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New Perspectives for light alkanes isomerization.

Robert Hubaut*, Alain Rives, Wenxing Kuang and Michel Fournier

Laboratoire de Catalyse, UMR CNRS N° 8010, Bâtiment C3, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France;

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* Corresponding author:
Hubaut Robert,
Laboratoire de Catalyse, UMR CNRS N° 8010, Bâtiment C3, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France;
Phone number: 33/320434503
Fax number: 33/320436561
E-mail address: Robert.Hubaut@univ-lille1.fr

Running title: n-alkane isomerization on heteropolyacids

Abstract

Isomerization of n-alkane into the high-octane number branched alkanes is an important challenge for petroleum refining industry. According to the literature, such a transformation needs two different active centres, one of them having a hydrogenating/dehydrogenating ability and the other a protonic acid function. From this point of view, hetero-polyacids (HPAs) in mixing with one or more transition metal appear promising. Mechanical mixtures of alumina-supported platinum or of mixed palladium (or nickel)-cerium oxides and silica-supported HPAs have been realized and tested for the n-hexane isomerization. The solids were characterized before and after tests. Presence of Pt, Pd (or nickel) and Ce gives rise to a better activity and a higher selectivity for di-branched isomers than pure silica-supported HPAs and is really beneficial for retaining the Keggin structure. Although pure silica-supported HPAs have an initial activity, they are very easily to deactivate by coke deposition unlike the mechanical mixtures. The results are strongly depending on the composition of the mechanical mixtures. Roughly, the activity is in the same order as the acid strength. ^1H and ^{31}P solid-state NMR of trimethyl phosphine adsorbed on heteropolytungstate put in evidence the acid sites. It is noteworthy that the presence of metallic Pt or Pd (or Ni) metal after the reduction instead of the original Pd^{++} or (Ni^{++}) species reinforces the generally admitted mechanism with an activation of the alkane- difficult to obtain by direct attack by an acid (proton) - by the metallic species to the corresponding alkene before formation of a carbenium intermediate on the acid site. However, the formation of alkenes directly by the HPA and the participation of metallic species for limiting the alkenes concentration are not excluded.

Keywords: alkane isomerization, heteropolyacids, bi-functional mechanism

Introduction

The number of vehicles on the road for the next years is foreseen in huge expansion. From 700 million cars in 2000, the expected amount is 1 billion for 2010 and up to 2.5 billions for 2060 [1]. In order to bring down the atmospheric pollution, standards of gasoline are more and more drastic: absence of lead additives, decrease for the toxic air pollutants (TAP) including benzene, and decrease for the sulfur amount (<0.05 %). Such latter specification can be reached, nowadays, by the help of hydro treatment of the petroleum feedstock but also through n-paraffin, more particularly with five or six carbon atoms, isomerization into multi-branched isomers. Thus, isomerization of n-alkanes, which are abundant in light naphtas, into the high octane number di-branched alkanes is an important challenge for petroleum refining industry. Besides, this process presents two main advantages i.e. total absence of TAP and secondly increasing of the octane number. The research octane number (RON) and the motor octane number (MON) for some n-alkanes and iso-alkanes are presented on the table 1. For thermodynamically reasons, lower the temperature for the isomerization higher the amount for di-branched isomers. The most current commercial catalyst (namely platinum on chlorinated alumina) works at low temperature (473 K) but presents many drawbacks as easily poisoning and not eco-friendly behavior. Thus, numerous researchers try to replace this catalyst by strong acidic catalysts, with or without metallic species, such as MoO_3 [2, 3], WO_3 [4, 5], zirconia [6-9], Zeolites [10-15], or various solids acids [16-20]. Due to their unique physico-chemical properties, heteropolyacids (HPAs), combined or not with a metallic atom, are also potentially interesting

Table 1: RON and MON values for some alkanes [1]

	RON	MON
n-pentane	61.7	61.9
n-hexane	24.8	26.0
2-methyl butane	92.3	90.3
2,2-dimethyl propane	85.5	80.2
2-methyl pentane	73.4	73.5
3-methyl pentane	74.5	74.3
2,2-dimethyl butane	91.8	93.4
2,3-dimethyl butane	103.5	94.5

Moreover, by respect to the others solid acids, HPAs present a strong and unique ability to “molecular tuning” through their salts; in addition to that, they have an oxidizing potential. Since the pioneer works of Ono *et al* [21], the supported HPAs have much been used [22-36], either pure or in mixture with metallic species as describer hereafter. Our recent works on the using of HPAs as solid acids for n-hexane isomerization are synthesized in this review.

