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Heteropolyanions based catalysts for paraffins isomerization

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Abstract

n-Hexane isomerization was carried over $Cs_xH_{3-x}PW_{12}O_{40}$ catalysts promoted with Pt by mechanical mixing with a Pt on alumina catalyst. Different parameters as caesium and platinum content in the catalyst, temperature and atmosphere of heteropolyacids pre-treatment were optimized. The catalytic performances of the best catalyst were compared with those of industrial Pt promoted mordenite. 0.3 wt.% Pt-promoted $Cs_2H_1PW_{12}O_{40}$ pre-treated under hydrogen flow at 473 K showed the highest conversion and selectivity. Its performances are very close to those of the industrial zeolitic catalyst in the same reaction conditions. The gain in dibranched isomers selectivity is really promising for the future. With this catalyst, the reaction proceeds by a non-ideal bifunctional mechanism resulting from the superposition of a monofunctional acid and a bifunctional metal–acid mechanism. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Caesium salts; Heteropolyanions; Paraffins; Isomerization

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1. Introduction

Paraffins isomerization is an important reaction in the frame of lead additive suppression and benzene reduction in gasoline. It allows to transform low octane *n*-paraffins, especially with five or six carbon atoms, into high octane *iso*-paraffins. For example, *n*-hexane (RON = 24.8) can be isomerized into monobranched (RON $\sim$ 74) and preferentially dibranched (RON $\sim$ 100) isomers. From a thermodynamical point of view, the formation of high octane dibranched isomers is favoured at low temperature. Consequently, the best isomerization catalysts will be strong acidic catalysts able to work at the lowest possible temperature.

Two types of catalysts are generally used in industrial processes:

- Pt on chlorinated alumina catalysts, which are very active at low temperature: 423 K. However, they are very sensitive to poisons like water, oxygen, organic nitrogen and sulphur. Moreover, the process requires a continuous addition of chloride precursor to the feed, which presents a major drawback.
- Pt on mordenite less active than the previous ones: they are operated at 523 K due to a lower acid strength. However, unlike Pt/chlorinated alumina, they are resistant to poisons.

For the future, an important challenge for the refiners is to develop new catalysts, resistant to poisons, environmental friendly, and giving in the best case, the same performances as industrial Pt on chlorinated alumina catalyst or at least intermediate performances between zeolitic and chlorinated ones.

With this aim in view, very strong solid acids as sulphated zirconia or heteropolyacids are potential candidates for hydroisomerization of alkanes. Both catalytic systems are able to isomerize alkane at low temperature, however, in the absence of a metallic function, these catalysts suffer from a strong deactivation. Metal promoted sulphated zirconia has been largely developed for alkane isomerization:

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conversions of light linear alkanes such as *n*-butane, *n*-pentane and *n*-hexane [1–5] have been investigated as well as those of higher alkanes [5–7]. Iglesia [5] reported that sulphated zirconia promoted with Pt catalyses *n*-hexane isomerization at temperatures lower than Pt/mordenite. However, the proportion of dibranched isomers remains low compared to that expected from the thermodynamic equilibrium [2,3,5]. For *n*-heptane and higher alkanes, high cracking selectivities are reported [5].

The major drawback of these materials seems to be the sulphur poisoning of the Pt function as shown by several groups [2,4–6,8]. Anyway, it must be stressed that in most cases a non-ideal bifunctional mechanism was observed, described as a consequence of the Pt poisoning by sulphur [6].

Other materials like heteropolyacids combined with a metallic function have been investigated for light alkane isomerization, namely n-C_4 and n-C_6.

To our knowledge, the pioneering studies related to these systems are those of Ono and co-workers [9,10] on palladium and silver salts of 12-tungstophosphoric acid. More recently, the acidic caesium salts of $H_3PW_{12}O_{40}$ promoted by Pt or Pd have been investigated by Misono [11,12] in skeletal isomerization of *n*-butane. A significant limitation of the catalyst deactivation was reported as regard to metal free heteropolyacids.

