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Isomerization of *n*-hexane over Pt-H₃PW₁₂O₄₀/SBA-15 bifunctional catalysts:

Effect of the preparation method on catalytic performance

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Graphical abstract



Highlights

- Development of Pt-H₃PW₁₂O₄₀/SBA-15 bifunctional catalysts using dual encapsulation or a combination of encapsulation/impregnation methods
- Their performance in *n*-hexane isomerization was compared to that of bifunctional catalysts obtained by mechanically mixing of acidic and metallic monofunctional materials
- The bifunctional catalysts where the Pt and HPW were immobilized within the same solid exhibit lower activity but higher selectivity than when the metal and HPW phases were physically separated
- All these results were interpreted by assuming a monomolecular mechanism for the isomerization and in terms of relative rates of initiation, propagation and termination.

Abstract

Pt-H₃PW₁₂O₄₀ based bifunctional catalysts immobilized on SBA-15 were prepared either by mechanically mixing of acidic (**HPW/SBA-15** or **HPW@SBA-15**) and metallic (**Pt/SBA-15**) monofunctional materials or by incorporation of the two active phases within the same composite

using dual encapsulation (Pt@HPW@SBA-15) and encapsulation/impregnation (Pt/HPW@SBA-15) methodologies. The phase structure, chemical composition and surface physico-chemical properties were characterized in details by XRD, FT-IR, ³¹P MAS NMR, N₂ adsorption-desorption and HRTEM, STEM and EDX microscopy techniques. All hybrid materials showed highly ordered mesostructuration of the SBA-15 matrix with homogeneous dispersion of both metallic and HPW phases. In the case of the *monophase* bifunctional catalysts, Pt/HPW@SBA-15 and Pt@HPW@SBA-15, both functions were found to coexist in close vicinity, with the HPW crystallites mainly located in the silica walls whereas Pt was found either in the channels or as part of the walls depending on the preparation route. Their catalytic performance was then evaluated in the isomerization of *n*-hexane. The catalysts prepared by mechanical mixing exhibited higher activity than those where the Pt and HPW were integrated within a single solid. These results were interpreted by assuming that the carbocations in the latter case were hydrogenated faster on the Pt particles thus decreasing their preponderance at the steady-state compared to the mechanical mixture.

Keywords: *isomerization, n-hexane, heteropolyacids, SBA-15, encapsulation, bifunctional catalyst, platinum*

1. Introduction

Current specifications for the production of cleaner fuels impose strong restrictions on the content of sulfur, aromatic compounds and olefins as well total interdiction of lead in the gasoline pool [1]. These restricted conditions led to the loss of the performance of internal combustion engine as these additives served as octane number enhancers [1, 2]. In this regard, the skeletal isomerization of linear alkanes represents a promising alternative since, with this process, low-octane straight chain paraffins are directly converted into high-octane branched molecules. Isomerization of linear alkanes can, thus, be considered as an efficient and economically acceptable way of increasing the octane number of motor gasoline and, unlikely aromatics and/or other toxic additives, the gasoline isomerizate is an ideal product that can satisfy the most stringent environmental legislation requirements.

Skeletal isomerization generally proceeds over acidic catalysts and is equilibrium-limited with branched isomers favored at low temperatures [3]. Bifunctional catalysts with both metallic and acid phases are currently being considered as key catalytic systems for this reaction. The metal

