Catalysis Letters Vol. 76, No. 1–2, 2001

From bifunctional site to metal–proton adduct site in alkane reforming reactions on sulphated-zirconia-supported Pt or Pd or Ir catalysts

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Received 14 February 2001; accepted 18 June 2001

Isomerization reactions of *n*-heptane, *n*-octane and *n*-nonane are studied on sulphated-zirconia-supported 0.2 wt% Pt, Pd or Ir catalysts. Evolutions of isomer selectivity *versus* total conversion and reaction temperatures are analysed. When total conversion (α_T) is increased, isomer selectivity ($\%S_{\text{isom}}$) is decreased and the slope of the curve $\%S_{\text{isom}} = f(\alpha_T)$ is more pronounced when the carbon number in the alkane is more important. At isoconversion, around 20%, below 473 K, cracking is favoured over isomerization reaction, and above 473 K it is the reverse. Moreover, with *n*-heptane, when the catalytic reaction occurred at 423 K and at low conversion, $\alpha_T \leqslant 20\%$, we observed a large decrease in the isomer selectivity percentages on Pd/SZ and Ir/SZ compared to Pt/SZ. What is remarkable is that, at this low temperature, both metals are inactive in the carbon–carbon bond rupture. To explain these results the following points are raised: (i) an associative mechanism is proposed for the adsorption step of the alkane involving an agostic intermediate species where the carbon–hydrogen bonds act as ligands to the transition metal centres forming covalent C–H···M systems, and (ii) a metal–proton adduct site, which gathers metallic and acidic sites is suggested. This approach seems to better explain our results than the "traditional" bifunctional mechanism.

KEY WORDS: *n*-alkanes; cracking; isomerization; bifunctional catalysis; bifunctional mechanism; metal–proton adduct; associative adsorption mechanism; agostic species; sulphated zirconia supported Pt or Pd or Ir catalysts

1. Introduction

Parallel to more and more severe environmental legislation, the petrochemical refining industry tries to find new alternatives for the production of clean-burning fuels. This enables the development of other promising fields such as solid acid catalysis. Their increasing importance has been demonstrated by Tanabe *et al.* [1] who presented a statistical survey of industrial processes using solid acid catalysts. In a same way Yadav *et al.* [2] set out the different industrial processes using sulphated zirconia (denoted as SZ) based catalysts, which are known to catalyse skeletal isomerization of hydrocarbons [3,4], and we are acquainted that the presence of isoalkanes increases the gasoline octane number.

SZ, a solid acid catalyst, is sometimes called superacidic. Based on Hammet's indicator technique it is claimed to present superacid sites. Nevertheless, some authors [5,6] asserted that the SZ sites are only strong acid sites. In spite of their superacidic properties those catalysts deactivate rapidly [7]. The addition of metal, like platinum [8–11], increases its stability. The presence of hydrogen is essential to maintain the catalytic activity [9]. Many studies concerning the physicochemical properties, the structure and the catalytic behaviour of SZ and of Pt-promoted sulphated zirconia (denoted as Pt/SZ) have been published. But the results are much debated [12–19], particularly for the reaction mechanisms of alkanes on such systems. Most of the publications concern the isomerization of *n*-butane to isobutane [4,5,9,12,13,20–27]. Two types of conclusions on the reaction mechanisms came out. Adeeva *et al.* [27] showed, using double ^{13}C-labelled *n*-C_4 ($^{13}CH_3$–$^{12}CH_2$–$^{12}CH_2$–$^{13}CH_3$), that this reactant isomerizes following a bimolecular mechanism, in which a C_8 intermediate is involved. Tomishige *et al.* [21] refuted this hypothesis and postulated a unimolecular mechanism. In general this intramolecular mechanism is accepted for hydrocarbons having more than five carbon atoms [10,20,23,28]. Moreover, about the metals present in the nature, only platinum, palladium and iridium have the power to isomerize *n*-alkanes [29,30]. In addition, from our knowledge, only a few publications concerning the isomerization mechanism of heptanes and heavier alkane molecules on Pt/SZ, Pd/SZ and on Ir/SZ exist. These three systems may behave as bifunctional catalysts since they possess metal and acid sites and they may follow the course of action proposed in 1953 by Mills *et al.* [31]. These authors have supposed that isomerization of a *n*-alkane is assumed to start with the dissociative adsorption of the feed molecule on a metal site, where it is dehydrogenated to an olefin. This latter moves to an acid site, where it is adsorbed and protonated as a secondary carbenium ion which can isomerize to a tertiary carbenium ion. Hence, this species is decomposed into