In the absence of metallic sites, acidic caesium salts are active in the conversion of different light alkanes as n-C_4 and n-C_6 and also in propane conversion but in a less extent [13], their rates of transformation depending strongly on their Cs content, therefore on their acid strength and/or on their protonic density. Compared to the mordenite catalysts, heteropolyacid catalysts are more active in n-C_3 and n-C_4 conversions, whereas the zeolitic material is the most active catalyst for *n*-hexane isomerization at 523 K, the rate remaining in the same order of magnitude.

The objectives of the present study were to investigate the potentialities of bifunctional Pt/heteropolyacid materials in *n*-hexane isomerization. In this work, heteropolyanions based catalysts, and particularly caesium salts of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) were prepared, evaluated in *n*-hexane isomerization and compared to our industrial reference Pt on mordenite catalyst.

2. Experimental

The caesium salt $Cs_3PW_{12}O_{40}$ was first prepared by precipitation in aqueous solution starting from a commercial $H_3PW_{12}O_{40}\cdot nH_2O$ and CsCl in stoichiometric ratio. CsCl solution (5 M) is added dropwise to an aqueous solution (0.1 M) of $H_3PW_{12}O_{40}$ under strong stirring. The resulting white colloidal solution was kept overnight at ambient temperature under stirring and then the precipitate was separated from the liquid phase by centrifugation [14]. The solid was finally dried at 110°C.

$Cs_xH_{3-x}PW_{12}O_{40}$ was prepared by mechanical mixing of $Cs_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}\cdot nH_2O$, in stoichiometric amount, following the procedure described previously [15] and pre-treated at different temperatures under various atmospheres (nitrogen, hydrogen, and air).

Platinum was then introduced in the acid catalyst ($Cs_xH_{3-x}PW_{12}O_{40}$) by mechanical mixing under inert atmosphere with a pre-reduced Pt on alumina catalyst.

Isomerization of *n*-hexane was performed in a fixed bed micro-reactor in the following conditions: total pressure $= 4$ bar, temperature ranging from 180 to 220°C, weight hourly space velocity $= 1.5\,h^{-1}$, molar hydrogen to *n*-hexane ratio $= 10$.

3. Results and discussion

First, the influences on the catalytic performances of the caesium and Pt content in the HPA, the temperature and the atmosphere of pre-treatment were successively considered. Then, the reaction mechanism was studied over the best catalyst. Finally, the optimized heteropolyanion based catalyst was compared with the industrial Pt on mordenite catalyst.

3.1. *Influence of the Cs content*

In a previous investigation, we have shown the possibility to prepare acidic caesium salts with improved catalytic performances in n-C_4 isomerization by a simple mechanical mixture of $Cs_3PW_{12}O_{40}$ with hydrated 12-tungstophosphoric acid [15]. Unlike the classical acidic salts obtained by precipitation in aqueous

Table 1
Influence of the Cs content

Cs/P	n-C_6 conversion (%)	Isomerization selectivity (%)	Dibranched selectivity (%)	S(BET) (m^2/g)	Microporous volume (cm^3/g)	VPT (cm^3/g)	B/L
1.5	6.3	84	13	60	0.0077	0.05	4.8
2	29.8	92	17	100	0.012	0.08	6
2.5	7.7	86	13	138	0.0093	0.13	1

solution [14] where the BET surface area (S), the pore size and the proton content are highly connected, the former preparation leads to catalysts with the highest superficial acidity. Hence, materials with more than 1.5 Cs atom per Keggin unit still exhibit BET surface area equal to 60 m^2/g. Such a result is not expected from the preparation in aqueous solution.

