JOURNAL OF CATALYSIS **169,** 397–399 (1997)
ARTICLE NO. CA971656

NOTE

Selective Isomerization of *n*-Butene into Isobutene over Deactivated H–Ferrierite Catalyst: Further Investigations

During the past decade, there was a renewed interest in the skeletal isomerization of *n*-butene due to the demand for isobutene used to produce methyltertiarybutyl ether (MTBE).

Various acid-type catalysts have been used such as oxides like MoO_3 or WO_3 or halogenated alumina and zeolites.

Recently, Cheng and Ponec (1) addressed the question of whether or not the selective isomerization of *n*-butene into isobutene over these catalysts proceeds through a common intermediate.

In a recent publication, we have shown that on MFI-type catalysts, two different pathways operate for the isomerization of *n*-butene into isobutene, one via a bimolecular mechanism and another one via a monomolecular mechanism, the last one being favored by high reaction temperature and low pressure (2). Identical conclusions were reached for nondeactivated ferrierite (2).

As has been clearly shown in the literature, medium pore zeolites like ZSM-22 (3) or ZSM-23 (4) are selective catalysts for this reaction.

More recently, a large number of papers were devoted to the study of ferrierite catalysts (5) which have been patented as effective catalysts for this isomerization reaction (6).

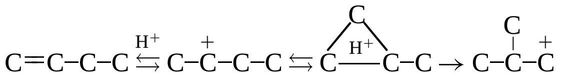
For ferrierite materials, it is observed that the isobutene selectivity increases with time on stream (5).

For these narrow pore materials, it has been suggested that a bimolecular mechanism is operating for fresh catalysts (7) acidic OH groups being the active sites, but for aged materials, which are highly selective, the reaction probably occurs via a monomolecular mechanism (8).

In a recent note, Mériaudeau *et al.* (9), using ^{13}C-labeled butene have demonstrated that for a selective ferrierite (aged solid), the monomolecular mechanism is operating.

Despite the fact that this reaction, over ferrierite catalyst, has been extensively studied several questions remain unsolved, among them, that of the nature of the active site and its location. Concerning the nature of the active site, Xu *et al.* (5) have shown that the aging of the solid with time on stream leads to a large increase in isobutene selectivity and that most of the porous volume of the solid is blocked by carbonaceous desposits; in addition, they observed that after coking the remaining number of acid sites, indirectly probed by ammonia or 1-butene TPD is quite low. Another group (10) has proposed that on the aged ferrierite catalyst, the active site for the squeletal isomerization of butene is a carbenium ion trapped within the carbonaceous residues formed in the ferrierite pores and responsible for its deactivation.

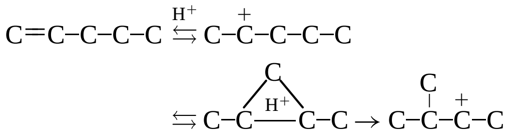
If the transformation of *n*-butene into isobutene via a monomolecular reaction mechanism is catalyzed by a proton, it is generally accepted that this transformation involves an unstable primary carbenium ion intermediate via a protonated cyclopropane intermediate:



[1]

This type of cyclopropanic intermediate has been first proposed by Brouwer and Hogeveen (11).

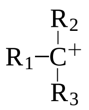
By contrast, for a larger olefin like pentene, the monomolecular reaction occurs via a secondary carbenium ion.



[2]

The reaction rate via [1] should be much smaller than via [2] since in the first scheme the reaction is occurring via secondary–primary carbenium ions, while for the second it is via secondary–secondary carbenium ions.

If the reaction is catalyzed by a carbonaceous carbenium ion (10)



$$R_1-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle R_3}{|}}{C^+}}$$

the formation of isobutene would occur via secondary–secondary carbenium ions as proposed in (10).

