Influence of hydrogen and of reaction temperature on the mechanism of *n*-butane isomerization over sulfated zirconia

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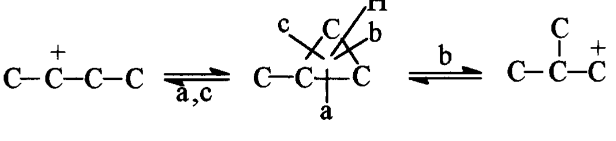
Received 30 January 1997; accepted 20 May 1997

Over HMOR zeolites, hydrogen inhibits *n*-butane isomerization which occurs through a bimolecular pathway and has practically no effect on *n*-hexane isomerization, of which the reaction mechanism is intramolecular. The large inhibiting effect found with butane isomerization is certainly related to the demanding character of the bimolecular process: two sec-butyl carbenium ions are necessary for the alkylation step. Hydrogen could react with carbenium ions limiting their concentration. Over sulfated zirconia hydrogen has also an inhibiting effect on *n*-butane isomerization, this effect being particularly pronounced at low temperature, and has no effect on *n*-hexane isomerization. It is suggested that the differences in the butane isomerization mechanisms proposed in the literature in the case of sulfated zirconia are mainly due to the "diluent" gas used (nitrogen and hydrogen) and for a small part to the reaction temperature.

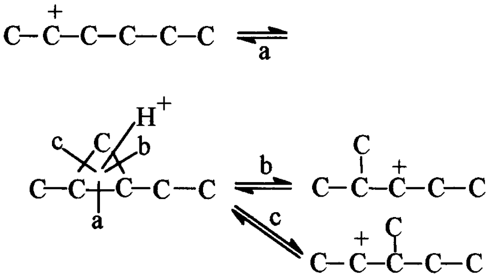
Keywords: *n*-butane isomerization, *n*-hexane isomerization, sulfated zirconia, intramolecular and bimolecular mechanisms

1. Introduction

Compared to C_{5+} alkane isomerization, butane isomerization over acid catalysts has some peculiarities. These peculiarities were emphasized a long time ago by Brouwer [1] in a homogeneous acid medium and by Chevalier et al. [2] over a bifunctional Pt–SiO_2–Al_2O_3 catalyst. By using ^{13}C-labelled butanes these authors have confirmed the existence of protonated cyclopropane intermediates. These intermediates explain why C_{5+} alkane isomerization is much faster than *n*-butane isomerization. Indeed contrary to *n*-butane isomerization (reaction (1)) C_{5+} isomerization (reaction (2)) does not involve primary carbenium ions as intermediates. Furthermore, the isomerization of [1-^{13}C] *n*-butane into [2-^{13}C] *n*-butane (isotopic scrambling) which involves the same intermediates as hexane branching (reaction (2)) occurred at a similar rate [2].



(1)



(2)

However, *n*-butane isomerization can also occur through a bimolecular pathway (figure 1), as has been shown over HMOR catalysts [3–5]. Except at a very low partial pressure of *n*-butane, this bimolecular isomerization is faster than the monomolecular pathway, for it does not involve primary carbenium ion intermediates. Sulfated zirconia (pure or doped with Pt, Mn or Fe) is also an active catalyst for butane isomerization [6–9]. Curiously, different conclusions were drawn on the mechanism of butane isomerization over non-doped sulfated zirconia by investigating the transformation of ^{13}C-labelled compounds. According to Garin et al. [10] butane isomerization would occur through an intramolecular mechanism while according to Adeeva et al. [11] it occurred through a bimolecular mechanism. We show here that this difference in mechanisms is mainly due to the nature of the "diluent" gas employed (hydrogen in the first case and nitrogen in the second); hydrogen inhibits the predominant bimolecular butane isomerization pathway and practically unaffects the intramolecular one. However, the temperatures chosen for the reaction

