

“Coke” molecules trapped in the micropores of zeolites as active species in hydrocarbon transformations

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Abstract

The formation in the channels or cages of zeolites of heavy side products (generally called “coke”) is often responsible for their deactivation owing to poisoning of active sites and/or to pore blockage. However, these coke molecules trapped in the zeolite micropores being relatively simple, are not generally inert with respect to the reactants or intermediates of the desired reactions and, hence can significantly affect the activity and selectivity. This participation in catalytic reactions of the coke molecules trapped in the zeolite micropores is shown here in several examples carried out in liquid or in gas phase, with large, medium or small pore molecular sieves: (i) isopropylation of naphthalene and alkylation of toluene with long chain *n*-alkenes over HFAU and HBEA zeolites; (ii) selective skeletal isomerization of *n*-butenes over HFER; (iii) selective hydroisomerization of long chain *n*-alkanes over PHTON; (iv) selective methanol conversion into light alkenes over SAPO 34. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zeolite catalysts are used extensively in refining and petrochemical processes and should know in the near future a large development in the synthesis of fine chemicals and in depollutants. Acid, base, acid–base, redox and bifunctional (hydrogenating acid) catalysis are involved in the reactions; acid and bifunctional catalysis playing, however, the major role.

One of the main problems with the use of acid zeolite catalysts is their deactivation by coking [1,2]. Heavy secondary products, designated as coke, can poison the active sites or block their access. It is well demonstrated that these products are formed and

trapped in the zeolite pores [2,3] and the formation of coke can be considered as a “ship in a bottle” process. The zeolite pores (channels, cages, channel intersections) being of molecular size, the growth of these products is limited, hence coke molecules are not very bulky in comparison to those found with conventional solid catalysts. Therefore, from the composition of zeolite coke, not only the chemical identity of the components but also their distribution as a function of their nature and their size can be obtained [3]. A simple method has been developed in our laboratory [2]. It consists of liberating the coke trapped in the pores by dissolving the zeolite in a solution of hydrofluoric acid. A large part of coke components can be solubilized in organic solvents (100% at low coke content for high reaction temperatures, and whatever the coke content at low temperatures), and analyzed

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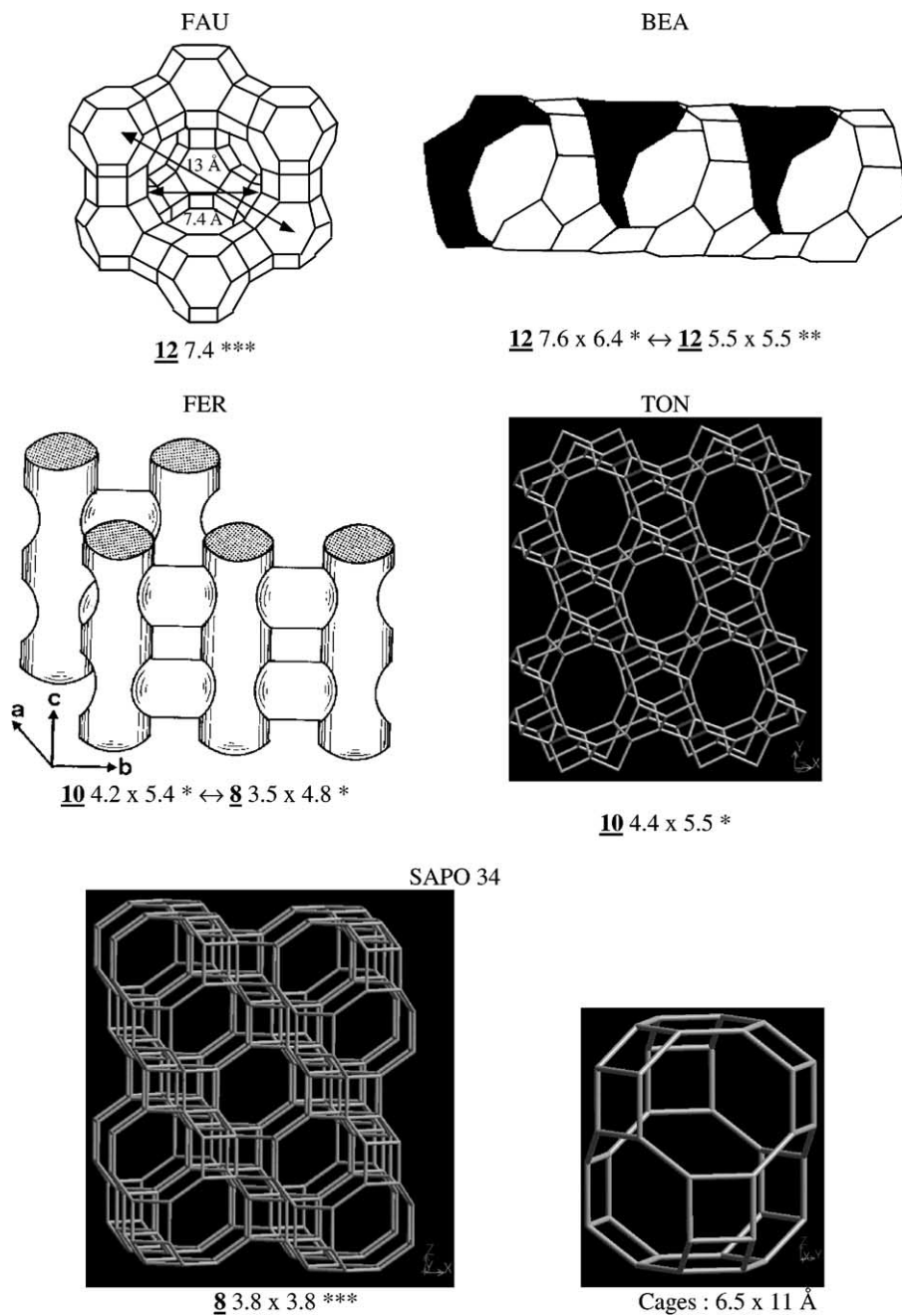


Fig. 1. Pore system of various zeolites and aluminophosphate molecular sieves FAU, BEA, FER, TON, SAPO 34.

by classical techniques such as GC, HPLC, NMR, IR, MS and especially GC–MS. This composition was particularly useful to specify the modes of coking and deactivation of zeolite catalysts [4].

Coke not always has a detrimental effect on the catalytic behaviour of zeolites. Thus, the deposit of coke can be used to increase the shape selective properties of zeolites, a well-known example being the toluene disproportionation process developed by Mobil. A very high selectivity to paraxylene can be obtained by using a MFI zeolite coked at a very high temperature [5]. At this very high temperature, a very polyaromatic coke is formed covering part of the outer surface of the crystallites. The selectivity increase has two origins [6]:

- (i) the access to the non-shape selective acid sites of the outer surface is blocked;
- (ii) the sieving properties of the zeolite are improved.

However, coke molecules of zeolites which are relatively simple, hence maintain a high reactivity, can also participate in the main reaction with sometimes a very positive effect on selectivity. The aim of this paper is to show in some examples chosen in acid catalysis that coke molecules trapped in the zeolite pores can be active species on the working catalysts. The pore system of the zeolites used in the various reactions is presented in Fig. 1.