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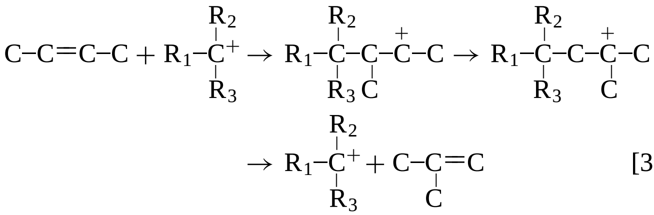

$$C{-}C{=}C{-}C + R_1{-}\overset{R_2}{\underset{R_3}{C^+}} \rightarrow R_1{-}\overset{R_2}{\underset{R_3}{C}}{-}\underset{C}{C}{-}\overset{+}{C}{-}C \rightarrow R_1{-}\overset{R_2}{\underset{R_3}{C}}{-}C{-}\overset{+}{\underset{C}{C}}{-}C$$
$$\rightarrow R_1{-}\overset{R_2}{\underset{R_3}{C^+}} + C{-}\underset{C}{C}{=}C \qquad [3]$$

If the site responsible for the skeletal isomerization of pentene is (over ferrierite covered by coke) again the previously cited carbenium ion (R_1) (R_2) (R_3) C^+, the pathway proposed for *n*-butene would also prevail and again would involve a secondary carbenium ion intermediate.

Thus if the skeletal isomerization of C_4 and C_5 olefins is catalyzed by a carbonaceous carbenium ion, the isomerization rates of *n*-butene and *n*-pentene are expected to be similar, while by contrast for H^+ catalyzed monomolecular reaction, the rate of *n*-pentene isomerization should be higher than that of *n*-butene. In order to discriminate between H^+ or (R_1) (R_2) (R_3) C^+ as the active site operating in coked ferrierite in the skeletal isomerization of linear olefins (butene, pentene), we have measured the respective rates of 1-butene isomerization and of 2-*cis*- and *trans*-pentene isomerization over coked ferrierite.

For this study, we have used a ferrierite, synthesized without templating agent, having Si/Al = 10. It has been checked by XRD that the ferrierite phase is pure and highly crystalline. After having exchanged the Na form with NH_4Cl, the protonic form was obtained by calcining the solid under N_2 at 773 K. 1-Butene reaction at 673 K, $P_{C_4H_8} = 26$ kPa, WHSV $= 6\ h^{-1}$ was run for 16 h until reaching an isobutene selectivity of 90% for a conversion of 40% (see Fig. 1); the reaction of 1-butene was then interrupted and the catalyst cooled to RT and the reactor was open to air.

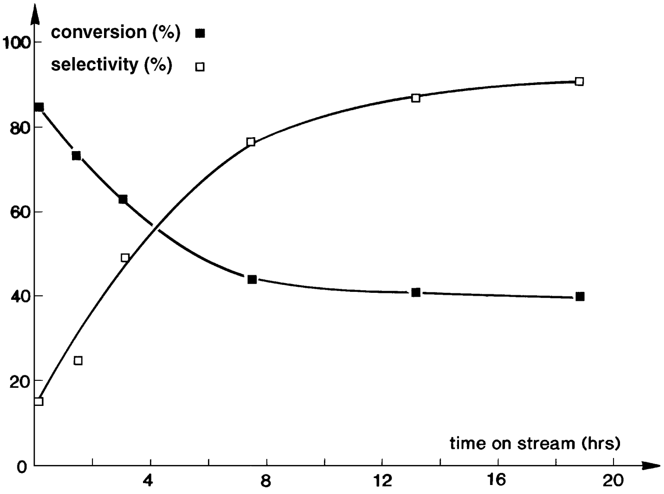

FIG. 1. Transformation of 1-butene on ferrierite. $T = 673$ K; WHSV $= 6\ h^{-1}$; $P_{C_4H_8} = 26$ kPa; complement to atmospheric pressure, N_2.

TABLE 1

Catalytic Properties of Fresh and Aged Solid for 1-C_4H_8 and 2-(*cis* + *trans*)-C_5H_{10} Transformation at 673 K

	Fresh catalyst	Aged catalyst[a]
n-Butene conversion,[b] (WHSV, h^{-1})[c]	4% (3,400) 3% (4,700)	2% (45)
Isobutene selectivity[d]	45%	92%
Isobutene rate formation[e] (butene conversion)[b]	1.1 (4%) 1.1 (3%)	0.015 (2%)
n-Pentene conversion,[b] (WHSV, h^{-1})[c]	12% (30,000) 8% (48,000)	3% (1700)
Isopentene selectivity[d]	92%	98%
Isopentene rate formation[e] (pentene conversion)[b]	45 (12%) 48 (8%)	0.7 (3%)

Note. $P_{olefin} = 26$ kPa; complement to atmospheric pressure, N_2.

