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Isomerization of 3-methyl(3-^{13}C)pentane over platinum supported sulphated zirconias: reaction mechanisms

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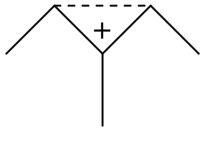
This paper studies the isomerization mechanisms of 3-methyl(3-^{13}C)pentane over Pt supported sulphated zirconias (SZs). Pt hydrogenates the reaction intermediates that desorbs, hinders successive isomerizations from occurring and reduces the isomerization steps to two (three with Pt-free SZs). The isomerization is a monomolecular process to which Pt does not participate. Lastly, it is suggested that the ratio between the proportions of methyl migration and ethyl migration could be appreciated as a catalyst intrinsic characteristic.

KEY WORDS: aluminium or gallium doped sulphated zirconia; platinum; isomerization; reaction mechanism; methylpentane; ^{13}C-labelled alkane.

1. Introduction

Sulphated zirconia (SZ) is a highly active catalyst for the skeletal isomerization of *n*-butane [1] but unfortunately, it rapidly deactivates [2]. To prevent such loss of activity, the addition of a metal, mainly platinum, is beneficial. The new catalyst, Pt/SZ, exhibits a better stability in presence of H_2 [3, 4] and is highly active for the nC_4 isomerization [5, 6]. The addition of Pt provides bifunctional properties to the catalyst. However, the role of Pt, the nature of the active site and the reaction mechanisms are still under discussion [7–14].

As underlined by Okuhara *et al.* [15], understanding the reaction mechanisms is indispensable for developing appropriate catalysts. An efficient way to make easier such mechanistic studies is the utilization of ^{13}C-labelled alkanes. For example, that tool has been helpful in throwing light on the mono- ($nC_4^+ \rightarrow iC_4^+$) [16, 17] and/or the bi-molecularity ($C_4^+ + C_4^= \rightarrow C_8^+ \rightarrow iC_4^+$) [15, 18–26] of the nC_4 isomerization. Keller *et al.* [27] have studied the isomerizations of various ^{13}C-labelled methylpentanes over tungsten carbide catalysts and have suggested reaction mechanisms involving protonated cyclopropanes as reaction intermediates as e.g.:



In a similar way, the skeletal rearrangement study of 3-methyl(3-^{13}C)pentane over Al or Ga doped SZs (without Pt) have suggested a reaction pathway involving similar reaction intermediates. At the knowledge of the authors, no paper deals with the isomerization of ^{13}C-labelled hexanes over Pt/SZ.

The 3-methyl(3-^{13}C)pentane is a very interesting ^{13}C-labelled alkane because its skeletal rearrangement provides a wealth of information useful for distinguishing between the methyl group migration and the ethyl group migration, which are important in acid and bifunctional catalysis. The present paper presents and analyzes the 3-methyl(3-^{13}C)pentane isomerization over different Pt supported SZs, the SZs being either pure or doped with Al or Ga. The primordial aim of this study is to understand the influence of the Pt addition on the mechanisms of the isomerization reactions.

2. Experimentals

The catalysts are Pt supported SZs. SZ is taken pure or doped whether by 3 mol% Al_2O_3 or 3 mol% Ga_2O_3. Aluminium and gallium were introduced either by impregnation or by coprecipitation. Platinum (0.3 wt%) was introduced by impregnation. The experimental procedure and the results of their characterizations are described elsewhere [28]. In the text, the abbreviations Pt/SZ, Pt/SAZi, Pt/SGZi, Pt/SAZc and Pt/SGZc point out the SZs modified by Al_2O_3 (A) or Ga_2O_3 (G), those lasts being added by impregnation (i) or coprecipitation (c).

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The synthesis of the 3-methyl(3-^{13}C)pentane molecule was performed in two steps as described elsewhere [29, 30]. 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 over Woelm alumina (1 g) at 180 °C and hydrogenated over 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 used for the catalytic reactions.