promotion, in presence of hydrogen, allows for the stabilization of the catalytic activity as well as enhancement of the selectivity to isomerization [4]. Indeed, this metal-hydrogen system proceeds through the monomolecular mechanism pathway where the final products are alkane isomers, without cracking [5]. Nowadays, the industrial catalysts consist of platinum supported on acidic zeolites [6, 7]. The zeolites have a high resistance to water and sulfur, making them stable catalysts with a long effective lifetime [6]. However, zeolites are less acidic than chlorinated alumina (commonly used in industry until very recently). As a consequence, the isomerization reaction requires high temperature (220-400 °C) and a high hydrogen pressure (15-30 bar) to proceed which is less favorable for the production of branched isomers [8-11]. Other acidic solids such as sulfated zirconia [12, 13], tungstated zirconia [14] and heteropolyacids (HPAs) [15-17] have also been applied to the skeletal isomerization of light alkanes. In particular, heteropolyacids, when used in conjunction with a noble metal, mainly platinum, were found to be highly efficient catalysts for the isomerization of *n*-alkanes in the C_4 - C_{10} range [18-22]. Their strong acidic strength allowed for the isomerization of alkanes at low temperature via the monomolecular reaction pathway, thus providing high conversion and selectivity to the isomeric products [22-25]. For instance, A. Miyaji et al. used Pt-Cs_{2.5}H_{0.5}PW₁₂O₄₀ as catalyst for the isomerization of *n*-butane with high selectivity (> 90%) [5]. Y. Xu et al. reported that the system Pt-H₃PW₁₂O₄₀/ZrO₂ provides a high and stable conversion (60 %) of n-pentane after 60 h of reaction at 200 °C [26]. A.V. Ivanov et al. also investigated the catalytic activity of Pt-HPW Keggin and Dawson tungstic acids supported on zirconia. The results showed a high activity for *n*-hexane isomerization with a yield of 80% and a selectivity of 96-98% at 190 °C [24]. However, partial degradation of the HPW structures was observed upon immobilization on the ZrO₂ support resulting in lower concentration of active sites.

In a previous work, we have reported on the acid-catalyzed isomerization of *n*-hexane by SBA-15 supported $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW) Keggin heteropolyacids [27]. The catalysts were found to be active at 200 °C exhibiting high selectivity (90%) towards isomerization, but a rapid deactivation was observed due to coke formation [27]. In a follow-up report, we studied the effect of the preparation method of these monofunctional acidic catalysts on the catalytic performance in *n*-hexane isomerization [28]. For this purpose, two strategies were considered for the synthesis of HPA modified hybrid materials: the classical impregnation technique where the HPA entities are held at the silica pores and the direct synthesis yielding embedded HPA clusters directly within the silica framework. The impregnated and encapsulated systems based on $H_3PW_{12}O_{40}$ exhibited nearly the same activity and selectivity while those based on $H_4SiW_{12}O_{40}$ showed markedly different behavior. The HSiW catalyst prepared by classical impregnation displayed an activity even higher than both HPW systems while that prepared by direct synthesis

was almost inactive. These results were correlated to acidity measurements by pyridine adsorption and it was proposed that in the encapsulated materials the heteropolyacid was located at the surface of the walls for HPW while, for HSiW derivatives, the active sites were more deeply embedded in the walls. Experiments in the presence of platinum and hydrogen as the carrier gas were also carried out with the impregnated HSiW based catalyst resulting in high and stable activity overtime with selectivity to isomerization as high as 95 % at 200 °C [29]. No catalyst deactivation was observed even after 3 days on stream in contrast to monofunctional catalysts emphasizing the crucial role of both Pt and hydrogen to achieve high reactivity and prevent any catalyst deactivation.

As a continuation of this work, we wish to further explore the effect of the preparation method of the bifunctional catalysts on the catalytic reactivity in *n*-hexane isomerization. Indeed, the metal and HPA phases can be physically separated (mechanical mixture of the two monofunctional catalysts) or present in close proximity within the same solid phase. In the latter case, the two components were introduced by direct encapsulation during the oxide synthesis or by a combination of both encapsulation and impregnation. One expects the catalytic reactivity to be substantially dependent on these synthetic parameters as the distance between the two functions may vary considerably. As the silicotungstic acid encapsulated material was not active in the isomerization of *n*-hexane, these studies were pursued by considering exclusively phosphotungstic acid based catalysts.

2. Experimental

2.1. Synthesis of the catalysts

H₃PW₁₂O₄₀ (HPW) and H₂PtCl₆.6H₂O, were purchased from Aldrich Chemical and used as received. Monofunctional **HPW/SBA-15** (impregnated) and **HPW@SBA-15** (encapsulated) catalysts were produced respectively by classical impregnation and sol-gel encapsulation methods following procedures described previously [28]. The HPW amount in these hybrid materials was determined from ICP-AES to be 33 wt.%. Monofunctional **Pt/SBA-15** was obtained by impregnation of H₂PtCl₆.6H₂O over SBA-15 through a solid-liquid route as reported elsewhere [29, 30] with a platinum content of 0.8 wt.%. Platinum was also incorporated in the monofunctional **HPW@SBA-15** catalyst by the same procedure, at quite the same loading (0.7 wt. % Pt), yielding the bifunctional catalyst **Pt/HPW@SBA 15**. Another type of bifunctional material was also prepared through the dual encapsulation of both platinum and HPW by adapting the procedure previously developed for **HPW@SBA-15** [28]. Typically, the silica precursor (TEOS) was introduced to an acidic solution (HCl 1.9 M) of a mixture of non-ionic (Pluronic 123) and ionic (CTAB) structure directing agents. After a short period of prehydrolysis (45 min), the

