

Isomerisation of butene in isobutene on ferrierite catalyst: A mono- or a bimolecular process?

P. Meriaudeau^{*}, R. Bacaud, L. Ngoc Hung, Anh. T. Vu

Institut de Recherches sur la Catalyse, CNRS-2, avenue A. Einstein, 69626 Villeurbanne Cédex, France

Received 12 April 1996; accepted 23 April 1996

Abstract

The isomerisation of n-butene into isobutene has been studied over a ferrierite catalyst being in a selective state (aged catalyst) or non-selective state (fresh catalyst). It is observed, by using $^{13}\text{C}=\text{C}-\text{C}-\text{C}$, that a bimolecular process operates on the non-selective catalyst whereas a monomolecular process exists on the selective catalyst.

1. Introduction

Isobutene is an important material needed for the synthesis of MTBE (methyl tert-butyl-ether) which is now used as an octane enhancer for unleaded gasoline.

The major source of isobutene is from the catalytic cracking of petroleum and a recent patent [1] and recent reports [2,3] have shown that ferrierite-based catalysts are effective to transform n-butene into isobutene.

Ferrierite, a natural or synthetic material, has an orthorhombic framework containing ten-membered ($4.2 \times 5.4 \text{ \AA}$) channels intersected by eight-membered ($3.5 \times 4.8 \text{ \AA}$) channels.

It is generally observed that ferrierite catalysts are not selective at the beginning of the reaction and that the selectivity increases with time-on-stream, reaching high values after a few hours. This behaviour is illustrated on Fig. 1

relative to commercial ferrierite from Tosoh. This ferrierite ($\text{Si}/\text{Al} = 9.5$) is formed of small elliptical grains having sizes in the range of 2–40 μm as observed by SEM. On Fig. 1, the change in isobutene selectivity and isobutene yield are plotted as a function of time-on-stream.

The exact nature of the active site and its location, are still under debate [4] and the reaction mechanism is not established. As for chlorinated alumina which is also active and selective for the isomerisation of n-butenes into isobutene [5], it has been postulated that butene could be transformed into isobutene either via a bimolecular reaction (oligomerisation and cracking producing $\text{C}_{4=} + i\text{-C}_{4=}$, $\text{C}_{3=} + \text{C}_{5=}$) or a monomolecular reaction (isomerisation).

For a ferrierite catalyst in its selective state (zone B of Fig. 1), it is observed that the isobutene selectivity changes with the butene pressure and the reaction temperature, this is interpreted to be in favour of the monomolecular reaction mechanism [6].

^{*} Corresponding author.

In order to clear this problem, we have decided to use ^{13}C labelled butenes as reactant: if the reaction is occurring via a monomolecular process, the isobutene molecules would have only one ^{13}C atom, by contrast in the case of a bimolecular process, some molecules will have no ^{13}C , some one ^{13}C and some more than one ^{13}C , depending on the rate of isomerisation of methylheptene relatively to its cracking rate.

2. Experimental

^{13}C enriched butane (99%, $^{13}\text{C}-\text{C}-\text{C}-\text{C}$) has been obtained from CEA (FRANCE). In order to obtain butenes from butane, the dehydrogenation of the labelled butane has been performed in a static reactor containing a Pt catalyst [7] highly selective and stable for the dehydrogenation of light alkanes. Reactant (butane) and products (butenes) were then trapped in a cold finger at 77 K and the hydrogen formed was removed. Then the mixture (butane, 60% and butenes 40%, 50 Torr) was introduced in a static reactor (17 ml) loaded with 100 mg of the ferrierite catalyst which is in its selective state (catalyst of Fig. 1, zone B). The reactants were analyzed by gas chromatography and mass spec-

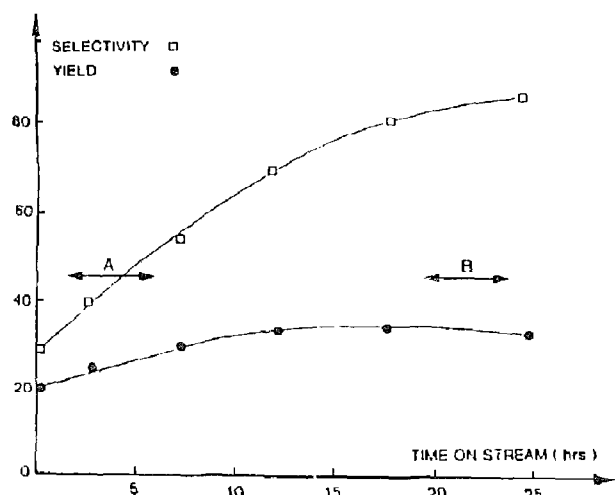


Fig. 1. Change in the isobutene yield and selectivity as a function of time-on-stream. Catalyst: Ferrierite from Tosoh; - WHSV: 5.6 h^{-1} ; $T = 673 \text{ K}$; reactant: n-butene/ N_2 (0.2 l/h/0.8 l/h).