Here, acidic caesium salts with different Cs/P ratio were prepared by mechanical mixture. Their main textural characteristics and their catalytic performances in n-hexane isomerization are presented in Table 1. Textural features are drawn from N_2 adsorption isotherms and B/L ratio (Brönsted to Lewis sites) are determined by IR of adsorbed pyridine at 150°C.

With the increase of the Cs/P ratio, a progressive increase of the BET surface area is obtained, while the microporous volume reaches a maximum value for the Cs/P ratio equal to 2. This effect of pore size on selectivity has already been reported by Misono [24] for different reactions. These observations are consistent with the fact that Cs salts, near the neutrality ($Cs/P > 2.5$), are partly mesoporous.

A remarkable influence of the Cs content on the catalytic activity is observed: a maximum in n-C_6 conversion and isomerization selectivities is observed over Cs_2P sample. A similar result was obtained for n-hexane isomerization over $Cs_xH_{3-x}PW_{12}O_{40}$ in the absence of metallic function; a maximum initial rate was measured for $Cs_{2.1}P$ [13]. The activity of Cs_2P sample can be related to its highest superficial acidity associated to a homogeneous porous framework. As far as acidity is concerned, the maximum of B/L observed for Cs_2P sample can be linked with previous results obtained with sulphated zirconia [16]. With caesium salt, the optimal ratio is close to 6, while with sulphated zirconia, it is close to 1. Over $Cs_{2.5}P$, it is most likely that the low protonic density combined with larger pores should increase the surface residence time of intermediate carbocations, and hence the cracking of secondary products.

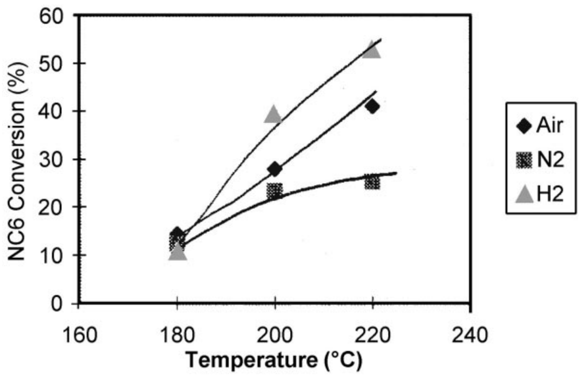

Fig. 1. Influence of the pre-treatment atmosphere on n-hexane conversion.

3.2. Influence of atmosphere and temperature for the pre-treatment

Cs_2P salt was pre-treated under different atmospheres (Fig. 1) at different temperatures (Fig. 2). The pre-treatment with H_2 leads to an important increase in conversion compared to the pre-treatments under air or nitrogen especially when the reaction temperature is higher than 473 K.

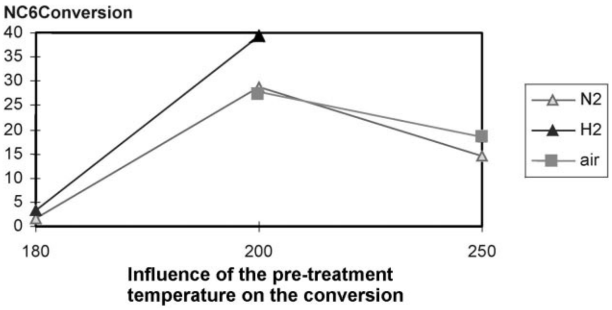

Fig. 2.

To understand the effect of the pre-treatment atmosphere, it is important to remind that in the absence of a metallic function, the activity of these heteropolyacids in alkane isomerization is only slightly affected by the nature of the pre-treatment atmosphere [10,19]. Therefore, the activity enhancement is linked to the presence of the metallic function. After promotion with Pt, the increased conversion observed after the pre-treatment with H_2 may be explained by several phenomena:

- Platinum sites can dissociate heterolytically the hydrogen molecule, generating hydride and protons as already suggested [5]. The rapid migration of these species, reported also by other authors [8], might enhance the initial hydride transfer ability of the catalyst, resulting in a higher isomerization yield.
- Moreover, as recently proposed by Iglesia [7] with tungsten oxide on zirconia, the activity increase could be caused by the improvement of acidity by protons generation through the reduction of tungsten clusters in the presence of H_2: $W^{6+} + \frac{1}{2}H_2 \rightarrow W^{5+} + H^+$. Indeed, in the case of HPA, such assumption is likely for the following reason: while their reduction with H_2 is strongly limited, the addition of Pt accelerates their reduction as proofed by the dark blue colour of Pt/HPA materials after TPR experiments [21].

