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A skeletal rearrangement study of a carbon-13 labelled 3-methylpentane on doped sulphated zirconia catalysts

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Abstract

The isomerization on sulphated zirconias of the 3-methyl(3-^{13}C)pentane, molecule chosen to distinguish between the methyl and ethyl migrations, is studied.

The products distribution shows 0% for the 3-methylpentane isotopomers (not detected? or not formed?), what makes the interpretations difficult. Supposing these molecules formed in low proportions but not detected, a reaction pathway involving protonated cyclopropanes is proposed: the isotopomers are obtained from one- two- or three-step reactions. However, it is envisaged the possible non-formation of these molecules and a reaction pathway involving protonated cyclopropanes, cyclobutanes and bicyclopropanes is suggested: the ^{13}C-label scrambling would be a two-step isomerization and the other isotopomers would be formed via a one-step reaction.

The relative proportions of methyl migration (MM) and ethyl migration (EM) are assessed. The MM/EM ratio could be appreciated as an intrinsic characteristic of the catalyst because of correlations with, e.g. the crystalline structure, the sulphate content and the activity. Such correlations knowledge could help preparing catalysts with high activity and selective reactivity.

Keywords: Sulphated zirconia; Isomerization mechanism; ^{13}C-label; Methylpentane; Protonated cycloalkane

1. Introduction

The identification of reaction mechanisms in the isomerization and cracking processes on mono- and bi-functional catalysts is often difficult. In general, this investigation is completely dependent on a single, but often not sufficient, tool, the distribution of the reaction products. For example, for the *n*-butane isomerization, the occurrence and the proportions of the mono- and bi-molecular mechanisms are difficult to assess by the simple analysis of products distribution [1–3]. Nevertheless, the use of ^{13}C-labelled alkanes makes it easier.

In metallic catalysis, the ^{13}C-labelling has been widely investigated to evaluate the relative importance of the cyclic and bond shift mechanisms [4,5]. For example, the 2-methyl(2-^{13}C)pentane isomerizes to 3-methyl(2-^{13}C)pentane by bond shift and to 3-methyl(3-^{13}C)pentane via cyclic mechanism (Fig. 1) [4–6].

About the solid acid sulphated zirconia catalysts, pure or transition metal modified, few publications deal with ^{13}C-labelled hydrocarbons. Some of them treat the *n*-butane conversion, the objective being to throw light on the mono- and/or bi-molecularity of the isomerization mechanism [1,3,7–17] (Fig. 2). Chao et al. [1] and Tomishige et al. [3] proposed that the isomerization of *n*-butane is monomolecular. By the use of ^{13}C-labelled butanes, Garin et al. [7] confirmed and suggested that the reaction involves the formation of a protonated cyclopropane intermediate. However, Sachtler et al. [8–12] supposed that the isomerization could not occur via this last species, because its formation involves the production of primary carbenium ions, which are thermodynamically unstable. They asserted, on the basis of investigations using *n*-butane molecules ^{13}C-labelled on the first and on the fourth carbon atoms ($^{13}CH_3$–CH_2–CH_2–$^{13}CH_3$), that the predominant mechanism is the intermolecular one, which requires the combination

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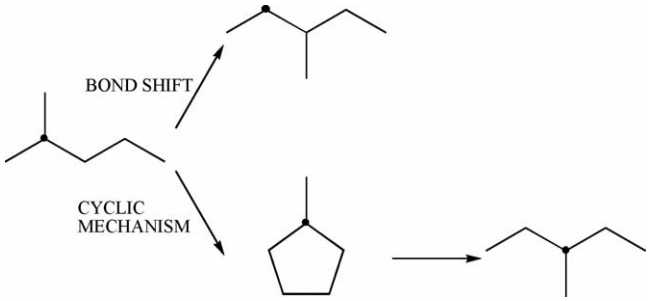


Fig. 1. Bond shift and cyclic mechanism for skeletal isomerization of 2-methyl(2-^{13}C)pentane [4–6].

of a butene molecule with a C_4^+ carbenium ion to form an octyl ion C_8^+. This last cation can then isomerize to a tertiary carbenium ion at the origin of *iso*butane formation. Tabora and Davis [13] were agreed with these last authors [8–12]. Using the same double ^{13}C-labelled *n*-butane, Okuhara et al. [14–16] studied the reaction mechanism of skeletal isomerization over typical solid acids, among which the sulphated zirconia catalyst. They suggested that the isomerization proceeds with an intermolecular rearrangement through a bimolecular pathway below 220 °C and via parallel (mono- and bi-molecular) pathway above 220 °C. Recently Luzgin et al. [17] provided evidences that the scrambling of the ^{13}C label in nC$_4$ (n-(1-^{13}C)butane → n-(2-^{13}C)butane) represents a monomolecular reaction, whereas skeletal isomerization into *iso*butane proceeds via a purely bimolecular mechanism, which is complicated with time to turn into conjunct polymerization.

This paper presents and analyzes the results of the 3-methyl(3-^{13}C)pentane isomerization on different doped sulphated zirconias, the aim being to provide information to understand the mechanisms and the intermediates of this reaction. 3-Methyl(3-^{13}C)pentane was chosen as reactant in order to distinguish between the methyl group and the ethyl group migrations, these reactions being important in acid catalysis.

2. Experimentals

2.1. The catalysts

The catalysts are sulphated zirconias modified whether by 3 mol% Al_2O_3 or 3 mol% Ga_2O_3 (kindly provided by Dr. Georges Poncelet, Université Catholique de Louvain, Belgium). Aluminium and gallium were introduced either by impregnation or by coprecipitation. The experimental procedure is described elsewhere [18]. These solid acids were completely characterized [18]. In the text, the abbreviations SAZi, SGZi, SAZc and SGZc point out these sulphated zironias (SZ) modified by aluminium (A) or gallium (G), these two last elements being added by impregnation (i) or coprecipitation (c).

2.2. The ^{13}C-labelled 3-methylpentane

The synthesis of the 3-methyl(3-^{13}C)pentane were performed in two steps according to the procedure described elsewhere [19,20]. According to the Grignard reaction, the 3-methyl(3-^{13}C)pentan-3-ol was obtained by the reaction of (2-^{13}C)ethylacetate with ethylmagnesium iodide, followed by acidic hydrolysis (H_2SO_4). The ^{13}C-labelled alcohol was dehydrated on Woelm alumina (1 g) at 180 °C and hydrogenated on platinum supported alumina (1 g) at 120 °C. The reaction products were collected in a cooled trap for 3 h, which was then put up on the purification bench. The undesired reaction products, the unreacted molecules and the ^{13}C-labelled hydrocarbons were separated using a purification column. The pure 3-methyl(3-^{13}C)pentane was then used for the catalytic reactions.