phosphotungstic acid was first added to the mother solution followed, after a 15 min period, by $H_2PtCl_6.6H_2O$. The resulting as-made solid was calcined under humid air at 400 °C for 20 h and then pre-treated at 300 °C for 3 h under nitrogen. Finally, the material was reduced under H_2 at 300 °C for 3 h leading to the dual encapsulated material referred to as **Pt@HPW@SBA-15**.

2.2. Characterization of the catalysts

KBr pellets were prepared and absorbance FTIR spectra were run on a Nicolet 5700 spectrometer. ³¹P MAS NMR spectra were recorded on a Bruker DSX-500 spectrometer. A Bruker D5005 diffractometer operating with the Cu K α monochromatic radiation ($\lambda = 1.54184$ Å) was used for the obtention of X-ray diffraction patterns. were performed on a A Micromeritics ASAP 2020 system was used for determination of the N₂ adsorption-desorption isotherms. Elemental analyses were performed by ICP-AES with an ICP spectroflamme-D. HRTEM (High Resolution Transmission Electron Microscopy) studies were made with a JEOL JEM 2100F microscope. The size distribution histograms were obtained from a manual measurement with J Image of at least 200 different nanoparticles assuming near spherical shapes and random orientations. Log normal fits were used to approximate the experimental size distribution histograms. The microscope was also equipped with a High Angle Annular Dark Field (HAADF) STEM detector with a resolution of 0.19 nm allowing to determine *in situ* the chemical composition of the samples using energy-dispersed X-ray (EDX). The platinum dispersion was determined by chemisorption of hydrogen on a Micromeritics ASAP2010 instrument. More informations on the methods used can be found in our previous works [27-29].

2.3. Catalytic experiments at atmospheric pressure

The catalytic experiments were made by using the same experiment than previously [29]. They were conducted during 12 hours at 200°C. The reactor was heated under a flow of argon (5 mL.min⁻¹) for 2 hours at 200 °C to remove any adsorbed water. The gas flow was then switched to hydrogen bubbled through hexane at room temperature (5 mL.min⁻¹, hexane/hydrogen ratio = 0.25). The carbon balances were determined in all cases in order to prove that all compounds were detected. In presence of platinum they were always very good. The reproducibility was also checked by repeating some experiments.

3. Results and discussion

3.1. Characterization of the catalysts

Four catalysts were evaluated in the isomerization of *n*-hexane: a mechanical mixture composed of impregnated **Pt/SBA-15** with either impregnated **HPW/SBA-15** or encapsulated **HPW@SBA-15**, a solid where platinum was subsequently impregnated on the encapsulated **HPW@SBA-15** and denoted **Pt/HPW@SBA-15** and a solid where both HPW and platinum were incorporated during the oxide synthesis leading to **Pt@HPW@SBA-15**. Prior to their use in catalysis, all solids were characterized by various physicochemical and spectroscopic methods. The texture and ordering of the materials was determined by X-ray diffraction and nitrogen sorption measurements. The molecular scale properties of the catalysts were analyzed by FT-IR and ³¹P MAS NMR. Finally, the platinum particles size and dispersion were characterized by chemisorption of hydrogen and electron microscopy (HRTEM and STEM with EDX analysis).

The low-angle powder XRD patterns of the monofunctional systems **HPW/SBA-15**, **HPW@SBA-15** and **Pt/SBA-15** were reported previously. In the three cases, the catalysts showed the three well-resolved peaks characteristics of the hexagonally ordered mesostructure of SBA-15 silica [27-29]. The low-angle XRD patterns of the bifunctional systems **Pt/HPW@SBA-15** and **Pt@HPW@SBA-15** are quite similar to those of the monofunctional ones and exhibit also the three reflection peaks at low scanning angles indexed as (100), (110) and (200) (Fig. 1). These results indicate that all solids had retained the long-range SBA-15 structure.