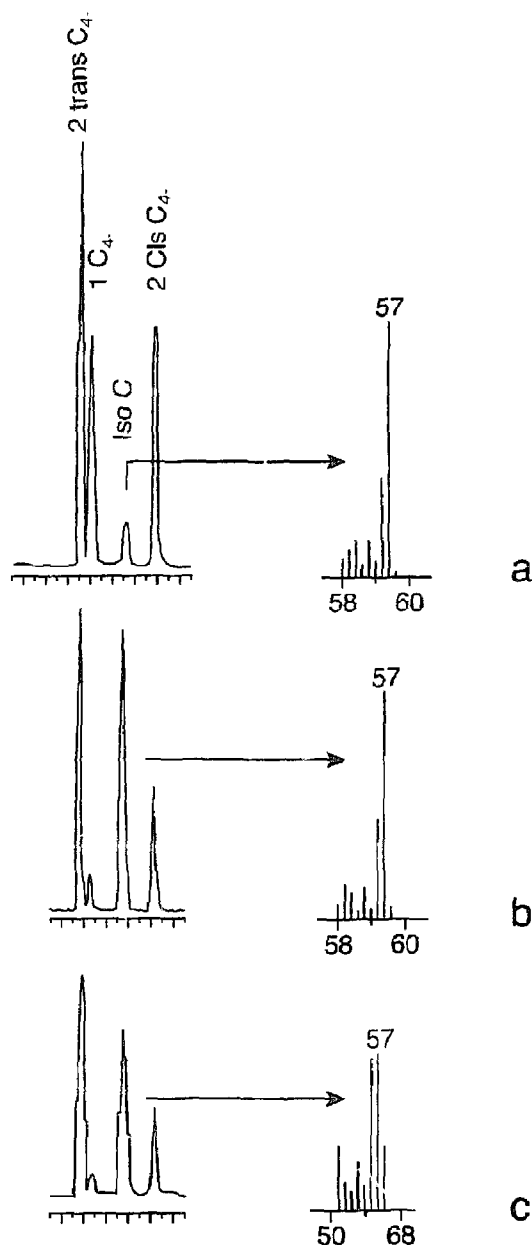


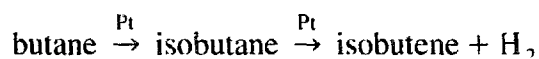
Fig. 2. Butene analysis by gas chromatography (left part) and mass analysis (right part). (a) Reactant. (b) after 30 min of reaction, in static conditions, on a selective ferrierite catalyst and (c) after 30 min of reaction, in static conditions, on a non-selective catalyst.

trometry before reaction (Fig. 2a) and after 30 min of reaction at 673 K (Fig. 2b).

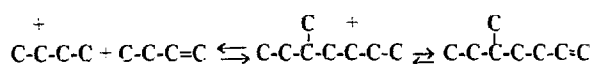
3. Results and discussion

Fig. 2a indicates that with the unreacted butane, there is a mixture of 1-butene, 2-butene

(*cis* and *trans*) having only one ^{13}C atom per molecule, this ^{13}C atom being randomly distributed. In addition to that, traces of isobutene are observed. These tiny traces of isobutene are probably formed on the dehydrogenation catalyst via:

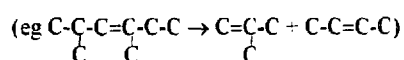


When the labelled butene is reacted with the catalyst, isobutene may be formed either via a monomolecular process (through a cyclopropane intermediate) and by consequence will have only one ^{13}C atom or via a bimolecular mechanism:

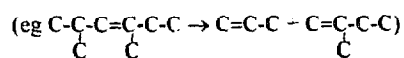


(each C_8 molecular containing two ^{13}C atoms)

The 3 MC_7 is isomerized rapidly into a mixture of MC_7 , DMC_6 and TMC_5 . Thus, the two ^{13}C atoms will randomly distributed in these C_8 molecules. The next step, the cracking reaction will transform the C_8 molecule either into two C_4 molecules:



or into $\text{C}_{3=} + \text{C}_{5=}$



These cracked products ($i\text{-C}_{4=}$, $\text{C}_{4=}$, $\text{C}_{3=}$ and $\text{C}_{5=}$) will have zero, one or two ^{13}C atoms.

The analysis of the products (Fig. 2b) indicates that indeed part of butenes are isomerised into isobutene and that isobutene contains only one ^{13}C atom clearly indicating that on the selective catalyst, the isobutene formation is occurring via a monomolecular mechanism.

The same reaction mixture has been reacted, in another experiment, on the ferrierite catalyst being in the non-selective state (state A, Fig. 1).

The results of Fig. 2c clearly indicate that the isobutene formed is a mixture of molecules containing two ^{13}C atoms (mass number 58), one ^{13}C atom (mass number 57) and no ^{13}C atom (mass number 56) the relative distribution being 1/2/1.

It will be of interest to know how the selectivity is modified as a function of time-on-stream: different factors could be at the origin of this modification:

1. poisoning of the non-selective sites
2. decrease in the pore dimensions by coke deposits defavoring bimolecular reaction
3. creation of selective isomerisation sites due to coke deposit [4]

These change in isobutene selectivity as a function of time-on-stream will be discussed in a different paper.

Thus, from this study it appears that the transformation of butenes over a selective ferrierite catalyst is occurring via a monomolecular mechanism but by contrast on a non-selective ferrierite catalyst, a bimolecular mechanism is operating.

References

- [1] US Pat. 711041 (1991) to Lyondell.
- [2] H. Mooiweer, K. de Jong, B. Kraushaar-Czarnetzki, W. Stork and B. Krutzen. Chem. Eng. News 25 (Oct. 1993) 30.
- [3] W.Q. Xu, Y.G. Yin, S. Suib, J. Edwards and C.L. O'Young. J. Phys. Chem. 99 (1995) 9443.
- [4] M. Guisnet, P. Andy, N. Gnep, C. Travers and E. Benazzi. J. Chem. Soc., Chem. Commun. (1995) 1685.
- [5] J. Szabo, J. Perrotey, G. Szabo, J.C. Duchet and D. Cornet. J. Mol. Catal. 67 (1991) 79.
- [6] P. Mériaudeau, H.N. Le, T. Vu, C. Naccache, in: Proc. 11th I.Z.C., Seoul, 1996, to be published.
- [7] Fr. Pat. 95/11926 to Total.