrometer using thin wafers of 4–8 mg/cm^2 activated *in-situ* in the IR cell. The activation was carried out in vacuum (10^{-5} Pa) at 523 K for 1 h. Ammonia was adsorbed on the sample at 323 K. The IR spectra were carried out at room temperature after an activation period and after desorption of ammonia in vacuum (10^{-5} Pa-1 h) at 323 K.

RESULTS

1. Influence of Time-on-Stream on the Formation of the Various Products

This study was carried out by using 0.05 or 0.5 g of ferrierite, the butene flow rate being equal to 18.4 $mmol\ h^{-1}$; i.e. the amount (g) of *n*-butene introduced per gram of ferrierite and per hour (WHSV) being 20.6 or 2.1. In both cases the reactions observed are in the order of significance— isomerization (I)—disproportionation (DIS): formation

of propene + pentenes and to a smaller extent of ethylene and hexenes—coking (C): formation of carbonaceous deposits—hydrogen transfer (HT): formation of *n*-butane and of very low amounts of ethane, propane and isobutane and—dimerization (D): formation of octenes. As shown in Fig. 1 for the longer contact time (WHSV = 2.1) there is a rapid decrease in the conversion of *n*-butene through DIS, C, HT reactions while a maximum is observed for I and D reactions. It should be emphasized that during the deactivation of *n*-butene isomerization there is only a very small increase in the coke content (from 6.5 wt% after 7.5 h reaction to 7.5 wt% after 20 h).

2. Characterization of Coked Ferrierite Samples

It has been previously shown (14, 15) that coke causes a blockage of the access of nitrogen to the zeolite pores, the decrease in the capacity of the ferrierite for nitrogen adsorption being proportional to the percentage of coke deposited. Complete blockage of the pores is obtained for a deposit of approximately 8 wt% of coke (Fig. 2).

Double bond shift of 1-butene at 323 K was used as a model reaction for characterizing the accessible acidity of coked samples. Figure 2 shows that the effect of coke on the

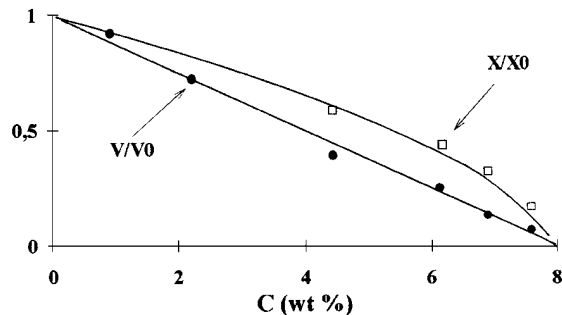


FIG. 2. Influence of coke content on the residual capacity for nitrogen adsorption (V/V_0) and on the residual activity (X/X_0) for 1-butene double bond shift.

rate of this reaction is significant but, however, lower than its effect on the capacity for nitrogen adsorption.

IR spectroscopy of the fresh and of the 6.9 wt% coked samples was carried out (Fig. 3). The band at 3600 cm^{-1} which corresponds to the acidic OH groups is strongly decreased (by approximately 75%), which shows that coke molecules can be adsorbed on the protonic sites. The decrease of this band is clearly shown in Fig. 3 by the negative peak observed in the difference between the spectrum of the coked sample and that of the fresh sample. New bands appear at approximately 1500 cm^{-1} (very intense) and at 3000 cm^{-1} (weak) (Fig. 3) which correspond to the coke molecules. They show the presence of aromatic rings (aromatic $\nu_{\text{C-H}}$ at 3085, 3062, 3037, and 3000 cm^{-1} , aromatic $\nu_{\text{C=C}}$ at 1524, 1583, and 1617 cm^{-1}) and of aliphatic groups ($\nu_{\text{as C-H}}$ (CH_3), C-H (CH_2) at 2963 cm^{-1} and 2925 cm^{-1} , $\nu_{\text{s C-H}}$ (CH_3) at 2865 cm^{-1} , $\delta_{\text{as C-H}}$ (CH_3 or CH_2) at 1447 cm^{-1} , $\delta_{\text{s C-H}}$ (CH_3) at 1372 cm^{-1}). A broad band is also observed at approximately $3300\text{--}3400\text{ cm}^{-1}$ which could correspond to a shift of part of the OH band at 3600 cm^{-1} to lower wavenumbers due to hydrogen bonding with coke species (17). With the coked sample, the adsorption of ammonia has practically no effect on the intensity of the band at 3600 cm^{-1} , although this band is totally suppressed in the case of the fresh sample (Fig. 4). This suggests that ammonia has no access to all the protonic sites of the coked sample which may or may not interact with coke molecules.

3. Characterization of the Carbonaceous Deposits

The composition of coke formed at the longer contact time (WHSV = 2.1) was determined for three values of the

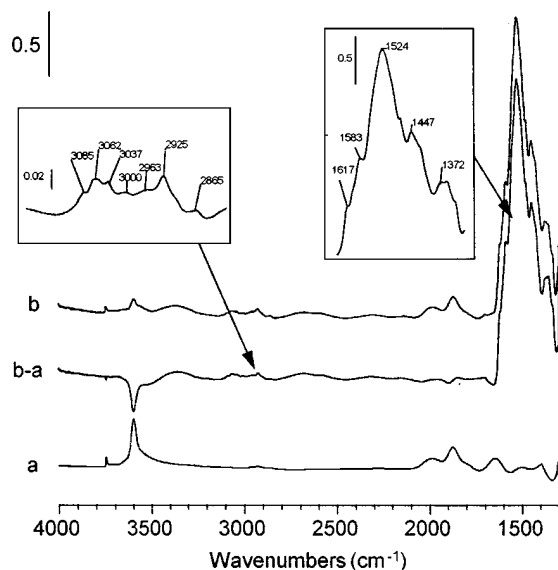


FIG. 3. IR spectra of fresh (a) and coked (b) samples and difference between the spectra (b-a).