The catalytic reactions were carried out in a pulse flow system with a fixed bed reactor working at atmospheric total pressure. In each run, 5 μL of the ^{13}C-labelled alkane were introduced into the gas flow of hydrogen (Air liquide, purity 4N, around 1 bar) at constant hydrocarbon partial pressure (around 7 mbar) 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) [29–31]. The experimental conditions were set to get the lowest total conversion. To perform it, a catalyst sample was tested with 3-methylpentane (Fluka, puriss. standard for GC). The reaction temperature was 150 °C, at which Pt is inactive to the carbon–carbon bond scission [32]. The other experimental parameters were kept constant. The catalyst weight was 0.1 g and the hydrogen flow was set to 30 mL min^{-1}. The procedure, the calculation of the isotopomer species distribution, as well as the location of the ^{13}C atom in the molecule have been described elsewhere [31, 33–35].

3. Results

For the clarity of the discussion to come, table 1 shows the results of the 3-methyl(3-^{13}C)pentane conversion over the Pt/SZ catalysts. Table 2 shows the distribution of the ^{13}C-labelled 3-methylpentane reaction products. In order to make easier the observation of the contribution of Pt, the isotopomers distributions calculated with the Pt-free SZ catalysts are also proposed in table 2. It is to note that the 2-methylpentane and 3-methypentane molecules 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.

Table 1
Products distribution for 3-methyl(3-^{13}C)pentane conversion over Pt/SZ catalysts at 150 °C

	^{13}C-labelled 2-methylpentanes conversion α_{2MP} (%)	^{13}C-labelled 3-methylpentanes conversion α_{3MP} (%)
Pt/SZ	9.9	90.1
Pt/SAZi	15.3	84.7
Pt/SGZi	18.3	81.7
Pt/SAZc	25.1	74.9
Pt/SGZc	15.9	84.1

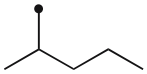
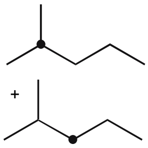
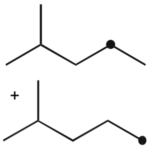
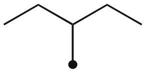
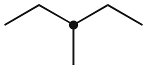
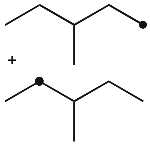
From table 2, three main observations stand out. They are listed below.

- *Statistical distribution*: The contribution of the isotopomers is different from the statistical distribution. The adsorption times of the reaction intermediates on the active sites of the catalyst are likely too short for the formation of all possible ^{13}C-labelled methylpentanes. The number of successive isomerization occurring in the adsorption phase is limited because of the hydrogenation ability of Pt.
- *2-methylpentane*: The 2-(^{13}C)methylpentane is a molecule stem from scrambling of the ^{13}C tracer: the ^{13}C atom shifts towards the primary carbon atoms of the alkane, what indicates the occurrence of successive isomerizations during the adsorption phase. In our conditions, that molecule is not detected with Pt/SZ, Pt/SGZi and Pt/SAZc while it is formed in very low proportions with Pt/SAZi and Pt/SGZc, what indicates that in presence of Pt the ^{13}C tracer scrambling does not really take place. If the isotopomers distributions got with SZs and Pt/SZS are compared, one can remark that the proportions in '2-methyl (4-^{13}C)pentane + 2-methyl(5-^{13}C)pentane' are similar while the percentages of '2-methyl(2-^{13}C)pentane + 2-methyl(3-^{13}C)pentane' are higher in presence of Pt. A quick calculation shows the non-formation of 2-(^{13}C)methylpentane benefits to the formations of '2-methyl(2-^{13}C)pentane + 2-methyl(3-^{13}C)pentane'.
- *3-methylpentane*: The 3-methyl(3-^{13}C)pentane does not self-isomerize into 3-(^{13}C)methylpentane, while it slightly self-isomerizes into 3-methyl(2-^{13}C)pentane and/or 3-methyl(1-^{13}C)pentane (1.0–7.0%).