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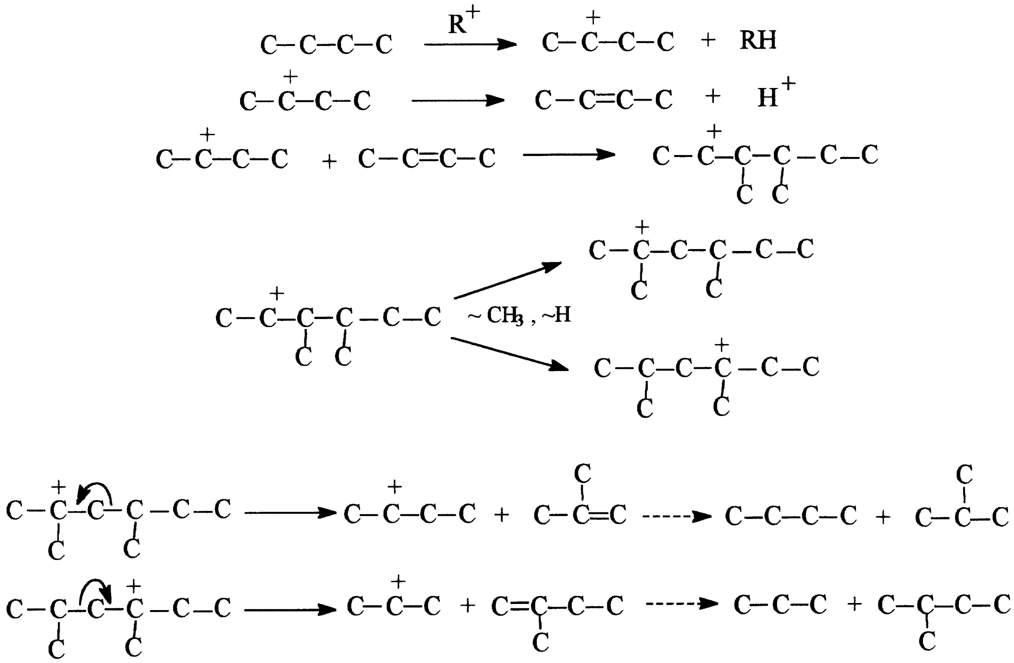


Figure 1. Mechanism of the bimolecular isomerization of *n*-butane over HMOR catalysts.

(523 K by Garin et al. [10], 453 K by Adeeva et al. [11]) can also influence the isomerization mechanism.

2. Experimental

H-mordenite HMOR20 (Si/Al = 20) was supplied from the "Institut Régional des Matériaux Avancés" (IRMA). Prior to being used, the zeolite sample was calcined in situ at 773 K under dry air flow (60 ml min^{-1}). Sulfated zirconia was prepared according to ref. [12] by impregnation of zirconium hydroxide $Zr(OH)_4$ with 0.3 N H_2SO_4 aqueous solution followed by filtration and drying at 383 K. $Zr(OH)_4$ was obtained by hydrolysis of $ZrO(NO_3)_2{\cdot}2H_2O$ (PROLABO) with 20% NH_4OH aqueous solution up to pH 10 followed by filtration and washing with distilled water. Sulfated zirconia was obtained by calcination at 873 K for 3 h under dry air flow (60 ml min^{-1}). Its sulfur content was equal to 2 wt%. Before the catalytic test, the catalyst was pre-treated in situ at 723 K in dry air (60 ml min^{-1}) for 2 h and cooled to reaction temperatures under a flow of dry air.

n-butane and *n*-hexane transformations were carried out in a flow reactor in the presence of nitrogen or hydrogen gas at 423–523 K under atmospheric pressure. The partial pressures of the reactants and of the "diluent" gas (N_2 or H_2) were equal to 0.1 and 0.9 bar respectively. The weight hourly space velocity (WHSV) was chosen equal to 0.6–10 in order to obtain an initial conversion lower than 10%. In order to obtain an accurate value of the initial activity, short values of time-on-stream were chosen (20 s to 3 min depending on WHSV). In every case, the minimum value of time-on-stream was chosen so as to have a constant value of the GC peak area, hence a constant value of the reactant pressure.