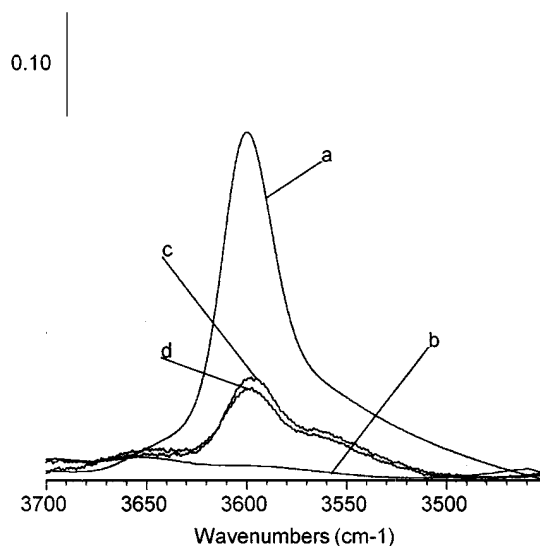


FIG. 4. IR spectra (transmittance) of HFER in the OH region after pretreatment of the fresh zeolite (a) and of the coked zeolite (b) and after desorption of NH_3 at 323 K from the fresh zeolite (c) and from the coked zeolite (d).

coke content: 1.8, 6.5, and 7.5 wt% (time-on-stream equal to 0.5, 7.5, and 20 h, respectively). In all cases all the coke components are soluble in methylene chloride after dissolution of the zeolite in a hydrofluoric solution. Less than 5% of the coke components can be recovered by simple soxhlet treatment of the coked samples, which shows that coke molecules are located in the zeolite pores. Furthermore, at low coke content part of the components cannot be analyzed. Due to their high volatility, they evaporate with methylene chloride.

The chromatogrammes in Fig. 5 show that coke is a complex mixture. The greater the coke content the more complex the mixture and the heavier the coke components. HNMR analysis (Fig. 6) shows the presence of a large proportion of aromatics. Thus for 6.5 wt% of coke, 71% of the protons are aromatics. Benzylic (20%) and aliphatic (9%) protons are also observed, which indicates the presence of alkyl groups. A small amount of protons of CH_2 groups α to the aromatic rings are also observed ($\delta = 3.5$ and 3.9 ppm). IR spectroscopy confirms the presence of both aromatic and alkyl groups (Fig. 7). The spectrum of coke is furthermore very similar to the difference spectrum in Fig. 3 between the spectra of coked and fresh samples.

All the coke components were identified by GC/MS. These components can be classified into seven families of alkylaromatics whose developed formulae are given in Table 1.

An estimation of the distribution of the coke components in the seven families was made by considering that the area of the chromatographic peaks was proportional to the amount (wt%) of corresponding compounds (no calibration). Figure 8 shows that compounds of families A, B,