4. Discussion

The following discussion uses as support the reaction mechanisms suggested for the acid-catalyzed isomerizations that involve protonated cyclopropanes as reac-

Table 2
Contribution of the ^{13}C-labelled methylpentanes (%) stem from the isomerization of 3-methyl(3-^{13}C)pentane over Pt supported SZ, SAZ and SGZ catalysts at 150°C (Black circles denote the ^{13}C-labelled carbon atoms)

					 Reactant	
Pt/SZ	0.0	75.0	25.0	0.0	97.6	2.4
Pt/SAZi	2.3	63.5	34.2	0.0	99.0	1.0
Pt/SGZi	0.0	69.5	30.5	0.0	94.4	5.6
Pt/SAZc	0.0	71.0	29.0	0.0	93.0	7.0
Pt/SGZc	1.4	66.0	32.6	0.0	96.0	4.0
SAZi [a]	17.0	49.0	34.0	1.0	99.0	0.0
SGZi [a]	15.0	52.5	32.5	1.0	99.0	0.0
SAZc [a]	11.0	55.0	34.0	0.0	100.0	0.0
SGZc [a]	8.0	63.0	29.0	1.0	99.0	0.0
Statistic [b]	16.7 × 2	33.3	33.3	16.7	16.7	33.3 × 2

[a] [36].

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

tion intermediates (figure 1) [27]. Those ones provide possible reaction pathways for all the 2-methylpentane and 3-methylpentane isotopomers, which are stem from isomerization reactions taking place in one, two or three steps.

4.1. Assumptions and interpretations

Few assumptions enable to detail the isotopomers distribution given in table 2.

(i) All ^{13}C-labelled 2-methylpentanes are formed with the same probability.
(ii) The 2-methyl(5-^{13}C)pentane proportion is similar to the 2-(^{13}C)methylpentane one. Hence, the remaining percentage (in its column of table 2) represents the 2-methyl(4-^{13}C)pentane proportion.

To formulate (ii), the isomerization pathway in figure 1 is regarded. From 3-methyl(3-^{13}C)pentane, the formations of 2-methyl(5-^{13}C)pentane and 2-(^{13}C) methylpentane involve three steps. The contributions of 2-methyl(5-^{13}C)pentane and 2-(^{13}C)methylpentane are supposed similar.

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

To formulate (iii), the isomerization scheme given in figure 1 is regarded. Both 2-methyl(4-^{13}C)pentane and 2-methyl(2-^{13}C)pentane are stem from the 3-methyl(2-^{13}C)pentanium ion.

(iv) 3-(^{13}C)methylpentane is not formed (0% in Table 2).

