$H_3PW_{12}O_{40}$ acid dispersed on its Cs salt: improvement of its catalytic properties by mechanical mixture and grinding

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Acidic cesium salts $Cs_xH_{3-x}PW_{12}O_{40}$ have been prepared by grinding together amounts of $H_3PW_{12}O_{40}$ and porous $Cs_3PW_{12}O_{40}$ compounds in varying stoichiometries. It is shown that this procedure leads to a dispersion of the acid on top of the high surface area $Cs_3PW_{12}O_{40}$ salt (160 $m^2\,g^{-1}$), and, subsequently, yields high surface area materials which exhibit a much higher catalytic activity for n-butane isomerisation at 473 K when compared with samples prepared directly by chemical precipitation. This improvement holds particularly true with low Cs content ($x < 2$).

Keywords: cesium salt of polyoxotungstate, heteropoly acid, acidity, n-butane isomerisation

1. Introduction

Keggin-type heteropoly acids have been widely studied in the last fifteen years for their acidic and subsequent catalytic properties [1–4]. Bulk heteropoly acids, such as $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, are strong Brønsted acids which is due to the large size of the anion, therefore a low negative charge density, and thus weak proton–anion bonds. For acidic type reactions, bulk heteropoly acids (HPAs) generally exhibit low catalytic performances due to their low surface areas. For this reason, the main criterion which can lead to highly active heterogeneous acid catalysts is an improvement of the HPA dispersion with respect to its primary acidic features. For this purpose, we can find in the literature two main approaches: (1) the impregnation of the HPA on classical porous materials, or (2) the direct preparation of the acidic porous salts of HPA.

The dispersion of the acid $H_3PW_{12}O_{40}$ through wet impregnation has been studied mainly on supports as silica [5], MCM-41 [6], activated carbon [7], etc. For acidic type reactions, it has been generally observed that only the materials charged with a high loading of the acid phase were active. With lower loadings of HPA, a neutralisation and even a transformation of the initial Keggin structure have been reported, resulting in a decrease of the acidity.

The second approach uses the precipitation in aqueous solutions of large alkaline ions salts of HPA (cations as Rb^+, Cs^+, NH_4^+ and K^+). It has long been known that such a preparation leads to microporous materials. Their adsorption capacity has already been studied by Gregg et al. in 1957 and 1978 [8,9]. The contribution of the works of Moffat in this field has covered the study of the microporosity of these large neutral alkaline salts [10] and the dependence of their textural features with their preparation conditions [11]. Although these solids were prepared stoichiometrically, the catalytic activity of these porous alkaline or ammonium salts of HPA was ascribed by Moffat et al. to the presence of residual quantities of protons [12]. Non-stoichiometric Cs salts, $Cs_xH_{3-x}PW_{12}O_{40}$, prepared by precipitation in aqueous solution, have been shown by Misono to be highly active catalysts in a number of acid-type reactions [13], including the isomerisation of n-butane, a reaction which requires strong acid sites [14]. The occurrence of catalytic shape-selective features in the presence of these catalysts was already suggested [12], however, a number of more recent papers have reported thoroughly the role of the shape-selective aspect with regard to their reactivity [4,15–17]. Nevertheless, some discrepancies can be found in the literature concerning the real nature of this "remaining acidity" of these acidic Cs salts. It has been proposed that solid solutions between the isostructural pure acid and the porous salts Cs_3P are formed, evidenced especially by ^{31}P NMR study, while it has also been proposed that the acidic properties could be attributed to the presence of $H_3PW_{12}O_{40}$ in strong interaction at the surface with the isostructural porous alkaline salt [4,15,18]. Whatever be the model, these Cs salts exhibit a high superficial protonic density as regard to the bulk acid. Finally, the preparation of non-porous alkaline salts by solid-state reaction has been investigated [19]. The resulting non-porous stoichiometric materials were seen to be much less active than those prepared by precipitation.