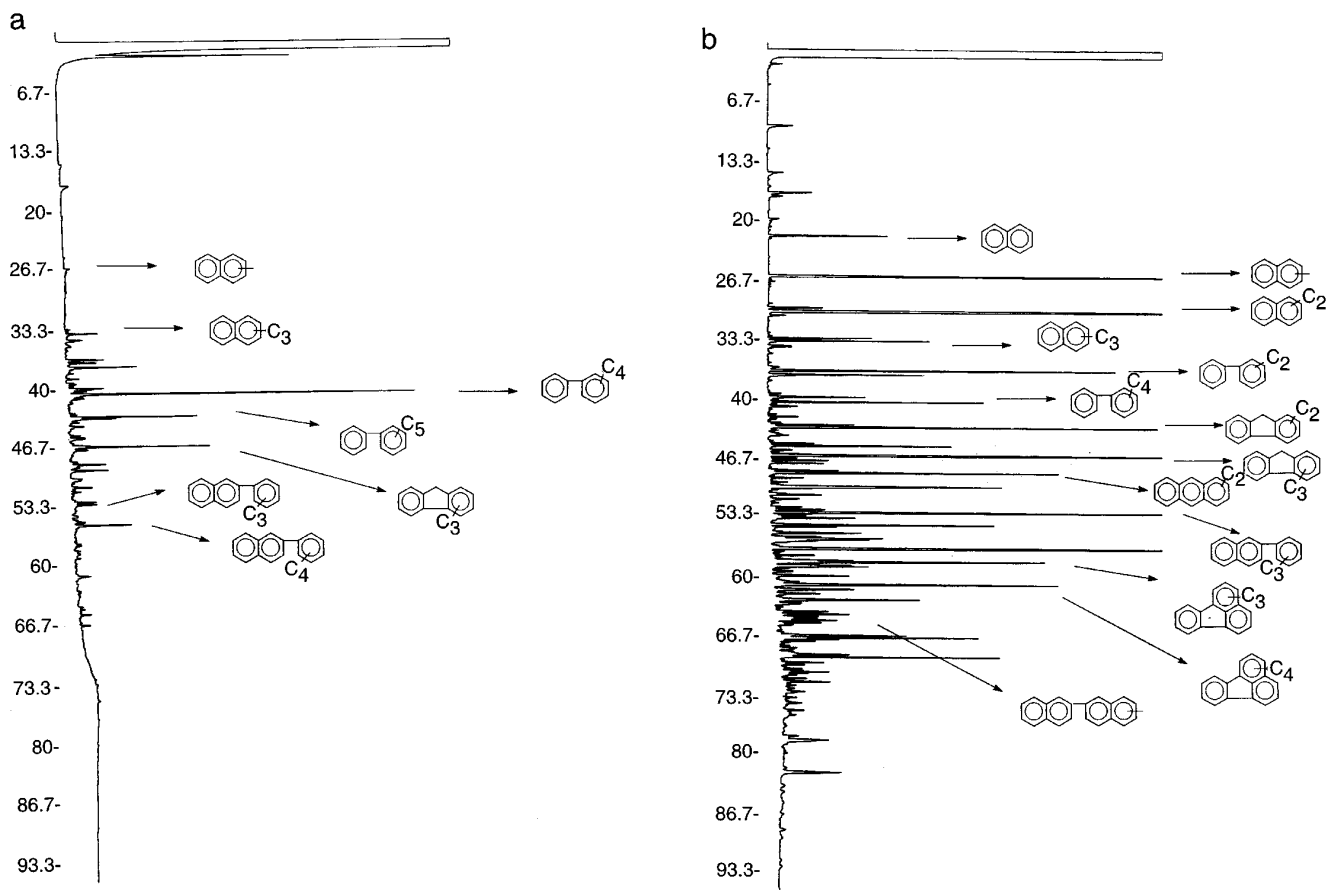


FIG. 5. Chromatogrammes of the carbonaceous compounds recovered from HFER samples coked for 0.5 (a) and for 7.5 h (b).

C, and E are formed from the low coke contents while the three other families D, F, G appear only at high coke content. A maximum is observed in the amounts of A, B, C families whose components are therefore transformed into components of the other families.

4. Removal of Carbonaceous Deposits

A simple treatment of coked samples under nitrogen flow ($60 \text{ cm}^3 \text{ min}^{-1}$) at the reaction temperature for 12 h allows elimination of only a small part of the carbonaceous

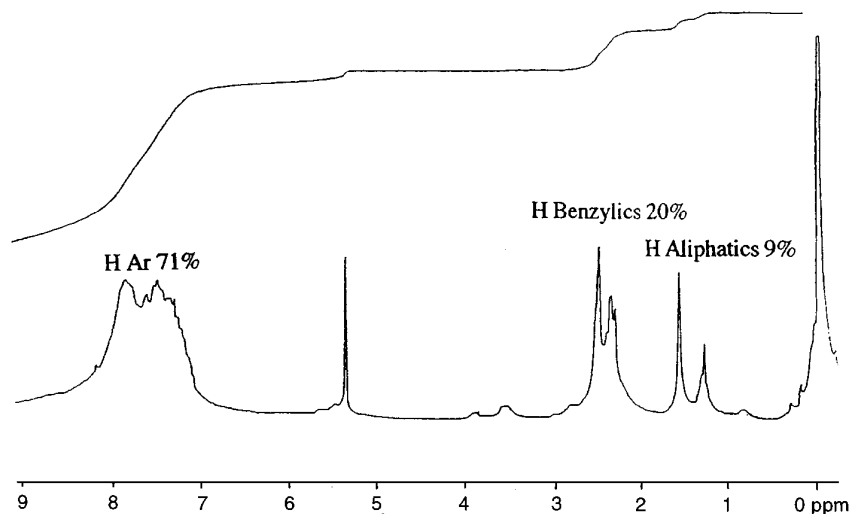


FIG. 6. HNMR spectrum of the carbonaceous compounds recovered from HFER sample coked for 7.5 h (6.5 wt% coke).