2.3. Apparatus and procedure

The catalytic reactions were carried out in a pulse flow system with a fixed bed reactor working at atmospheric total pressure. In each run approximatively 5 μl of the ^{13}C-labelled alkane were

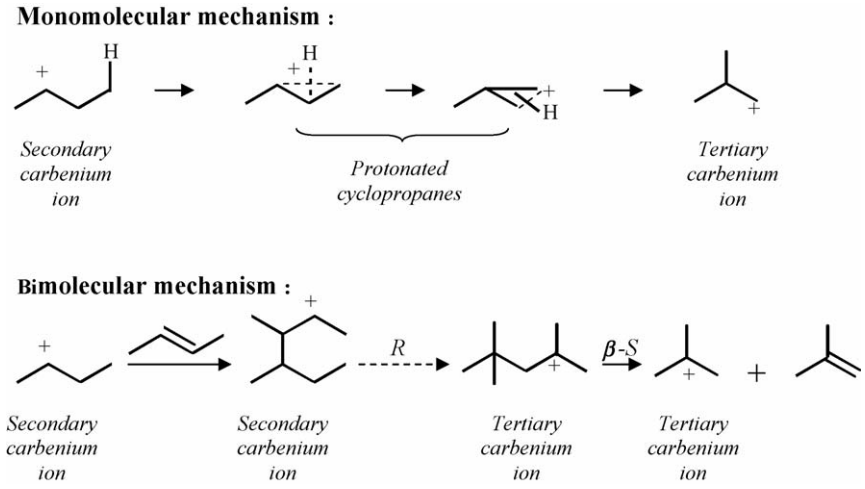


Fig. 2. Monomolecular and bimolecular mechanisms for skeletal isomerization of nC$_4$ (initiation step that is activation of nC$_4$ to nC$_4^+$, and termination step by hydride transfer to iC$_4^+$, are missed out; *R* is the rearrangement of the C$_8$ carbenium ion via protonated cyclopropanes, and β-S is the β-scission of the carbenium ion).

introduced into the gas flow of hydrogen (air liquide, purity 4N, around 755 Torr) at constant hydrocarbon partial pressure (around 5 Torr) thanks to a cooled trap kept at a constant temperature. At the outlet of the reactor, three samples of reaction products were taken by three syringes (250 μl). The different isotopic species were characterized by a gas chromatograph–mass spectrometer couple (FISONS Instrument, MD800 GC8000 series, capillary column CP Sil 5CB length 60 m diameter 0.323 mm) [19,21].

The experimental conditions were set to get total conversion of approximatively 10% and to be identical for all catalysts. This conversion of 10% could be considered as very close to the initial distribution. To perform it, a sample of all the catalysts was tested with 3-methylpentane (Fluka, puriss. standard for GC). The reaction temperature was 150 °C, the catalyst weight 0.1 g and the hydrogen flow 30 ml min^{-1}.

The procedure, the calculation of the isomer isotopic species distribution, as well as the location of the ^{13}C atom in the molecule have been described elsewhere [21–24].

3. Results and discussion

3.1. Isomerization of 3-methyl(3-^{13}C)pentane on SAZ and SGZ catalysts

Isomerization of 3-methyl(3-^{13}C)pentane was studied on the four SZ samples at 150 °C. Table 1 shows the distribution of the ^{13}C-labelled 3-methylpentane reaction products. It is to note that the 2-methylpentane and 3-methypentane were separated by GC, while the different isotopically substituted molecules were distinguished by their fragmentation patterns in mass spectra. Molecules given in the same column, 2-methyl(2-^{13}C)pentane and 2-methyl(3-^{13}C)pentane, 2-methyl(4-^{13}C)pentane and 2-methyl(5-^{13}C)pentane, as well as 3-methyl(2-^{13}C)pentane and 3-methyl(1-^{13}C)pentane, could not be distinguished by MS because their mass spectra were very similar.

From Table 1, three main observations stand out. They are listed below.

3.1.1. Statistical distribution

From a statistical point of view, all the isotopomers should be formed at similar percentages (around 16.7%), that would suppose that the adsorption time of the reaction intermediates on the catalyst active sites are long enough to let the formation of all possible ^{13}C-labelled methypentanes. As shown in Table 1, the contribution of the different isotopomers is different from the statistical distribution. The adsorbed species are likely not adsorbed sufficiently in time [25]. The number of successive isomerization steps occurring in the adsorption phase is hence limited in our conditions.

3.1.2. 2-Methylpentane

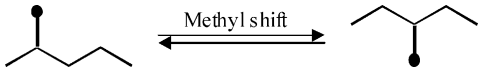
The relative distribution of the ^{13}C-labelled 2-methylpentanes show the presence of 2-(^{13}C)methylpentane among the reaction products: 8–17% from SGZc to SAZi. This molecule is stem from a scrambling of the ^{13}C tracer, indicating the occurrence of successive isomerizations during the adsorption phase [25].

3.1.3. 3-Methylpentane

It is amazing to note that the 3-methyl(3-^{13}C)pentane does not self isomerize in ^{13}C-labelled 3-methylpentanes, particularly in 3-methyl(2-^{13}C)pentane via an ethyl group shift (0%). This observation is the fundamental point for the following discussion.

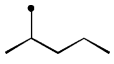
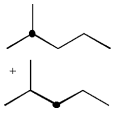
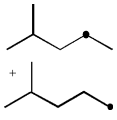
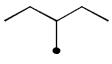
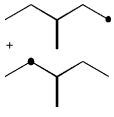
3.2. Assumptions and interpretations

The 2-(^{13}C)methylpentane and 3-(^{13}C)methylpentane are two molecules for which the carbon 13 is located on the methyl group. Their formation results from successive isomerizations in the adsorbed phase [25]. The isomerization of 2-(^{13}C)methylpentane to 3-(^{13}C)methylpentane involves a methyl group shift. The reverse isomerization is also right:



From Table 1, the 3-(^{13}C)methylpentane is formed in negligible amount while 2-(^{13}C)methylpentane is detected in relatively large amounts (8–17%). The adsorbed intermediate at the origin of 2-(^{13}C)methylpentane would be likely first formed, which would desorb by hydride transfer before the occurrence of a consecutive isomerization that would lead to the formation of 3-(^{13}C)methylpentane. Therefore the maximum number of steps

Table 1
Contribution of the ^{13}C-labelled methylpentanes (%) stem from the isomerization of 3-methyl(3-^{13}C)pentane on SAZ and SGZ catalysts at 150 °C

					Reactant	
SAZi	17.0	49.0	34.0	1.0	99.0	0.0
SGZi	15.0	52.5	32.5	1.0	99.0	0.0
SAZc	11.0	55.0	34.0	0.0	100.0	0.0
SGZc	8.0	63.0	29.0	1.0	99.0	0.0
Statistic[a]	16.7 × 2	33.3	33.3	16.7	16.7	33.3 × 2

Black circle denotes the ^{13}C-labelled carbon atom.

[a] Percentage multiplied by two '×2' when the labelling is possible on two similar carbon atoms of the alkane; as for example for the methyl carbon atom and the main chain first carbon atom in 2-(^{13}C)methylpentane.

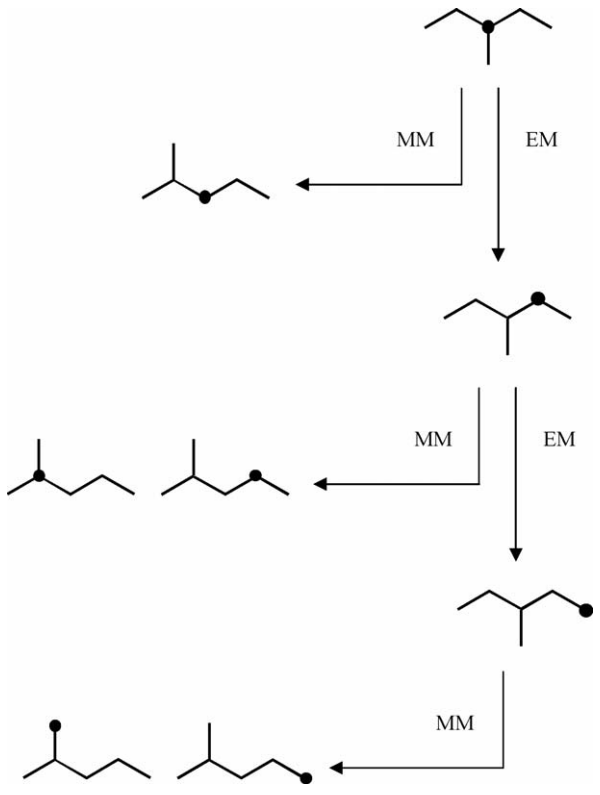


Fig. 3. Reaction sequences of the 3-methyl(3-^{13}C)pentane isomerization involving protonated cyclopropane intermediates (MM: methyl group migration; EM: ethyl group migration).

for successive isomerization would be the one determined by the 2-(^{13}C)methylpentane formation.