< Fig. 1 >

The wide-angle powder XRD patterns of monofunctional **HPW/SBA-15**, **HPW@SBA-15** and **Pt/SBA-15** did not show any peaks in the 10 - 70° 2θ range, indicating that both HPW and platinum were finely dispersed throughout the solids [27-29]. The wide-angle XRD patterns of the bifunctional catalysts are shown in Fig. 2. As for the monofunctional materials, no diffraction peaks were found for **Pt/HPW@SBA-15** evidencing again highly dispersed metallic and acidic phases all over the solid. On the other hand, **Pt@HPW@SBA-15** displayed small broad diffraction peaks at 20 values of 24°, 33°, 41°, 50° and 54°, characteristic of monoclinic WO₃ [31]. These peaks are probably due to a partial decomposition of the polyoxometalate ions which may occur during the thermal treatment and/or the reduction step [32]. However, no characteristic peaks associated with either HPW or Pt crystallites were observed which is indicative of well-dispersed active sites in the mesoporous SiO₂ framework [33].

Table 1 lists the textural data deduced from X-ray diffraction and N₂ adsorption-desorption isotherms together with chemical analyses. For all materials, the isotherms are characteristic of mesoporous materials with uniform cylindrical channels and narrow pore size distribution (see for example Supporting Information, Fig. S1-S2 for encapsulated based hybrids, while data for impregnated materials have already been reported elsewhere [28]). As expected, all isotherms present a hysteresis loop at quite the same relative pressure range than SBA-15 (P/P₀ values between 0.6 and 0.8). The d₁₀₀ and a₀ parameters are quite the same for all catalysts if we take into account the errors on the measurements. In contrast, the BET surface areas vary between 360 and 844 m².g⁻¹ and the porous volume between 0.5 and 1.1 cm³.g⁻¹. For the two supported catalysts **HPW/SBA-15** and **Pt/SBA-15**, the surface area variation can be directly correlated to the real amount of silica in the samples respectively of 75 wt. % and \approx 99 wt. %. As HPW clusters are located in the channels, the porous volume is lower than for **Pt/SBA-15**. For the encapsulated materials, all results are comparable if we take into account the fact that the **Pt/HPW@SBA-15** solid was prepared from another batch of **HPW@SBA-15**.

< Table 1 >

The ³¹P MAS NMR spectra of **Pt/HPW@SBA-15** and **Pt@HPW@SBA-15** (Fig. 3) showed that the primary Keggin structure was mostly retained. Indeed, in the case of the **Pt/HPW@SBA-15**, the ³¹P MAS NMR spectrum showed a sharp peak at -15 ppm which is characteristic of the $[PW_{12}O_{40}]^{3-}$ anion [34]. Another weak resonance was also observed at -14.1 ppm which can be ascribed to HPW in slight interaction with the silica surface as suggested by Yun and Hamad [35, 36]. In addition to the resonances at -15 and -14.1 ppm, the **Pt@HPW@SBA-15** catalyst showed two other small peaks at 0.4 and -6.1 ppm. The resonance around 0 ppm is clearly identified with phosphate species suggesting that partial decomposition of some HPW has occurred during the material synthesis. This result is in good agreement with the wide-angle XRD data which showed the formation of WO₃ confirming some degradation of the Keggin structure into its composition elements. The weak resonance observed at -6.1 ppm could be due to some degraded HPW species, for example one isomer of the lacunary PW₉ polyoxometalate.

< Fig. 3 >

The FT-IR spectra of SBA-15, **Pt@HPW@SBA-15**, **Pt/HPW@SBA-15** and pure HPW are displayed in Fig. 4. Pure HPW shows the typical IR bands at 1080 (v_{as} (P-Oa)), 982 (v_{as} (W-Od)), 890 (v_{as} (W-Ob-W)), and 800 cm⁻¹ (v_{as} (W-Oc-W)) associated with Keggin anions [37]. The FT-IR spectrum for pure SBA-15 displays the classical absorption bands at 1080, 800 and 465 cm⁻¹ assigned to Si-O-Si vibrations. These latter are clearly observed for the bifunctional catalysts. **Pt/HPW@SBA-15** also clearly exhibits the characteristic bands of the Keggin ions indicating that the structural integrity of the HPA Keggin unit was preserved during the two-step preparation process. In the case of the **Pt@HPW@SBA-15** material however, these bands are broadened and difficult to observe, in agreement with a partial decomposition of the Keggin unit.