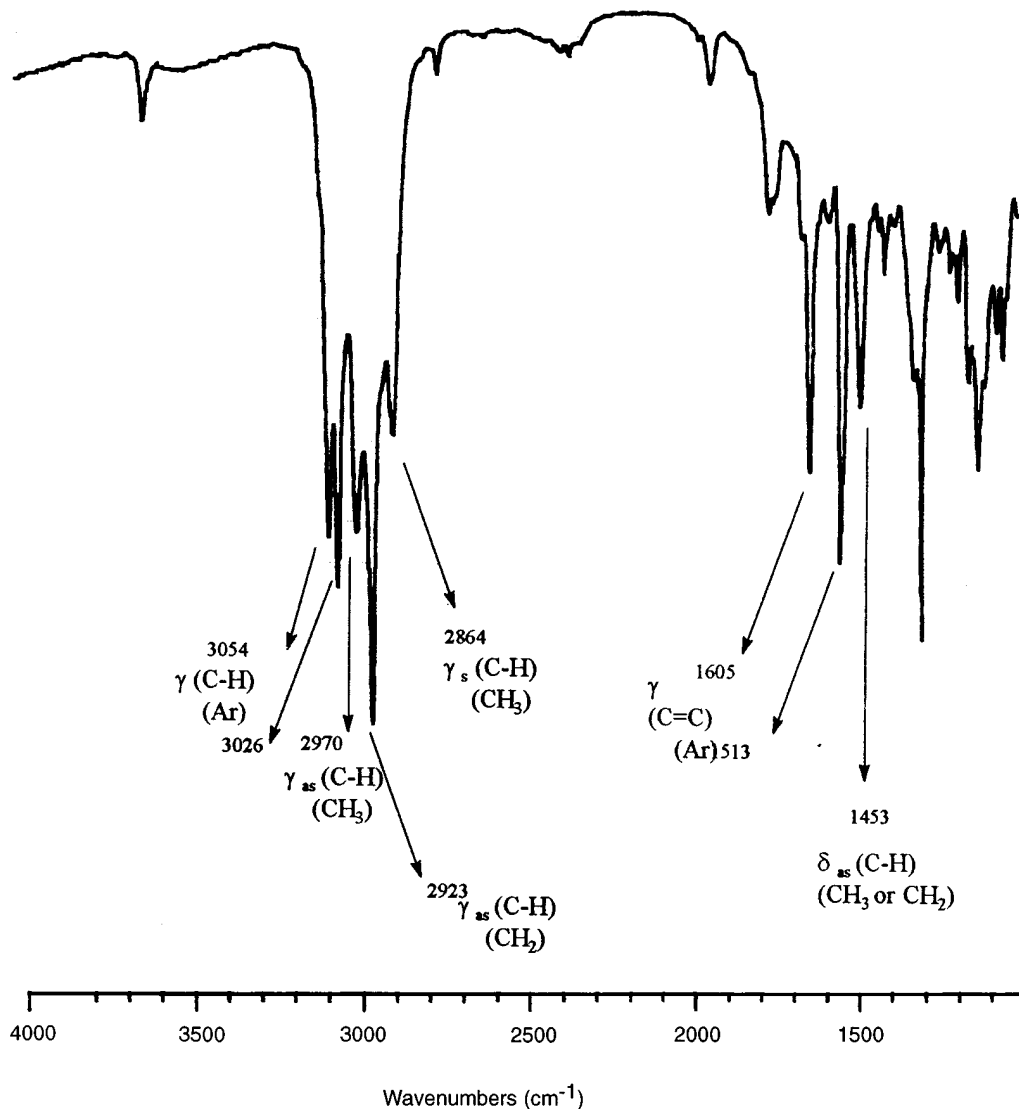


FIG. 7. IR spectrum of the carbonaceous compounds recovered from HFER sample coked for 7.5 h (6.5 wt% coke).

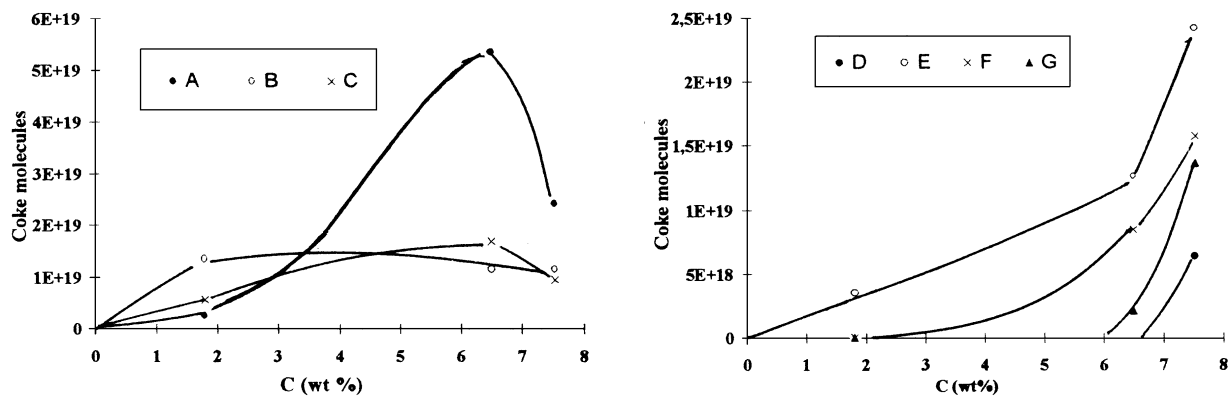
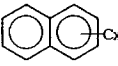
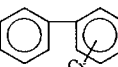
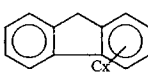
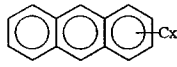
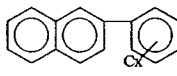
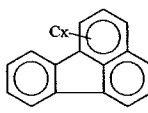
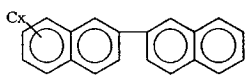


FIG. 8. Number of coke molecules of the seven families versus coke content.

TABLE 1

Formulae of the Main Coke Components and Approximate Values of Their Boiling Point

Family	General Formulae	Developed Formulae	x	Boiling Point (K)
A	C_nH_{2n-12}		0 to 5	490 to 540
B	C_nH_{2n-14}		0 to 5	530 to 570
C	C_nH_{2n-16}		0 to 5	> 570
D	C_nH_{2n-18}		1 to 4	515 to 665
E	C_nH_{2n-20}		0 to 4	> 545
F	C_nH_{2n-22}		3 and 4	650
G	C_nH_{2n-26}		1 to 5	> 635

deposits. Thus the coke content of a sample used for 3.5 h in *n*-butene transformation with WHSV = 20.6 passes from 6.2 to 5.5 wt%. However, this treatment completely changes the nature of the carbonaceous compounds. Indeed less than 15% of the coke of the treated sample is soluble in methylene chloride although all the coke components of the non treated sample were soluble. Furthermore, the capacity for nitrogen adsorption increases from 0.036 cm³ g⁻¹ for the non treated sample to 0.052 cm³ g⁻¹ for the treated sample. Despite this increase a decrease in the activity is observed (Fig. 9).

Complete removal of coke can be obtained by treating the deactivated sample under dry air flow (60 cm³ min⁻¹) at 773 K for 12 h. The first regeneration of a sample used for 7.5 h in *n*-butene transformation with WHSV = 20.6 (coke content = 6.9 wt%) causes a slight decrease in the initial activity. However, the increase in isobutene yield becomes more significant than that observed with the fresh sample and the stability of the catalyst is slightly improved. The IR

spectra of fresh and regenerated samples were compared in the region of the zeolite framework bands. A shift of the bands (especially of the more intense around 1080 cm⁻¹) towards higher values of the wavenumber is observed, which

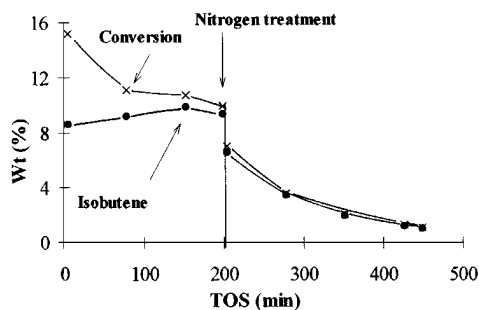


FIG. 9. Influence of the treatment under nitrogen flow of a HFER sample on *n*-butenes conversion (x) and on the yield in isobutene (●), WHSV = 20.6.

seems to indicate a slight dealumination of the zeolite during the removal of coke (18).