The protonated cyclopropanes are the reaction intermediates generally proposed for the acid catalyzed isomerization. On the basis of the general reaction pathway for ^{13}C-labelled methylpentanes proposed by Keller et al. [25], Fig. 3 proposes a general reaction pathway completely devoted to the 3-methyl(3-^{13}C)pentane isomerization into methylpentane isotopomers. The reaction intermediates are exclusively protonated cyclopropanes. The following assumptions have as support the reaction schemes given in Fig. 3.

Keeping in consideration the previous observations, we assume that:

i. All the ^{13}C-labelled 2-methylpentanes are likely formed with the same probability.

ii. The proportion in 2-methyl(5-^{13}C)pentane is likely similar to the proportion of 2-(^{13}C)methylpentane. In consequence, the remaining percentage (in its column of Table 1) represents the 2-methyl(4-^{13}C)pentane proportion.

To formulate the assumption (ii), we considered the isomerization pathways involving protonated cyclopropane-like rings (Fig. 3). The formation of 2-methyl(5-^{13}C)pentane from 3-methyl(3-^{13}C)pentane involves three steps during the successive isomerizations in adsorption phase. The formation of 2-(^{13}C)methylpentane needs three steps too. These two isotopomers are stem from the 3-methyl(5-^{13}C)pentanium ion via a methyl group shift. Therefore, we supposed with the assumption (ii) that the 2-methyl(5-^{13}C)pentane contribution is similar to the 2-(^{13}C)methylpentane one (Table 1).

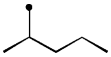
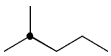
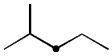
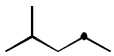
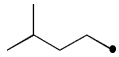
iii. The proportions in 2-methyl(4-^{13}C)pentane and 2-methyl(2-^{13}C)pentane are similar.

To formulate the assumption (iii), we took into account the isomerization scheme given in Fig. 3. The isotopomers 2-methyl(4-^{13}C)pentane and 2-methyl(2-^{13}C)pentane are stem from the 3-methyl(2-^{13}C)pentane-corresponding reaction intermediate, which undergo a methyl group migration.

iv. The absence of the self-isomerized 3-methylpentanes could be explained by either (a) fast isomerization into 2-methylpentanes or (b) their non-formation.

The assumption (iv) takes its origin in the amazing 0% calculated for all the 3-methylpentane isotopomers. According to Fig. 3, the 3-methylpentane isotopomers should have been observed as it was the case for Keller et al. [25] with their tungsten carbide catalysts. According to the equilibrium constant of the isomerization reaction between 3-methyl(2-^{13}C)pentane and 2-methyl(2-^{13}C)pentane in favour of the second molecule (K∼3), it is likely that the 3-methyl(2-^{13}C)pentane would be formed in low proportion but insufficiently for its detection. This might be the explanation of the non-self-isomerization of the reactant (iv, a). However, as already reported [25], compounds in proportion lower than 1% were detected and their proportion were calculated from the mass spectrum. The non-formation of

Table 2
Corrected distribution of the ^{13}C-labelled 2-methylpentanes (%) according to the reaction pathway given in Fig. 3

					
SAZi	17.0	17.0	32.0	17.0	17.0
SGZi	15.0	17.5	35.0	17.5	15.0
SAZc	11.0	23.0	32.0	23.0	11.0
SGZc	8.0	21.0	42.0	21.0	8.0
Statistic	16.7 × 2	16.7	16.7	16.7	16.7
First step alkyl migration[a]	EM	EM	MM	EM	EM
Number of steps[b]	3	2	1	2	3

[a] This row gives information about the alkyl group migration which occurs during the first step of the isomerization according to Fig. 3 (MM: methyl group migration; EM: ethyl group migration).

[b] This row gives information about the number of isomerization steps involved to their formation according to Fig. 3.

the 3-methylpentane isotopomers is thus a possibility that is not dismissed (iv, b).

Table 2 presents the corrected 2-methylpentane isotopomers distribution, where the previous assumptions are taken into account.

The distribution of each isotopomer in Table 2 was calculated from Table 1 values:

- The proportion in 2-(^{13}C)methylpentane is unchanged.
- The proportion in 2-methyl(2-^{13}C)pentane is equal to the 2-methyl(4-^{13}C)pentane one (iii).
- The proportion in 2-methyl(3-^{13}C)pentane is calculated by substracting its percentage in Table 1 by the 2-methyl(4-^{13}C)pentane one (iii).
- The proportion in 2-methyl(4-^{13}C)pentane is calculated by substracting its percentage in Table 1 by the 2-(^{13}C)methylpentane one (ii).
- The proportion in 2-methyl(5-^{13}C)pentane is equal to the 2-(^{13}C)methylpentane one (ii).

From Table 2, two observations arise:

- The 2-methyl(3-^{13}C)pentane percentage is between 32% and 42% depending of the catalyst nature. This molecule can be formed from our reactant, 3-methyl(3-^{13}C)pentane, via a single methyl group shift. It suggests that the contribution of the methyl migration, a single step reaction, is between 32% and 42%.
- It is likely that the reaction intermediate in the adsorption phase which leads to the formation of 2-methyl(3-^{13}C)pentane has the lower stability. The reaction intermediate leading to the four other isotopomers likely has higher stability because 58–68% of the ^{13}C-labelled 2-methylpentanes are stem from it after two or three isomerization steps (Fig. 3). These percentages represent the contribution of the ethyl migration in the isomerization first step.
- The steps number of the isomerization process increases with the ^{13}C-label shift, step by step, toward the end of the alkane main chain from its initial position. The first stage can be seen as the methyl group migration giving the 2-methyl(3-^{13}C)pentane. The second stage is the shift of the ^{13}C-label to a next carbon. The third stage is the shift of the ^{13}C-label to an end carbon. The ^{13}C-label scrambling is a three-step process.

The isotopomer 2-(^{13}C)methylpentane is formed via successive isomerizations in the adsorption phase. Considering the occurrence of successive protonated cyclopropane rings as intermediate [25], the intermediate of the isomerization first step is likely the carbenium ion of 3-methyl(2-^{13}C)pentane (Fig. 3). Hence, this first isomerization leading to the 2-(^{13}C)methylpentane is an ethyl group migration (Table 2). From these, we propose that the isomerization reactions of 3-methyl(3-^{13}C)pentane on SZ catalysts take place according:

- Successive isomerizations (three steps) for the ^{13}C-label scrambling (formation of 2-(^{13}C)methylpentane), with a first step as being an ethyl group migration.
- Successive isomerizations (three steps) for the 2-methyl(5-^{13}C)pentane formation, with a first step as being an ethyl group migration.
- Single step isomerization for the 2-methyl(3-^{13}C)pentane (methyl group migration).
- Ethyl group migration as initial step for the 2-methyl(2-^{13}C)pentane and 2-methyl(4-^{13}C)pentane formations. But the non-detection or the non-formation of 3-methyl(2-^{13}C)pentane make arising one question: are the 2-methyl(2-^{13}C)pentane and 2-methyl(4-^{13}C)pentane formed via successive isomerizations or via a one-step isomerization?

3.3. Evaluation of the relative proportions of methyl migration and ethyl migration on SAZ and SGZ catalysts

The evaluation of the relative proportions of methyl migration and ethyl migration on SAZ and SGZ catalysts could allow us to determine the relative stability of the reaction intermediates which undergo methyl or ethyl shift via protonated cyclopropane rings.