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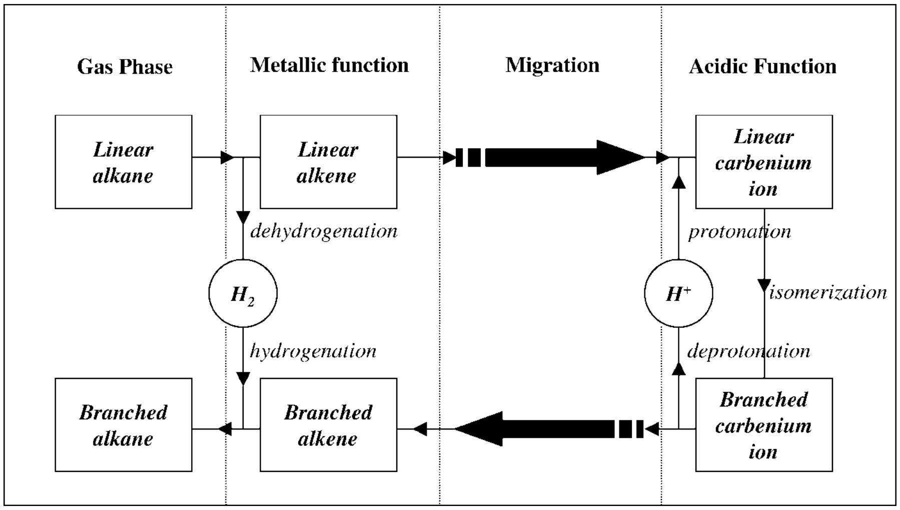


Scheme 1. Schematic representation of the mechanism of skeletal isomerization of alkanes following a bifunctional process, according to Mills *et al.* [31].

a surface proton and a branched olefin which travels from the acid site to a metal site, where it is hydrogenated. Then a branched alkane molecule is obtained. Scheme 1 shows the steps of this mechanism.

However, recent investigations [8,28,32,33] have introduced some modifications to this way of thinking based on the "traditional bifunctional mechanism". From experimental results obtained on zeolite-encaged palladium clusters, Bai and Sachtler suggested the presence of a $[Pd_nH]^+$ adduct, to explain their results concerning the conversion of methylcyclopentane [34]; the metal being "electron-deficient". This "hybrid metal–proton site" was defined as responsible for ring enlargement of the methylcyclopentane [35]. Then from the work performed on Pt/SZ and on Pt/H-Mor by Liu *et al.* [20], these authors suggested that a "collapsed bifunctional mechanism" is more appropriate to explain their results. At the same time, Buchholz *et al.* [32] used the denomination "compressed bifunctional mechanism" to interpret their results on Pt/SZ. These two expressions have the same signification. It is suggested that isomerization on such catalysts does not follow the "traditional" bifunctional route and it is considered thus that ensembles containing metallic and acidic sites are the active sites. Yet the bifunctional catalysis still arouses interrogations and discussions.

The aim of the present study is to investigate the isomerization reactions of three *n*-alkanes – *n*-heptane, *n*-octane and *n*-nonane – on platinum-, palladium- or iridium-promoted sulphated zirconia and to contribute to better understanding the mechanisms through which those reactants are rearranged.

2. Experimental

2.1. Materials

Hydrocarbons *n*-heptane and *n*-octane from Fluka (puriss. standard for GC), and *n*-nonane, from Aldrich (purity >99%), were used without further purification. Hydrogen and helium were purchased from Air liquide (purity 4N).

2.2. Catalyst preparation

A one-step sol–gel synthesis of sulphated zirconia was used [36,37]. It consisted in addition of water to alcohol solution (*n*-propyl alcohol) of zirconium alkoxide (zirconium *n*-propoxide), the sulphuric acid being introduced through the hydrolysis water. The solid was dried at 353 K for 18 h and calcined at 898 K for 4 h. Then 0.2 wt% of metal was added from $Pt(NH_3)_4(NO_3)_2$, $Pd(NH_4)_2Cl_6$ or from H_2IrCl_6. The mixture was stirred for 2 h and then was dried in an oven for 12 h. The hydrogen reduction was performed at 623 K for 2 h.

2.3. Apparatus and procedure

The catalytic reactions were carried out in a pulse flow system with a fixed-bed reactor working at the atmospheric total pressure. In each run *n*-alkanes were introduced into the gas flow of hydrogen at constant hydrocarbon partial pressure (around 5 Torr) thanks to a cooled trap kept at a constant temperature. To obtain different conversions at constant temperature we changed the reaction conditions by increasing or decreasing either the gas flow or the weight of catalyst used.