DISCUSSION

1. Influence of the Carbonaceous Deposits (Coke) on the Catalytic Activity of HFER Samples

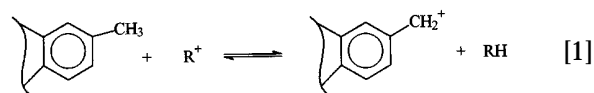
On the fresh HFER catalyst, *n*-butene isomerization is accompanied by a direct formation of propene and pentenes, which suggests a dimerization–cracking process most likely catalyzed by the protonic sites of this zeolite (13). Other primary products, the most significant being *n*-butane resulting from hydrogen transfer, are also observed. The change with time-on-stream in the rates of formation of the various products is most likely due to the formation of carbonaceous deposits in the zeolite pores (coke). These carbonaceous deposits block the access of nitrogen to the pores (Fig. 2), hence the access of the reactant to the inner active sites. This explains why coke provokes a decrease in the rates of side transformations of *n*-butene at 623 K: disproportionation, hydrogen transfer, and coke formation (Fig. 10) and in the rate of 1-butene double bond shift at 323 K (Fig. 2). However, as already emphasized, a curious increase in the rate of *n*-butene isomerization into isobutene (with therefore an increase in the selectivity) is observed (Fig. 1).

Obviously, while an increase in selectivity can easily be explained by a preferential deactivation of nonselective sites, this is not the case for an increase in the isomerization rate. However, it can be suggested that this latter increase results from the suppression of rapid secondary transformations of isobutene. This seems most unlikely for, over the fresh HFER zeolite, the main side products, i.e. propene, pentenes, and *n*-butane, result from a direct transformation

of *n*-butene. Moreover, with this zeolite, the rate of their formation is slower from isobutene than from *n*-butene (13).

Furthermore, it must be emphasized that the 6.9 wt% coked HFER sample which is practically inactive for disproportionation, hydrogen transfer, and coking is still active (and very selective) for *n*-butene isomerization (Fig. 10). On this sample, all the OH groups are either in interaction with coke molecules or inaccessible to NH₃ molecules (hence, to the reactant molecules). This demonstrates that, on this coked sample, butene isomerization is no longer catalyzed by the protonic sites of the HFER zeolite.

To explain these observations, it has been proposed that molecules of carbonaceous compounds located near the pore mouth and adsorbed on protonic sites could be active sites for a selective skeletal isomerization of *n*-butene. A pseudomonomolecular reaction (only one reactant molecule is involved) catalyzed by stable tertiary cations resulting from the adsorption of coke molecules on the protonic sites was firstly suggested (14). However, the analysis of the coke composition led us to propose as active sites benzylic cations instead of the tertiary cations (15). The formation of these benzylic carbocations from alkylaromatics is generally admitted. In particular these carbocations, which are stabilized by resonance, are proposed as intermediates in the disproportionation of methylaromatics over acid catalysts (19). The carbocations would be formed according to the following equation:



in which R⁺ are preexisting carbocations, benzylic or not.

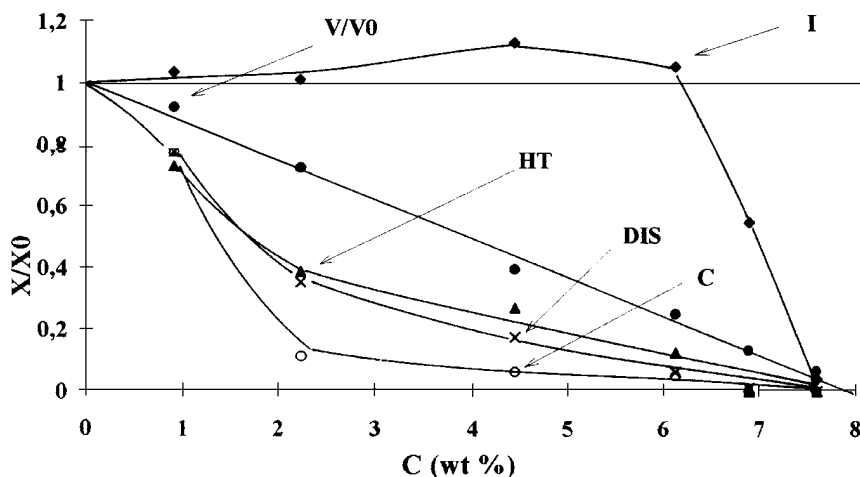


FIG. 10. Influence of coke content on the residual activity of HFER for the various transformation of *n*-butenes (operating conditions: 623 K, $P_{n\text{-butenes}} = 0.1$ bar; WHSV = 20.6. I, isomerization; DIS, disproportionation; C, coking; and HT, hydrogen transfer) and on the residual capacity for nitrogen adsorption (V/V₀).