2. Liquid phase alkylation of aromatic hydrocarbons

Two alkylation reactions carried out in liquid phase over large pore zeolites (HFAU and HBEA zeolites) will be considered:

- (i) The isopropylation of naphthalene by isopropanol with decaline as a solvent (1:2:6 mol mixture) at 350 °C and 40 bar [7–9]. The desired products 2-alkyl and 2,6-dialkyl products are precursors of high-value chemicals, i.e. dyes, pharmaceuticals, perfumes and speciality polymers.
- (ii) The alkylation of toluene with long chain 1-alkenes (1-heptene and 1-dodecene) at 90 °C, the toluene/alkene ratio being equal to 3 [10,11]. These reactions are well representative of the synthesis of linear alkylbenzenes (LABs) which

are used in the production of biodegradable surfactants.

In both cases, transalkylation between the aromatic substrate and polyalkylated compounds trapped in the zeolite nanopores was shown to play a role.

2.1. Isopropylation of naphthalene

Mono-, di- and triisopropyl naphthalenes referred as IPNs, DIPNs and TIPNs were formed in amounts depending on catalysts and on time-on-stream (TOS). Various by-products resulting mainly from dehydration–oligomerization–cracking of isopropanol were also observed. With most catalysts, the conversion of naphthalene increases first with TOS then becomes stable (Fig. 2). The lower initial conversion can be related to limitations in the desorption of alkylated products from the zeolite nanopores. In agreement with this proposal,

- (i) the smallest products, e.g. 2-isopropyl-naphthalene, 2,6-diisopropyl-naphthalene are largely predominant at short TOS in the IPNs and DIPNs mixtures;
- (ii) a large amount of carbonaceous products (“coke”) is retained in the zeolite during the first hour of reaction (Table 1);
- (iii) no activation period and practically no coke formation can be observed with an amorphous silica-alumina sample (Fig. 2), which confirms that these phenomena are related.

Only a small amount of carbonaceous products can be recovered by direct soxhlet treatment of the coked samples with CH₂Cl₂, whereas a large part of them are soluble in this solvent after dissolution of the zeolites in a hydrofluoric solution (Table 1). With HFAU and HBEA zeolites, soluble coke was shown to be mainly constituted by polyisopropyl (two to four

Table 1
Apparent conversion of naphthalene, amount of carbonaceous species retained on the zeolite and amount of soluble species

TOS (h)	HFAU 4			HBEA 15		
	X	C	Soluble	X	C	Soluble
	(wt.%)		(wt.%)	(wt.%)		(wt.%)
1	40	15	80	33	12	80
6	71	17	35	60	12	80

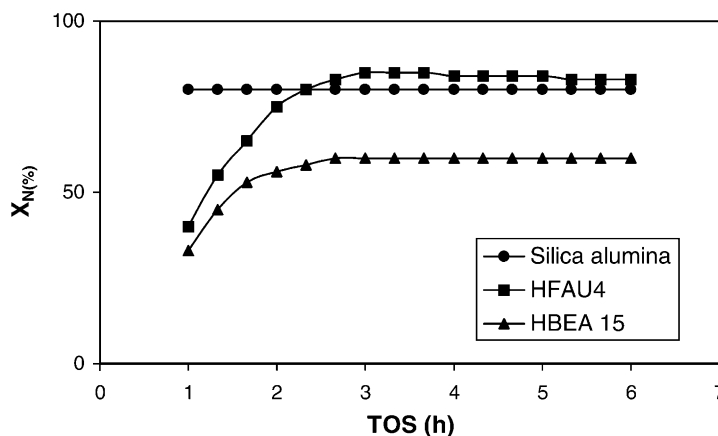
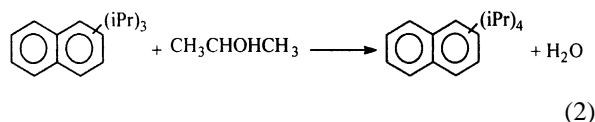
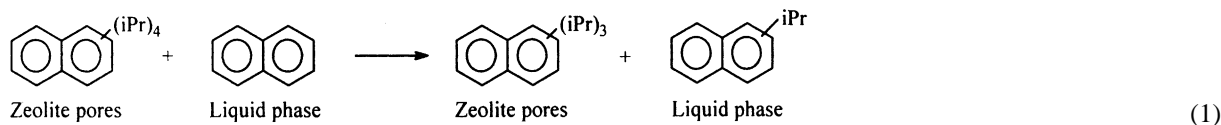


Fig. 2. Transformation of the naphthalene–isopropanol mixture over HFAU 4, HBEA 15 and silica-alumina. Conversion of naphthalene (X_N) as a function of TOS (min).

isopropyl groups) naphthalene compounds: polyisopropyl pyrenic and indenopyrenic compounds were also observed with HFAU 4 and C₄–C₅ alkylnaphthalenes with HBEA 15.

Nitrogen adsorption experiments were carried out on the coked zeolite samples. Curiously, whereas the activity of both zeolites increases with TOS (Fig. 2) the micropore volume accessible to nitrogen is practically zero after 1 h of reaction. Therefore, it can be concluded that isopropyl naphthalenes are not formed in the micropores but on active sites located on the outer surface of the zeolite crystallites or at the entrance of the pores (pore mouth catalysis). However, the nature of the active sites, i.e. protonic sites as generally proposed, carbonaceous species adsorbed on protonic sites, etc. remained to be proved. Indeed carbonaceous species being constituted of polyisopropyl naphthalene, isopropyl transfer from molecules trapped near the entrance of the pores to molecules of naphthalene reactant is quite possible (reaction (1)). Furthermore, the loss of the isopropyl group can be rapidly compensated by realkylation of the entrapped compounds with the small molecules of isopropanol (reaction (2)). Both reactions require the participation of protonic sites.



The possibility of reaction (1) was clearly demonstrated by substituting naphthalene for the naphthalene–isopropanol reactant mixtures: with both zeolites (Fig. 3), the production of isopropyl naphthalene products continues for a certain time. Therefore, the transalkylation/alkylation scheme (reactions (1) and (2)) is quite likely. On the other hand, the initial increase in activity could not be explained if the active sites were protonic sites of the outer surface, whereas with the transalkylation/alkylation scheme, it is simply due to the progressive formation of polyisopropyl derivatives near the entrance of the pores.