As shown in Fig. 3, the 3-methyl(3-^{13}C)pentane can isomerize in 2-methyl(3-^{13}C)pentane via a methyl shift or 3-methyl(2-^{13}C)pentane via an ethyl shift. In our conditions, 3-methyl(2-^{13}C)pentane was not detected or not formed. The formation in similar amounts of 2-methyl(2-^{13}C)pentane and 2-methyl(4-^{13}C)pentane could be due to the presence of adsorbed 3-methyl(2-^{13}C)pentane carbenium intermediate. This last could undergo a second immediate transformation. In this case, it is possible to evaluate the relative proportions of methyl migration and ethyl migration on SAZ and SGZ catalysts. Similarly, the molecules 2-(^{13}C)methylpentane and 2-methyl(5-^{13}C)pentane could be formed via a 3-step isomerization with the 3-methyl(2-^{13}C)pentanium ion as reaction intermediate in the first step (Fig. 3). The results are given in Table 3.

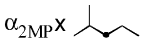
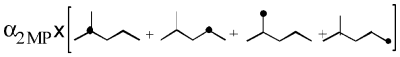
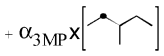
To set up Table 3, we applied the calculations and values, listed below:

- X-methylpentane conversion α_{XMP}: ratio between the mole number of X-methylpentane and the sum of the total mole number of products and the mole number of unreacted reactant.
- $\alpha_{2MP} = 7.6\%$, 8.1%, 7.0%, 7.2% for SAZi, SGZi, SAZc, SGZc, respectively.
- Percentages of 2-(^{13}C)methylpentane, 2-methyl(2-^{13}C)pentane, 2-methyl(3-^{13}C)pentane, 2-methyl(4-^{13}C)pentane and 2-methyl(5-^{13}C)pentane from Table 2 and of 3-methyl(2-^{13}C)pentane from Table 1.

This Table 3 presents two main particularities:

- The proportion of ethyl migration is always greater than the methyl migration one.
- SAZ and SGZi catalysts present ratios between methyl and ethyl migrations that are similar and close to 0.5, while the SGZc catalyst has a value close to 0.7.

Table 3
Relative proportions of methyl and ethyl migrations according to the reaction pathway given by Fig. 3

	α_{2MP}  Methyl Migration[a]	α_{2MP}  + α_{3MP}  Ethyl Migration[a]	MM/EM[b]
SAZi	2.43	5.17 + 0.0 = 5.17	0.47
SGZi	2.84	5.27 + 0.0 = 5.27	0.54
SAZc	2.24	4.76 + 0.0 = 4.76	0.47
SGZc	3.02	4.18 + 0.0 = 4.18	0.72

[a] α_{XMP} is the conversion in X-methylpentanes (in decimal).
[b] Ratio between methyl migration and ethyl migration.

Table 4
Characterization and conversion data of the SAZ and SGZ catalysts [18]

	SAZi	SGZi	SAZc	SGZc
Sulphate content (wt.%, TGA)	7.65	6.87	8.15	6.50
Water content (wt.%, TGA)	5.97	5.03	5.25	3.93
Monoclinic fraction (%)	12.8	14.3	5.4	<5
Conversion of nC$_4$ at 450 °C				
After 5 min (%)	53.0	58.3	58.2	66.6
Steady regime (%)	23.5	14.3	35.5	40.3

It seems that on these acid catalysts the ethyl migration is preferred to the methyl migration during the isomerization process.

This MM/EM ratio is a value that could be appreciated as an intrinsic characteristic of the catalyst. It could be compared to characteristics of the physical and chemical properties of the solid acid in order to verify if there exists any correlation betwen these values.

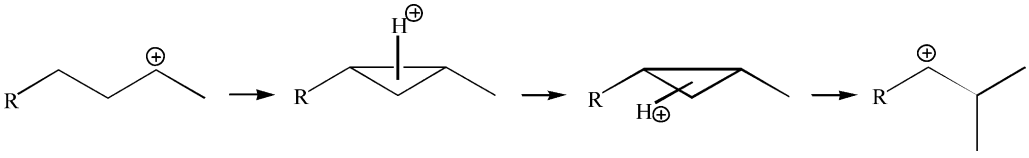
Table 4 summarizes few physical characteristics and catalytic activity values of the SAZ and SGZ catalysts [18]. The comparison of Tables 3 and 4 seem to show a correlation between the MM/EM ratio and the sulphate content, the water content as well as the catalytic activity. In fact high catalytic activity seems to favor the methyl migration, high catalytic activity being observed for catalysts with low sulfate and low water contents (SGZc solid acid). Moreno and Poncelet [18], who provided us these catalysts, showed that Ga was more efficient promoter than Al when introduced by coprecipitation, and that the best catalytic performances were obtained over SGZc nearly free of monoclinic structure and with nearly monolayer sulfate coverage.

All of these remarks suggest that the solids cristalline structure as well as the sulfate content, and so the acidity and/or the redox activity, play an important role in the alkyl group migrations during isomerization and in the relative stabilities of the reaction intermediates. As it is commonly admitted, each physical/chemical property and so the experimental synthesis procedure of the catalyst have great importance in the catalytic activity and the reaction mechanisms. The knowledge of such correlations could allow preparing catalysts combining high activity and selective reactivity. At this stage, further studies are needed to determine more precisely such correlations that are completely dependent on an accurate determination of the isotopomers distribution and an accurate knowledge of the reaction mechanisms.

Finally, one can remark that the MM/EM ratio can be viewed as the ratio between the percentage of the molecules formed through a one-step isomerization and the percentage of isotopomers formed through a multi-step isomerization.

3.4. General idea of the literature about isomerization reactions mechanisms

In acid catalysis, only the branched isomers are generally formed. The skeletal rearrangements of linear alkanes with more than four carbon atoms occur via the formation, from a secondary carbenium ion, of a protonated cyclopropane intermediate [26]:



For the acid catalysts, pure or loaded with a transition metal (mostly Pt), except a unique metallocycle mechanism proposed for molybdenum oxycarbonate [27], carbenium ions are considered to be responsible for the skeletal rearrangements [28]. Catalysis via “chemisorbed carbenium ions” on heterogeneous catalysts resembles catalysis via “solvated carbenium ions” in liquid acids [29].

3.4.1. Carbenium ion formation

In the skeletal isomerization of n-butane over solid acids, one of the critical steps is the activation of n-butane to a secondary carbenium ion. Two processes would be possible, protonation of n-butane by Brønsted acid and dehydrogenation

$$n\mathrm{CH_4} + \mathrm{H^+} \rightarrow n\mathrm{CH_5}^+ \rightarrow n\mathrm{CH_3}^+ + \mathrm{H_2}$$

or hydride abstraction by Lewis acid

$$n\mathrm{CH_4} + \mathrm{L^+} \rightarrow n\mathrm{CH_3}^+ + \mathrm{L^+} - \mathrm{H^-}$$

These two steps are supposed to require high acid strength for the acidic sites [14]. However numerous papers show that the SZ and metal modified SZ catalysts are not superacidic [28,30–32]. It follows that their acid sites may not activate butane molecules and that the surface properties other than acidity are involved in alkane activation [28]. Dumesic et al. [30,31] proposed that the unique catalytic properties of sulphated zirconia may be related to the combination of acid sites with sites capable of undergoing oxidation-reduction cycles. The redox sites generate olefins by dehydrogenation of butanes that are then protonated at the acid site forming carbenium ions. An intimate contact or close proximity between the metal site and the acid site is required for reactivity [33]. Cao et al. [34] studied the promoting effect of gallium on sulphated zirconia for $n\mathrm{C_6}$ isomerization and showed that gallium increases the redox capability of the promoted catalyst. The studies about the promotion of sulphated zirconia with metal as Al [18], Ga [18,34], Mn [29,33] or Fe [29,33] showed improved catalytic properties and better catalyst stability for *n*-alkane isomerization relative to pure SZ.