Experimental

Heteropolyacids, phosphotungstique acid – $H_3PW_{12}O_{40}$ - (HPW), silicotungstic acid - $H_4SiW_{12}O_{40}$ -(HSiW) and borotungstic acid - $H_5BW_{12}O_{40}$ - (HBW) were prepared in a classical way [37]. Silica-supported heteropolyacids were prepared by the wet impregnation method. The 1 wt. % Pt/Al_2O_3 sample was prepared by impregnating the γ-Al_2O_3 (100 $m^2.g^{-1}$) support with a solution of hexachloroplatinic acid as reported by Granger *et al* [38]. Ce-Ni oxides were prepared by the reverse homogeneous co-precipitation method as described in the literature [39] from Cerium nitrate Ce $(NO_3)_2.6H_2O$ (Prolabo Co) and nickel nitrate Ni $(NO_3)_2.6H_2O$ (Prolabo Co). The Ce-Pd oxides were prepared in the same manner from $Pd(NO_3)_2.6H_2O$ (Prolabo Co). The catalytic reactions were performed in a flow reactor (U-type glass) at 498 K for the Ni-Ce-O and Pt/Al_2O_3 containing samples and 553 K for the Pd-Ce-O containing samples respectively, under atmospheric pressure. The products were analyzed by gas chromatography with a SE-30 capillary column and a flame ionization detector. Chemical analysis of the samples was performed by the CNRS microanalysis centre using atomic absorption spectroscopy. The surface area measurements were performed on a Quantasorb Jr instrument (N_2 absorption at 77 K). X-Ray diffraction patterns were obtained in a Siemens D 5000 diffractometer with Cu K_α radiation. Thermogravimetric measurements were carried out in a Sartorius 4102 microbalance. Electron paramagnetic resonance spectra were recorded at 77 K and at room temperature on an EMX Brucker spectrometer. F.T.Raman spectra were taken with a Labram-Infinity spectrometer. I.R. spectra were obtained at room temperature using a Fourier transformed infra red (FT-IR) spectrometer (Nicolet Protected 460). NMR spectra were recorded at room temperature on a Bruker Advance ASX-400 spectrometer with a WVT triple resonance probe, with a 14 kHz spinning speed. Larmor frequency used for ^1H was 400.13 MHz and 161.97 MHz for ^{31}P.

Results and Discussion

The heteropolyacids (HPAs) with Keggin structure were chosen for two main reasons. The first one is their thermally stability at temperature used for isomerization reactions, and the second one is the less pronounced acidity [40], by respect to the other kinds of solid acids, which, if too strong, could lead to intensive cracking. Owing to their very low surface area (typically ~ 1or 2 $m^2.g^{-1}$), pure HPAs have a poor catalytic activity. Thus, supported HPAs appear more performing in their catalytic abilities [41]. Many supports have already been tested such as sulfated Zirconia [22-27], Zeolites [25], silica [24, 27-36]. Recently, Vedrine *et al* asserted that hexagonal silica is one of the best supports because it does not modify the catalytic activity and, thus, the acid properties of the HPA [27]. Moreover, the thermal stability of the phosphotungstic acid (HPW) was reported as enhanced when supported on silica [42]. That stability could be due to the hydrogen bonding of the protonated silanol groups in interaction with bridged oxygen atoms in the HPW structure [43]. The interaction is almost independent of the heteropolyacids content in a large range of concentration [31,32].

Surface areas

The surface area of pure silica (HNO_3 re-treated Aerosil 380 Degussa) is ~ 320 $m^2.g^{-1}$ with a large porosity. This surface area decreases drastically from 267 to 105 $m^2.g^{-1}$ when the HPW loading increases from 1 wt % up to 60 wt% (table2).

We note that the surface area per gram of silica remains almost unchanged. The particle size of HPW in the samples with 30-60 wt % loading calculated by XRD results using the Scherrer 's equation is c.a. 24-27 nm. Based on these results one can conclude that most of the HPW mainly exists as small crystalline particles and cannot totally block silica which has a remaining macroporosity. Thus, we can assume that the decrease in the surface area, probably results from the increase content of the non-porous component.

F.T Raman and Infra-Red spectroscopy

F.T.Raman of silica-supported HPW (figure 1) shows the characteristic HPW bands at around 1009 and 992 cm^{-1} [27, 44], their intensity increases with the HPA loading. For the higher loading (c.a.50-60 wt %) we observe a broad peak at 905 cm^{-1} which can implies a relatively large crystalline particles distribution. After reduction at 498 K for 4h no new peak appears and the characteristic bands never totally disappear. Contrarily, after the reaction, the bands assigned to the heteropolyacids totally disappear, probably because the surface of the samples is covered by coke deposition. This coke deposition would be the cause of the activity deactivation as explained hereafter. In presence of a metallic component, as reduced CeNi oxide, the bands assigned to HPW does not disappear indicating that the surface structure of silica-supported heteropolyacids is maintained during the reaction.

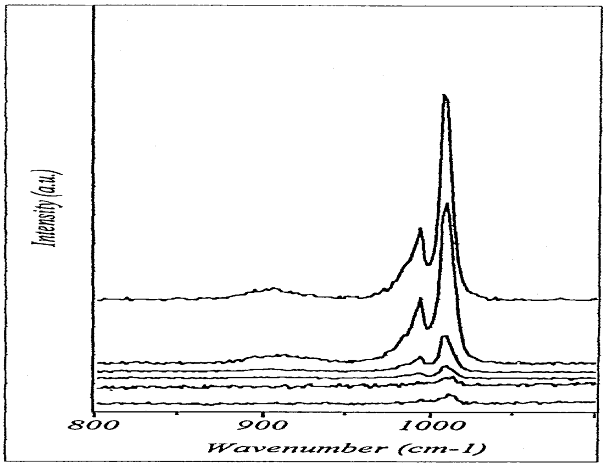

Figure 1: FT-Raman of silica-supported HPW samples after treatment at 383 K under vacuum with different loading (the samples from bottom to top are, respectively, with 10, 20, 30, 40, 50 and 60 wt % loading).