Analysis of reaction products was performed on-line by gas chromatography with a Varian 3400 equipped with a 50 m fused silica chrompack CPSil-5 (1.2 μm thickness) capillary column in the case of *n*-hexane and with a 50 m fused silica PLOT Al_2O_3/KCl capillary column for *n*-butane reaction, with a flame ionisation detector and a valco multiposition valve (ten positions).

3. Results and discussion

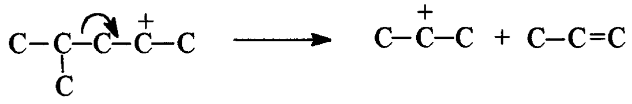
From the transformation of ^{13}C-labelled compounds over HMOR catalysts it is well demonstrated that butane isomerization occurs through a bimolecular pathway [3], while hexane isomerization occurs through a monomolecular one [2,13,14]. To confirm these conclusions a kinetic study of *n*-butane and *n*-hexane transformations was carried out on HMOR20 at 523 K under nitrogen. As expected from the bimolecular mechanism the isomerization order with respect to *n*-butane was close to 2 (1.7), while the reaction order with respect to *n*-hexane was close to 1. We can thus consider *n*-hexane and *n*-butane isomerization over HMOR as typical monomolecular and bimolecular pathways respectively.

The effect of hydrogen on the rates of *n*-butane and of *n*-hexane isomerizations was determined at 523 K on a series of mordenite samples differing by their framework Si/Al ratio. Whatever the sample and the diluent gas the products are only paraffinic: isobutane, propane and pentanes from *n*-butane, isohexanes and C_3–C_5

alkanes from *n*-hexane. Hydrogen strongly inhibits *n*-butane transformation while it has only a limited effect on *n*-hexane transformation. Thus, initially, over HMOR20, *n*-butane isomerization is approximately seven times slower under hydrogen than under nitrogen, while *n*-hexane isomerization occurs at similar rates under nitrogen and under hydrogen (figure 2). For *n*-hexane transformation, deactivation is very fast under nitrogen and under hydrogen. For butane transformation, deactivation is relatively rapid under hydrogen, while a short period of activation is observed under nitrogen. This period of activation is generally not reported in the literature for the first analysis is carried out after relatively long time-on-stream (e.g. 30 min in ref. [5]). This activation period could correspond to a progressive increase in the concentration of the carbenium ions adsorbed on the zeolite (R^+ in the bimolecular chain isomerization process of figure 1) [15]. Another point to note is that, for both reactants, hydrogen causes an increase in the isomerization selectivities: from 70 to 83% for *n*-butane transformation (at 1% conversion) and from 55 to 65% for *n*-hexane transformation (at 2% conversion). In the case of *n*-butane isomerization, this increase can be explained by the preferential decrease in the bimolecular pathway which, contrary to the monomolecular one, leads both to isobutane and to propane plus pentanes. This means that under hydrogen a non-negligible part of isomerization (estimated at approximately 50% from the selectivity) occurs through the monomolecular pathway involving a primary carbenium ion as an intermediate. Even if this monomolecular pathway occurs very slowly its existence indicates the presence of very strong acid sites on the HMOR samples. In the case of *n*-hexane isomerization, the increase in isomerization selectivity can be explained by the slight decrease observed in the formation of C_3–C_5 products which most likely results from an alkylation–cracking process [16]:

$$C_6^+ + C_3^= \longrightarrow C_9^+ \longrightarrow C_5^+ + C_4^=$$
$$\longrightarrow C_4^+ + C_5^= \qquad (3)$$

In this process propene results from the following cracking reaction:



$$C-\underset{C}{C}-C-\overset{+}{C}-C \longrightarrow C-\overset{+}{C}-C + C-C=C \qquad (4)$$