3.4.2. Skeletal rearrangement in adsorbed phase [28]

In the isomerization of alkanes, elementary reaction proceeds via protonated cyclopropane intermediate. In the case of butane, the isomerization via a protonated cyclopropane intermediate is not easy because the reaction involves the conversion of a secondary carbenium ion into a primary one [8–16]. In the case of pentane or hexane isomerization, the intermediates are secondary carbenium ions [28]. In many cases the rate determining step is the skeletal rearrangement of carbenium ions. The nature of carbenium ions on the surface determines the rate and the selectivity of the isomerization. Ono [28] in his review titled "A survey of the mechanism in catalytic isomerization of alkanes" concluded that the dependence of the behaviours of "carbenium ions" on the acidic properties of the catalyst has to be more focused.

In this paper, we will focus our discussion on the skeletal rearrangements, and on the occurrence and the relative stability of the carbenium ions. We will not discuss the activation step of the reactant on acidic and/or redox active sites. We will consider the reactant as being activated into carbenium ion.

3.4.3. Monomolecular and/or bimolecular isomerization mechanisms

As discussed in Section 1, the light alkanes isomerizations occur via monomolecular and/or bimolecular mechanisms [1,3,7–17]. For *n*-butane, it is mainly suggested a bimolecular isomerization [8–17]. For heavier alkanes, the bimolecular mechanism is less important, because the isomerization via monomolecular mechanism is much faster [28]. The isomerization of $\mathrm{C_6}$ hydrocarbons is suggested to proceed predominantly through a monomolecular carbocation mechanism [35,36]. Monomolecular mechanism is generally accepted for hydrocarbons containing more than five carbon atoms [11,36–38]. Nevertheless Comelli et al. [39] observed that the isomerization of $n\mathrm{C_6}$ was always accompanied by hydrocracking, independently of reaction conditions, allowing them to consider a common intermediate, a polymeric species, for both processes. Within the scope of our discussion, we will consider that the isomerization of our reactant follows mainly a monomolecular pathway. This rests on the analysis of our isotopomers distribution. We never detected among the reaction products the presence of double labelled molecule that is formed via a bimolecular route. The same number of $^{13}\mathrm{C}$ label on reactant and products is only possible if a monomolecular mechanism is realized [29]. Nevertheless we think that the bimolecular pathway might occur but its contribution would be minor or even negligible in our conditions.

3.4.4. Carbenium ions

We exclude, in our mechanism schemes, the implication of primary carbenium ions, which are thermodynamically unstable. The energy levels of the carbenium ions are in the order of tertiary carbenium ion > secondary carbenium ion > protonated methyl cyclopropane > primary carbenium ion [40,41].

3.5. Proposition of mechanisms for isomerization reactions

3.5.1. Cyclopropane intermediates-based mechanism following the assumption (iv, a)

To explain the distributions of the $^{13}\mathrm{C}$-labelled reaction products got via 3-methyl(3-^{13}C)pentane isomerization on the SAZ and SGZ catalysts, our reasoning was based on the last observations. The formation of 2-(^{13}C)methylpentane is an indication of successive isomerizations, where the first isomerization can be the step leading to the 3-methyl(2-^{13}C)pentane. An amazing observation was that the 3-methyl(3-^{13}C)pentane did not self isomerize. This result made the interpretations quite difficult. Because the 2-methyl(2-^{13}C)pentane and the 2-methyl(4-^{13}C)pentane isotopomers were formed in great amounts, while according to Fig. 3 they are stem from the 3-methyl(2-^{13}C)pentane carbenium ion and this one was not formed. From this, we suggest that the formations of the 2-methyl(2-^{13}C)pentane and the 2-methyl(4-^{13}C)pentane follow a very fast two steps isomerization. A similar argument can be proposed for both 2-(^{13}C)methylpentane and 2-methyl(4-^{13}C)pentane, for which fast three-step isomerizations occur.

Another difficulty was to identify the reaction mechanisms. For this, we proceeded as it follows. Firstly, we drew all the possible isomerization reaction schemes from our reactant, the 3-methyl(3-^{13}C)pentane, according to three-step processes according to the Keller et al.'s work [25]. We excluded the formation of primary carbenium ion and the occurrence of bimolecular mechanism. The reaction intermediates were protonated cyclopropanes. Secondly, we discarded the schemes giving undetected reaction products. Finally we considered that the maximum number of steps in the successive isomerization is three, because it is the one of the 2-(^{13}C)methylpentane formation.

This exercise provided in fact the reaction pathway given in Fig. 3. The first step corresponds to the formation of the 2-methyl(3-^{13}C)pentane via a methyl group migration

and to the formation of the 3-methyl(2-^{13}C)pentane via an ethyl group migration. This second isotopomer was likely not detected and probably not calculated from the mass spectra. As assumed in the assumption (iv, a), this molecule was probably formed but in undetectable amounts. The equilibrium constant between it and the 2-methyl(2-^{13}C)pentane is highly in favour of the 2-methyl(2-^{13}C)pentane. Hence, the 3-methyl(2-^{13}C)pentane isomerizes into 2-methyl(2-^{13}C)pentane and into 2-methyl(4-^{13}C)pentane as well via methyl group migrations and into 3-methyl(5-^{13}C)pentane via an ethyl group migration. This step is the second of the isomerization process. As a third step, the 3-methyl(5-^{13}C)pentane, for the same reason than for the 3-methyl(2-^{13}C)pentane, isomerizes fastly providing three possible isotopomers: 2-(^{13}C)methylpentane and 2-methyl(5-^{13}C)pentane via methyl group migrations; 3-(^{13}C)methylpentane via an ethyl group migration. These three-step isomerization justifies the formation of all the detected isotopomers, particularly all the ^{13}C-labelled 2-methylpentanes.

The reaction pathway presented in Fig. 3 introduces three remarks. It seems that the product desorption systematically occurs after a methyl group migration step and more particularly when a carbenium ion corresponding to a 2-methylpentane is formed. The isomerization of a 3-methylpentanium ion into a 2-methylpentanium ion is faster than the 3-methylpentanium ion desorption and hydrogenation. And it seems then that the isomerization of a 2-methylpentanium ion is slower than its desorption and hydrogenation. The second remark is relative to the number of steps of the isomerization. All the different isotopic species produced are obtained from reactions that take place in one, two or three steps. For tungsten carbide catalysts, Keller et al. [25] reported one or two steps to justify the formation of all the isotopomers produced. This second remark introduces the third one, i.e. the adsorption of the surface species is stronger with sulphated zirconias in comparison with the tungsten carbides [25]. However, the adsorption is not strong enough to allow a statistical distribution for the isotopomers. Therefore the desorption rate is rather important.

3.5.2. Cycloalkane intermediates-based mechanism following the assumption (iv, b)

It is obvious that the reaction schemes given in Fig. 3 justify the formation of all the observed isotopomers in our conditions. Nevertheless, as suggested in assumption (iv), it is possible that the 3-methylpentane isotopomers are not formed at all. As previously stressed on, the formations of the 2-methyl(2-^{13}C)pentane and the 2-methyl(4-^{13}C)pentane follow a very fast two-step isomerization, where the first carbenium ion which should give the 3-methyl(2-^{13}C)pentane does not desorb. Therefore it could be made this very fast two-step isomerization similar to a single step isomerization. In this context, we wish for suggesting a possible different reaction mechanism, which would suppose the non-formation of the 3-methylpentane isotopomers. Hence, except for 2-(^{13}C)methylpentane, a mechanism by which the reactant isomerization would take place in a single reaction could be suitable, but where one or two carbon–carbon bonds could break. In this last case, the two carbon–carbon bonds breaking would occur simultaneously, making similar to a single step reaction. By this suggestion, it could be proposed the occurrence of protonated cyclopropane and protonated cyclobutane as reaction intermediates, but also of protonated bicyclopropane.