< Fig. 4 >

Classically, the dispersion of metallic catalysts is determined by hydrogen chemisorption. We thus used this method for the platinum containing solids, Fig. S3. For the **Pt/SBA-15** solid, the Pt dispersion was found to be 25 %, which corresponds to a particle size of 4.5 nm if we assume a spherical shape. These results are in agreement with data reported by Seok Oh, et al., who prepared Pt/SBA-15 catalysts with 1 wt. % of Pt by impregnation (with H₂PtCl₆ as the precursor) [38]. They measured a dispersion of 29.4 %, a value close to that obtained in this work [38, 39]. In the case of the bifunctional systems **Pt/HPW@SBA-15** and **Pt@HPW@SBA-15** unreliable results were obtained. Blank experiments were then undertaken with the supported heteropolyacid alone. Clearly, the polyoxometalate reacts with hydrogen as the material instantaneously turned to a dark blue color. This reaction is only partially reversible thus preventing any conclusive determination of the Pt dispersion in presence of the polyoxometalate.

As a consequence, other methods needed to be used for the characterization of the bifunctional catalysts. This can be accomplished by transmission electron microscopy.

The morphology and distribution of platinum nanoparticles in the HPW containing materials were assessed by HRTEM and dark-field STEM images coupled with EDX analysis. The bifunctional catalysts presented the typical hexagonal organized channels of SBA-15 in agreement with the low-angle XRD data which showed highly ordering of the mesostructure. Typical HRTEM images are shown in Fig. 5 and 6. They provide direct observation of the distribution of Pt nanoparticles in the SBA-15 solids.

< Fig. 5 and 6 >

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The **Pt/HPW@SBA-15** (0.7%_{wt} Pt) solid showed the presence of well dispersed and narrowsized nanoparticles of 2.3 ± 0.6 nm, generally spherical and mostly inside the channels of the host SBA-15 (Fig. 5). The **Pt@HPW@SBA-15** catalyst (0.4%_{wt} Pt) (Fig. 6) exhibited also welldispersed platinum nanoparticles with a mean size of 2.8 ± 1.2 nm which is close to **Pt/HPW@SBA-15** but with a broader distribution of particles size. In both cases, the particle size was smaller than that achieved on the **Pt/SBA-15** catalyst (4.5 nm). This could be ascribed to the presence of tungsten, as already mentioned in other reports, which may play an important role in the nucleation-growth process during the nanoparticles formation [40].

Representative HAADF-STEM images of Pt/HPW@SBA-15 and Pt@HPW@SBA-15 catalysts are displayed in Fig. 7 and 8 respectively. For both catalysts, one can see the highly ordered pore structure of SBA-15 with the presence of very small white dots uniformly dispersed throughout the organized domains which can be either Pt or W heavy elements given that the intensity in HAADF images depends on the atomic number. HAADF images taken at higher magnification provide direct evidence of the particles location. Fig. 7 (right) shows that for Pt/HPW@SBA-15 the white particles were mainly confined in the channels of the SBA-15 whereas in the case of dual encapsulated Pt@HPW@SBA-15 catalyst they were chiefly located at the surface or within the core of the silica framework (Fig. 8, right). To get deeper insight into the chemical composition of these white particles, EDX analysis was performed on both samples. Fig. S4 shows that the white spots in Pt/HPW@SBA-15 were mainly constituted of Pt with an atomic ratio Pt/Si of ca. 45 % while the W/Si one was found at ca. 5 %. In the dark gray areas, only Si, O and W could be detected with a W/Si atomic ratio of ca. 5 %. This confirmed that the HPW clusters, introduced by encapsulation during the gel synthesis, are mainly located within the walls of the materials with the Pt nanoparticles mostly in the channels or above the walls. In the case of Pt@HPW@SBA-15 (Fig. S5), one clearly sees the presence of very small crystallites of 1 to 2.5 nm size exclusively located within the framework walls of the solid. EDX analysis of the different zones indicated that the brighter particles were more likely attributed to Pt nanoparticles whereas the lighter ones corresponded to W. The dual encapsulation method of both Pt and HPW has thus produced a hybrid material where Pt and HPW active sites are found in very close vicinity as a structural part of walls.