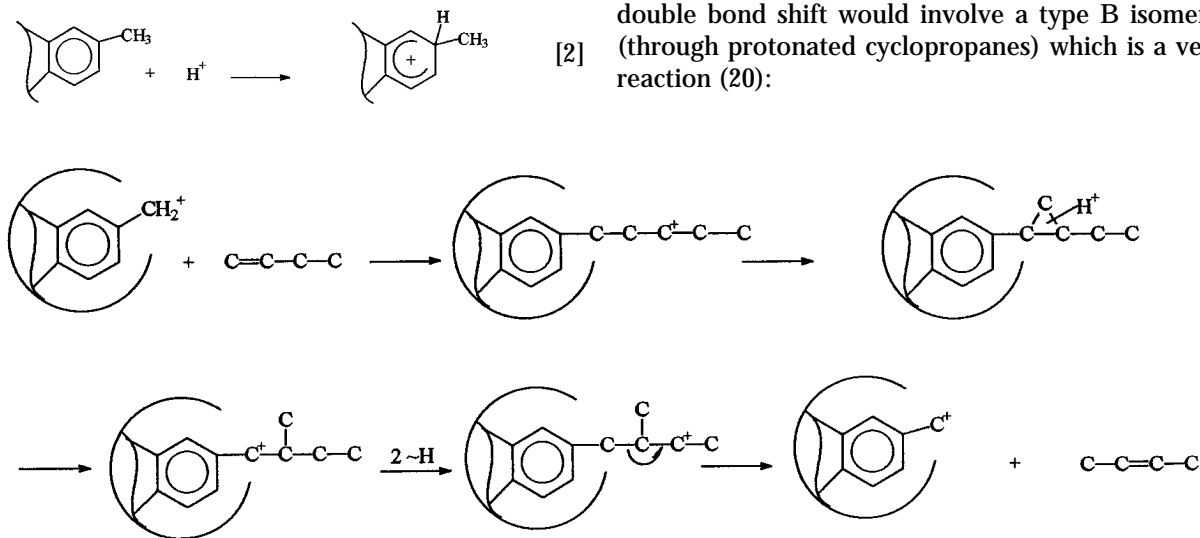
Figure 11 shows how the pseudomonomolecular mechanism allows the selective isomerization of *n*-butene into isobutene. The alkylation of *n*-butene by a benzylic carbocation located near the pore mouth leads to a secondary carbenium ion which isomerizes through hydride and methyl shifts into a tertiary carbenium ion which in turn cracks to isobutene with regeneration of the initial benzylic carbocation. This mechanism does not allow propene and pentenes to be formed. Moreover, all steps which are involved in this chain mechanism: alkylation of an alkene by a benzylic cation, hydride shift, methyl shift (type A isomerization (20)), cracking of a tertiary carbenium ion are known to be very rapid reactions. Therefore, it is not surprising that, despite the relatively small number of benzylic carbocations located near the pore mouth, the skeletal butene isomerization which they provoke is fast or at least occurs at a rate similar to that of the dimerization–cracking transformation of *n*-butene catalyzed by the inner acid sites of HFER.

Experiments performed by Meriaudeau *et al.* (21) with *n*-butene having one ^{13}C atom confirm the change with time-on-stream of the isomerization mechanism. Over a fresh HFER sample, the resulting isobutene was found to be a mixture of molecules containing two ^{13}C atoms, one ^{13}C atom, and no ^{13}C atoms, which confirms the dimerization–cracking mechanism. On the other hand, as can be expected from the pseudomonomolecular mechanism (Fig. 11), isobutene formed over the aged (after 20 h reaction) HFER sample contains only one ^{13}C atom (21).

In agreement with this pseudomonomolecular mechanism the coke molecules are found to be adsorbed on or to interact with (hydrogen bonding) the inner protonic sites (Fig. 4). However, it should be emphasized that a large part of this adsorption is under the form of benzenium ions:

Nevertheless this means that the components of coke are located near the acid sites and, hence, can also be transformed into benzylic carbocations through reaction [1].

Figures 2 and 10 show that the deactivating effect of the carbonaceous compounds depends on the reaction considered. With double bond shift of 1-butene at 323 K the deactivating effect of coke is lower than the blockage of nitrogen adsorption (Fig. 2) while the reverse is found with the transformations of *n*-butene at 623 K (disproportionation, hydrogen transfer, and coking). The very pronounced effect that coke has on its own formation has often been observed. Indeed coking can be considered as a nucleation-growth phenomenon (22) and the growth of the first coke molecules leading to more and more bulky molecules is obviously more sterically inhibited than their formation. Moreover, the first coke molecules limit or block the access of other molecules to acid sites, hence limiting the rate of growth reactions. The greater effect of coke on disproportionation and hydrogen transfer (compared to its effect on nitrogen adsorption) can be explained either by the greater size of the reactant (or product) molecules or by the fact that both reactions involve bimolecular intermediates and, hence, are very sensitive to steric constraints. The smaller effect of coke on butene double bond shift is unexpected. Indeed butenes being bulkier than nitrogen (5.3 Å, instead of 4.2 Å) should enter the pores occupied by coke molecules with more difficulty. This slow deactivation could be due to the participation in butene isomerization of acid sites located on the outer surface of the zeolite crystallites whose deactivation by coke would be very slow. However, this is most unlikely, since HFER is completely inactive for a model reaction developed for characterizing the acidity of the outer surface of medium pore zeolites (23), i.e. isooctane cracking at 623 K and even at 773 K. Another possibility is that coke molecules which catalyze the skeletal isomerization of *n*-butenes at 623 K could also catalyze their double bond shift at 323 K. However this is most unlikely, for this double bond shift would involve a type B isomerization (through protonated cyclopropanes) which is a very slow reaction (20):



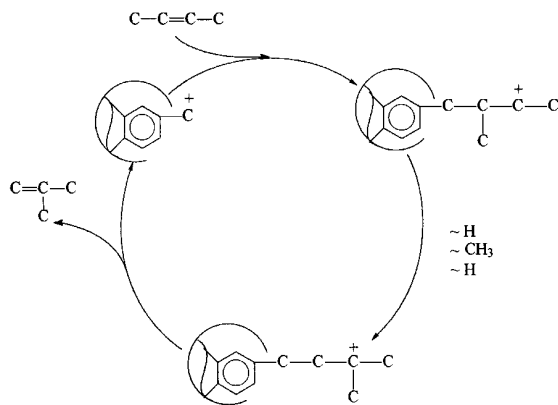


FIG. 11. Pseudomonomolecular mechanism of *n*-butenes isomerization into isobutene over coked HFER samples.