[a] Solid aged for 16 h (see Fig. 1).

[b] For butenes (or pentenes) the conversion is defined as $(C_{in} - C_{out})/C_{in} \times 100$, with C_{in} being the number of moles of 1-C_4H_8, $C_{out} = \Sigma$(1-C_4H_8 + 2-*cis* C_4H_8 + 2-*trans*-C_4H_8). Same assumptions for linear pentenes. Contact times chosen to have conversion ≤ 12%.

[c] WHSV adjusted to have conversions ≤ 12%.

[d] Carbon basis, all linear butene (1-butene, 2-*cis*- and 2-*trans*-butene) are considered as reactants. Same assumption for pentene.

[e] Rate in mol · h^{-1} g^{-1} catalyst.

Part of this catalyst was pressed in a form of a disk for IR studies and another part was mechanically mixed with silica (Aerosil, Degussa) and loaded in a microreactor for catalytic studies.

Additional experiments have shown that the contact with air of the catalyst at RT does not modify the catalytic properties of the aged solid.

The catalyst which has been aged during the reaction of 1-butene and was in a selective state was then used without further treatment for a series of 1-butene and 2-(*cis* + *trans*)-pentene isomerization reaction experiments. The reactant space velocity was selected such that the reaction kinetics were not controlled by external mass transfer.

In Table 1 are listed the results of the isomerization experiments performed on the fresh ferrierite and the aged ferrierite, coked as indicated above.

The conversions obtained are low and of same magnitude for the aged solid reacted with either butene or pentene. By contrast, for the fresh solid used for *n*-pentene isomerization it has not been possible to have a very low conversion even for this highest WHSV but since the isopentene rate formation is nearly constant when calculated with conversion of 12 and 8%, this strongly suggest that the rate so calculated is very close to the true rate value.

From Table 1, two features are clearly apparent:

—the rate of isobutene (or isopentene) formation is strongly depressed on the aged ferrierite;

—the rate of isobutene formation (starting from 1-butene) is much smaller than that of isopentene (starting from 2-pentene) on both fresh and aged ferrierites.

It is improbable that the mechanism involving the carbonaceous carbenium ion active site for the skeletal isomerization of *n*-butene over aged ferrierite (10) would not operate for *n*-pentene isomerization. Since our results have clearly shown that on aged ferrierite *n*-pentene is isomerized much faster than *n*-butene, it appears also improbable that the isomerization steps involve the same skeletal intermediates namely secondary–secondary carbenium ions. This precludes the carbonaceous carbenium ion residues, on the aged ferrierite, from being the active site for the *n*-butene isomerization. The selective isomerization of *n*-butene is probably catalyzed by proton acid sites on the internal surface of ferrierite crystals, with a monomolecular reaction path via cyclopropane intermediates prevailing on aged catalysts (9).

The decrease in the butene conversion, as a function of time on stream, is due to two phenomena induced by coke deposits:

—a partial pore blocking as evidenced by Xu *et al.* (5);

—a partial site poisoning as indirectly evidenced by butene TPD (5). Direct evidence of this was obtained by using IR spectroscopy: we have observed that the vibration at 3600 cm^{-1} attributed to acidic OH groups is reduced by a factor of 2.4 after 16 h on stream. Indeed, the rate of isobutene (or isopentene) formation is reduced by a much larger factor (73 for isobutene and 64 for isopentene) suggesting that either part of the acidic OH groups are no more accessible to reactants and/or that the rate of the isomerization reaction is diffusion controlled.

Further work is needed to clarify this question.

ACKNOWLEDGMENT

Total Raffinage Distribution is acknowledged for funding.

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Received November 1, 1996; revised February 10, 1997; accepted February 13, 1997

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