2.4. Gas chromatography

The products were analysed by a gas chromatograph (Varian 3300) equipped with a flame ionisation detector and a capillary column (CP Sil 5CB, length 50 m, diameter 0.53 mm). The GC was coupled to the outlet of the catalytic reactor.

3. Results

3.1. Catalyst characterisations

From microanalysis performed at Vernaison (CNRS – Lyon), the sulphur content of the support was equal to

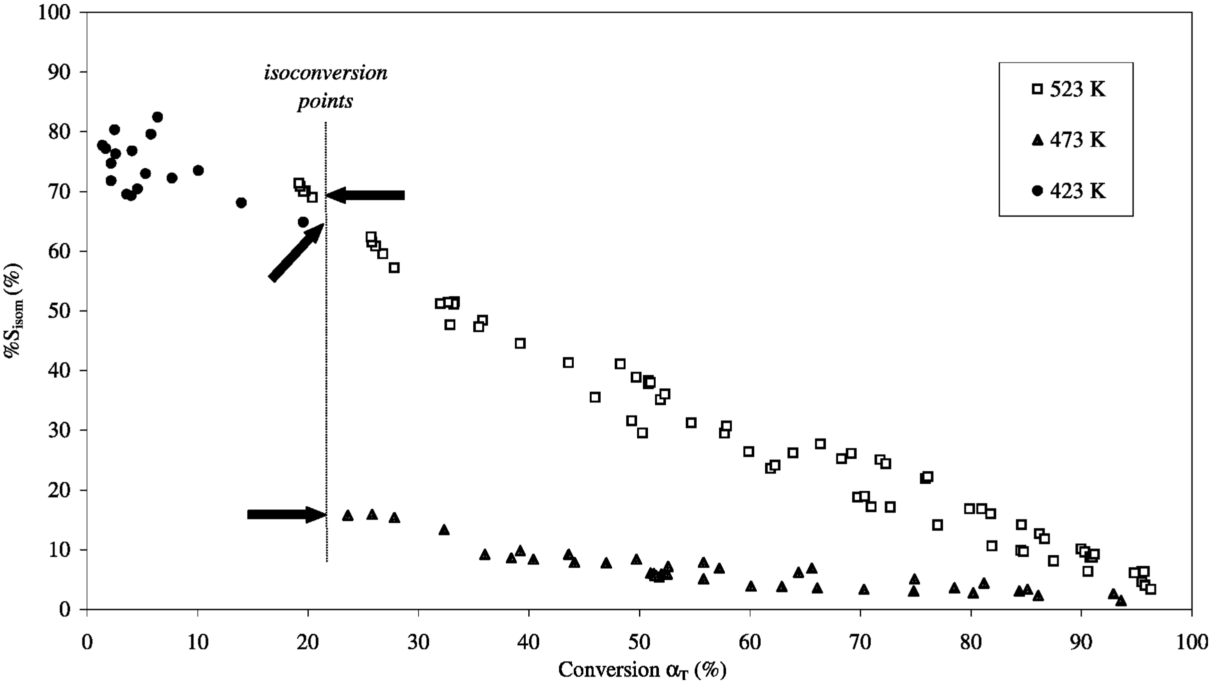


Figure 1. n-heptane reactivity on Pt/SZ. Evolution of the isomerization selectivity $\%S_{\text{isom}}$ as a function of the total conversion α_T, at three different temperatures. The black arrows point to results obtained at isoconversion but at three different temperatures.

1.14 wt%. The BET of the support was equal to 81 m^2/g; and from TEM we were unable to detect metallic particles.

3.2. Catalytic reactions of the alkanes

The contact reactions of the n-alkanes, n-C_7, n-C_8 and n-C_9, were performed at three different temperatures, 423, 473 and 523 K. We have defined:

- the total conversion α_T in percent as

$$\alpha_T\ (\%) = [100 - \text{amount of unreacted reactant}];$$

- the isomerization selectivity, $\%S_{\text{isom}}$ as

$$\%S_{\text{isom}}\ (\%) = \frac{\sum \text{isomer formed}}{\sum \text{isomer formed} + \sum \text{cracked products}} \times 100. \qquad (1)$$

The denominator of equation (1) is equal to $\%\alpha_T$, and all the calculations are in moles.