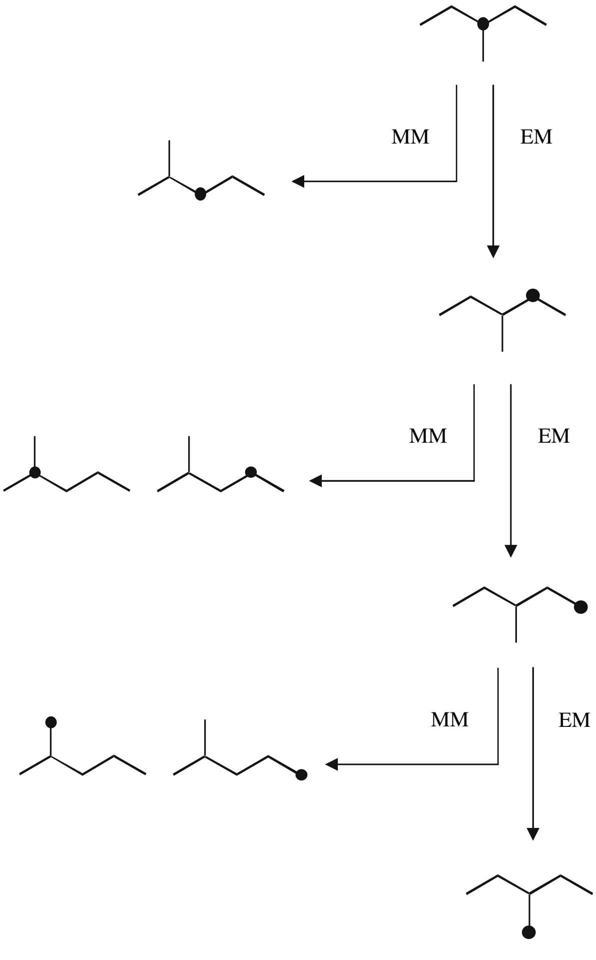


Figure 1. Isomerization of 3-methyl(3-^{13}C)pentane over SZs: reaction sequences involving protonated cyclopropane intermediates (MM: methyl group migration; EM: ethyl group migration).

(v) The proportion in 3-methyl(1-^{13}C)pentane is supposed negligible. The remaining percentage (in its column of table 2) represents the 3-methyl (2-^{13}C)pentane one.

According to figure 1, the 3-methyl(1-^{13}C)pentane isotopomer is formed prior to both 2-(^{13}C) methylpentane and 2-methyl(5-^{13}C)pentane. The 2-methyl (5-^{13}C)pentane proportion is supposed nil or negligible. According to the equilibrium constant of the isomerization reaction between 3-methyl(1-^{13}C)pentane and 2-methyl(5-^{13}C)pentane in favour of the second molecule ($K \sim 3$), it is likely that 3-methyl(1-^{13}C)pentane is formed in undetectable proportions.

Table 3 presents the corrected 2-methylpentane isotopomers distribution, where the previous assumptions are taken into account.

The distribution of each isotopomer in Table 3 is calculated from the values of table 2:

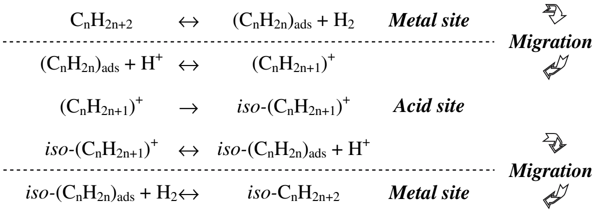
- The proportion in 2-(^{13}C)methylpentane is unchanged.
- The proportions in 2-methyl(5-^{13}C)pentane and 2-(^{13}C)methylpentane are equal (ii).
- The proportion in 2-methyl(4-^{13}C)pentane is calculated by subtracting its percentage in table 2 by the 2-(^{13}C)methylpentane percentage (ii).
- The proportions in 2-methyl(2-^{13}C)pentane and 2-methyl(4-^{13}C)pentane are equal (iii).
- The proportion in 2-methyl(3-^{13}C)pentane is calculated by subtracting its percentage in table 2 by the 2-methyl(4-^{13}C)pentane percentage (iii).

From table 3, three observations arise:

- The 2-methyl(3-^{13}C)pentane percentage is between 31.6% and 50% depending on the catalyst nature. That molecule can be formed via a single methyl group migration from 3-methyl(3-^{13}C)pentane (figure 1). That suggests that the contribution of the methyl group migration, which can be seen as a single-step reaction, is between 31.6% and 50%.
- The contribution of the ethyl group migration at the time of the first step of the isomerization is higher than the contribution of the methyl group migration, except for Pt/SZ for which both contributions are similar.
- With the Pt/SZs, the maximum number of isomerization steps can be regarded as being two.