The positive effect of hydrogen on the catalytic activity of silver salts of 12-tungstophosphoric acid has already been observed by Ono et al. [9] and studied by spectroscopic techniques [10]. The authors proposed that acid sites are generated through reduction of the Ag^+ cation into silver metal particles: $Ag^+ + \frac{1}{2}H_2 \rightarrow Ag^0 + H^+$. A similar behaviour was also reported for $Pd–H_3PW_{12}O_{40}$ catalyst by the same group [22]. In contrast with the previous explanation of the role of H_2, Misono [12] suggested that this mechanism is not true over $Pt–Cs_xH_{3-x}PW_{12}O_{40}$.

Our interpretation of the possible role of hydrogen is the following one: it is most likely that some kind reduction may occur during the pre-treatment releasing water molecules. We believed that the enhanced activity measured after the H_2 treatment originates rather from this water. In a previous study, we have shown that water molecules can regenerate the Brönsted acid sites of heteropolyacids and in addition participate to H–H exchanges between the hydrocarbon and the protonic sites [23].

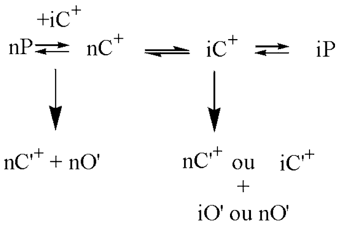

Fig. 3. Monofunctional mechanism (P: paraffin, O: olefin, C: carbonium ion).

Concerning the effect of the temperature of pre-treatment, whatever the atmosphere, an optimum in conversion for a pre-treatment temperature of 473 K is observed (Fig. 2). This result is consistent with the thermal stability of HPA. It is now well established that deprotonation of heteropolyacids occurs when thermal treatment is realized at too high temperature ($T > 473$ K) leading to lower activity in reaction sensitive to the protonic density as *n*-butane isomerization [17–20]. At lower temperatures, moisture may remains, lowering the acid strength.

3.3. Reaction mechanism

Two types of mechanism are currently involved in isomerization reactions. The first one is a monofunctional acid mechanism (Fig. 3) in which the carbocation is formed by hydride abstraction from the paraffin and whose limiting step is the reaction of hydride transfer.

The second one is a bifunctional metal–acid mechanism (Fig. 4), whose first step is the formation of an olefin by dehydrogenation of the paraffin on the metallic site. This olefin is then protonated on the acid

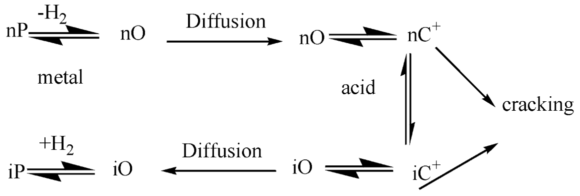

Fig. 4. Bifunctional mechanism.

Table 2
Isomerization mechanism

Mechanism	Activation energy (kJ/mol)	Order/n-C_6	Order/H_2	Isomer selectivity
Monofunctional acid	40–50	1	0	2,2-DMC_4: secondary product
Bifunctional metal/acid	105–135	1	0 to −1	2,2-DMC_4 and 2,3-DMC_4: secondary products

site to generate the carbocation. In this case, the limiting step is the carbocation rearrangement on the acid site.