2.2. Alkylation of toluene with 1-alkenes

The first experiments were carried out in a batch reactor with a 3:1 mol mixture of toluene and 1-heptene [10]. Over a HFAU 6 zeolite, monoheptyltoluenes are rapidly and selectively formed. Only a small amount of biheptyltoluenes appear above 50% conversion. In

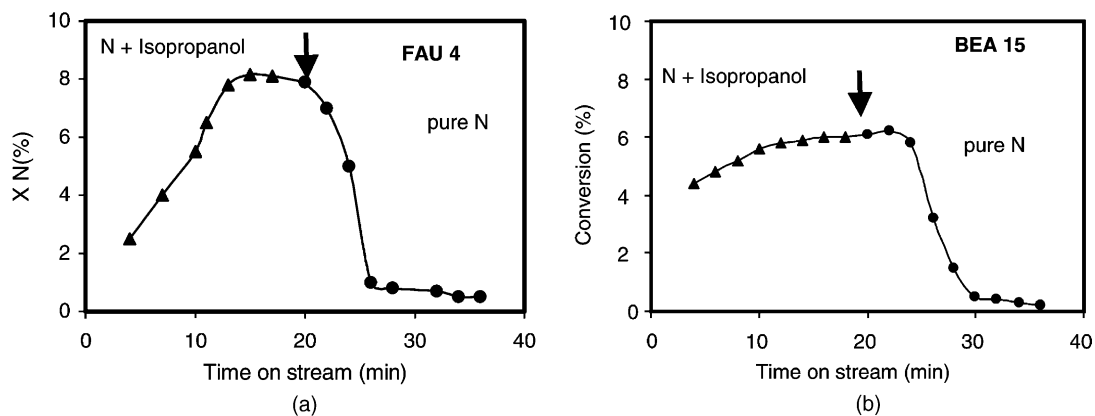


Fig. 3. Naphthalene conversion, X_N , over HFAU 4 (a) and HBEA 15 (b) vs. TOS (min) for naphthalene reaction with isopropanol and after interruption of the feed in isopropanol.

addition to these products, reaction products are also found to be trapped in the zeolite nanopores. Indeed these products (called here coke), cannot be removed by direct soxhlet treatment with CH_2Cl_2 . The amount of coke increases very rapidly during the first few minutes of reaction then much more gradually. It should be remarked that this slow increase occurs despite the total disappearance of heptenes from the liquid phase (Fig. 4), hence the related coke formation does not involve heptene molecules.

Coke is constituted by mono-, bi- and triheptyltoluenes. The total number of coke molecules increases with time, which is due to an increase in the

amount of monoheptyltoluenes; on the other hand, the amounts of biheptyltoluene and especially triheptyltoluene molecules decreases. However, this decrease cannot be related to the desorption of these latter molecules from the zeolite pores; in the liquid phase no triheptyltoluenes appear and there is a slight decrease in the percentage of biheptyltoluenes: from 10% after 20 min to 7% after 360 min. Therefore, the only way to explain the decrease in the amount of bi- and triheptyltoluenes trapped in the zeolite pores is their transalkylation with toluene (reaction (3)) which remains present in the liquid phase after total consumption of heptenes.

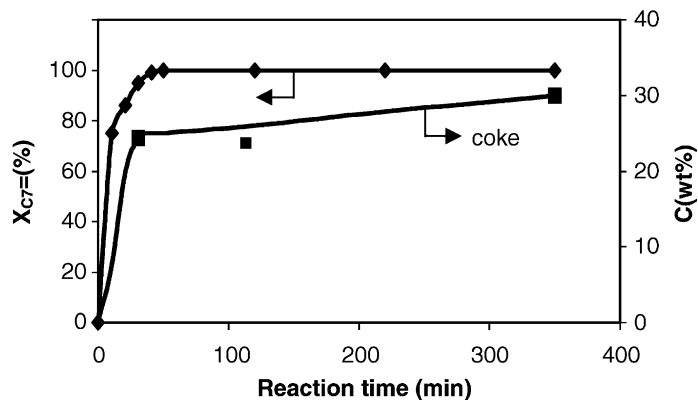
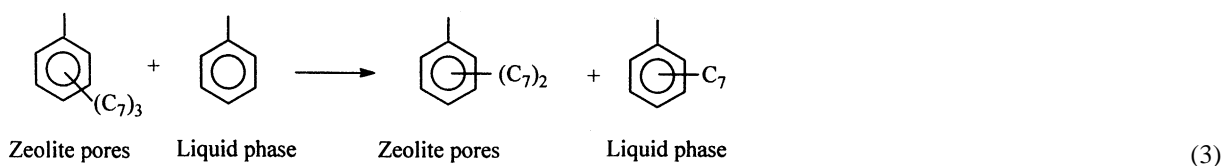
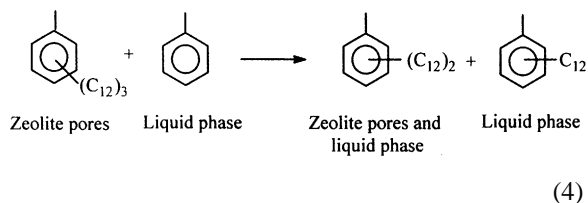


Fig. 4. Heptene conversion into alkylation products ($X_{C7=}$) and coke formation (C, wt.%) over 0.25 g of HFAU 7.5 as a function of reaction time (min).



Experiments in a fixed bed reactor with a 3:1 mol mixture of toluene and 1-dodecene as a reactant show that bi- and trialkyltoluenes blocked in the HFAU 25 pores are responsible for the deactivation of this zeolite (Fig. 5). Adsorption of nitrogen on the completely deactivated sample shows a complete blockage of the access to the zeolite nanopores. As transalkylation between toluene and bi- or trialkyltoluenes was previously demonstrated [10], the treatment of the completely deactivated samples under toluene flow was attempted, the objective being to remove the ‘‘coke’’ molecules and hence to regenerate the catalyst. Very good results were obtained [11]: after 1 h treatment, the ‘‘coke’’ content was decreased by 35% and part of the catalyst activity was recovered; after 12 h treatment, all the ‘‘coke’’ was removed from the zeolite pores and the catalyst activity was completely recovered. Mono- and bidodecyltoluenes (90 and 10 wt.%) were obtained but no tridodecyltoluenes were found in the toluene used for treating the deactivated

sample. This confirms that the bulky tridodecyltoluene molecules cannot desorb from the zeolite micropores. Their removal from the zeolite pores results from reaction (4):



Part of bidodecyl molecules may diffuse in the liquid phase, the other part reacts with toluene molecules with the formation of two monododecyltoluene molecules which desorb easily from the zeolite pores.

It should be remarked that the first alkylation steps occur most likely at the pore mouth because the access to the pores of the completely deactivated samples is blocked. However, after the removal of part of tridodecyltoluenes, the access of toluene molecules

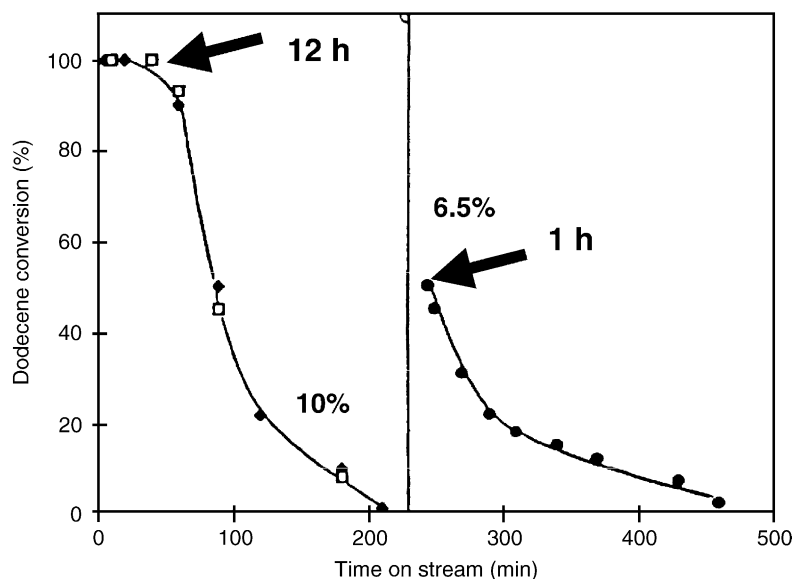


Fig. 5. Dodecene conversion into alkylation products over HFAU 25 as a function of TOS (min) over fresh (\blacklozenge), partially regenerated (1 h treatment under toluene flow (\bullet)) and totally regenerated (12 h treatment under toluene flow (\square)).