4.2. Isomerization reactions mechanisms

Pt/SZ is a catalyst for which many aspects are still under discussion [7–14]. Regarding the Pt state, Sayari and Dicko [37] and Zhao *et al.* [38] show that Pt is metallic. For Hattori *et al.* [6, 39–42], Pt is mainly cationic (mixture of Pt oxide and Pt sulphate) with a small fraction of metallic Pt. Nevertheless, in studies published later, those authors [43, 44] suggest the coexistence of metallic Pt (particle core) with cationic Pt as PtO_x (particle shell). Lastly, according to Föttinger *et al.* [45], Pt on SZ is partially electron-deficient. Regarding the role of Pt, Iglesia *et al.* [47, 48] and Chao *et al.* [16] suppose that Pt catalyzes the H_2 dissociation as a hydride and a proton. The proton acts as a Brønsted acid site, while the hydride reacts with the isomerized carbenium ion. However, for many groups [6, 17, 39–45, 49, 50], Pt adsorbs and dissociates H_2 into atomic hydrogens, which spillover onto SZ and convert to a proton and a hydride, the former one acting as a Brønsted acid active site.



$$\mathrm{C_nH_{2n+2}} \leftrightarrow \mathrm{(C_nH_{2n})_{ads} + H_2}$$

$$\mathrm{(C_nH_{2n})_{ads} + H^+} \leftrightarrow \mathrm{(C_nH_{2n+1})^+}$$

$$\mathrm{(C_nH_{2n+1})^+} \rightarrow iso\text{-}\mathrm{(C_nH_{2n+1})^+}$$

$$iso\text{-}\mathrm{(C_nH_{2n+1})^+} \leftrightarrow iso\text{-}\mathrm{(C_nH_{2n})_{ads} + H^+}$$

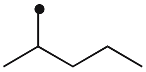
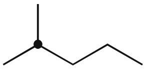
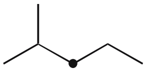
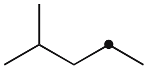
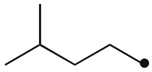
$$iso\text{-}\mathrm{(C_nH_{2n})_{ads} + H_2} \leftrightarrow iso\text{-}\mathrm{C_nH_{2n+2}}$$

Pt/SZ is a bifunctional catalyst, on which generally the isomerization is believed to proceed following the "traditional" bifunctional mechanism [51]:

The bifunctional mechanism comprises dehydrogenation of the alkane over the metal surface, isomerization of the protonated alkene over the acid site and hydrogenation of the isomerized alkene on the metal surface. However, recent investigations have introduced modifications. In a previous paper [32], we have suggested the presence of a metal–proton adduct $[\mathrm{H\text{-}(M_m)(H^+)_{\mathit{x}}}]^{x}$ + , which combines metal and acid sites and with which the migration steps between these two sites are suppressed. That concept is in agreement with the $[\mathrm{Pd}_n\mathrm{H}]^+$ and $[\mathrm{Pt}_n\mathrm{H}]^+$ adducts that act as "collapsed bifunctional sites" proposed by Sachtler *et al.* [21, 52–54] and with the "compressed bifunctional sites" suggested by Paàl *et al.* [55, 56].

The following discussion supposes the metal–proton adduct as the active site and envisages thus an intimate contact between the metallic site and the acidic site. At 150 °C, the Pt role is the dehydrogenation–hydrogenation of the hydrocarbon, while the acid site role is the skeletal rearrangement of the carbenium ion [32]. In metallic catalysis, the alkane isomerization takes place according to two mechanisms (figure 2). The first is the bond shift mechanism. The second is the cyclic mechanism: in the case of methylpentane, it implies the dehydrocyclization of an adsorbed methylcyclopentane species by ring opening. With Pt, a statistical bond breaking could take place [57]. In our conditions, no hexane and no cyclic product have been detected, what

Table 3
Corrected distribution of the ^{13}C-labelled 2-methylpentanes (%)

					
Pt/SZ	0.0	25.0	50.0	25.0	0.0
Pt/SAZi	2.3	31.9	31.6	31.9	2.3
Pt/SGZi	0.0	30.5	39.0	30.5	0.0
Pt/SAZc	0.0	29.0	42.0	29.0	0.0
Pt/SGZc	1.4	31.2	34.8	31.2	1.4
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 figure 1 (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 figure 1.

suggests that Pt does not participate to the skeletal rearrangement of the carbenium ion and is inactive towards C–C bonds.