Fig. 4 proposes the reactions (I)–(V) involving these last species, which could be at the origin of the formed ^{13}C-labelled 2-methylpentanes (the reaction schemes for the ^{13}C-labelled 3-methylpentanes are proposed as well). The reaction (II), i.e. the 2-methyl(3-^{13}C)pentane formation, is the same than the one given in Fig. 3.

The isomerization of 3-methyl(3-^{13}C)pentane in 2-methyl(4-^{13}C)pentane could be a single step process where two carbon–carbon bonds could be simultaneously broken. The reaction (IV) could take place via a reaction intermediate we called protonated bicyclopropane. This reaction (IV) is developed in Fig. 5. We could detail it as follows. There would be a formation of a protonated cyclopropane with the participation of the carbons denoted 2, 3 and 4. This intermediate is the species which would justify the formation of the 3-methyl(2-^{13}C)pentane. Because of the σ-basicity of the C–H bonds of the methyl group on carbon 1, a second protonated cyclopropane would be simultaneously formed between the carbons 1, 2 and 4. The "A + B" set could be seen as the formation of a protonated bicyclopropane between the carbons 1, 2, 3 and 4. Two protons would be then shared by four carbon atoms, and these carbon atoms could be considered as carrying partial positive charges $\delta+$. This would amount to consider a cycle between four carbon atoms with two σ–π hyperconjugations. In the case of carbenium ions, the σ–π hyperconjugation [42–45] involves σ-type-electrons and empty p-orbitals. The bonding σ-type-electrons pair can delocalize to an empty p-orbital, and this interaction has a stabilising effect of the electron-deficient-centre. The transformation of this bicyclopropane intermediate to an isomer would take place in accordance with a mechanism which would imply simultaneous breakings and formations of bonds. Similarly, the formation of 2-methyl(2-^{13}C)pentane would involve a bicyclopropane as intermediate. Fig. 6 illustrates it. In this case, the reaction could be detailed as follows: formation of a protonated cyclobutane between the carbons 1, 2, 3 and 4, and simultaneous intervention of a protonated cyclopropane between the atoms 1, 3 and 4. This "A′ + B′" (Fig. 6) set could be seen as a protonated bicyclopropane (Fig. 4, reaction (V)) with the participation of the carbons 1, 2, 3 and 4.

The formation of 2-(^{13}C)methylpentane would suppose successive isomerizations involving two steps (reaction (III)). The first step would be the formation of 2-methyl(3-^{13}C)pentane, as for the reaction (II). The second step would be an ethyl group migration via a protonated cyclobutane, which would lead to 2-(^{13}C)methylpentane by ring opening (reaction (III)). The intervention of the protonated cyclobutane, in the same time than the protonated cyclopropane, has been already suggested in the literature to justify the formation on bifunctional catalysts of all *n*-heptane isomers [46]. In consequence, the isomerization reactions on the SAZ and SGZ catalysts would be at most two steps processes.

The reaction mechanisms in Fig. 4 suggest the possible participation of protonated cyclobutane and bicyclopropane intermediates in addition to protonated cyclopropanes. Their occurrence

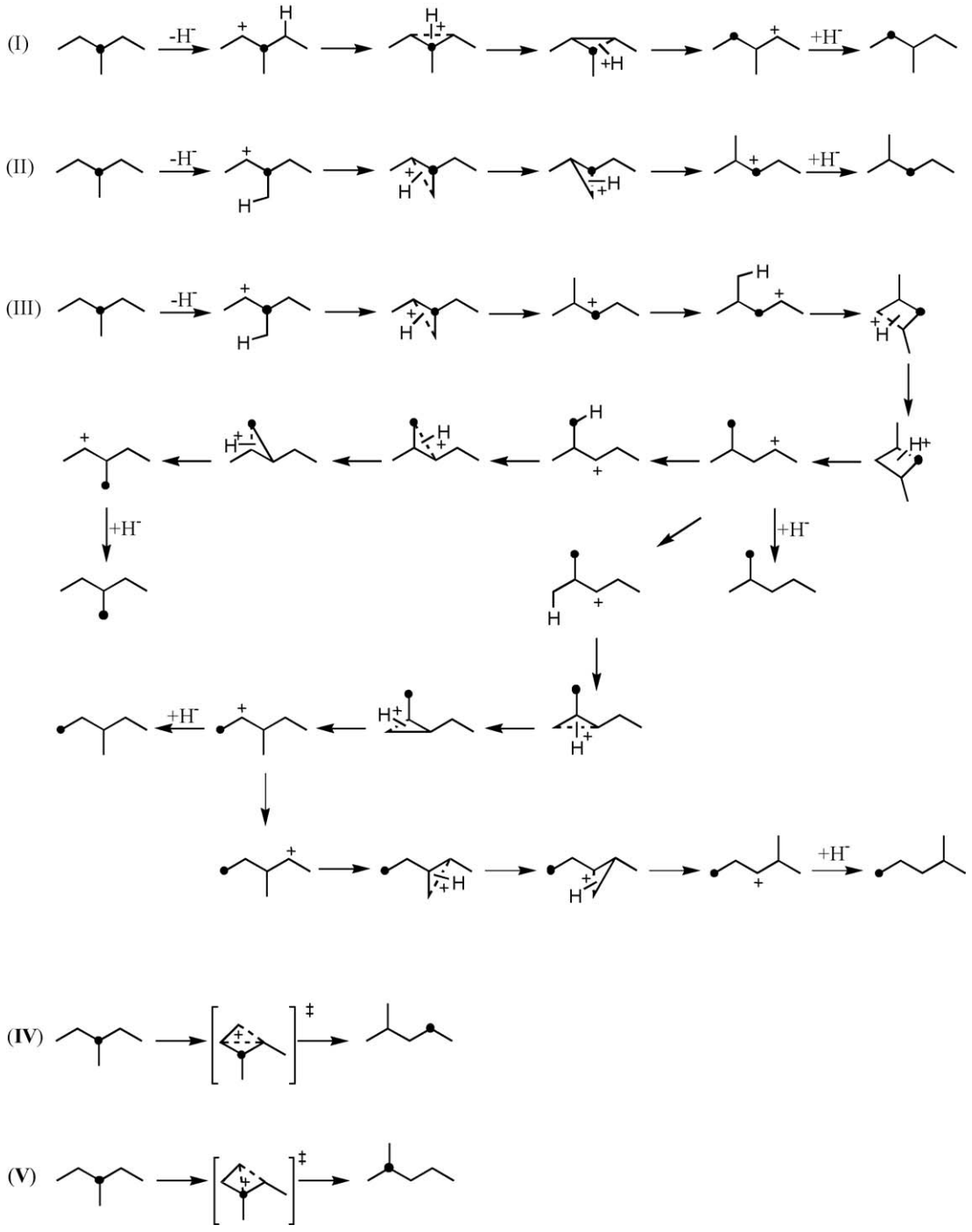


Fig. 4. Reaction sequences of the 3-methyl(3-^{13}C)pentane isomerization involving protonated cyclopropane, cyclobutane and bicyclopropane intermediates (reactions (IV) and (V) are given in details by Figs. 5 and 6, respectively).

rationalizes reasonably the lack of the 3-methylpentane isotopomers. Moreover, they allow to decrease the number of successive steps of isomerization from three (Fig. 3) to two (Fig. 4). This reaction mechanism could be used to calculate the corrected 2-methylpentane isotopomers distribution, the maximum number of isomerization steps being two (Table 5).