The discrimination between these two mechanisms can be made on the basis of kinetic data like activation energy, reaction order and isomer selectivity.

In the case of the monofunctional mechanism, the apparent activation energy is about 40–50 kJ/mol, the H_2 order is null and only the 2,2-dimethylbutane (2,2-DMC_4) appears as secondary product. In the case of the bifunctional mechanism, the apparent activation energy is higher and close to 100 kJ/mol, the H_2 order is negative and both 2,2-DMC_4 and 2,3-DMC_4 appear as secondary product (Table 2).

The kinetic study was performed on 0.3 wt.% $Pt/Cs_2HPW_{12}O_{40}$ pre-treated at 200°C under H_2 flow. The apparent activation energy obtained is found equal to 71.2 kJ/mol. This value is intermediate between the two characteristic activation energies of the previous described mechanisms. Fig. 5 shows that only the 2,2-DMC_4 isomer is formed as a secondary product indicating that the mechanism could be a monofunctional mechanism. These results suggest that there is most likely participation of both mechanisms for this reaction with this type of catalyst.

3.4. Influence of Pt content

To elucidate the role of the metallic function in the mechanism, we studied the influence of the Pt content on both activity and selectivity.

Fig. 6 shows that there is a maximum of conversion for a Pt content of 0.3 wt.% and that selectivity in dibranched isomer and particularly in 2,2-DMC_4 increases when Pt content decreases.

Adding Pt makes the reaction easier, improving the acid sites feeding with olefinic intermediates. As for usual well-known bifunctional catalysts, catalytic performances depend on the ratio between the number of hydrogenating sites and the number of acidic sites (nPt/nA), proving the participation of a bifunctional mechanism with these heteropolyanions based catalysts. Nevertheless, the 2,3-DMC_4 isomer never appears as a secondary product like in the ideal bifunctional mechanism.

With these so prepared heteropolyanions based catalysts, the mechanism is a non-ideal bifunctional mechanism whose limiting step is no longer the carbocations rearrangement step on the acid sites, but the diffusion step between hydrogenating and acid sites. This can be related to the preparation of the catalyst,

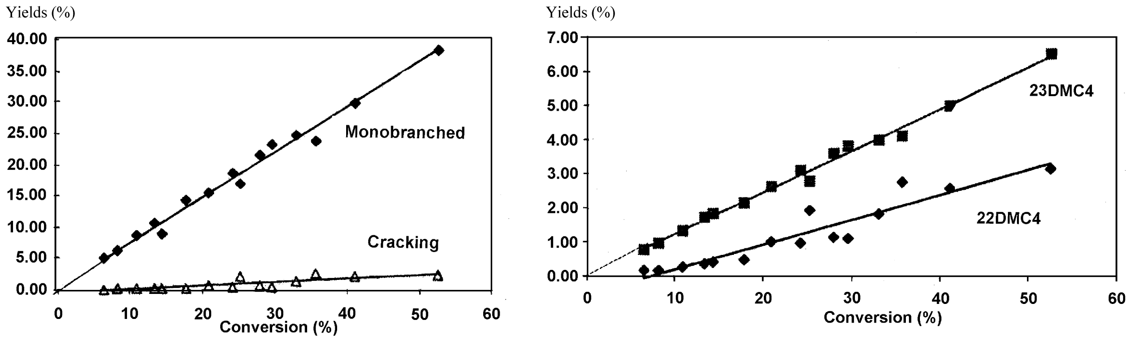

Fig. 5. Yields in different products versus conversion.