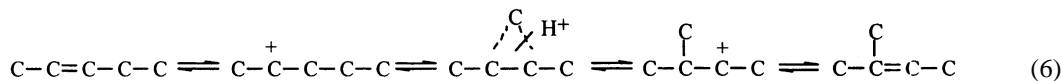
to the micropore volume becomes again possible, and transalkylation then occurring inside the supercages.

2.3. Conclusion

The existence of transalkylation reactions between polyalkylaromatic molecules trapped in the micropores of large pore zeolites and aromatic molecules of the liquid phase was demonstrated. Transalkylation plays a significant role in the production of isopropyl-naphthalene during the transformation at 350 °C of naphthalene with isopropanol over HFAU and HBEA zeolites. It also allows the regeneration under mild conditions of HFAU samples used in the synthesis of LABs. Transalkylation generally occurs at the pore mouth (pore mouth catalysis).

3. Skeletal isomerization of butenes over HFER zeolites

The suppression of lead additives in gasoline has caused an increase in the use of methyltertiobutylether

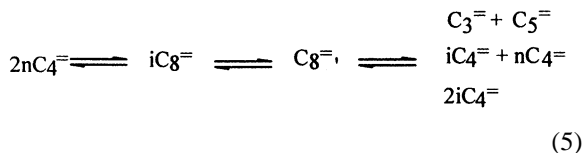


(MTBE), hence in the demand in isobutene. This has initiated a great deal of academic and industrial studies on the skeletal isomerization of *n*-butene, especially after the discovery by Shell that HFER, a medium pore zeolite was an excellent catalyst for this reaction, capable of operating in the absence of water at a relatively low temperature (350 °C) with a high selectivity to isobutene and a high stability [12,13].

3.1. The particular behaviour of HFER in *n*-butene isomerization

The behaviour of this zeolite catalyst is very particular. The high selectivity to isobutene is only obtained after an initiation period, propene and pentenes being formed in large amounts on the fresh catalyst [12–19]. Most of the authors agree that selectivity is related to the formation of carbonaceous compounds. The product distribution observed on the fresh catalyst is the

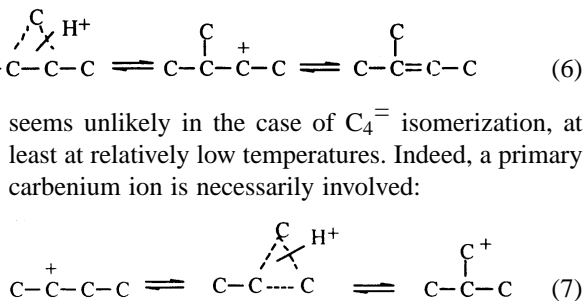
one expected from a bimolecular mechanism involving successive steps of dimerization, isomerization and cracking [19]:



whereas the high selectivity to isobutene found after the initiation period would be typical of a monomolecular mechanism.

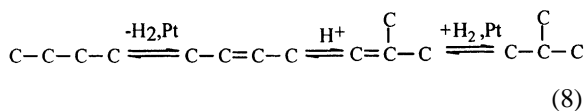
This change in reaction mechanism was confirmed by experiments with ¹³C-labelled butenes. The extensive scrambling which occurs on the fresh samples shows that butene isomerization occurs through a bimolecular mechanism (reaction (5)). On the other hand, ¹³C scrambling is no longer observed over aged samples, which is characteristic of a monomolecular mechanism [20,21].

However, the classical monomolecular mechanism which is well demonstrated for the isomerization of C₅⁺ alkenes:



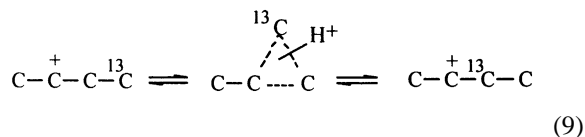
seems unlikely in the case of C₄⁺ isomerization, at least at relatively low temperatures. Indeed, a primary carbenium ion is necessarily involved:

In agreement with that, it has been demonstrated that on bifunctional Pt/SiO₂-Al₂O₃ catalysts, the formation of isobutane from *n*-butane:



was much slower than the formation of isopentane from *n*-pentane [22]. It should be emphasized that under the operating conditions of these experiments, the percentage of olefinic intermediates is very low, hence bimolecular isomerization is also very slow. Reaction (8) is also much slower than the scrambling of ¹³C in

n-butane [22], the acid step of which does not involve primary carbenium ions as intermediates:



On the other hand, the bimolecular mechanism involves only stable carbocation intermediates [19].

3.2. How to explain the selectivity by carbonaceous deposits?

Various proposals have been put forth to explain the selectivity of butene isomerization by carbonaceous species. These proposals can be classified into three categories:

1. Change in the zeolite acidity due to (a) a preferential poisoning of acid sites, non-selective either because of their location on the outer surface of the crystallites [23,24] or because of their too high strength [25,26] or (b) a decrease in the density of protonic sites [27,28]: the bimolecular process which could involve two acid sites for its catalysis would be more affected than the monomolecular process which requires only one acid site.
2. Restriction of channel dimensions by carbonaceous deposits [25,26,29,30] with a consequent increase in the steric constraints on the formation of transition states or intermediates. The steric constraints would affect more significantly the formation of the bulky intermediates of the bimolecular process.
3. Participation of carbonaceous species in a very selective isomerization process [16,31,32].

It would be remarked that whatever the proposal, selectivity is related to the quasi complete disappearance of the bimolecular mode of isomerization. However, within proposals 1 and 2, it has to be supposed that on the protonic sites of the fresh HFER samples, the monomolecular and the bimolecular modes of 2-butene isomerization coexist and at comparable rates. This implies that very unstable primary carbenium ions could be formed at a relatively high rate. In proposal 3, a mechanism of butene isomerization involving carbonaceous compounds as active species has to be found, the mechanistic scheme involving only one molecule of *n*-butene reactant

(no ¹³C scrambling). Moreover, this mechanism could be retained only if it leads to a selective formation of isobutene, this formation thus involving only facile steps (no very unstable intermediates).

Some experimental results cannot be explained by proposals 1 and 2 and seem in agreement with proposal 3.

3.2.1. The effect of TOS hence of the coke content on the yield in isobutene

An increase with TOS of the yield in isobutene was observed by various authors [14–16,21,33]. Unfortunately in most of the studies [14,15,21,33], the contact time was too long, hence the isobutene/*n*-butene ratio which was obtained close to its thermodynamic equilibrium value and the amount of propene and pentenes very high. Therefore, in these experiments, deactivation (which can be considered as similar to a decrease in contact time) affects preferentially the secondary formation of propene and pentenes from isobutene, with consequently an apparent increase in isobutene yield.

However, at low conversion as it is the case in the results reported in Fig. 6 (isobutene/*n*-butene ratio of 0.1, i.e. far from the thermodynamic equilibrium value: 0.65) the increase in isobutene yield which is also observed [16] can no longer be explained by this way (more especially as on the fresh FER sample the by-products are formed more slowly from isobutene than from *n*-butene [19]). Therefore, the only possible explanation is the development of a new and very selective mode of *n*-butene isomerization.