Here, it will not be discussed the activation step of the reactant. The reactant will be considered as being activated into a carbenium ion.

In our conditions, the isomerization follows a monomolecular pathway. The analysis of the isotopomers distribution has shown that no double-^{13}C-labelled molecule formed via a bimolecular route has been detected. In fact, Pt in presence of H_2 stabilizes the catalyst activity by hydrogenating the olefins [24, 46, 58, 59] and the presence of both is unfavourable for the occurrence of a bimolecular mechanism [15, 24, 60].

The reaction pathway in figure 3 summarises the isomerization of 3-methyl(3-^{13}C)pentane over Pt/SZs in our conditions (tables 2 and 3). The first step corresponds to the formation of 2-methyl(3-^{13}C)pentane via a methyl group migration and to the formation of 3-methyl(2-^{13}C)pentane via an ethyl group migration. During those first step, Pt hydrogenates a certain amount of the 3-methyl(2-^{13}C)pentanium ions because the hydrogenation reaction is in competition with the skeletal isomerization of that intermediate. The surface lifetime of the carbenium ion is thus reduced and the occurrence of successive transformations is decreased. The second step is the formation of both 2-methyl(2-^{13}C)pentane and 2-methyl(4-^{13}C)pentane via a methyl group migration. The second step could be also the formation of the 3-methyl(1-^{13}C)pentanium ion via an ethyl group migration (figure 1). However, it is supposed that those isotopomer is not formed for two reasons: the first one is given by the assumption (v) (Section 4.1.); the second one is because the hydrogenation of the carbenium ions formed during the first isomerization step is certainly faster than the skeletal rearrangement via an ethyl migration. In presence of Pt, the adsorption time of the carbeniums ion is not long enough for two steps of skeletal rearrangement via ethyl group migrations.

To summary, the 3-methyl(3-^{13}C)pentane isomerization over the Pt/SZs is a one- or two-step process. The

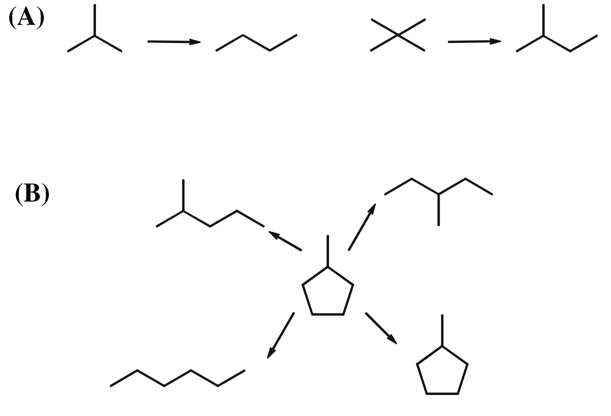


Figure 2. Metallic catalysis: bond shift mechanism (A) and cyclic mechanism (B) [56].

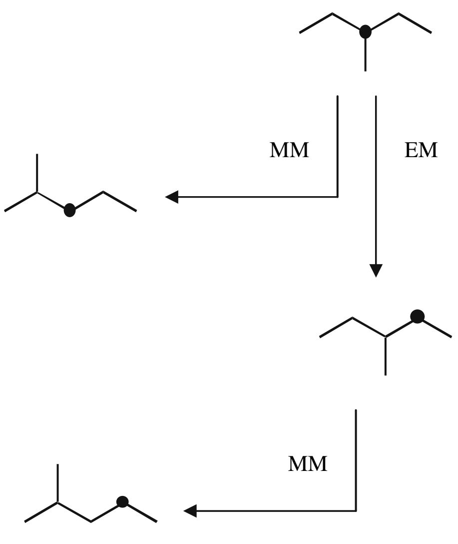


Figure 3. Isomerization of 3-methyl(3-^{13}C)pentane over Pt supported SZs: reaction sequences involving protonated cyclopropane intermediates (MM: methyl group migration; EM: ethyl group migration).