The very large inhibiting effect of hydrogen on the bimolecular butane isomerization could be explained by a large decrease in the concentration of the sec-butyl carbenium ions caused by the following reaction:

$$C-\overset{+}{C}-C-C + H_2 \longrightarrow C-C-C-C + H^+ \qquad (5)$$

This type of reaction has previously been proposed to explain the decrease in the rate of toluene disproportionation caused by hydrogen [17,18]. The large decrease in this concentration would render practically impossible the encounter between sec-butyl carbenium ions and butene molecules formed from these carbenium ions. Hydrogenation of butenes over traces of iron impurities could also explain the inhibiting effect of hydrogen on *n*-butane isomerization. On the other hand, hydrogen would have practically no effect on hexane isomerization: firstly, because the monomolecular isomerization process is less demanding in carbenium ions than the bimolecular one and secondly, because carbenium ions and alkenes are formed by cracking (reaction (4)).

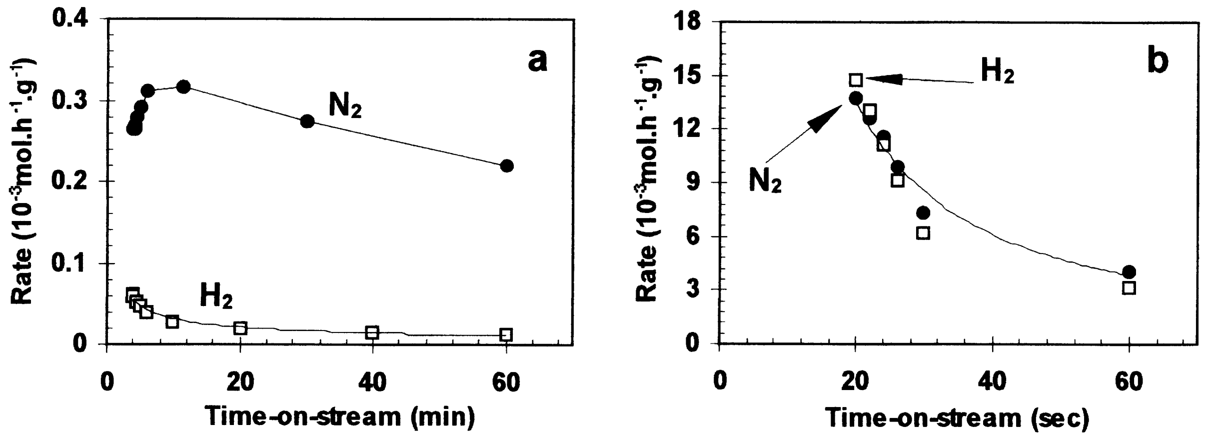


Figure 2. *n*-butane (a) and *n*-hexane (b) isomerization over HMOR20 at 523 K. Influence of the "diluent" gas (N_2 or H_2) on the reaction rate.