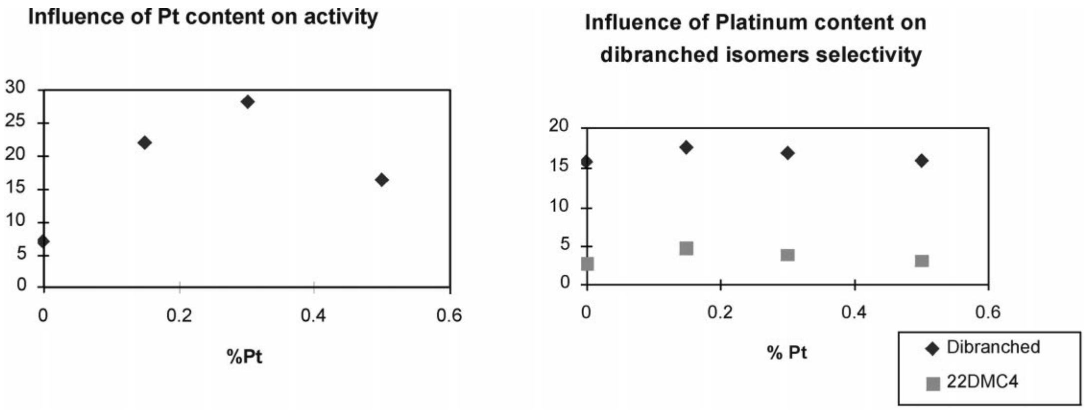

Fig. 6. Influence of Pt content.

and particularly to the way of Pt deposit. Mechanical mixing does not favour the proximity between hydrogenating and acid sites.

3.5. *Comparison with the industrial Pt/mordenite catalyst*

The optimized 0.3 wt.% $Pt/Cs_2HPW_{12}O_{40}$ catalyst was compared with the industrial zeolitic one. Fig. 7 and Table 3 present the results.

0.3 wt.% $Pt/Cs_2HPW_{12}O_{40}$ gives n-C_6 conversions closed to those obtained with the industrial zeolitic catalyst. For a same conversion level, dibranched isomers selectivity is increased, leading to an increase of nearly 1 point for the octane number, which is of great interest from an industrial point of view, particularly if the 2,2-DMC_4 isomer selectivity remains higher in the presence of the HPA catalyst due to the higher acid strength of these compounds.

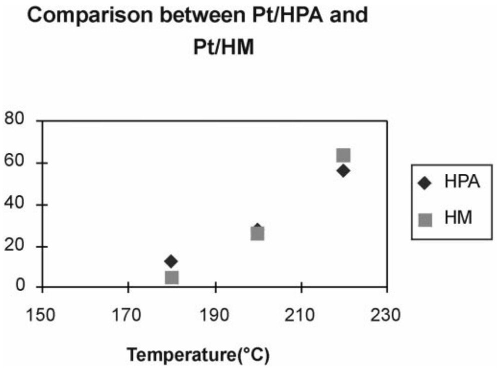

Fig. 7. Comparison with industrial catalyst.

Table 3
Comparison between Pt/HM and Pt/HPA (C = 25%)

Selectivity	Pt/HM	Pt/HPA
2,2-DMC_4	3.1	3.95
2,3-DMC_4	12.55	13.05
Monobranched isomers	82.8	79.2
Cracking	0	0.5
RON	38.2	39.1

4. Conclusions

This work shows that Cs salts of $H_3PW_{12}O_{40}$ are promising solids for n-paraffin isomerization. The best activity is obtained with the Cs salt developing the highest microporosity and a Brönsted/Lewis ratio close to 6. Acidity is enhanced by H_2 pre-treatment either directly by the protons coming from W^{6+} reduction or by the intermediate of water molecules formed through the reduction step.

With these bifunctional catalysts prepared by mechanical mixing, the reaction proceeds through the superposition of a monofunctional acid mechanism and a non-ideal bifunctional one. The non-ideality is due to diffusion limitations bound to the distance between hydrogenating and acid sites. This could be largely improve by improving the Pt deposit method. At the present time, this catalyst leads to an improved octane of about 1 point due to a higher production of dibranched isomers.

From an industrial point of view, the possible improvement in the catalyst preparation gives strong hope to obtain a much more performant catalyst than the zeolitic one in the near future.

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