< Fig. 7 and 8 >

Note that for both **Pt/HPW@SBA-15** and **Pt@HPW@SBA-15** catalysts, crystalline Pt nanoparticles with a face-centered cubic structure were obtained (Fig. S6).

3.2. Catalytic experiments

The skeletal isomerization of alkanes is an acid-catalyzed stepwise process leading to the formation of branched isomers. In order to achieve good conversions without catalyst deactivation the experiments are usually carried out under hydrogen in the presence of platinum particles [41-43]. In previous work, we have shown that bifunctional Pt-HSiW based systems provided high selectivity to isomerization (> 90%) with a stable *n*-hexane conversion (60%) even after 3 days on stream [29].

The use of the Pt-H₂ system in addition to the HPA acidic phase prevents the formation of olefins, improving the selectivity towards isomerization. Furthermore, elimination of the olefins will also suppress the formation of coke and so deactivation of the catalyst by this way [44-50]. Another consequence is that the presence of the Pt-H₂ system leads to the monomolecular mechanism [4] which favors the formation of only hexane isomers. The acid sites protonate the alkane and form a secondary carbocation which rearranges into a tertiary one. Upon reaction with a new alkane molecule, the initial carbocation is reformed. However, there is probably a great influence of the distance between the two functions (metal and acid site) on the performance of the catalysts. Indeed, if this distance is infinite no effect of the metal should be expected and the mechanism could be bimolecular. Keeping this in mind, our bifunctional catalysts, where both the distance between sites and their spatial location can strongly vary, were then evaluated in the isomerization of *n*-hexane. In order to allow for a direct and meaningful comparison, all systems contained the overall same amount of tungsten and platinum. All the experiments were carried out with a dynamic reactor during 12 hours in order to study the deactivation of the catalyst. The global conversions and selectivities to C₆ isomers for each catalyst are given in Table 2.

< Table 2 >

The bifunctional catalyst prepared by a mechanical mixture of **Pt/SBA-15** and **HPW/SBA-15** (entry 1) showed an initial global conversion around 44 % which gradually increased until 62 % and remained stable after 12 h of reaction. The selectivity to isomerization of up to 95 % is in agreement with the proposed monomolecular mechanism. The selectivity of each isomer is constant with the conversion, the mono-branched isomers being the major products with more than 50 % for 2-methylpentane (2MP) and 30 % for 3-methylpentane (3MP). These two

products stem from a single carbon shift, whereas the minor 2,2- and 2,3-dimethylbutanes (2.2DMB and 2.3DMB) necessitate two successive rearrangements and thus are produced more slowly.

The other bifunctional catalyst prepared by a mechanical mixture of **Pt/SBA-15** and **HPW@SBA-15** (entry 2), showed similar performance. Initially, the conversion was rather low, around 19 %, which can be due to slow initiation due to the HPW localization which is held more deeply in the pore walls of the encapsulated **HPW@SBA-15** material. *n*-Hexane conversion steadily increased with time on stream up to 66 % after 12 h, where it remained stable. The distribution of the various hexane isomers was quite similar to that achieved with the (**Pt/SBA-15** + **HPW/SBA-15**) catalyst, in agreement with previous results for this type of catalyst [27].

Both bifunctional catalysts where the metallic and acidic functions are immobilized in closer proximity within a single composite showed lower activity compared to the mechanically mixed catalysts but exhibited higher selectivity. The **Pt/HPW@SBA-15** catalyst, entry 3, presented an initial conversion around 19 % which increased and remained stable at up to 25 % after 12 h of reaction. This catalyst showed also a high selectivity to C₆ isomers (97 %). The **Pt@HPW@SBA-15**, entry 4, had an initial conversion of 20 % which increased to 34 % in the initial four hours and then remained stable over 12 h on stream with a selectivity of 98.6 %. As in this material some HPW had been destroyed, part of the lower conversion compared to the mechanical mixtures can be ascribed to the lower amount of acid sites. However this explanation cannot explain the factor 2 between these conversions as only a small part (and not 50 %) of HPW has been destroyed, as shown by all analyses.