It should be remarked that at very short TOS (not considered in Fig. 6) a significant decrease of the yield in isobutene (from 16 to 8%) can be observed. During this period, the decrease in the yield in propene + pentenes is still more pronounced (from 15 to 4.5%). This simultaneous decrease in isobutene, propene and pentenes production can be related to a decrease in *n*-butene transformation through the dimerization–isomerization–cracking mechanism.

3.2.2. The composition and the location of coke molecules

The carbonaceous compounds were found to be mainly constituted by polymethylaromatic compounds with two or more aromatic rings [31]. These compounds are more basic than butene, which makes

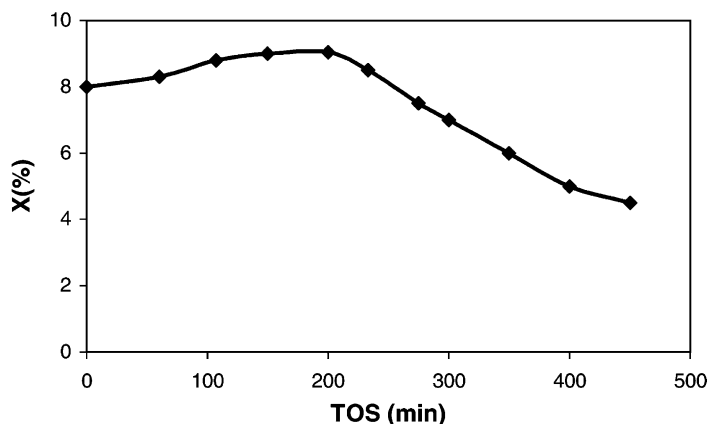


Fig. 6. Change with TOS (min) in the conversion X (%) of n -butenes into isobutene.

most unlikely the adsorption of butene molecules on protonic sites close to coke molecules (i.e. proposal 2).

The carbonaceous compounds were shown to be mainly located inside the zeolite micropores. Indeed, only less than 5% of coke can be recovered in methylene chloride through a direct soxhlet treatment, whereas all the coke components are soluble in this solvent up to long TOS. Outer coke, constituted by highly polyaromatic molecules appear only at very long TOS. These molecules responsible for deactivation result from the growth (and overflowing onto the outer surface) of internal coke molecules. The preferential location of carbonaceous compounds inside the zeolite pores suggests that on the fresh catalyst, n -butene transformation occurs inside the pores. Therefore, proposal 1a in which the bimolecular non-selective reaction would occur on acidic sites of the outer surface of the crystallites cannot be retained.

The location of coke molecules inside the pore system of HFER was specified by molecular modelling techniques. Monte Carlo docking showed that most of these molecules are well solvated by the zeolite framework and are preferentially sited within one or two intersections along the 10-membered ring channel [34].

3.2.3. The effect of coke on the accessibility to pore volume and on the acidity

Carbonaceous deposits cause a blockage to the access of nitrogen to the zeolite pores [16]. At the maximum in isobutene yield which was obtained at approximately 200 min, the coke content is between

5 and 6 wt.% and only 30% of the micropore volume remains accessible to nitrogen hence to the reactant. The quasi complete suppression of propene + pentenes production confirms that the bimolecular transformation of n -butene into isobutene, propene and pentenes occurs inside the zeolite micropores. After 450 min, the yield in isobutene is equal to half of the yield at the maximum, the coke content is equal to 6.9 wt.% and less than 15% of the micropore volume remains accessible to nitrogen.

As was suggested by one of the referees, the blockage of the access of nitrogen to the zeolite pores could be due to the very low temperature (-196°C) of adsorption measurements. Indeed, at this low temperature, coke molecules cannot move within the pores, preventing the diffusion of smaller molecules, whereas at the reaction temperature coke molecules are able to move making free the diffusion of smaller molecules. However, as it is shown below by NH_3 adsorption, pore blockage exists also at 50°C . Furthermore, the size of coke molecules is such that the diffusion of reactant molecules in pores containing coke is most unlikely.

The IR spectra of the fresh and coked samples are compared in Fig. 7 before and after NH_3 adsorption at 50°C [31]. The band at 3600 cm^{-1} which corresponds to the acidic OH groups (Si–OH–Al) is strongly decreased by coke deposits (by 75%), which shows that coke molecules can be adsorbed on the protonic sites. With the coked sample, a broad band is observed at $3300\text{--}3400\text{ cm}^{-1}$ resulting from the shift of the OH

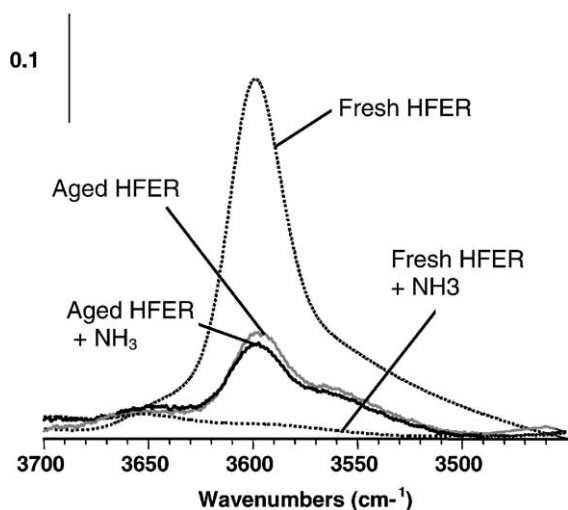


Fig. 7. IR spectra of the OH groups of a HFER 14 sample after pretreatment of the fresh zeolite and of the aged sample, and after adsorption of NH_3 at 50°C on the fresh and aged zeolites.

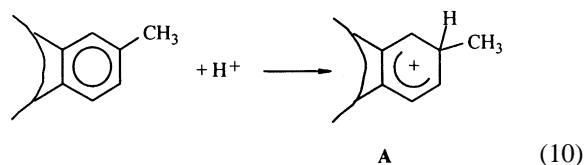
band at 3600 cm^{-1} due to hydrogen bonding with coke species. As it could be expected, NH_3 adsorption on the fresh sample causes the complete disappearance of the band at 3600 cm^{-1} . With the coked sample, NH_3 adsorption has practically no effect on the intensity of this band. This means that NH_3 , hence reactant molecules, cannot accede to the protonic sites of the coked HFER sample. Indeed if the protonic sites would be accessible to NH_3 , this very basic molecule would substitute coke molecules adsorbed on 75% of the protonic sites and would also adsorb on the 25% of the protonic sites which do not interact with the coke molecules.

The complete blockage of the access to the protonic sites of a HFER sample capable to catalyze selectively the skeletal *n*-butene isomerization cannot be explained by proposals 1 and 2. On the other hand, proposal 3 is quite suitable, provided, however, to admit that the selective isomerization process catalyzed or cocatalyzed by carbonaceous species occurs at the pore mouth.