All these observations remain valid for the other heteropolyacids used such as silicotungstic acid (HSiW) [45, 46] and borotungstic acid (HBW) [46].

A complete study in infra-red spectroscopy presents similar kind of results and leads to the same conclusions. If numerous I.R. spectra of pure silica-supported HPA exist in the literature, few spectra of these HPA after reaction are reported [25, 34]. In our works, the spectrum of pure silica presents a broad and strong band at 1100 cm^{-1} and a strong band at 806 cm^{-1}. A weak shoulder attributed to the surface OH groups [47] evidenced by ^{1}H solid state NMR [48] is visible at 974 cm^{-1}. On pure HPW, four strong bands (c.a. 1079, 983, 893 and 810 cm^{-1}) can be respectively assigned to the typical anti-symmetrical stretching vibration of P-O, W-O and W-O-W [31]. On the silica-supported solid, (figure 2-A), we observe, before treatment, two bands at 982 and 893 cm^{-1} and a slight overlapping of the two other bands with those of silica. The spectra of the mechanical mixtures with the mixed oxides are identical to the pure supported one. Concerning the silicotungstic acid, we observe, for the pure HSiW, four strong bands around 978, 924, 879 and 783 cm^{-1} respectively assigned to the typical anti symmetrical stretching vibration of W-O, Si-O and W-O-W. Three bands at 980, 927 and 878 cm^{-1} are visible for HSiW/SiO_2 and the mechanical mixtures (figure 2-B) , two broads lines at 1102 and 795 cm^{-1} resulting from the overlapping with bands of silica are also visible. We do observe any change neither after reduction nor after reaction. These results confirm that the Keggin structure is kept. This keeping of the structure was also indicated by Essayem *et al* [25] who, working with the ammonium salts of HPW, show that the I.R. spectra of the fresh and used ammonium salts have always the vibrations due to the Keggin unit and conclude that the deactivation with the time on stream, observed in alkane isomerization on the Pt-free catalysts, is not caused by a structural modification of the heteropolyacids. Okuhara *et al* [34] shown ,for their part, that I.R. spectra of the used Pd-20wt% $H_4SiW_{12}O_{40}/SiO_2$, prepared by successive impregnation, also give the peaks relative to the Keggin structure with a similar shape and intensity of those of the fresh solids. In our works, infra-red spectroscopy relative to HSiW/SiO_2 gives one another important information: there is absence of characteristic Si-O band at 925 cm^{-1} on the solid after test, that means phosphorus as central atom is not replaced by silicon from silica as proposed in the literature [49].

NMR results

MAS-NMR is a powerful tool to obtain some information about the interaction of the active catalyst and its support. ^{1}H MAS NMR and ^{31}P MAS NMR spectra were recorded for pure and silica-supported HPW [43]. The observed shift at about -15.3 ppm for ^{31}P MAS NMR of the “wet” silica-supported HPW is due to the HPA. This band can be decomposed in two lines. The former being due to the bulk HPA while the latter is due to the more or less hydrated species without interaction with the support

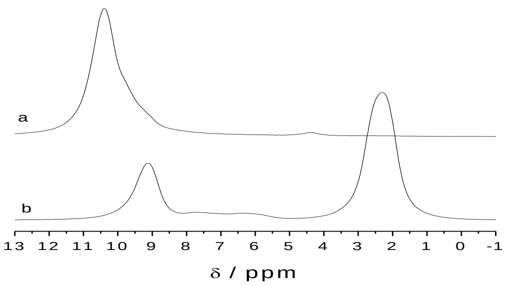

Figure 3-A: ^{1}H MAS NMR spectra of
a) $H_3PW_{12}O_{40}$ b) TMP adsorbed on
$H_3PW_{12}O_{40}$

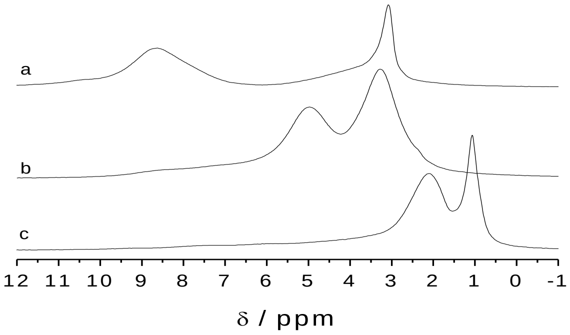

Figure 3-B: ^{1}H MAS NMR spectra of:
a) 20 wt%HPW/SiO_2
b) + TMP weakly adsorbed
c) + TMP saturated

Thus, without care, the silica-supported HPW balance between a bulk-like state and a quasi-liquid state without interaction with the support. On the contrary, the samples kept under inert atmosphere show a band at -11.8 ppm attributed to dry dispersed species with strong interaction between HPW and the silanol groups of silica. For measuring the acidity of HPA, adsorption of trilmethyl phosphine (TMP) on the solid acids-technique which has been extensively studied but not on HPAs- was used [48]. The ^{1}H NMR spectrum of pure fully dehydrated HPW shows an intense resonance at 10.4 ppm, characteristic of the proton linked to the bridging oxygen atoms of the anhydrous HPW [50]. TMP adsorbed on HPW gives rise to a peak at 2.35 ppm attributed to interaction between TMP and HPW (figure 3-A). A peak located at 9.15 ppm is attributed to a weak acidity of HPW which is revealed by TMP forming trimethyl phosphonium ($TMPH^+$) at 6.36 ppm. This is confirmed by ^{31}P NMR spectrum with a peak at -2 ppm which was previously assigned to $TMPH^+$ [51]. For the 20 wt % HPW/SiO_2, (figure 3-B), ^1H NMR spectrum shows a peak at 3.10 ppm due to the remaining silanol groups linked by hydrogen bond and a second broad peak located at 8.65 ppm which can be attributed to the hydrated protons of HPW. We note that the peak at 1.85 ppm of pure silica, assigned to isolated silanol groups hardly joined by water molecules [52], totally disappear. Thus, HPW interacts with the most basic groups of silica and is in a semi-liquid phase.