When looking at all these results, two conclusions can be pointed out. Firstly, in all cases the activity increases during the first several hours on stream. This fact could be explained by a modification of the catalyst which becomes more active with time but it seems more reasonable to search an explanation in the mechanism of isomerization itself. In a first step (initiation), a *n*-hexane molecule is activated by a proton of the heteropolyacid leading to a carbocation which will then rearrange. Upon reaction with another hexane molecule, the isomerized product is formed and the carbocation is regenerated (propagation). The initial increase in activity should then be related to the increase of the number of carbocations in the catalyst. When the termination rate is equal to the initiation one the activity becomes constant. The formation of hexane by dehydrogenation of hexane on the metallic phase can be excluded in our conditions as a blank experiment performed with **Pt/SBA-15** did not show any trace of hexenes. The variation of the conversion of the four catalysts as a function of time is shown in Fig. 9. If one compares the two mechanical mixtures, clearly the rate of carbocations formation is higher on **HPW/SBA-15** than on **HPW@SBA-15**

based system. This phenomenon is probably related to the accessibility of the HPA. Indeed, in the impregnated material all HPA are located at the pore surface and can readily react with *n*-hexane while in the case of the encapsulated material they are more likely located inside the walls, near the surface and so are less accessible to the reactants.

< Fig. 9 >

Secondly, when looking at the steady-state activities, the catalysts can be separated into two groups: the two mechanical mixtures which exhibit similar catalytic activity and the two materials where platinum and HPW sit nearby within the same support for which differences in activity can be noticed probably arising from the lower tungsten amount in the Pt/HPW@SBA-15 material (see Table 1). By assuming the same explanation as aformentioned, the steady-state activity is related to the propagation rate (reaction of the carbocation with *n*-hexane leading to the isomer and reformation of a carbocation). It is reasonable to assume that the rate of reaction of a carbocation is the same in all materials as all experiments were performed under the same reaction conditions and all materials are based on the same SBA-15 scaffold. As a consequence, the steady-state activity is directly related to the number of carbocations present at the steady-state. We can then conclude that, at the steady-state, the materials where Pt and HPW are included within the same support have a lower amount of carbocations than those where they are located in separate matrices. The explanation could also be found in the mechanism. The number of carbocations is obtained when the initiation rate is equal to the termination rate. The termination rate can be the elimination of a proton of the carbocation leading to an alkene molecule or the hydrogenation of the carbocation leading to the alkane. This second possibility is the most reasonable as the reaction is run in presence of hydrogen. As platinum is a well-known hydrogenation catalyst, a marked increase of the termination rate, and so a decrease of the amount of carbocations at equilibrium, is expected when both Pt and HPW are immobilized in close proximity rather than apart from each other in separate solids.

4. Conclusion

Different strategies were developed towards the synthesis of Pt-HPW bifunctional catalysts supported on SBA-15, either by mechanically mixing Pt and HPW containing monofunctional solids or by combining both functions within the same material via encapsulation and encapsulation/impregnation methodologies. After thorough characterization to attest of the structural ordering and the state of the metallic and acidic inclusions, all materials were tested in *n*-

hexane isomerization. The present results confirmed the essential role of both Pt and hydrogen to achieve efficient and stable catalytic systems. In all cases, the activity increased initially before reaching a steady-state. The bifunctional catalysts prepared by mechanical mixture were highly active and selective, whatever the nature, impregnated or encapsulated, of the HPW derived material. The bifunctional catalysts prepared with the two active phases immobilized within the same solid exhibited a lower catalytic activity. The main conclusion of this work is then that in contrast to what could be expected, the separation of the two phases, metallic and acidic, is required to achieve the best catalyst.

All results were interpreted by assuming a monomolecular mechanism for the isomerization and in terms of relative rates of initiation, propagation and termination.

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FIGURE CAPTIONS

Fig. 1. Low-angle XRD patterns of (a) Pt@HPW@SBA-15 and (b) Pt/HPW@SBA-15.

Fig. 2. Wide-angle XRD patterns of (a) Pt@HPW@SBA-15 and (b) Pt/HPW@SBA-15.

Fig. 3. ³¹P MAS NMR of Pt/HPW@SBA-15 and Pt@HPW@SBA-15.