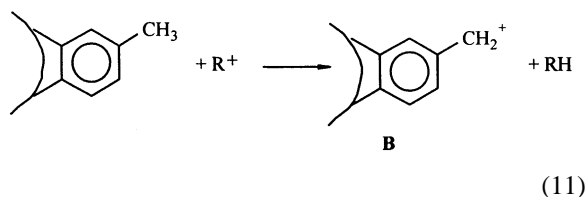
3.3. Mechanism of butene isomerization over aged HFER samples

Coke molecules located near the pore mouth and interacting with protonic sites are most likely the active

sites for the selective butene isomerization observed on the aged HFER samples. The methylarenes which are the main coke components can be adsorbed on the protonic sites as arenium ions (A):



or as benzylic carbocations (B):



These primary carbocations B stabilized by resonance are generally proposed as intermediates in the transalkylation of methylarenes over acid catalysts, the benzenium ions A as intermediates in the isomerization of methylarenes [35]. No isomerization of *n*-butene seems possible over arenium ions, whereas this reaction can occur on benzylic carbenium ions through the mechanism described in Fig. 8 [31]. All the necessary conditions are fulfilled by this mechanism:

- Only one molecule of butene is involved (it is a pseudo monomolecular mechanism).

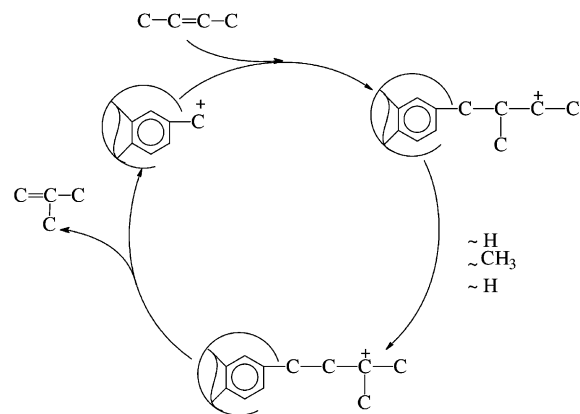


Fig. 8. Mechanism of *n*-butene isomerization into isobutene over coked HFER samples.

- Only facile steps (involving stable intermediates) are required.
- This mechanism leads selectively to isobutene with no formation of propene and pentenes.

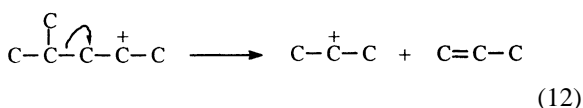
It can also be proposed that coke molecules react with *n*-butylcarbenium ions resulting from *n*-butene adsorption over protonic sites at the pore mouth. However, adsorption of butene on these sites is strongly inhibited by the basic coke molecules. Moreover, the corresponding mechanism of skeletal butene isomerization would involve necessarily a very unstable primary isobutyl carbocation.

3.4. Conclusions

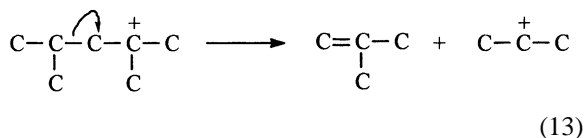
Carbonaceous compounds formed and trapped in the micropores of HFER during the skeletal isomerization of *n*-butenes cause a significant increase in the selectivity to isobutene. On the fresh samples, butene transformation occurs in the micropores through a bimolecular mechanism with consequently parallel formation of isobutene, propene and pentenes. On the aged samples, the micropores are largely filled with carbonaceous deposits and *n*-butene isomerizes selectively at the pore mouth of the 10MR channels. The latter reaction occurs most likely through a pseudo-monomolecular mechanism involving as active species, benzylic carbocations resulting from adsorption of the carbonaceous species on the protonic sites.

4. Hydroisomerization of long chain *n*-alkanes over PtHTON catalysts

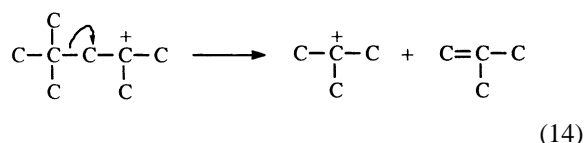
Whereas it is easy to carry out selectively the isomerization of *n*C₅–C₆ alkanes over bifunctional Pt/acid catalysts, this is not generally the case for heavier hydrocarbons because of easier cracking steps. Indeed whereas with C₆ alkanes only the very slow C type of acid cracking can occur:



with C₇ alkanes, B cracking appears:



and with the longer alkanes it is the case for the very fast A cracking (at 200 °C, A cracking was found to be 50 times faster than B cracking and 10,000 times faster than C cracking [36]):



At 200 °C, on an ideal bifunctional PtHFAU catalyst, i.e. a catalyst on which acid isomerization and cracking are the limiting steps, the cracking products of *n*-decane transformation were shown to result mainly from β-scission of tribranched decene intermediates through mode A [36,37] and for a small part from β-scission of dibranched decenes through mode B. The maximum yield of isodecanes which could be obtained was equal to 50–55%.

With PtHMFI catalysts the maximum yield is much lower (≈20%) [37]. This is due to limitations in the diffusion of isodecene intermediates which undergo secondary cracking during their long residence time in the narrow pores of HMFI [37,38]. However, with another average pore size zeolite as acid component (TON) an exceptional high yield of isodecanes (75%) can be obtained [37]. This suggests that PtHTON does not operate through the classical bifunctional mechanism. Pore mouth catalysis was proposed to explain this high selectivity of PtHTON to isodecanes. Indeed molecular graphics showed that the pores of TON can accommodate neither the protonated cyclopropane intermediates of B isomerization nor branched decane and decene molecules, hence that isomerization could not occur entirely inside the micropores [37].

Isomerization would be catalyzed by protonic sites on the external surface of the TON crystal [37,39]. However, another possibility could be that, like in the skeletal isomerization of *n*-butenes over HFER and HTON zeolites [40], molecules of products trapped in the micropores near the external surface be the active species. To discuss this possibility, *n*-decane transformation was carried out at 220 °C, *p*_{H₂} = 0.9 bar,

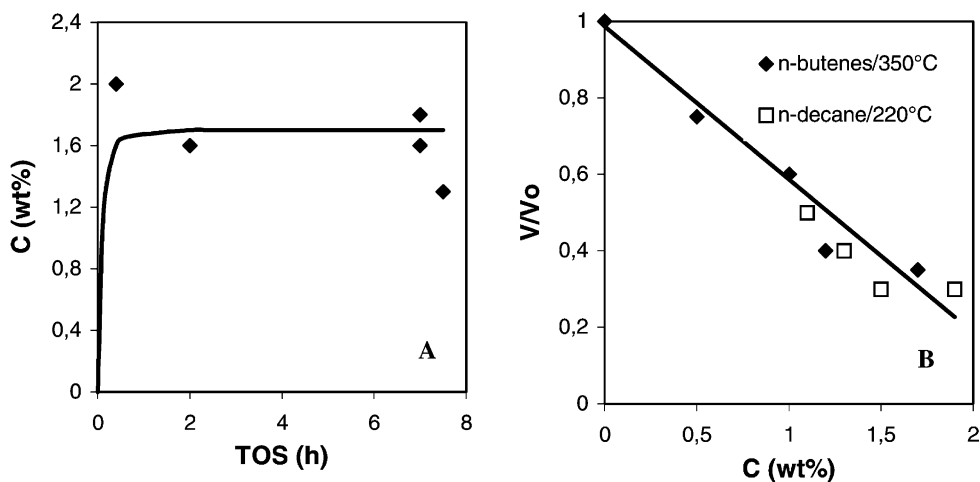


Fig. 9. (A) Percentage of coke (wt.%) on a PtHTON catalyst used for *n*-decane hydroisomerization as a function of TOS. (B) Influence of coke (wt.%) on the capacity for nitrogen adsorption of PtHTON samples.