An important point that has to be stressed here, is that we have observed, whatever the conversion, only one carbon–carbon bond breaking during the cracking reactions; no multiple processes occurred, which means that with n-C_7 we have $[C_3] = [C_4]$, with n-C_8 we have $[C_5] = [C_3]$ and with n-C_9 we have $[C_3] = [C_6]$ and $[C_4] = [C_5]$.

3.2.1. Results obtained on Pt/SZ

Figure 1 displays the variation of $\%S_{\text{isom}}$ *versus* α_T for n-C_7 on Pt/SZ at 423, 473 and 523 K. At increasing conversion, isomerization selectivity decreases. Above 90% of conversion there is only a few percent of isomerization, while for α_T below 10%, $\%S_{\text{isom}}$ reaches values of 80%. This trend is similar but more striking for n-C_8 and n-C_9, as illustrated in figure 2 (A) and (B), respectively. The highest values of $\%S_{\text{isom}}$ are observed at low conversions, but these ones did not reach 40%.

Moreover, a closer observation of the figures 1 and 2 (A) and (B) shows an original characteristic. The modification of

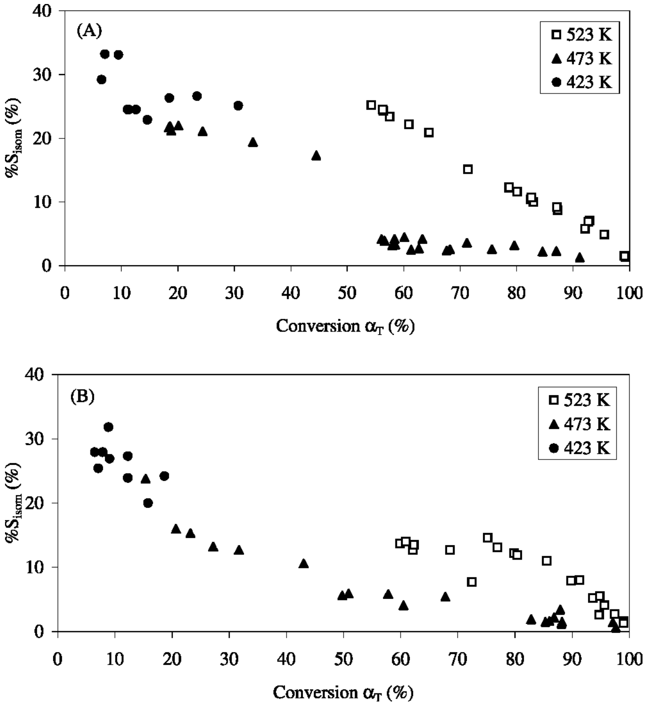


Figure 2. Reactivity of n-octane (A) and n-nonane (B) on Pt/SZ. Evolution of the isomerization selectivity $\%S_{\text{isom}}$ as a function of the total conversion α_T, at three different temperatures.

$\%S_{\text{isom}}$ *versus* α_T also differs for each experimental temperature used. This behaviour is more striking and more clear for n-heptane (figure 1, black arrows). If one considers the points at isoconversion around 20%, $\%S_{\text{isom}}$ is different for each reaction temperature and one can distinguish the corresponding points: at 423 K, $\%S_{\text{isom}}$ is equal to ∼65%, at 473 K to ∼20% and at 523 K to ∼70%. The experimental conditions were completely identical from one temperature to the other, except that hydrogen flow was changed to get similar conversions. Moreover, this result can be observed whatever the conversion was and the hydrocarbon used.

Typical isomer distributions are reported in table 1. We can notice that 2- and 3-methylhexanes (2MH, 3MH) are always formed in the same amount and are the predominant isomers produced.

Table 1
Isomers distributions, in moles, from n-C_7 on 0.2 wt% Pt/SZ. The figures in bold are those pointed by the black arrows in figure 1.

Temperature (K)	$\%\alpha_T$	$\%S_{\text{isom}}$	Isomers selectivity[a] (%)				
			2MH	3MH	EP	DMP	223TMB
423	**19.6**	**64.9**	**25.5**	**25.3**	**1.6**	**12.5**	**0**
423	10.1	73.5	29.1	29.2	1.6	13.6	0
423	2.2	74.7	30.4	29.7	2.1	12.5	0
473	93.7	1.5	0.4	0.6	traces	0.4	traces
473	51.4	6.0	1.8	2.6	0.3	1.3	traces
473	**23.8**	**15.5**	**5.0**	**6.8**	**0.5**	**3.1**	**0.1**
523	99.0	1.4	0.4	0.5	traces	0.4	traces
523	49.9	38.4	14.6	15.6	1.1	6.9	0.2
523	**19.3**	**70.5**	**27.8**	**30.1**	**2.2**	**10.3**	**0.1**

[a] 2MH = 2-methylhexane, 3MH = 3-methylhexane, EP = 3-ethylpentane, DMP = 2,2-, 2,3-, 2,4- and 3,3-dimethylpentanes, 223TMB = 2,2,3-trimethylbutane.