n-hexane isomerization

Despite the advantages of silica, there are two drawbacks for using pure silica-supported HPAs. The first one is the rapid poisoning of the catalyst on time [31]. The table 3 displays one example of such a deactivation for the n-hexane isomerization on the 40 wt % HPW/SiO_2. The conversion of sample with 10, 20, 30, 40, 50 and 60 wt % loading respectively decreases to 0.8, 1.3, 3.6, 4.4, 5.7 and 5.6 after 22 minutes of reaction time and, in the same time, the selectivity of all silica-supported HPW samples drops to 75-79 %. Thus, the acid sites on phosphotungstic acid surface are easily deactivated. Besides, we observe after reaction an E.P.R signal at 2.0008 G which can be assigned to the coke deposition [53]. However, there is no obvious difference between the infra-red spectra of the sample before and after the reaction (see the spectroscopy part) suggesting that the structure of silica-supported HPW is relatively preserved. The protection of HPW on silica has also been reported by Ponzi *et al* [54].

The second drawback is the low conversion obtained in the first minutes whatever the HPA loading and the central atom (table 4), in contrast with the results observed in presence of metal component (see hereafter). As we can see table 4, the isomerization selectivity decreases when the HPA loading increases and is better on HPW than on HSiW. Nevertheless, it is interesting to note that, even in absence of promoter, silica-supported HPAs have initial activity. The selectivity for the isomerization always remains higher than for cracking and the main products are methylpentanes (MP) and dimethylbutanes (DMB) while the main cracking products are isopentane and isobutane.

It was previously proposed by Travers *et al* [55] that the discrimination between the two mechanisms generally admitted for n-alkane isomerization, c.a. mono-functional acid mechanism and the bi-functional metal-acid mechanism can be made on the basis of kinetic data, reaction order and isomerization selectivity. According to these authors, the mono-functional mechanism would lead to only 2-2 DMB as secondary products while the bi-functional one could lead to 2-2 DMB and 2-3 DMB. In our case, we obtain the two isomers in absence of metal. Probably the mechanism of isomerization is not that simple. Ono [56] proposes that the alkanes are activated by the acid species; the metal component, even though its positive effect is obvious, mainly stabilizes the catalytic activity reducing the concentration of alkenes by the help of its hydrogenating power. We do not totally agree with these authors because, if pure silica-supported HPA are effectively active, the results displayed hereafter show the important improvement in presence of a metal component. We think that a small part of the intermediate alkene comes from HPA which is capable to form this organic compound by a one-electron oxidation step while the main part is due to the metal component if it is present. The mechanism of alkenes formation by a one-electron oxidation step has been proposed by Farcasiu and Lee [57]. Anyway, whatever the real mechanism, it is obvious that the presence of a metal component strongly is beneficial for both activity and selectivity for the isomerization of alkanes. As the current commercial process is platinum-based, numerous authors choose this metal [22-26, 45, 58-62]. We have to notice that, in our experimental conditions, no products were detected with the pure 1wt% Pt/Al_2O_3. As expected, promotion of HPA/SiO_2 by 1 wt% Pt/Al_2O_3 has a remarkable impact on the properties and the stability of the catalyst. The table 5 displays the results obtained with various silica-supported HPAs loading. By comparing with the same solid without platinum (table4), the selectivity is now close to 100% and the conversion is strongly improved. If we focus on the 50 wt% HPAs, the activity is improved by a factor 2 for HPW, 3 for HsiW and up to 20 for HBW.

Clearly, the addition of platinum is tremendously efficient for promoting heteropolyacids. The figure 4 shows the excellent stability on time of the catalyst and we can see that the initial activity of HSiW is even increased in such a manner that, finally, the conversion follows the order: HSiW > HPW > HBW which is not consistent with the order of their acid strength as usually claimed in the literature [44]. The change in the conversion on the three different HPAs could come from the different behavior of surface reactive species during reaction.