$p_{nC_{10}} = 0.1$ bar over a PtHTON catalyst [41]. Whatever the contact time, there was a slight decrease in conversion with TOS. Catalyst samples were recovered after various TOS and their “coke” content determined by elemental analysis. Fig. 9A shows that there is a quasi immediate retention in the catalyst of carbonaceous compounds. These compounds cause a blockage of the access of nitrogen hence of the reactant molecules to zeolite pores. This quasi immediate pore blockage is a good confirmation of pore mouth catalysis. It should be remarked that the pore blockage which is observed is quite comparable to that caused by carbonaceous compounds trapped during *n*-butene transformation at 350 °C (Fig. 9B).

Only a very small part of the carbonaceous compounds (<5%) can be recovered by direct soxhlet treatment of the “coked” samples, whereas after dissolution of the catalyst in a hydrofluoric acid solution all these compounds are soluble in methylene chloride. This confirms that the carbonaceous compounds are trapped in the zeolite pores. GC–MS coupling analysis shows that the carbonaceous compounds are mainly constituted by C_{12} – C_{20} linear and monobranched alkanes in a 2:1 ratio; traces of alkenes were also detected.

The pore volume really occupied by the carbonaceous compounds is much lower than the pore volume made inaccessible to nitrogen, which suggests a preferential location near the pore mouth. Therefore, like

in *n*-butene isomerization, the carbonaceous compounds could participate in the hydroisomerization of *n*-alkanes. Moreover, it can be suggested that the molecules of monobranched alkanes are preferentially located near the outer surface of the crystals where they block the desorption of *n*-alkane molecules located in the same channels but in their inner part.

A simple isomerization mechanism involving active sites tertiary carbenium ions formed from these monobranched alkanes can be proposed (Fig. 10). The first step is the alkylation by the tertiary carbenium ions of decene molecules resulting from decane dehydrogenation on the platinum sites. The other steps depend on the decene molecules participating in the first step:

- With 1-decene molecules (Fig. 10A) there is a branching of the resulting carbenium ions through protonated cyclopropane intermediates (B isomerization) followed by hydride shift and A cracking steps via tertiary carbenium ion intermediates with formation of 2-methylnonene molecules only which can be hydrogenated into 2-methylnonane which is the monobranched alkane preferentially formed on PtHTON [37,39,41].
- With the other decene molecules, 2-, 3-, 4- and 5-methylnonanes can be formed through the

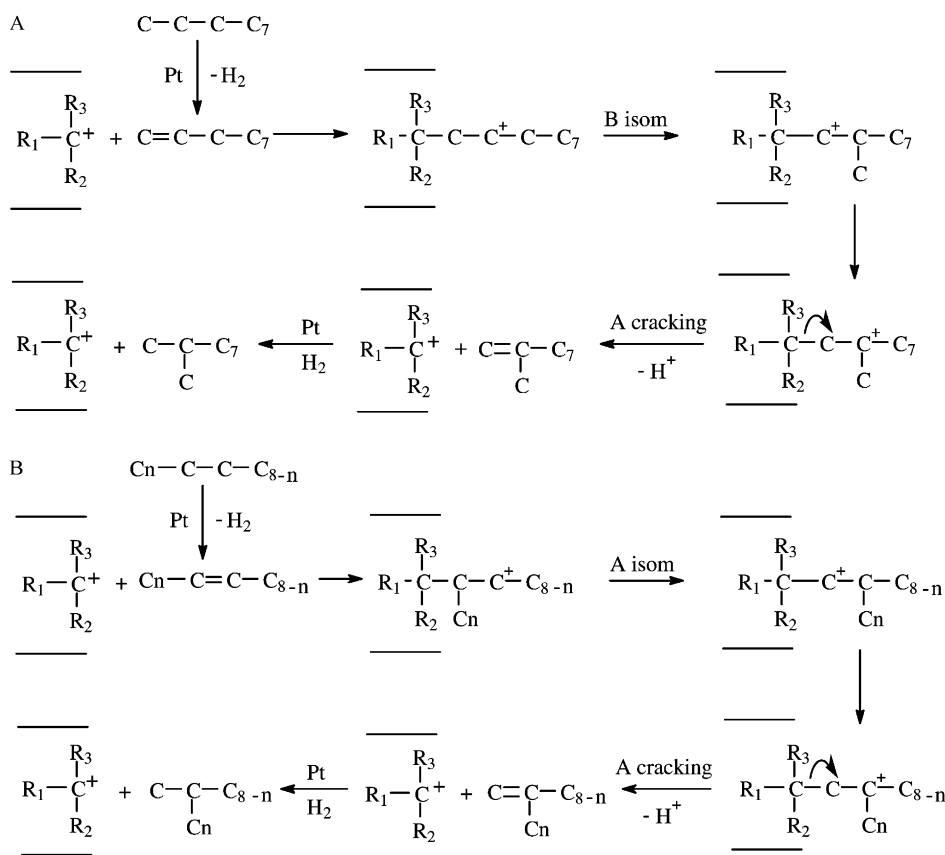


Fig. 10. Mechanism of *n*-decane hydroisomerization over tertiary carbenium ions resulting from adsorption on protonic sites of the TON pore mouth of carbonaceous compounds trapped in the zeolite nanopores.

following successive steps: A isomerization (through alkyl shift), hydride transfer, A cracking and hydrogenation (Fig. 10B). In the absence of steric constraints, this pathway which involves only very facile steps should occur more rapidly than the previous one (Fig. 10A). As at the pore mouth of TON the steric constraints should increase with the number of carbon atoms of the smaller alkyl substituent of the double bond (*n*), a preferential formation of 2-methylnonane is also expected from this pathway.

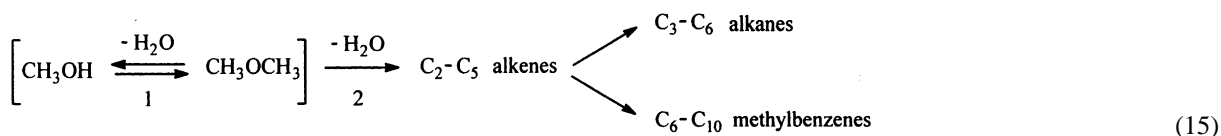
In conclusion, it can be said that the hydroisomerization of long chain *n*-alkanes over PtHTON catalyst most likely occurs at the pore mouth of the zeolite (even if recent investigations [38,42] dispute this proposal). This reaction may involve as active sites

tertiary carbenium ions formed at the pore mouth by adsorption of methyl alkenes trapped in the zeolite pores during the first minutes of reaction.

5. Conversion of methanol into light alkenes

The methanol to gasoline (MTG) process developed by MOBIL allows the selective production of gasoline with a high octane number [5]. This process, quite remarkable in selectivity, was used in New Zealand to convert natural gas to gasoline via methanol synthesis but due to economical reasons, the MTG unit was closed down.