3.2.2. Results obtained with n-C_7 on Pd/SZ and Ir/SZ

We have compared the results obtained at low conversion, $\alpha_T < 20\%$, and at 423 K, on Ir/SZ and Pd/SZ to those obtained on Pt/SZ. These results are reported in figure 3. The main point to notice is that, in such experimental conditions, the isomer selectivity values are lower on Pd/SZ and Ir/SZ than on Pt/SZ. The values of $\%S_{\text{isom}}$ are divided by a factor of four between those obtained on Pt/SZ and on Ir/SZ.

4. Discussion

The catalytic behaviour of such systems *versus* the skeletal rearrangement of alkanes is very interesting. Our experiments have pointed out several fascinating results that will be discussed now. We noticed that the more carbon atoms the n-alkane molecule had, the smaller the isomerization selectivity was, and the more important the cracking reaction contribution was. This is confirmed by Iglesia *et al.* [10] who noticed that the cracking selectivity increases markedly with the carbon chain length. Their investigations focused on n-C_5, n-C_6, n-C_7, n-C_8 and n-C_{10} molecules on Pt/SZ: the n-C_5 and n-C_6 isomerization selectivities were around 99%; for n-C_7, $\%S_{\text{isom}}$ was only about 50% even at low conversions; and the isomerization selectivities of n-C_8 and n-C_{10} were below 35% at a conversion of 20%. On the one hand, according to the published results in the literature, n-C_4, n-C_5 [10,20] and n-C_6 [10,32] isomerization contributions reach values over 90% for $\%S_{\text{isom}}$ at low conversions. On the other hand, as presented in fig-

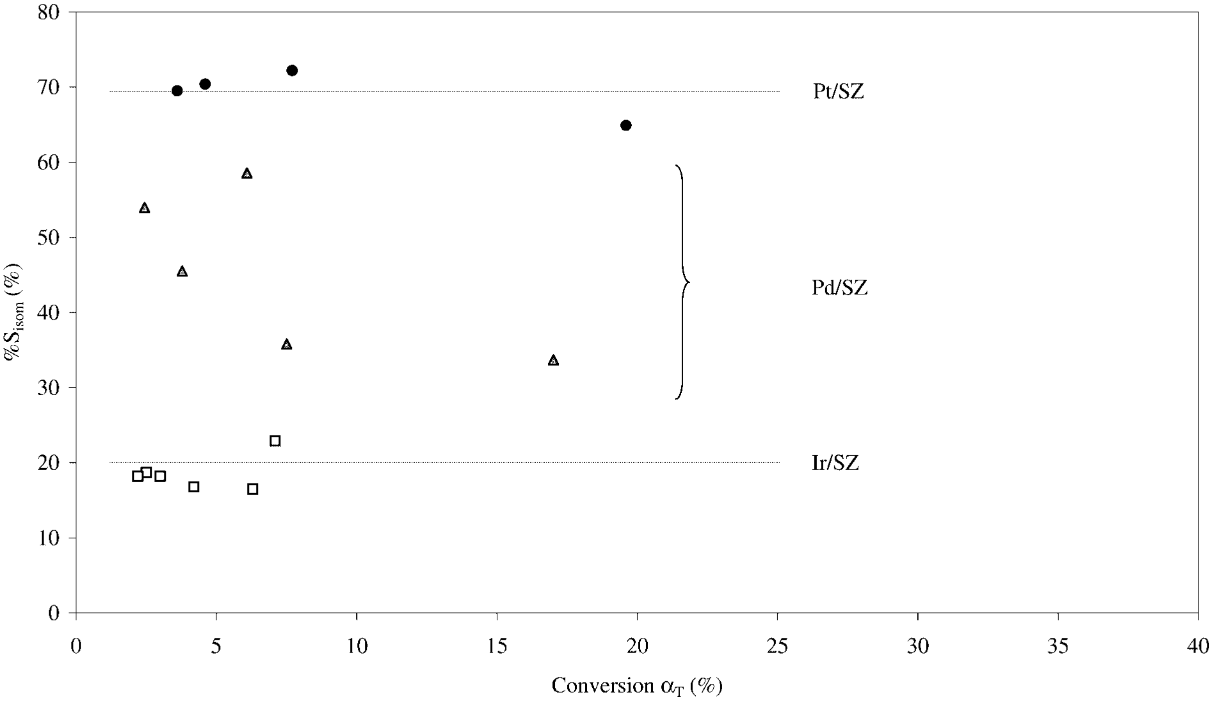


Figure 3. n-heptane selectivity in isomers on Pt/SZ, Pd/SZ and Ir/SZ. The reaction temperature is 423 K.

