# Origin of the Positive Effect of Coke Deposits on the Skeletal Isomerization of n-Butenes over a H-FER Zeolite

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The curious positive effect of carbonaceous deposits on the skeletal isomerization of n-butenes over a H-FER zeolite can be related to the development of a new reaction mechanism involving as active sites tertiary carbenium ions blocked in the zeolite pores.

Methyl tert-butyl ether (MTBE) is now a significant part of the gasoline pool. The availability of isobutene, a key component in its synthesis, is a limiting factor for expanding the production of MTBE. This gives particular importance to the process of skeletal n-butene isomerization.[1–3] This apparently simple isomerization is generally complicated by the simultaneous production of dimers and of propene and pentenes and by a rapid catalyst deactivation by coke. This does not seem to be the case with a H-FER zeolite catalyst recently developed for n-butene skeletal isomerization.[3] However this zeolite leads initially to a large amount of secondary products, becoming selective only after a partial deactivation by coke deposits.[3] With the fresh catalyst the isomerization of n-butenes into isobutene would proceed through a dimerization-cracking mechanism with consequently a large simultaneous formation of propene and pentenes,[4] Scheme 1.

We show here that after selectivation of the catalyst by coke, n-butene isomerization occurs through another mechanism involving as active sites tertiary-carbenium ions blocked in the zeolite pores.

H-FER (Na + K < 50 ppm) was prepared by three successive $NH_4^+$ ion exchanges (10 mol dm$^{-3}$ $NH_4NO_3$ solution, 4 h at 373 K) followed by calcination under dry air flow at 773 K from a sample (Laboratoire des Matériaux Minéraux-Mulhouse). n-Butene isomerization was carried out under the following conditions: flow reactor, 623 K, n-butene and nitrogen pressures of 0.1 and 0.9 bar respectively, mass hourly space velocity equal to 20.6. Reaction products were analysed on-line by GC (50 m Chrompack PLOT $Al_2O_3/Na_2SO_4$ capillary column).

At short time-on-stream (TOS), the skeletal isomerization of n-butenes is accompanied by the formation of a large amount of propene and pentenes. This formation can be explained through the above dimerization–cracking mechanism, this mechanism also being responsible for the skeletal isomerization of n-butenes. Octenes, heptenes and hexenes are also formed in small amounts. The initial rate of dimer formation is about 100 times lower than that of isobutene, that of heptenes 50 times and that of hexenes 25 times. n-Butane is also formed (ten times more slowly than isobutene) probably through hydrogen transfer from coke precursors to n-butenes.

Fig. 1(a) shows that the conversion of n-butenes into isobutene increases slightly with TOS then decreases for TOS greater than 4 h. This slight increase in the rate of skeletal n-butene isomerization was confirmed by experiments for identical or greater contact times. On the other hand, there is a rapid decrease in the formation of all the other products: propene and pentenes [Fig. 1(b)], hexenes, heptenes, octenes and n-butane. This deactivation is certainly due to the formation of carbonaceous deposits ('coke') (Fig. 2). These carbonaceous deposits cause a pronounced blockage of the access to the

zeolite pores as shown by adsorption experiments. Indeed the pore volume accessible for nitrogen passes from 0.15 cm$^3$ g$^{-1}$ with the fresh zeolite to 0.02 with H-FER deactivated during 7.5 h and containing 6.9 mass% coke.

The rapid deactivation observed for the formation of all the products except for isobutene can be explained by this blockage. Curiously, although isobutene is formed through the same dimerization–cracking process as propene and pentenes there is initially no deactivation and even a slight activation. This shows that the dimerization cracking is replaced by a new isomerization process which is quite different namely: (i) it is much more selective with practically no simultaneous formation of propene
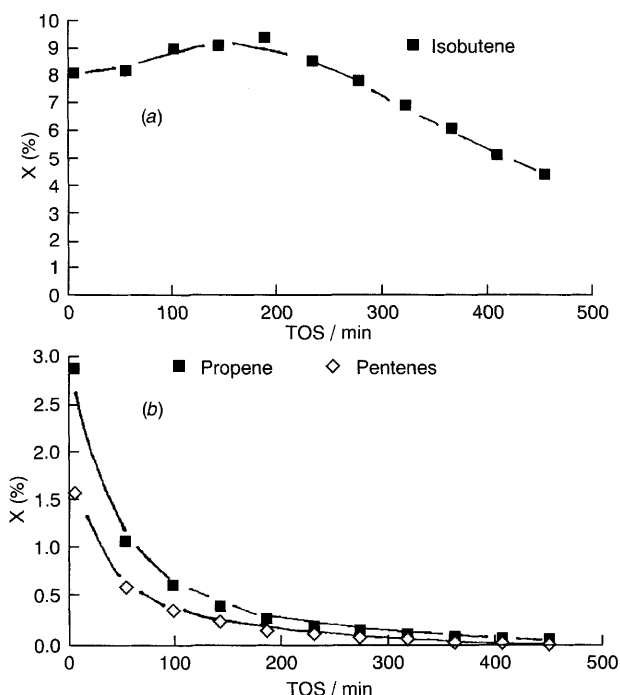