metallic function decreases the surface adsorption lifetime of the carbenium ions by hydrogenating, hinders successive skeletal transformations from occuring, limits the number of successive skeletal rearrangement to two steps and does not enable a statistical distribution of the isotopomers.

4.3. *Evaluation of the relative proportions of methyl migrations and ethyl migrations*

The relative proportions of methyl migrations (MM) and ethyl migrations (EM) over Pt/SZ catalysts are assessed by regarding the alkyl migration during the first step of the isotopomer skeletal formation (figures 1 and 3). The MM/EM ratio can be calculated. This value could be appreciated as an intrinsic characteristic of the catalyst. It can be compared to some physical/chemical properties of the catalysts in order to check if there exists any correlation between all of those values. The knowledge of such correlation(s) could enable to prepare catalysts combining high activity and selective reactivity. Table 4 proposes the relative proportions of MM and EM as well as the ratio MM/EM.

To set up table 4, the calculations and the values listed below are applied:

- 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 (Table 1).
- 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 3 and percentages of 3-methyl(2-^{13}C)pentane from table 2.

Table 4 presents two main particularities:

- The proportion of ethyl migration is always greater than the proportion of the methyl migration.
- The Pt/SAZ and Pt/SGZ catalysts present similar MM/EM ratios with values between 0.4 and 0.5, while the Pt/SZ catalyst shows a ratio of 0.7.

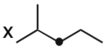
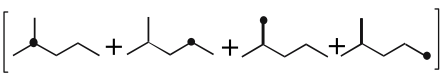
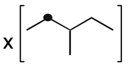
On those bifunctional catalysts, the ethyl migration is preferred to the methyl migration. The calculated MM/EM ratios can be compared to data from the catalysts physical/chemical characterization. Table 5 summarizes few of them [28]. On the one hand, no correlation can be done with the catalytic activity. On the other hand, the comparison of Tables 4 and 5, shown by figure 4, seems to show a certain correlation between the MM/EM ratio and either the sulphate content, the water content or the acidity. However, care must be taken because the data have been determined for the Pt-free catalysts. Besides, a correlation between the MM/EM ratio and the crystalline structure could be suggested (figure 4). For the isomerization of alkanes, it is commonly admitted that the tetragonal crystalline phase of SZ shows higher catalytic activity than the monoclinic crystalline form [61–65]. Here, the ethyl migration would increase with the increase of the fraction of the catalyst tetragonal phase. The strongest metal-support interaction existing with the tetragonal materials [65, 66] could justify that observation thanks to strongest adsorptions and longer surface lifetimes of carbenium ions.

At that stage, further studies are required to determine more precisely such correlations that are completely dependent on an accurate determination of the isotopomers distribution. It is to remark that most of the physical/chemical characteristics of the catalysts are interdependent: e.g. the presence of water in some extent has influence on the sulphur species properties which depend on the crystalline structure, what affects the solid acid strength and the active sites nature, and thus the catalytic activity. Hence, a similar interdependence could also exist with the MM/EM ratio.

Finally, one can remark that the MM/EM ratio can be viewed as the ratio between the percentage of the

Table 4

Relative proportions of methyl and ethyl migrations according to the reaction pathways given by figures 1 and 3

	α_{2MP} x  Methyl migration [a]	α_{2MP} x  + α_{3MP} x  Ethyl migration [a]	MM/EM [b]
Pt/SZ	4.95	4.95 + 2.16 = 7.11	0.70
Pt/SAZi	4.84	10.47 + 0.85 = 11.32	0.43
Pt/SGZi	7.14	11.16 + 4.58 = 15.74	0.45
Pt/SAZc	10.54	14.56 + 5.24 = 19.80	0.53
Pt/SGZc	5.53	10.37 + 3.36 = 13.73	0.40

[a] α_{XMP} is the conversion in X-methylpentanes (in decimal) from table 1.