ure 2 (A) and (B), cracking reactions occurred mainly for n-C_8 and n-C_9. From these observations we should consider n-C_7 as a "transition" molecule between n-C_4 and n-C_6 alkane molecules having $\%S_{\mathrm{isom}}$ above 90% and n-C_8 and heavier n-alkanes for which cracking reactions predominate. The simplest way to explain this observation is to correlate the relative contribution of the cracking reactions to the probability to form "multi-branched" alkane isomers which give tertiary carbenium ions, and, via a carbon–carbon β-scission bond, secondary or tertiary cracked carbenium ions are formed [38]. The heavier the reactant molecule is, the more "multi-branched" alkanes can be obtained; but the influence of the metal used may play a role and at that point two questions arise:

(i) Why do the isomer selectivity values, *versus* the total conversion, follow a "U evolution" when the reaction temperature is increased?

(ii) Why did such differences in isomer selectivity occur when changing the nature of the metal, the experiments being performed at 423 K, on the same support of sulphated zirconia?

To answer the first question, we have to keep in mind that two sites, acidic and metallic, are present on that catalyst, but they are not active in the same range of temperature. At 423 K, on Pt/SZ with n-C_7 (figure 1), the relative contribution of the isomers is 65%. When the temperature is increased up to 473 K the cracking selectivity rises markedly. We should have expected more cracking at 523 K but this was not the case. On the contrary, $\%S_{\mathrm{isom}}$ was greater at 523 K than at 473 K. This original behaviour is also noticeable on Ir/SZ and Pd/SZ catalysts and is, in addition, observed for the three studied n-alkanes, even if it is less significant for n-C_8 and n-C_9 (figure 2 (A) and (B)). This latter point can be explained by the predominance of cracking reactions for the heavier molecules, that does not allow large differences in isomerization selectivity values with the temperature of reactions [38]. To explain such results, let us consider that we are above the isokinetic point in both cases and that isomerization and cracking apparent activation energy values are E_{isom} and E_{crack}, respectively. When we analyze our results at isoconversion, $\alpha_{\mathrm{T}} \approx 20\%$, we see that when the temperature increases from 423 to 473 K the isomer selectivity decreases from ~65 to ~20%. In other words it means that E_{crack} is higher than E_{isom} in this range of temperatures. But, when the temperature is raised by 50 K, from 473 K, the $\%S_{\mathrm{isom}}$ is raised up to ~70%. In that domain of temperatures, 473–523 K, E_{isom} is higher than E_{crack}. Such opposite situation is due to the fact that, at low temperatures, the metallic site is only active in the carbon–hydrogen bond breaking and bond formation and the acidic site is responsible for the carbon–carbon bond rearrangements. While, at high temperature the metallic site has the two powers for C–H and C–C bond ruptures and bond recombinations. The fact that platinum is involved in skeletal rearrangement of the alkane leads to E_{isom} value higher than E_{crack} value, and it is the reverse when only acid sites are responsible for reforming reactions. These two sites are not active in the same range of temperatures.

Table 2

Lowest temperatures used, on alumina-supported Pt, Pd or Ir catalysts, in order to get some reactivity in alkane reforming reactions. The reactant is 2-methylpentane, and the experimental conditions are all identical.