To explain this slow deactivation it can be suggested that the butene double bond shift is diffusion limited. Coke would decrease the length of the diffusion path rendering the apparent activity of the residual acid sites more significant than the average activity of the acid sites of the fresh zeolite sample.

2. Location of Coke Molecules

Coke is constituted of slightly condensed aromatics (with two to four aromatic rings). These compounds are located inside the zeolite pores. Indeed, they cannot be recovered in methylene chloride by a direct soxhlet treatment of the coked zeolite sample. Moreover, their boiling point is close to or lower than the reaction temperature. As these compounds are not very polar, their retention in the zeolite pores can be attributed to their steric blockage. The steric blockage of most of the coke molecules can be confirmed by comparing their size and the size of channels or of channel intersections. From preliminary molecular mechanism calculations (24) it can be proposed that the main part of the coke molecules are trapped at the intersections between the 10- and 8-membered-ring channels.

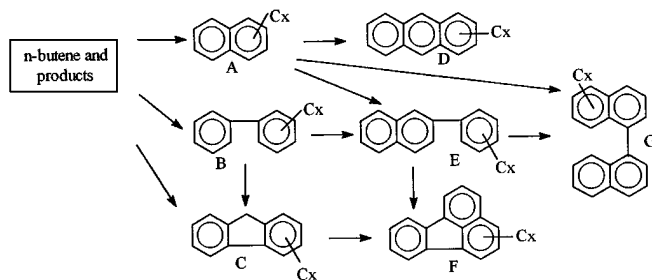
This location of the coke molecules can be confirmed from the measurement of the acidity by ammonia adsorption on the fresh and on the coked zeolite samples. The protonic acid sites of H Ferrierite have been classified into three categories by Xu *et al.* (25): H^+ (XL), H^+ (L), and H^+ (S). The O^{2-} ions corresponding to the H^+ (XL) are located in both 10- and 8-membered-rings (hence, at the channel intersections) so that they have a very large space around them (XL: extralarge). H^+ (L) (L: large) are located inside the channels of the 10-membered-rings and of the 8-membered-rings, O^{2-} of H^+ (S) (S: small) are located on 5-membered-rings so that the space around them is very limited. By assuming a random distribution of Al^{3+} ions inside ferrierite the number of H^+ (XL), H^+ (L), and H^+ (S) was estimated to be equal to 33, 39, and 28%, re-

spectively, in the case of the fresh ferrierite sample. All the protonic sites are accessible by the small molecule of NH_3 as shown by the suppression of the OH band after NH_3 adsorption (curve b, Fig. 4). Coke molecules interact with about 75% of the protons, i.e. certainly with all the H^+ (XL) and H^+ (L) (72%). The other protons (H^+ (S)) do not remain accessible by ammonia; hence, their access is blocked by the coke molecules. The number of coke molecules was estimated for various coke contents and compared to the total number of protonic sites and to the number of sites located at the channel intersections (H^+ (XL)). The total number of protonic sites, calculated from the unit cell formula (6.8×10^{20} sites g^{-1}), is very close to the number of NH_4^+ ions determined from the IR experiment with the fresh zeolite sample (7.5×10^{20} sites g^{-1}). For 1.8 wt% coke, the number of coke molecules is equal to 7% of the total number of protonic sites and 22% of the number of H^+ (XL) while for 6.5 and 7.5% coke the number of coke molecules is equal to 31% of the total number of protonic sites and to 94% of the number of H^+ (XL). This is in agreement with the location of coke molecules at the channel intersections. However, these coke molecules could interact not only with the H^+ (XL) but also with the H^+ (L) (by hydrogen bonding in the later case).

The IR characterization of the 6.9 wt% coked HFER sample shows that all the protonic sites of this sample either interact with coke molecules or are inaccessible to NH_3 molecules. This indicates that all the pores close to the outer surface of the crystallites are occupied by coke molecules. As this sample is still active (and very selective) in butene isomerization, this confirms the role of active sites played by the coke molecules located near the pore mouth (pore mouth catalysis).

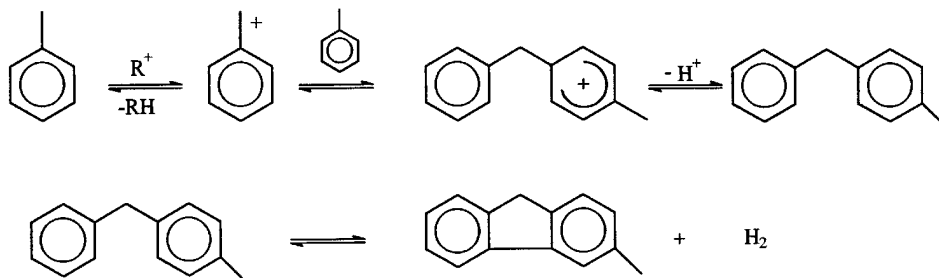
3. Mode of Coke Formation

From the nature of the coke molecules (Table 1) and from the change in their number as a function of the coke content (Fig. 8) the following scheme can be proposed:

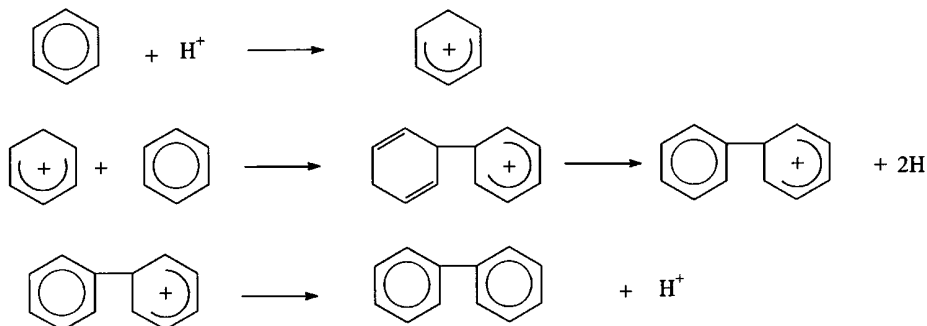


Benzenic compounds are formed through the classical scheme of aromatization described in detail in the case of HMFI catalysts (26). This aromatization involves oligomerization-cracking, cyclization, and hydrogen transfer steps. The benzenic molecules are too small to be blocked

in the zeolite pores and most of them are desorbed from the zeolite. However, their diffusion in the zeolite pores is slow and some of them are transformed into naphthalenic and then into anthracenic compounds through alkylation by alkene, cyclization, and hydrogen transfer steps. Fluorenic can also result from condensation of two methylbenzenics into diphenylmethane compounds (which are intermediates in the disproportionation of methylaromatics (19)) followed by their dehydrogenative coupling:



Dehydrogenative coupling of benzenic and/or of naphthalenic molecules is also responsible for the formation of the compounds of the families B, E, and G. It should be emphasized that with ferrierite this coupling plays a very important role in the formation of coke molecules (this reaction intervenes in the formation of the molecules of families B, C, E, F, and G) while with other zeolites its role is generally limited to the formation of very polyaromatic molecules. According to Gates *et al.* (27) dehydrogenative coupling would occur on acid catalysts through the following mechanism written below with benzene as the reactant:



The large role played by this reaction, which is generally considered to be much slower than the classical mode of coke formation (through aromatic alkylation by alkenes, cyclization, and then hydrogen transfer), indicates that the probability of encounter in the pores of HFER between two aromatic molecules is much higher than that between one aromatic and one alkene molecule. This may be due (i) to the small size of the channel intersections which therefore can accommodate only slightly condensed aromatics (with one or two rings) and (ii) to their proximity which favours the coupling between these aromatics.

4. Origin of the Deactivation for Isobutene Formation

As indicated in paragraph 1 of the Results section, the deactivation of isobutene formation which occurs after 7.5 h reaction is accompanied by only a small increase in the coke content (from 6.5 to 7.5 wt% after 20 h). This slight increase in coke content is not due to an increase in the number of coke molecules but only to an increase in their molecular size. Exactly the same number of coke molecules is found for 6.5 and 7.5 wt% coke, but there is an increase in the number of coke molecules of families D, E, F, G at the expense of the smaller coke molecules (especially of family A) (Fig. 8). Therefore, deactivation is most likely due to the growth of coke molecules. The bulkier molecules would result from the growth of molecules trapped at the channel intersections. Because of the larger number of aromatic rings they are either less easily transformed into benzylic cations or less easily accessible by the reactant molecules.

Much bulkier molecules (very polyaromatic hence insoluble in methylene chloride) can be formed by treatment of the coked ferrierite sample under nitrogen flow for a long time. This formation of polyaromatic coke has already been

observed with other zeolites: HFAU (28), HEMT (29). This formation of polyaromatic coke is accompanied by an increase in the pore volume accessible to nitrogen. This means that during this treatment coke molecules migrate in the pores, leaving free the channel intersections. Despite this increase in the pore volume accessible to nitrogen, hence most likely to the reactant, a decrease in the isomerizing activity is observed. This decrease can be related to the decrease in the number of coke molecules which play a role in the skeletal isomerization of *n*-butene.

Coke can be completely removed by oxidative treatment at 773 K. The catalyst recovers the same behavior in butene transformation: initial increase, then decrease, in the formation of isobutene; rapid initial decrease in the secondary reactions of disproportionation, hydrogen transfer, and coking. However, an increase in stability is observed, most certainly due to a slight dealumination of the zeolite during coke removal.

CONCLUSIONS

From this study of the formation of carbonaceous compounds during *n*-butene transformation over a HFER zeolite the following main conclusions can be drawn:

1. Carbonaceous deposits (coke) provoke a significant change in the selectivity of *n*-butene transformation. On the fresh zeolite *n*-butene undergoes various reactions: dimerization–cracking leading to isobutene, propene and pentenes, hydrogen transfer, and coke formation. Coking causes a significant decrease in these reactions but also the apparition of a selective process of butene isomerization. A mechanism is proposed for this reaction involving benzylic carbocations formed from coke molecules trapped in the pores near the outer surface of the crystallites (pore mouth catalysis).

2. Coke is constituted of slightly condensed aromatics (with two to four aromatic rings) located at the intersections of the 8- and 10-membered-ring channels. They result from the transformation of benzenics (formed from butene aromatization over the acid sites and slowly desorbed from the zeolite) through two different ways: (i) the classical route by alkylation of benzenics by alkenes followed by cyclization and hydrogen transfer and (ii) dehydrogenative coupling. Contrary to what is observed with many other zeolites, this latter reaction is very much favoured with ferrierite.

3. Deactivation of isobutene formation is due to the growth of coke molecules. The bulkier the coke molecules the less active they are in butene isomerization.

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