The distribution of each isotopomer in Table 5 was calculated from Table 1 values:

- The proportion in 2-(^{13}C)methylpentane is unchanged.
- The proportion in 2-methyl(2-^{13}C)pentane is equal to the 2-methyl(4-^{13}C)pentane one (iii).
- The proportion in 2-methyl(3-^{13}C)pentane is calculated by substracting its percentage in Table 1 by the 2-methyl(4-^{13}C)pentane one (iii).
- The proportion in 2-methyl(4-^{13}C)pentane is the one given in its column of Table 1.

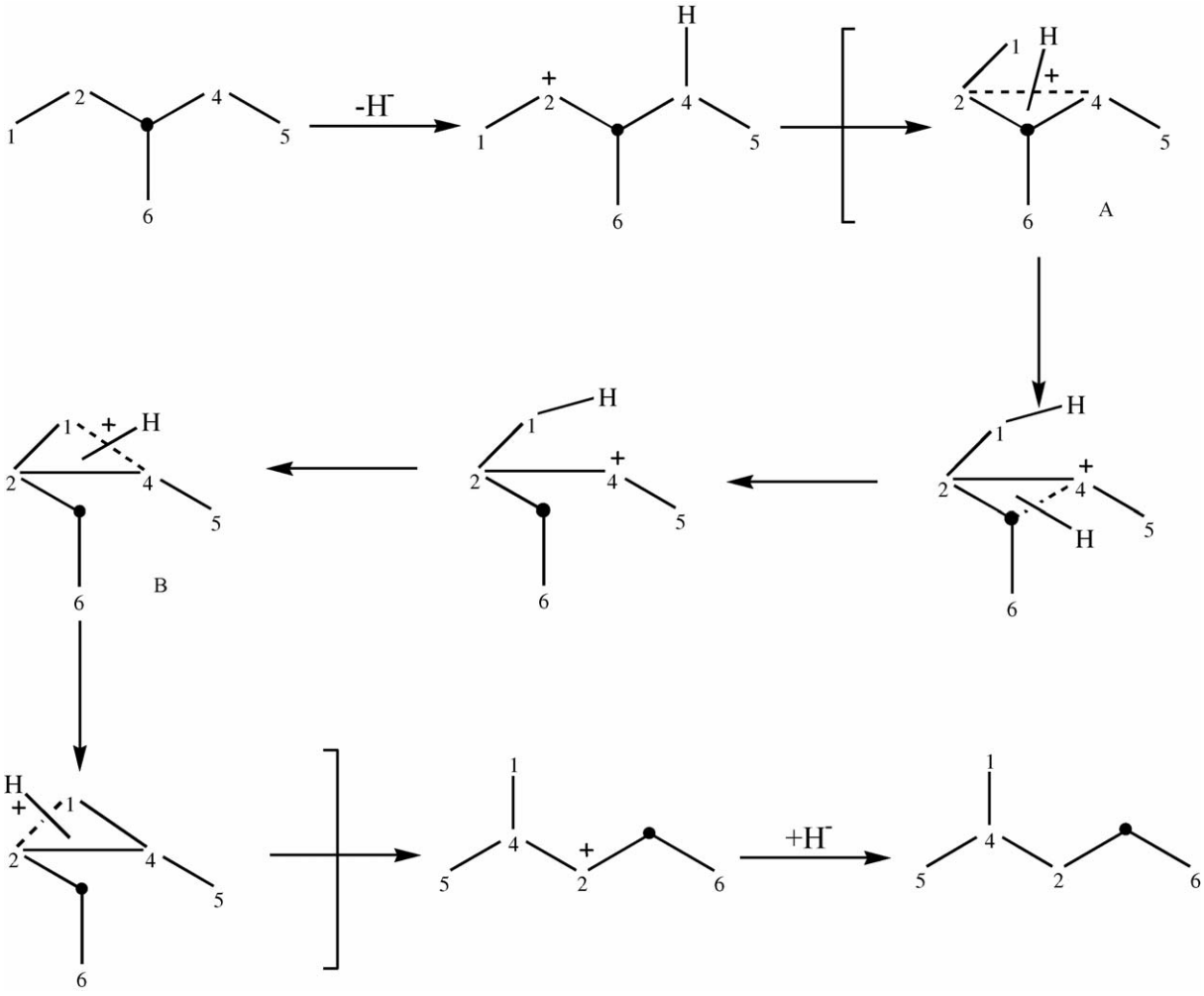
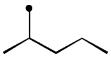
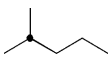
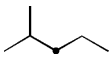
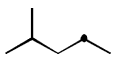
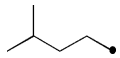


Fig. 5. Isomerization mechanism of 3-methyl(3-^{13}C)pentane in 2-methyl(4-^{13}C)pentane: what is in parentheses is a likely detail of the protonated bicyclopropane of reaction (IV) in Fig. 4.

- The proportion in 2-methyl(5-^{13}C)pentane is nil. Because, the formation of 2-methyl(5-^{13}C)pentane from 3-methyl(3-^{13}C)pentane would involve more than two steps during the successive isomerizations in adsorption phase while the formation of 2-(^{13}C)methylpentane would need two steps, which would be the maximum of steps.

From the data of Table 5, the relative proportions of methyl migration and ethyl migration on SAZ and SGZ catalysts could be calculated as for Table 3 (Section 3.3). The MM/EM ratios provided in Tables 3 and 6 are exactly the same, what does not affect the discussion proposed in Section 3.3.

Table 5
Corrected distribution of the ^{13}C-labelled 2-methylpentanes (%) according to the reaction pathway proposed in Fig. 4

					
SAZi	17.0	34.0	15.0	34.0	0
SGZi	15.0	32.5	20.0	32.5	0
SAZc	11.0	34.0	21.0	34.0	0
SGZc	8.0	29.0	34.0	29.0	0
Statistic	16.7 × 2	16.7	16.7	16.7	16.7
First step alkyl migration[a]	MM	EM	MM	EM	–
Number of steps[b]	2	1	1	1	–

[a] This row gives information about the alkyl group migration which occurs during the first step of the isomerization according to Fig. 4 (MM: methyl group migration; EM: ethyl group migration).

[b] This row gives information about the number of isomerization steps involved to their formation according to Fig. 4.