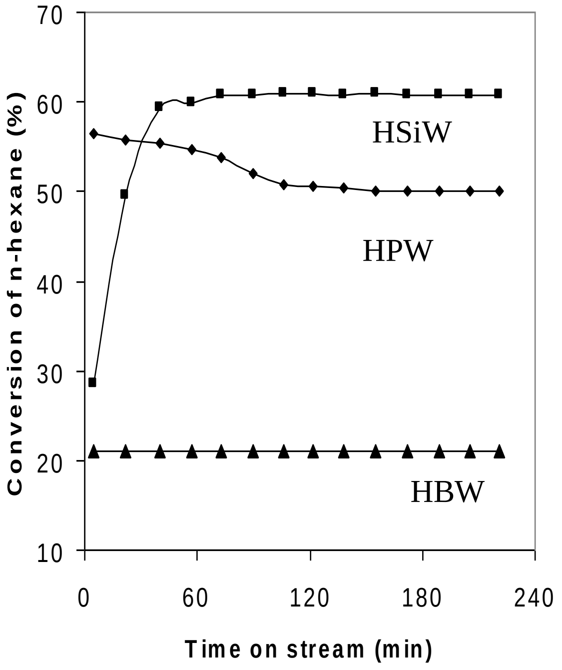

Fig. 4 Conversion of n-hexane over
[50wt % HPA/SiO_2] promoted by 1 wt % Pt/Al_2O_3.

The F.T. Raman spectra (figure 5) indicates that the presence of platinum allows to keep the intensities of the bands associated with HSiW in a best manner that with the two others HPAs. Thus, in presence of Pt, HSiW is the best sample for keeping the surface structure of HPA and its surface acid strength.

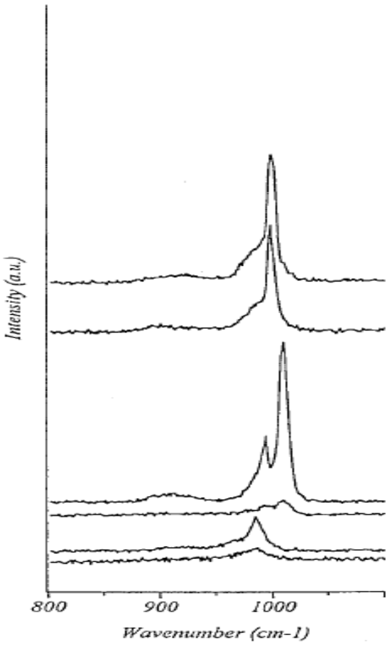

Figure 5: FT-Raman spectra of, respectively
(from top to bottom): 50 wt % $HSiW/SiO_2$,
50 wt % $HSiW/SiO_2$ promoted by 1wt % Pt/Al_2O_3 after reaction,
50 wt % $HSiW/SiO_2$,
50 wt % $HSiW/SiO_2$ promoted by 1wt % Pt/Al_2O_3 after reaction
50 wt % $HSiW/SiO_2$,
50 wt % $HSiW/SiO_2$ promoted by 1wt % Pt/Al_2O_3after reaction

These beneficial effect of Pt on HPA or their alkali salts have also been evidenced in skeletal isomerization of n-butane [23,58,59,62], n-pentane [25,26,60], n-hexane [22,26,55,61] and n-heptane [24,61] but the explanation is still matter of debate. Timofeeva *et al* [22] propose, in the case of Pt-HPW/ZrO_2 a partially distorted grafted Keggin ion, Ono [56] assumes that the metal dissociates H_2 to form H atoms which, in turn, react with heteropolyanion to form proton and reduced form of the anion. However, numerous authors agree with a bi-functional metal-acid mechanism in which olefin is formed by dehydrogenation of the paraffin on the metal component and secondly protonation to lead to a carbocation on an acid site. The carbocation, at last, is the seat of either cracking or isomerization [55]. This mechanism is rejected by Lunsford *et al* [63], at least on Pt/H-β Zeolites, who propose a mechanism in which the acid sites are mainly responsible for isomerization via a cyclic reaction. The role of Platinum would only be to keep the local alkenes concentration small by hydrogenation. We can remark that, in our experimental conditions, no alkenes were detected. Moreover, it is well known that double bond migration is very common during the hydrogenation of olefins. Catalysts differ widely in the extent in which they affect this double bond migration [64]. The order for the double bond migration is: palladium > nickel >> rhodium ~ ruthenium > osmium ~ iridium ~ platinum. So, in the case where the metal component is present only to hydrogenate the alkenes and that this step is not too rapid, the using of various metals could drive to different products distributions. Palladium [21,33,34,65,66] and nickel [46,67] have already been tested in some metal-HPA mixtures for alkane isomerization. Perez-Luna *et al* [67] worked on a series of catalysts with various nickel concentrations on sulfated zirconia and found that the catalytic activity and the 2,3-DMB selectivity seem to be correlated with the NiO well dispersed phase rather than with their acidic properties. This result is in favor of the bi-functional mechanism. This mechanism is also favored by Okuhara *et al* for the skeletal isomerization of n-pentane [24] and n-heptane [33] on Pd-$H_4SiW_{12}O_{40}$ supported on silica. Ono *et al* [21] were the first to incorporate palladium as metallic species to prevent destruction of the Keggin structure. In some cases, a third component was added to more improve the protection of the heteropolyacids [20,46,66,68]. We had previously shown that cerium is able to prevent the poisoning of metals during some hydrogen treatments [69]. The only presence of cerium does not play an important role in term of activity but acts as a powerful tool for protecting Pd (Ni) by the help of its Ce^{4+}/Ce^{3+} Red-Ox system which imposes the rate of the reducibility of the Pd (Ni) ion during the reaction. As a proof, we note a slight decrease on time for the conversion in absence of cerium in our experimental conditions. This is the reason why we introduce cerium in a mixed oxide with palladium or nickel (these solids are called Pd_xCeO or Ni_xCeO where x is the atomic ratio Pd(Ni)/Ce). We can notice that the conversion is very weak on pure mixed palladium(nickel)-cerium oxide. The best mechanical mixture of mixed oxide and HPA which leads to the highest conversion and the optimal amount of di-branched isomers (DC6) is constituted of 50% $Pd_{0.1}CeO$ and 50% of (20 wt % HPW/SiO_2) (table 6). On these mechanical mixtures, the order of the reactivity is in the range usually admitted of the acid strength. The fifty-fifty mixture is probably the one which provides the maximum of close vicinity between the metallic species and the acid sites. Strangely, the co-impregnated catalysts give rise to very similar results [70] indicating that it is unlikely that the metal species acts only as a promoter of the acid sites but more probably as active sites itself either through bi-functional mechanism or by the help of its hydrogenating power (control of the alkene concentration).