[b] Ratio between methyl migration and ethyl migration.

Table 5
Characterization data of the SZ, SAZ and SGZ catalysts and conversion data of the Pt supported SZ, SAZ and SGZ catalysts [28]

	SZ	SAZi	SGZi	SAZc	SGZc
Sulphate content (wt%, TGA)	4.34	7.65	6.87	7.15	5.82
Water content (wt%, TGA)	3.12	5.97	5.03	5.25	3.93
Monoclinic fraction (%)	40.6	12.8	14.3	5.4	< 5
Acidity NH_4^+-IR 250 °C (a.u m^{-2})	1.42	2.41	2.45	2.14	2.44
	Pt/SZ	Pt/SAZi	Pt/SGZi	Pt/SAZc	Pt/SGZc
Conversion of nC$_4$ at 450 °C					
After 5 min (%)	38.3	36.5	48.2	46.5	59.5
Steady regime (%)	30.2	30.9	37.5	38.1	51.7

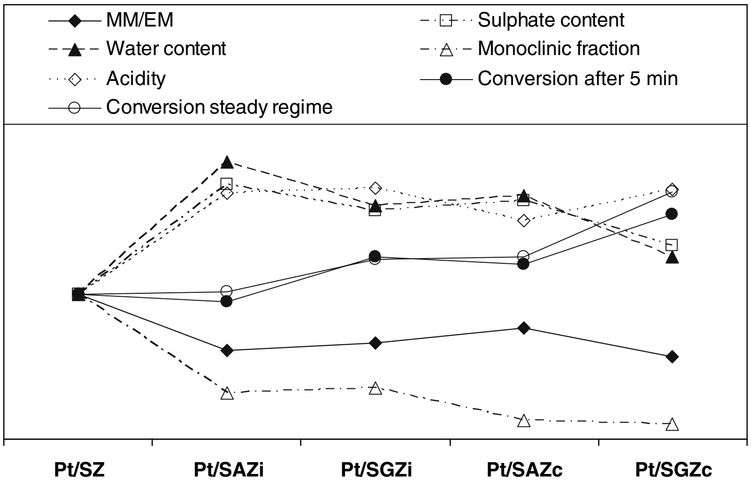


Fig. 4 Evolutions of data from tables 4 and 5 (all the data belonging to Pt/SZ are normalized to 1 and the data of the other catalysts are calculated according to this normalization)

molecules formed through a one-step isomerization process and the percentage of the molecules formed through a two-step isomerization process.

5. Conclusion

The isomerization of 3-methyl(3-^{13}C)pentane over Pt supported on SZs, pure or doped with either Al or Ga, has been studied. That molecule has been chosen as reactant because it enables to distinguish between the migrations of methyl group and ethyl group.

With the addition of Pt to the SZ solids, the number of steps of successive isomerizations becomes two, while it is three with the Pt-free SZs. The Pt metal, thanks to its hydrogenation ability, quickly hydrogenates the carbenium ions and hinders a further isomerization step from taking place. The hydrogenation reaction is in competition with the skeletal rearrangement and the surface lifetime of the reaction intermediates is decreased. In the present conditions, i.e. at 150 °C, no metallic catalysis occurs. Pt does not participate to the isomerization, which is a monomolecular process, and is not active towards the C–C bonds.

The MM/EM ratios are calculated but no relevant correlation between those ratios and either data from the catalysts physical/chemical characterization or catalytic activity data is obvious. In fact, the MM/EM ratio could be regarded as an intrinsic characteristic of the catalyst but further studies are required for developing the use of such ratio.

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