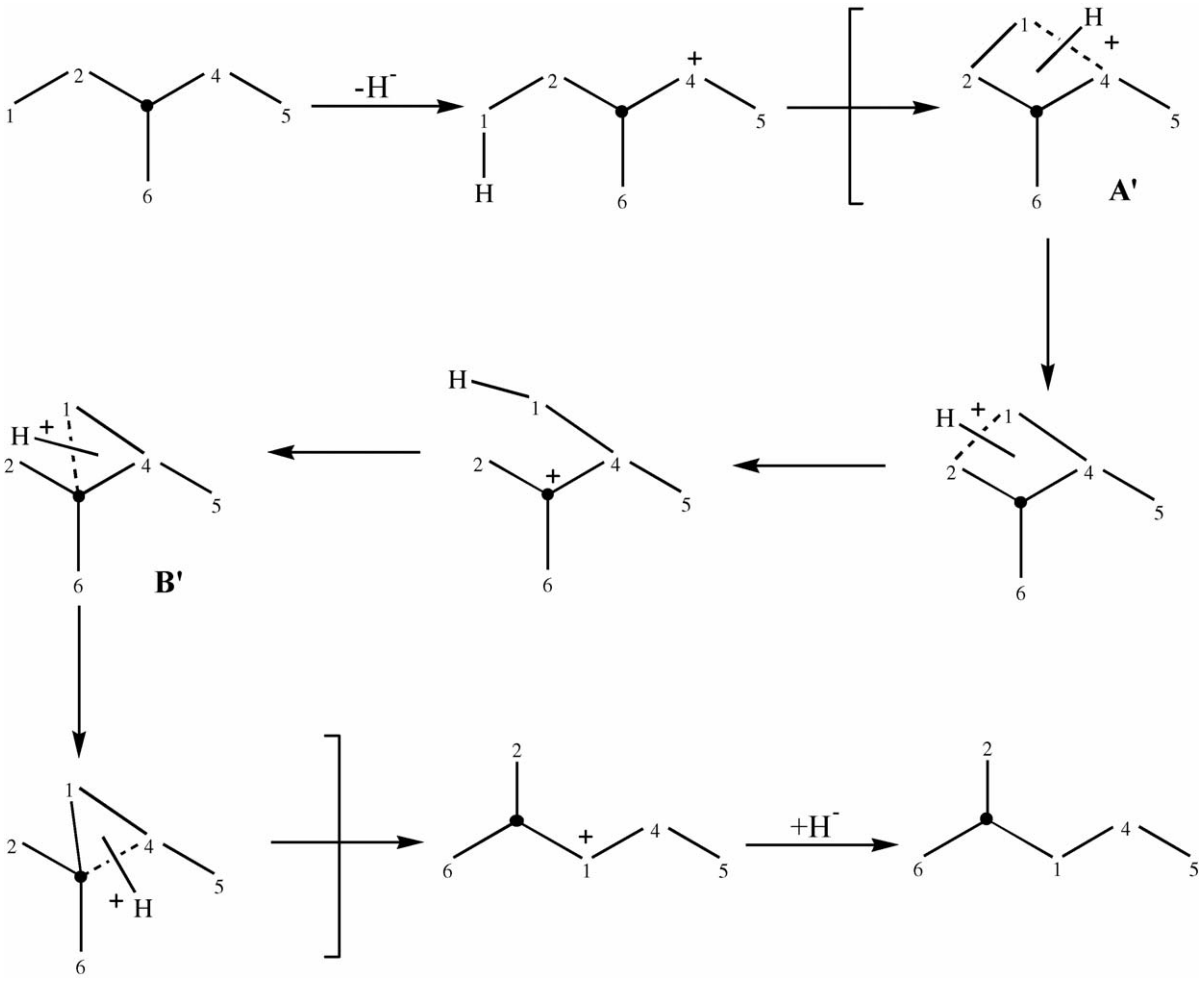


Fig. 6. Isomerization mechanism of the 3-methyl(3-^{13}C)pentane in 2-methyl(2-^{13}C)pentane: what is in parentheses is a likely detail of the protonated bicyclopropane of reaction (V) in Fig. 4.

The lack of 3-methyl(2-^{13}C)pentane is the base of the suggested bicyclopropane mechanism.This suggested mechanism requires further studies in order to highlight dark points. In fact two questions arise:

- Does the 0% for the 3-methylpentane isotopomers (calculated from the mass spectrum) mean that these molecules are not formed? Or are they not detected (formed in low proportions, but insufficiently to their detection)?
- Is the relative stability of the two suggested bicyclopropanes similar?

To answer the first question, the 0% value must be reliable and no doubt must remain. However, it is to remark that, in a previous paper [25], calculations from mass spectra provided product selectivity below 0.5%, what could support the non-formation of the 3-methylpentane isotopomers. The answer to the second question is essential because a negative answer could call in

Table 6
Relative proportions of methyl and ethyl migrations according to the reaction pathway proposed in Fig. 4

	α_{2MP} x [2-MP + 3-MP]	α_{2MP} x [2-MP + 3-MP] + α_{3MP} x [3-MP]	
	Methyl Migration[a]	Ethyl Migration[a]	MM/EM[b]
SAZi	2.43	5.17 + 0.0 = 5.17	0.47
SGZi	2.84	5.27 + 0.0 = 5.27	0.54
SAZc	2.24	4.76 + 0.0 = 4.76	0.47
SGZc	3.02	4.18 + 0.0 = 4.18	0.72

[a] α_{XMP} is the conversion in X-methylpentanes (in decimal).
[b] Ratio between methyl migration and ethyl migration.

question the supposed equality of the proportions of 2-methyl(4-^{13}C)pentane and 2-methyl(2-^{13}C)pentane. The drawn schemes explaining the two bicyclopropanes are different (Figs. 5 and 6), but they could be not realistic. Hence, the intermediates on their whole could be similar (Fig. 4) and likely could have similar stabilities. Such reaction mechanism involving such bicyclopropane intermediates could occur but it must be confirmed by additional studies.

3.5.3. In short

According to the first reaction pathway (Fig. 3) involving only protonated cyclopropanes, all the different isotopic species produced are obtained from reactions that take place in one, two or three steps. However, according to the second reaction pathway (Fig. 4) involving protonated cyclopropanes, cyclobutanes and bicyclopropanes, all the different isotopic species produced are obtained from reactions that take place in one or two steps. In both pathways, there is no strong adsorption of the surface species and the desorption rate is rather important [25].

Taking into consideration the ethyl migration, which occurs preferentially (Table 3), the isotopomers distribution (Table 2) and the reaction schemes of Fig. 3, it is proposed that the relative stability of the carbenium rings are in the order of protonated cyclopropane (322) > protonated cyclopropane (321), where the figures 1, 2, 3 in parentheses represent, respectively the primary, secondary and tertiary carbon atoms involved in the rings formation. In fact, the three steps of the isomerization involve only these two types of protonated cyclopropanes. For the first step, the protonated cyclopropanes (322) and (321) are, respectively, at the origin of the ethyl and methyl groups migrations. Hence, the classification of the alkyl groups migration is the following: ethyl > methyl. This is in agreement with the ratios MM/EM of Table 3, showing the favoured ethyl migration.

According to the reaction pathway regarding the 3-methylpentane isotopomers as non-formed molecules, the relative stability of the carbenium rings could be in the order of protonated bicyclopropane (3221) > protonated cyclopropane (321). This classification is in agreement with the preferential occurring of the ethyl migration. A parallel can be made with the previous classification. The protonated cyclopropane (322) is one part of the protonated bicyclopropane (3221) and these two rings could have similar stabilities. Further studies more devoted to the reaction intermediates could provide more information about their respective stability.

4. Conclusion

The isomerization of the 3-methyl(3-^{13}C)pentane on Al or Ga modified sulphated zirconia was studied. The 3-methyl(3-^{13}C)pentane was chosen as reactant in order to distinguish between the methyl and the ethyl migrations. From the experimental data, an amazing observation was the 3-methyl(3-^{13}C)pentane did not self isomerize (0%). This result made the interpretations quite difficult. One question arose: what does the 0% mean? Not detected or not formed? This ambiguity urged to envisage the two possibilities.

First, it was considered the 3-methylpentane isotopomers as being not detected but likely formed in low proportions. The acid catalyzed isomerization involves generally the protonated cyclopropanes as reaction intermediates. Hence, according to reaction schemes involving only these intermediates, all the different isotopic species produced are obtained from reactions taking place in one, two or three steps.

Second, it was supposed that the 3-methylpentane isotopomers were not formed at all. In this case, a mechanism by which the reactant isomerization would take place in a single reaction was suggested, but where one or two carbon–carbon bonds could break implying protonated cyclopropane or cyclobutane or bicyclopropane as intermediates.

For both reaction pathways, the relative proportions of methyl migration (MM) and ethyl migration (EM) were assessed and were equal. The MM/EM ratio could be appreciated as an intrinsic characteristic of the catalyst. On our acid catalysts, the ethyl migration was preferred to the methyl migration during the isomerization process. It was suggested that the solids crystalline structure as well as the sulphate content, and so the acidity and/or the redox activity, play an important role in the alkyl migrations during isomerization. The knowledge of such correlations could allow preparing catalysts combining both high activity and high selective reactivity.

Acknowledgment

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