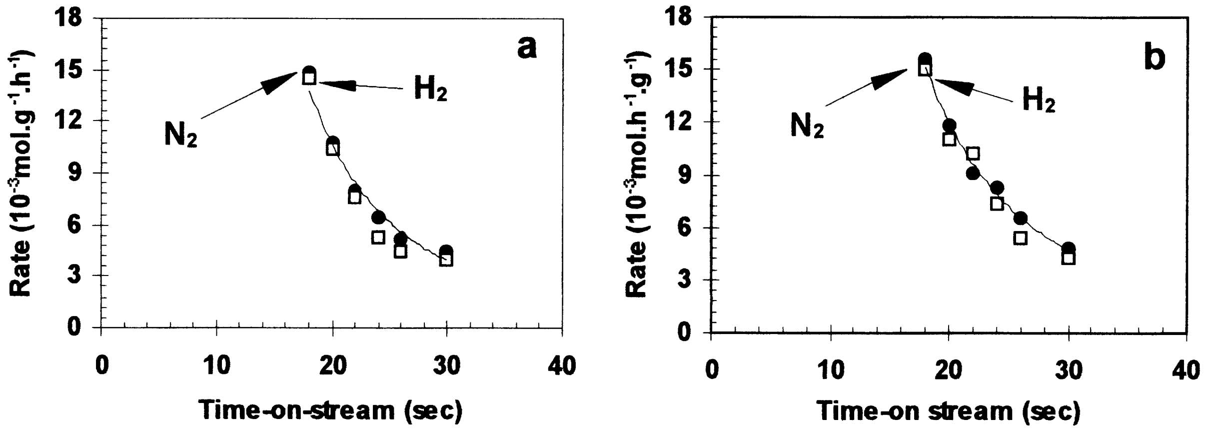


Figure 3. n-hexane isomerization over sulfated zirconia: (a) at 473 K, (b) at 523 K. Influence of the "diluent" gas (N_2 or H_2) on the reaction rate.

The effect of hydrogen on n-butane and n-hexane isomerization was determined over sulfated zirconia at various temperatures. Whatever the temperature (473 and 523 K) hydrogen has practically no effect on n-hexane isomerization (figure 3), which confirms that this reaction occurs (similar to that carried out over mordenite) through a monomolecular mechanism.