These interesting results lead us to prepare directly some palladium salts of HPA with the Keggin structure [71] and these salts will be tested later. At this point of our discussion, we can do two remarks : i) the maximum of conversion obtained in presence of Pd is not so far from the one obtained in presence of platinum although the preparation are different (c.a. 65.7 of conversion on the [30 % $Pd_{0.1}CeO$ - 70 % $HPW^{/}SiO_2$] and 61 % on the [50 wt % $HSiW/SiO_2$ promoted by 1 wt % Pt/Al_2O_3]) ii) the C6 isomers are not in equilibrium with each other (thermodynamic equilibrium concentrations at 523 K : 2,2-DMB= 38.8%, 2,3-DMB =10%, 2-MP = 25%, 3-MP = 12.9% and n-hexane = 13.3% [72]. That is to say, in absence of n-hexane, a DC6/TC6 ratio of ~ 56%. The variation of the Pd/Ce atomic ratio does not bring any improvement neither for the activity nor for the DC6/TC6 ratio (table 7).

A similar study of the mechanical mixtures of silica-supported HPA and mixed Ce-Ni oxide leads to the same conclusions. The table 8 shows the strong influence of the composition on both the conversion and the isomerization selectivity; with 20 wt% HPW/SiO_2, the conversion reaches a maximum value for 30 % of mixed Ce-Ni oxide but the selectivity decreases continuously from ~ 92% to ~ 4% as the amount of the mixed oxide increases. The pure reduced Ni-Ce oxide leads to 92 % of cracking.

On the 50 wt % HPA/SiO_2 we observe similar results (maximum of conversion for 30 % of CeNi oxide) and the reactivity is one more time in the range of the proposed acid strength (HPW > HSiW > HBW) (table 9). For a better understanding of the role of each species, we plotted the n-hexane conversion versus the Ni/(Ni+W) (figure 5a) and Pd/(Pd+W) (figure 5b) atomic ratio. This latter ratio might be really representative of the metallic sites/ acidic sites relative amount and consequently of the magnitude of the synergy phenomenon and in the case of a pure bi-functional mechanism, representative of the hydrogenating-dehydrogenating power versus the isomerization ability.

As we can see, for the mechanical mixtures (figures 5) the highest conversion is reached for about 66% moles of nickel by respect to the total (Ni+W) amount, that is to say 2 moles of nickel per moles of W while the best conversion is obtained with 40% moles of Pd by respect to the total (Pd+W) amount that is to say 0.66 mole of Pd per mole of W. The product distributions and more particularly the DC6/TC6 ratio obtained for the different cases are not enough different to choose a particular mechanism and probably as previously proposed by Travers *et al* [55], on the mechanical mixtures, able to provide bi-functional mechanism, the reaction proceeds through the two possible mechanisms: the mono-functional acid mechanism and the bi-functional one.

This latter is more or less important depending on the proximity of the two kinds of active sites. Thus, the improvement of the preparation method remains preponderant and the Pt (Pd) HPA salts can have a great importance.

Conclusion

The current commercial process used for n-alkane isomerization is not eco-friendly. Many researches are in progress to replace the chlorinated alumina supported platinum by solid acid. Sulfated zirconia and Zeolites are interesting but heteropolyacids (HPAs) have a conclusive advantage which is the possibility to accurately tune the acidity through their salts. The numerous examples presented in this review show the interesting potentiality of HPAs as acid catalysts for n-paraffin isomerization. The mechanical mixtures of single (Pt/Al_2O_3) or mixed oxides (Ce-NiO, Pd-CeO) are promising catalysts. They stabilize the catalytic properties of the HPAs which are easily poisoned by coke deposition during the reaction. They maintain the Keggin structure as indicated by the F.T.-Raman and infra-red spectra, and they increase noticeably the activity and the isomerization selectivity compared to pure silica-supported HPAs. In presence of metallic species, the isomerization selectivity is close to 100% deleting quasi totally the cracking. Concerning the dibranched alkanes which are the most interesting products, their amount is not very high but is like the ones obtained with others kinds of solid acids (selectivity of about 15-20 %). The results obtained on our solids are in agreement with the bi-functional mechanism which needs a metallic centre for the dehydrogenation of the alkane in alkene, and the hydrogenation of the alkene after isomerization on the acidic centre. However, we cannot exclude that HPAs also form alkene by a one-electron process while the metallic active sites limit the olefin concentration. For the bi-functional mechanism, the direct preparation of Pd or Pt salt of HPA may be will allow avoiding the mechanical mixtures and will lead to an optimum proximity of the active sites.