M on Al_2O_3	Temperature (K)	$\%\alpha_{\mathrm{T}}$	$\%S_{\mathrm{isom}}$	Ref.
0.2% Pt	539	~10	65	[42]
1.0% Pd	593	~10	70	[43]
0.2% Ir	493	<3	~20	[44]

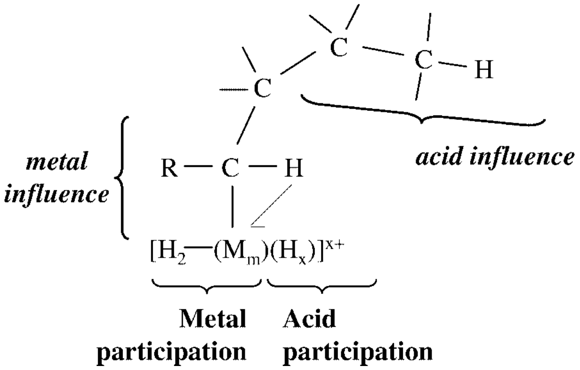
How to interpret such results if we suppose that we are faced to the bifunctional mechanism, and at this stage we can doubt on the validity of the Mills *et al.*'s bifunctional mechanism [31] which is still hugely used. In respect with it, after dehydrogenation steps on the metallic sites, the alkene formed shuttles to the acidic site where it is protonated and isomerized or cracked. This model is based on dissociative adsorption steps on metal (2) in accordance with the Langmuir–Hinshelwood kinetic scheme which hinders the platinum participation in other processes than dehydrogenation–hydrogenation steps.

$$\begin{array}{rcll} C_nH_{2n+2} + 2\text{ free sites} & \rightleftharpoons & (C_nH_{2n+1})_{\mathrm{ads}} + H_{\mathrm{ads}} & (2) \\ (C_nH_{2n+1}) + 1\text{ free site} & \rightleftharpoons & (C_nH_{2n})_{\mathrm{ads}} + H_{\mathrm{ads}} & \text{metal} \\ 2H_{\mathrm{ads}} & \rightleftharpoons & H_2 + 2\text{ free sites} & \\ \hline C_nH_{2n+2} + 1\text{ free site} & \rightleftharpoons & (C_nH_{2n})_{\mathrm{ads}} + H_2 & \end{array}$$

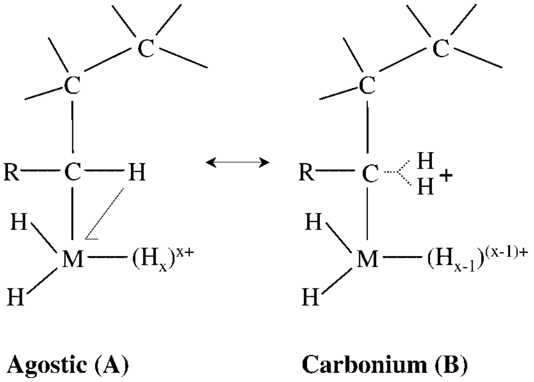
$$\begin{array}{rcll} (C_nH_{2n})_{\mathrm{ads}} + H^+ & \rightleftharpoons & (C_nH_{2n+1})^+ & \text{acid} \\ (C_nH_{2n+1})^+ & \rightleftharpoons & \text{isomers or cracked products} & \end{array}$$

However, investigations using isotopic molecules (D_2 or ^{13}C-labeled alkanes) showed that the first step of adsorption would rather be associative [39–41].

Now we are going to discuss the second point. First of all, if we compare the catalytic reactivity and selectivity of our catalysts to those already studied in the laboratory, we can notice the thresholds of reactivity for alumina-supported Pt, Pd or Ir catalysts, under the same experimental conditions as those used in this work (table 2). From this table 2 we can observe that low-loaded platinum, palladium and iridium will be unreactive for carbon–carbon bond breaking in a range of temperatures between 423 and 473 K. But we noticed that, even at a temperature where Pd, Ir and Pt are inactive *versus* carbon–carbon bond ruptures, we observed large differences in isomer selectivity values. At low conversion, $\alpha_{\mathrm{T}} \approx 20\%$, and at 423 K, the isomer selectivity values are around 70, 50 and 20%, respectively, on Pt/SZ, Pd/SZ and Ir/SZ. This point can be interpreted by a dual approach of the active site and of the adsorbed species. Therefore our results would suggest, firstly, the co-operation of a metal–acid site rather than the participation of two sites where the reactant and the products must undergo migration steps. Secondly, to reinforce this proposal, we will introduce the participation of metal–hydrogen interactions with



Scheme 2. Alkane adsorbed species on a metal–proton adduct site. Metal and acid participations are underlined.