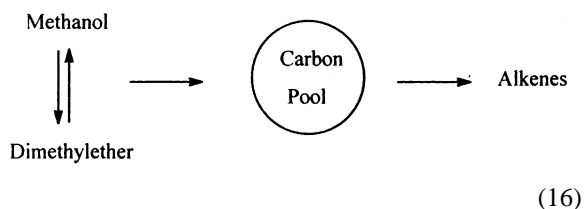
With the HMF1 zeolite catalyst used in MTG, methanol conversion was shown to occur through the following successive scheme [43]:



Under chosen operating conditions [5] or by using other zeolites (e.g. highly dealuminated mordenite [44]) or SAPO type molecular sieves (e.g. SAPO 34 [45]), methanol conversion can be directed to the formation of light alkenes: methanol to olefin (MTO) processes. UOP-Norsk Hydro announced in 1996 the construction of a 250,000 t per year plant for production of ethylene from natural gas via their SAPO 34 MTO process [46].

5.1. Methanol to olefin transformation

The discovery that methanol could be selectively converted to gasoline on HMF1 has attracted world wide attention and initiated a significant number of studies on the catalytic applications of MFI as well as on the mechanisms of the steps involved in methanol conversion. Despite that, the mechanism of alkene formation (step 2 in Eq. (15)) is still the subject of controversy. Four types of intermediates: carbenes, radicals, carbocations and oxonium ions were proposed for the formation of the first C–C bond on the fresh catalysts [46]. Moreover, as an induction period is observed with most of the catalysts, the reaction mechanism could be different on fresh and on working catalysts. In this latter case, there is evidence for a scheme based on a pool of adsorbed intermediates which react with methanol or dimethylether, the resulting products splitting up after rearrangement into alkene molecules (carbon pool mechanism [47–49]).

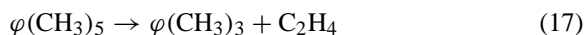


5.2. "Coke" molecules as active species for methanol transformation over SAPO 34

Various adsorbed species were proposed as pool components: carbenium ions, oxonium ions,

cyclopentenyl cations, benzenium ions, etc. resulting respectively from proton addition to alkenes, ethers, cyclopentadienes and aromatic compounds. Carbonaceous compounds ("coke") trapped in the zeolite pores during the first times of reaction were also proposed as pool components [49,50]. As previously emphasized, due to the molecular size of the cages and channels of zeolites, "coke" molecules can be very simple. This is the case for coke molecules formed during methanol conversion of SAPO 34 which has cages of 6.5 Å × 11 Å with apertures of 3.8 Å. Coke is mainly constituted by polymethylbenzenes, with one to six methyl groups, polycyclic aromatics appearing at long TOS (high coke content) [51].

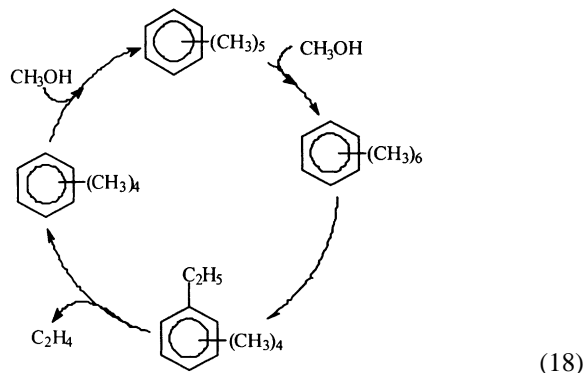
According to Arstad and Kolboe [49], the observation that methylarenes are dominantly trapped molecules formed in parallel with the MTO reaction suggests that they may be intimately connected to this reaction. In agreement with this suggestion, the same authors show that after a short flushing with nitrogen the amount of penta- and hexamethylbenzenes in coke significantly decreases at the benefit of xylenes and trimethylbenzenes. Light alkenes could be the complementary products of this transformation:



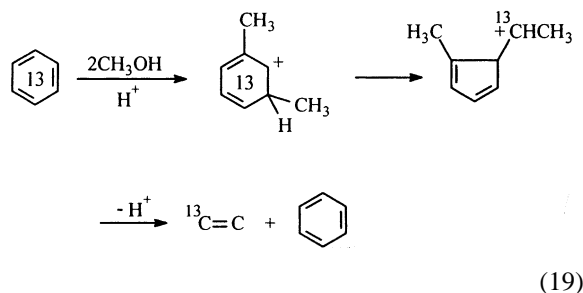
Experiments of methylation of benzene and toluene by ¹³C methanol [50] carried out over HMF1, HMOR and HBEA confirm that this type of reaction is quite possible. (Similar experiments with ¹³C benzenes or toluene and light methanol have been carried out 20 years ago by Mole and co-workers [52,53] over a MFI zeolite.) Indeed, ethene and propene products were isotopically mixed, containing only 50–75% ¹³C instead of 100%. This indicates that arenes participate in their formation. Furthermore, polymethylbenzenes which were formed contained up to six ¹³C atoms in the benzene ring. Therefore, the expected fast methylation of benzene and toluene with ¹³C methanol was followed by rearrangement leading to ¹³C scrambling. Another important information is that the rate of methanol conversion to hydrocarbons over HMF1

zeolite is enhanced by the addition of aromatic hydrocarbons to the feed [54].

Polymethylbenzenes trapped in the cages of SAPO 34 also have a significant positive effect on the rate of methanol conversion [51]. Thus, with the fresh catalyst, the conversion was only 14% but the SAPO 34 sample pretreated with a methanol pulse achieved nearly 100% conversion of the second methanol pulse. This provides strong evidence that in order to be active for MTO reaction, SAPO 34 must have polymethylbenzenes trapped in its cages. Therefore, the most likely scheme for methanol conversion to light alkenes over SAPO 34 after the fast initial formation of polymethylbenzenes in its cages can be described as indicated below for ethylene formation (reaction (18)):



The transformation of hexamethylbenzene into ethyltetramethylbenzene is most likely the limiting step of this reaction. The following mechanism with 6,5-ring contraction and 5,6-ring expansion was proposed for this step [55] to explain the formation of mono ^{13}C -labelled ethylene from ^{13}C benzene and methanol observed in the experiments of Mole and co-workers [52–54]:



Another mechanism involving an exo-methylene-cyclohexadiene intermediate was also proposed [53,56].

5.3. Conclusion

It seems established that the mechanism of methanol transformation into light alkenes is different on the fresh and on the working catalysts. On the fresh catalysts, alkenes are *directly* formed from methanol molecules, the oxonium-ylide mechanism proposed by van den Berg et al. [57] being the most likely. On the working catalysts, a large part of alkenes would be *indirectly* formed from methanol molecules, methylarenes trapped in the zeolite cages (e.g. SAPO 34) or resulting from secondary transformation of alkenes (e.g. MFI) acting as cocatalysts.

6. Conclusion

The results presented in this paper demonstrate that the simple “coke” molecules trapped in the zeolite channels or cages of molecular size may participate as active species in various acidic reactions. The examples, chosen in commercially important processes of hydrocarbon production, show that the catalytic action of “coke” molecules is relatively general. Indeed it is observed for reactions carried out in gas as well as in liquid phase and with small, medium or large pore zeolites. Furthermore, depending on the reactants–zeolite couple which is considered, the catalytic action of coke molecules occurs within the zeolite pore system or only at the vicinity of the outer surface of the crystal (pore mouth catalysis).

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