Fig. 4. FT-IR spectra of (a) SBA-15, (b) Pt@HPW@SBA-15, (c) Pt/HPW@SBA-15 and (d) pure HPW.

Fig. 5. HRTEM image and particle size distribution of Pt/HPW@SBA-15.

Fig. 6. HRTEM image and particle size distribution of Pt@HPW@SBA-15.

Fig. 7. Representative HAADF-STEM images of Pt/HPW@SBA-15.

Fig. 8. Representative HAADF-STEM images of Pt@HPW@SBA-15.

Fig. 9. Variation of the conversion as a function of the reaction time for the four catalysts. Reaction conditions: 1 bar, 200 °C, 5 mL.min⁻¹ hydrogen flow, ratio hexane/hydrogen = 0.25, 0.5 g of catalyst (0.5 g of each monofunctional solids in the case of the mechanical mixture).



< Fig. 1 >



< Fig. 2 >



< Fig. 3 >



< Fig. 4 >



< Fig. 5 >



< Fig. 6 >



< Fig. 7 >



< Fig. 8 >



< Fig. 9 >

Table 1

Textural and physical properties of Pt-HPW catalysts.

| Catalysts | wt. % W | wt. % Pt | $d_{100}{}^a$ (Å) | a_0^b (Å) | Wall thickness ^c (Å) | $V_p \qquad ^d (cm^3/g)$ | ${D_p}^e (\mathring{A})$ | S_{BET} (m^2/g) | C_{BET}^{f} |
|----------------------------|------------|-------------|----------------------|----------------|---------------------------------------|--------------------------|--------------------------|---------------------|---------------|
| SBA-15 | - | - | 99 | 114 | 48 | 1.13 | 75 | 859 | 151 |
| HPW/SBA-15 | 25 | - | 97 | 111 | 46 | 0.9 | 65 | 639 | 204 |
| Pt/SBA-15 | - | 0.8 | 101 | 117 | 52 | 1.1 | 64 | 844 | 168 |
| HPW@SBA-15 | 26 | - | 96 | 111 | 35 | 0.6 | 76 | 451 | 203 |
| Pt/HPW@SBA-15 ^g | 20 | 0.7 | 95 | 109 | 33 | 0.5 | 76 | 360 | 261 |
| Pt@HPW@SBA-15 | 26 | 0.4 | 99 | 114 | 38 | 0.7 | 77 | 474 | 163 |

 $^a\,d_{(100)}$ spacing (the error is estimated as 3 Å).

^b $a_0 = 2d(100)/\sqrt{3}$, hexagonal lattice parameter calculated from XRD.

 c Calculated by a_0 – pore size.

^d Total pore volume at $P/P_0 = 0.980$.

^e Pore size from desorption branch applying the BJH pore analysis.

^f Derived from the BET equation of the nitrogen adsorption isotherms.

^g The parent HPW@SBA-15 used to impregnate the Pt is different from HPW@SBA-15 used in the mechanical mixture.

Table 2

Conversions and selectivities of the Pt-HPW bifunctional catalysts.

| Entry | Catalysts | Conversion (%) | | Select. iC ₆ (%) | Distribution of C_6 isomers (%) | | | |
|-------|---------------------------|----------------|------|--------------------------------|-----------------------------------|------------|---------|---------|
| | | 0 h | 12 h | 12 h | 2.2 DMB | 2.3 DMB | 3 MP | 2 MP |
| 1 | Pt/SBA-15 + HPW/SBA-15 | 44.4 | 62.4 | 95.7 | 5.1 | 10.3 | 30.0 | 50.3 |
| 2 | Pt/SBA-15 + HPW@SBA-15 | 18.9 | 66.5 | 96.4 | 5.8 | 11.3 | 29.6 | 49.7 |
| 3 | Pt/HPW@SBA-15 | 18.9 | 24.7 | 97.5 | 1.4 | 8.1 | 32.4 | 55.6 |
| 4 | Pt@HPW@SBA-15 | 19.8 | 34.4 | 98.6 | 1.9 | 10.3 | 31.2 | 55.2 |

Reaction conditions: 1 bar, 200 °C, 5 mL.min⁻¹ hydrogen flow, ratio hexane/hydrogen = 0.25, 0.5 g of catalyst (0.5 g of each monofunctional solids in the case of the mechanical mixture).