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Table 2: Structure of various samples dried at 383K under vacuum

Samples	Surface area $m^2.g^{-1}$	Particle size nm [a]	Average pore Diameter (Å)
Silica	320	-	176
5wt % HPW/SiO_2	286	n.d	173
10wt % HPW/SiO_2	267	n.d	177
30 wt % HPW/SiO_2	192	24.3	200
40 wt % HPW/SiO_2	150	26.0	
50 wt % HPW/SiO_2	124	27.0	213
60 wt % HPW/SiO_2	105	27.6	-
50 wt % HSiW/SiO_2	111	-	-
50 wt % HBW/SiO_2	115	-	-

a: Calculated by XRD results

Table 3: Isomerization of n-hexane: %conversion over 40 wt % HPW/SiO_2 on stream at 498K

Sample	Time on stream (min)				
	5	22	40	57	75
Methane	-	-	-	-	-
Ethane	-	-	-	-	-
Propane	4.7	3.0	4.3	3.5	4.0
Butane	1.0	2.5	2.0	3.5	1.8
Isobutane	16.4	7.9	7.5	7.4	8.0
Pentane	2.2	1.8	1.7	3.9	2.0
Isopentane	12.4	6.6	5.9	2.8	4.8
2,2-Dimethylbutane	2.9	3.2	2.2	3.1	1.6
2,3-Dimethylbutane	8.4	9.3	9.0	8.2	7.8
2-Methylpentane	32.7	40.3	40.9	39.5	39.8
3-Methylpentane	19.3	25.4	26.5	28.1	30.2
Conversion (%)	17.3	4.4	3.1	2.6	2.2
Isomerization (%)	63.3	78.2	78.6	78.9	79.4
Cracking (%)	36.7	21.8	21.4	21.1	20.6

Note: dash indicates trace amount

Table 4: reactivity of pure silica-supported HPA after 5 min on stream at 498K

catalyst		Conversion %	Isomerization selectivity	2MP (%)	3MP (%)	2,2DMB (%)	2,3DMB (%)	DC6/TC6
HPW /SiO_2	Loading wt%							
	10	3.7	78	39.8	25.5	3	9.4	15.9
	20	5.6	76.7	40	24.7	2.2	9.8	15.6
	30	16.6	68	30	18.2	2.4	7.9	17
	40	17.3	63.3	32.7	19.3	2.8	8.4	18
	50	28	55.9	33.5	17.4	2.7	2.3	9
	60	29	52.1	26.1	15.8	2.8	7.4	19.6
HSiW /SiO_2	50	21	39.8	20.7	12.6	1.9	4.6	16.3
HBW /SiO_2	50	1	17.8	13.7	-	4.1	-	23

Table 5: reactivity of silica-supported HPA promoted by 1 wt % Pt/Al_2O_3 (1:1 ratio in weight) at 498K (stationary state)

Catalyst : HPA/SiO_2 + Pt 1w t%		Conversion %	Isomerization selectivity	2MP (%)	3MP (%)	2,2DMB (%)	2,3DMB (%)	DC6/TC6
HPW /SiO_2	Loading wt%							
	10	9.8	99.5	54.2	38.5	0.6	6.2	6.8
	20	25.2	99.5	55.4	35.1	1.1	7.9	9
	30	37.7	99.5	54.7	34	1.6	9.2	10.8
	40	46.6	99.3	53.1	32.6	2.6	11	13.7
	50	50.1	99.2	52.6	32.2	2.8	11.6	14.5
	60	46.1	98.9	52.7	32.1	2.6	11.5	14.3
HSiW /SiO_2	50	61	99.3	52.5	32	3.6	11.2	14.9
HBW /SiO_2	50	21	99.6	55.9	35.3	1.3	7.1	8.4

Table 6: Catalytic properties of various Pd-based catalysts

catalyst		Conversion (%)	Isomerization Selectivity (%)	DC6/TC6 (%)
$Pd_{0.1}CeO$		0.5	37.7	1.6
Mechanical mixtures Y % $Pd_{0.1}CeO$ + (100-Y) % (20wt % HPW/SiO_2)	Y %			
	25	20.8	98.9	6.8
	40	47.8	98.5	13.3
	50	56.2	98.2	14.4
	60	48.7	98.5	13.5
	75	5.7	93.7	4.3
Co-impregnation/SiO_2 Y % $Pd_{0.1}CeO$ + (100-Y) % 20wt % HPW	20	23.5	98.7	7.8
	30	65.7	96.3	16.6
	40	59.3	96	16.4
	50	49	92.3	15
	60	33.6	93.6	13.6
50 % $Pd_{0.1}CeO$ + 50 % (20 wt % HSiW/SiO_2)		47	99.3	11.6

Table 7 Effect of the Pd/Ce ratio on the catalytic properties of mechanical mixture with HPW/SiO_2

Catalyst*	Conversion (%)	Isomerization Selectivity (%)	DC6/Tc6 (%)
X (Pd_xCeO)			
0	13.3**	93.2	14
0.05	26.4	99.2	9.5
0.1	56.2	98.2	14.4
0.15	49.8	98.6	11.1
0.2	39	98.9	8.9

* mixture of 50 wt % Pd_xCeO – 50 % (20 wt % HPW/SiO_2)