Scheme 3. Schematic representation of the agostic species (**A**) and of the carbonium species (**B**) according to the reactions (3).

the C–H groups in the adsorbed phase. Transition metals Pt, Pd and Ir can interact with a nearby C–H bond to obtain a share in the C–H bonding electron pair. This interaction appears to arise between an electron-deficient metal centre and a C–H bond of an alkyl group [45,46]. In our case, we propose that surface atoms located at the corners or edges of the metallic aggregates, in strong interaction with the acid solid support, may bind to C–H groups to give M···H–C "hydrogen-bonding" type interactions in which, formally, the C–H group donates two electrons to the metal. The term "agostic" has been coined by Green [47]. The word "agostic" is used to refer specifically to situations in which a hydrogen atom is covalently bonded simultaneously to both a carbon atom and to a transition metal atom [47]. Taking into account the points raised above, we have presented the adsorbed species in scheme 2. We have pointed out the mutual participations and influences of the acid and of the metal in the reaction process. Now we can understand why the selectivity in isomers was different between Ir/SZ, Pd/SZ and Pt/SZ. The M···H–C interactions arise between an electron-deficient metal centre and a C–H bond of an alkyl group; hence, the electron withdrawing of iridium and palladium should be more important than from the platinum. In that case "partially" positive hydrocarbon entities will be formed, and, *via* β-scission reactions, more cracked products will appear on iridium and palladium than on platinum.

Then we propose that the active site is a metal–proton adduct $[(M_m)(H_x)^{x+}]$ (m being the number of Pt, Pd or Ir atoms in the metallic aggregates, and x the number of surface protons linked to Pt, Pd or Ir atoms) as suggested by Sachtler *et al.* [20,28]. This site has metallic and acidic functions. These adducts are able to act as "collapsed bifunctional sites"; then alkane isomerization is visualized taking place on such sites without the need of the intermediates to shuttle between metal and acid sites. All of the reaction steps can be achieved during a single residence of the molecule. In addition, the adsorption step is associative and, as these experiments are performed under an excess of hydrogen, we have some hydrogen atoms adsorbed on the metallic sites. The reactive site is then $[(H{-}M_m)(H_x)^{x+}]$. We suggest the following reactions (3):

$$\begin{aligned}
&C_nH_{2n+2} + [(H{-}M_m)(H_x)^{x+}] \rightleftharpoons [C_nH_{2n+3}]_M \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{agostic species } (\mathbf{A}) \\
&[C_nH_{2n+3}]_{\text{M participation}} \rightleftharpoons [C_nH_{2n+3}]^+_{\text{ACID participation}} \\
&\quad \text{agostic species} \qquad\qquad\quad \text{carbonium ion } (\mathbf{B}) \\
&[C_nH_{2n+3}]_{\text{ACID participation}} \\
&\quad \rightleftharpoons [C_nH_{2n+1}]^+_{(\text{M}-\text{ACID})\text{participation}} + H_2 \\
&[C_nH_{2n+1}]^+_{(\text{M}-\text{ACID})\text{ participation}} \\
&\quad \rightarrow \text{isomers or cracked products}
\end{aligned} \tag{3}$$

This equation (3) follows the Eley–Rideal kinetic model. We suggest (scheme 3) that an agostic species (**A**) is formed on the metallic part of the adduct site and that an equilibrium occurs between (**A**) and a carbonium ion (**B**) formed with the proton of the acidic part of the adduct site. Finally a carbenium ion is formed giving isomers and/or cracked products. Such agostic species $[C_nH_{2n+3}]_M$ were already suggested [48] to explain our results concerning the isomerization of 2-methylpentane on platinum–alumina catalyst.

5. Conclusion

The conversions of n-C_7, n-C_8 and n-C_9 molecules on Pt/SZ, Pd/SZ and Ir/SZ correspond mainly to cracking reactions at high conversions. On these solid acid catalysts the carbon chain length affects the reactivity. The n-heptane seems to be a "transition" molecule between the n-alkanes that predominantly isomerize, like n-C_4 to n-C_6, and the ones for which cracking reactions predominate, like those with more than seven carbon atoms.

The original variation of the catalytic activity of Pt/SZ, Pd/SZ and Ir/SZ with the reaction temperature is in contradiction with both the "traditional" bifunctional catalysis and the dissociative adsorption step. Our results are rather in favour of a metal–proton adduct model, in our case $[(H{-}M_m)(H_x)^{x+}]$, and an associative adsorption step. This adduct gathers together the metallic and the acidic sites. Moreover, the presence of an agostic species, as the adsorbed species, explains the difference in isomer selectivities observed on Ir/SZ, Pd/SZ and Pt/SZ when both metals are inactive in carbon–carbon bond rupture. In fact the

M···H–C interaction appears to arise between an electron-deficient metal center and a C–H bond of an alkyl group; and the electron withdrawing of Ir, Pd and Pt are different.

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