Fig. 1 Change with time-on-stream (TOS) in the conversion (X%) of n-butenes into isobutene (a) and into propene and pentenes (b)
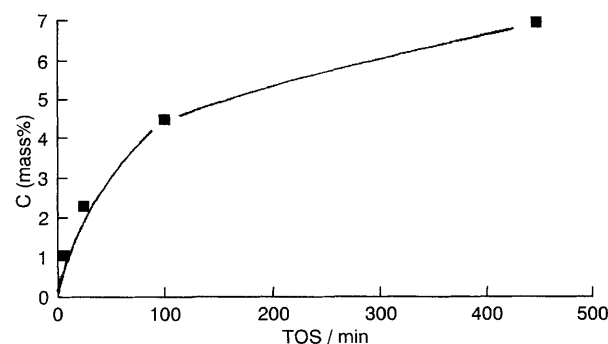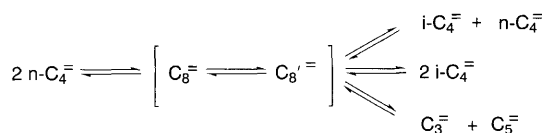


Fig. 2 Formation of coke (C) as function of TOS



Scheme 1

and pentenes, (*ii*) the active sites are most likely the carbonaceous deposits rather than the protonic acid sites, (*iii*) the process cannot occur within the inner zeolite pores which are blocked by the carbonaceous deposits.

The mechanism in Fig. 3 allows us to explain all these points. The active species would be tertiary-carbenium ions formed from 'coke' molecules and blocked in the pores near the outer surface of the crystallites. The alkylation of these carbenium ions leads to secondary carbenium ions, which isomerize through hydride and methyl shifts into tertiary-carbenium ions, which in turn crack into isobutene with regeneration of the initial tertiary carbenium ions [type A cracking[5]]. Hydride and
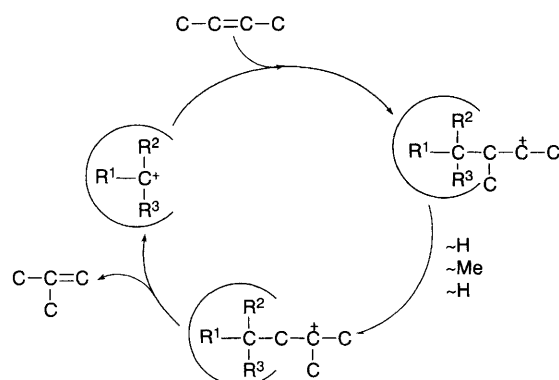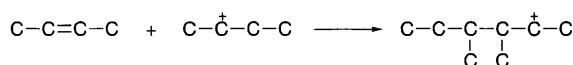


**Fig. 3** Mechanism of n-butene isomerization into isobutene on a coked H-FER sample



**Scheme 2**

methyl shifts and type A cracking being very rapid,[5] the slowest step of this process is the alkylation. However, this alkylation, which involves tertiary and secondary carbenium ions (Fig. 3), is faster than the alkylation step of the dimerization–cracking mechanism that involves two secondary carbenium ions,[5] Scheme 2. Moreover, this mechanism does not allow propene and pentenes to be formed.

This pseudo-monomolecular mechanism could also explain the significant differences of the selectivity of variously modified aluminas in butene isomerization.[6] These differences were related to the coexistence of monomolecular and bimolecular processes catalysed by Lewis and Brønsted acid sites, respectively. Allylic species were proposed as intermediates in the monomolecular process.[6] However, it seems difficult to envisage a mechanism of skeletal isomerization involving such intermediate species. The pseudo-monomolecular mechanism constitutes an interesting alternative to this proposal. The key step would be the quasi-irreversible adsorption of branched alkenes (such as isobutene) on strong Lewis acid sites with formation of tertiary carbenium ions.

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