For n-butane isomerization at 423 K, hydrogen

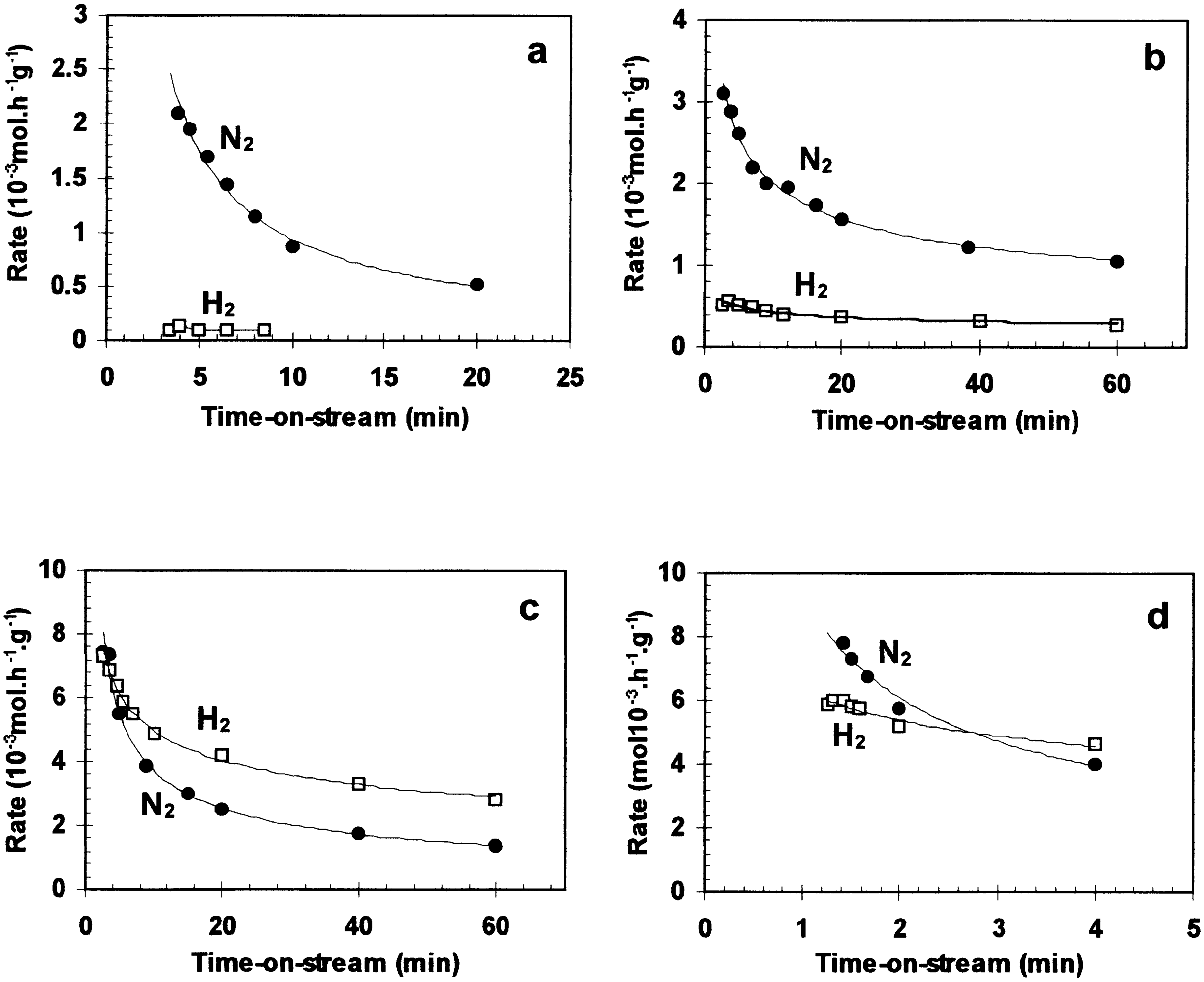


Figure 4. n-butane isomerization over sulfated zirconia (a) at 423 K, (b) at 473 K, (c) and (d) at 523 K. Influence of the "diluent" gas (N_2 or H_2) on the reaction rate.

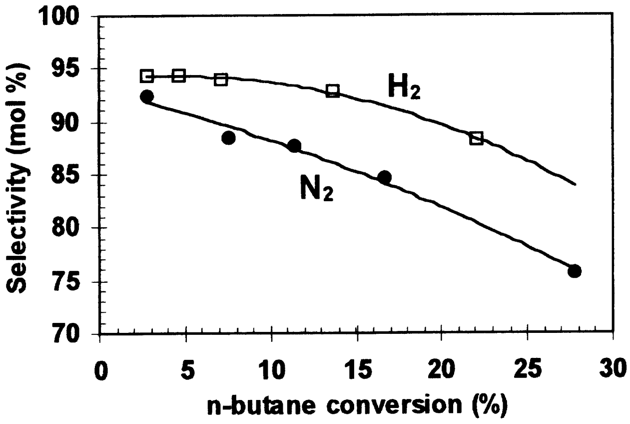


Figure 5. *n*-butane isomerization over sulfated zirconia at 523 K. Influence of the "diluent" gas (N_2 or H_2) on the selectivity to isobutane.

causes a decrease in the rate by a factor of 30 (figure 4a); the effect is less pronounced at 473 K (/7) (figure 4b) and is very small at 523 K (figure 4c) even at very low time-on-stream values (figure 4d). This indicates that at least at low temperatures butane isomerization occurs through a bimolecular pathway. Even at 523 K a substantial part of isomerization is bimolecular as shown by the significant increase in the isomerization selectivity caused by hydrogen (figure 5). However, at this temperature the initial deactivation under nitrogen is very fast (much faster than under hydrogen), which makes the inhibiting effect of hydrogen less apparent.

Therefore, the difference in the butane isomerization mechanisms over sulfated zirconia which was found by Adeeva et al. [11] and Garin et al. [10] is mainly due to the diluent gas used for the experiments. In the experiments carried out by Garin et al. [10], the inhibiting effect of hydrogen on the bimolecular butane isomerization is particularly pronounced because of the very high hydrogen/butane ratio (~ 90) used and the intramolecular isomerization is predominant. Temperature can also play a role, however more limited. Indeed the higher the reaction temperature the less pronounced the inhibiting effect of hydrogen, which could indicate that the relative significance of the monomolecular pathway increases with the reaction temperature. This could be expected from the difficulty of the reaction involved: the activation energy for the difficult monomolecular butane isomerization is certainly greater than that for the bimolecular one.

Acknowledgement

One of the authors (M-TT) is grateful to TOTAL S.A. for financial support.

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