** conversion after few minutes

Table 8: Catalytic properties of mechanical mixture of Ce_1NiO and 20 wt % HPW/SiO_2

Catalyst		Conversion (%)	Isomerization Selectivity (%)	DC6/Tc6 (%)
Mechanical mixtures Y % Ni_1CeO + (100-Y) % (20wt % HPW/SiO_2)	Y			
	2.5	2.4	91.8	19
	5	5.9	88.7	18
	10	14.5	86.7	17
	20	19	87.3	15
	30	21.9	80.4	11
	40	20.6	76.6	11
	50	16.9	50.4	9
	60	14	41.6	4
	80	10.2	3.2	0
	100	14.2	3.8	0

Table _9: Catalytic properties of mechanical mixture of CeNiO and [50 wt % HPA/SiO_2]

Catalyst (mechanical mixtures)		Conversion (%)	Isomerization Selectivity (%)	DC6/TC6 (%)
Y % Ni_1CeO + (100-Y) % (50wt % HPW/SiO_2)	Y			
	20	27.8	91.2	17.9
	30	34.2	86.7	18
	40	31.6	84.3	17.4
20 % Ni_1CeO + 80 % (50wt % HSiW/SiO_2)		23.3	94.2	13.1
20 % Ni_1CeO + 80 % (50wt % HBW/SiO_2)		2.1	67	8

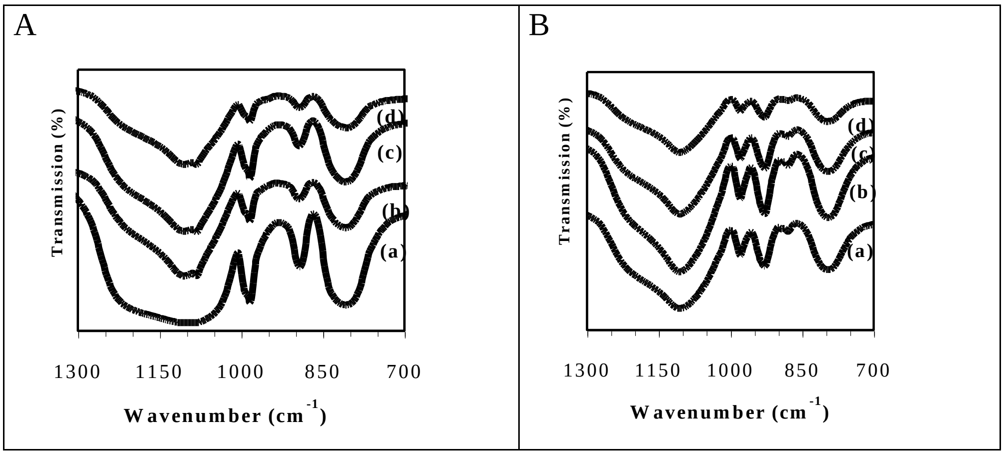
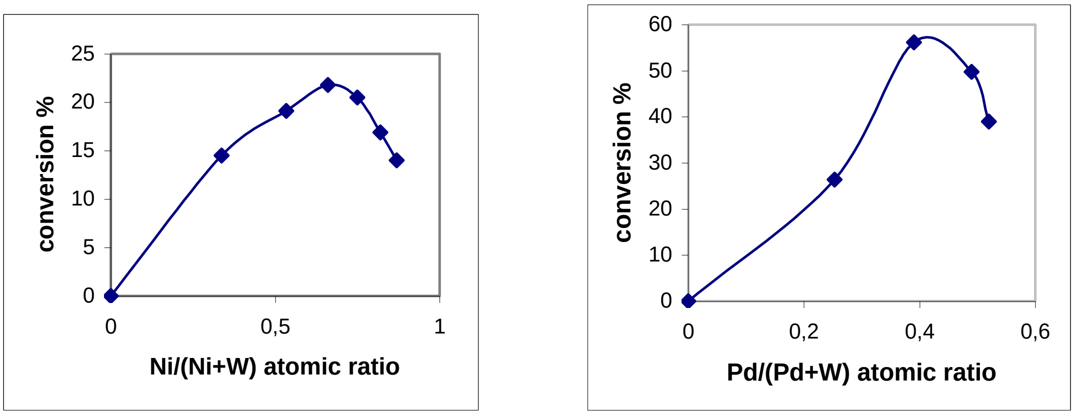


Figure 2: FT-IR spectra of various samples containing:

A- (a) 20wt% HPW/SiO_2,(b) 20wt% HPW/SiO_2 after reduction, **(c)** 20wt%HPW/SiO_2 after reaction and **(d)** mechanical mixture of 50wt% $Pd_{0.1}Ce$ and 50wt% [20wt% HPW/SiO_2] after reaction.

B - (a) 20wt% HSiW/SiO_2, **(b)** 20wt% HSiW/SiO_2 after reduction, **(c)** 20wt% HSiW/SiO_2 after reaction and **(d)** mechanical mixture of 50wt% $Pd_{0.1}Ce$ and 50wt% [20wt% HSiW/SiO_2] after reaction.



5a 5b

Figure5. n-hexane isomerization conversion versus the tungsten content in the mechanical mixtures of MeCeO-HPW/SiO_2 (1a: Ni_1CeO-20wt%HPW/SiO_2; 1b: $Pd_{0.1}$CeO-20wt%HPW)