Concerning the direct preparation of the porous salts of HPA by precipitation, it is quite obvious that the dispersion of the acid depends on several preparation parameters, such as concentrations of both solutions, stirring rate upon mixing the two solutions, temperature, etc. In particular, we have shown that if the excess solution after precipitation

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was eliminated by centrifugation one could not get a precipitate with a H^+/P ratio larger than 1 [15]. Ratios larger than 1 were possible if the excess solution was not eliminated and the water solvent evaporated thermally [13,17]. Moreover, it was shown by Moffat [11] that the porous features of the stoichiometric alkaline salts depend on the conditions of precipitation: precursor ratio and also nature of the alkaline ions. Similar effects were observed in the synthesis of acidic salts [4,15]. It is clear that the preparation of highly active acidic alkaline salts requires two conditions: a high BET surface area value combined with a high amount of residual protons. However, the BET surface area decreases with the increase of the precursor ratio of H_3P/alkaline. In other words, the solid with the highest proton content exhibits also the lowest BET surface areas and the smallest pore apertures [4,15,16]. Consequently, obtaining highly active acid catalysts by this method is limited by these two factors and, therefore, the best catalyst corresponds to a narrow optimum.

The wet impregnation of $H_3PW_{12}O_{40}$ on the high surface area alkaline salt as K_3P or Cs_3P was an alternative method. This supporting procedure was seen to preserve the Keggin structure of the acid-phase $H_3PW_{12}O_{40}$ even for low amount of HPA, contrary to impregnation using classical supports. It was demonstrated that an epitaxial layer was formed at the alkaline salt surface [18]. However, the main drawback was that the impregnated catalyst exhibited a low surface area with regard to that of the stoichiometric porous salt, due to pore blockage; the BET surface area value was around 20–30 m^2/g, while that of the neutral salt reached 160 m^2/g [18].

In the present work, we have studied the possibility of improving the $H_3PW_{12}O_{40}$ dispersion on a porous stoichiometric salt (namely $Cs_3PW_{12}O_{40}$) by vigorous grinding of a mixture of the pure acid $H_3PW_{12}O_{40}\cdot xH_2O$ and its stoichiometric Cs_3P salt within a wide range of H/P ratio values, in the hope that the textural features of the Cs_3P salt would be at least partly preserved.

2. Experimental

2.1. Preparation of the samples

The $H_3PW_{12}O_{40}\cdot 21H_2O$ acid (designated $H_3P\cdot 21H_2O$) was supplied by Aldrich and was used without further purification. $H_3P\cdot 13H_2O$ was obtained after drying $H_3P\cdot 21H_2O$ on a Büchner filter. Crystals of the highest hydrate $H_3P\cdot 30H_2O$ were isolated from water recrystallisation of H_3P. $H_3P\cdot 30H_2O$ crystals were removed from the solution and dried quickly on a filter paper. The hexahydrate $H_3P\cdot 6H_2O$ was obtained through heating $H_3P\cdot 21H_2O$ in a drying oven at 353 K. The hydration states of the various hydrates were checked, immediately after their preparation, by thermogravimetric analysis.

The Cs_3P salt was prepared by precipitation upon adding, under vigorous stirring, at room temperature, a 5 M aqueous solution of CsCl into a 0.1 M solution of the H_3P in the desired stoichiometric proportion. The precipitate was separated by centrifugation and simply dried under ambient atmosphere for 48 h. The hydration state obtained by this procedure was $Cs_3P\cdot 10H_2O$. Its chemical composition was checked by elemental analysis of W and Cs content ($Cs/P = 2.96$).

Mechanical mixtures were prepared by mixing $H_3P\cdot xH_2O$ and Cs_3P samples in the desired stoichiometry. Grinding was carried out in an automated device using an alumina mortar with three agate balls. 2 g of sample were ground at a time in the open air for varying times.

A wet impregnation of the neutral Cs salt and a soft mixing method were tested for comparison. To this end, two samples with a stoichiometry $H_3P/Cs_3P = 1.3/1.7$ were prepared; one by gentle mixing of the solids in a simple vibrator for 25 min and the other by impregnating the Cs_3P salt with an aqueous solution of H_3P and evaporating the water at 313 K under reduced pressure.

For convenience, all the samples prepared by mixing will be designated as $H_xCs_{3-x}\,t.n$, where x is the final amount of protons per Keggin unit (KU), t the duration of the grinding and n the number of constitutional water molecules per KU of the particular acid H_3P used in the grinding (6, 13, 21 or 30). The sample prepared through mild mixing will be abbreviated as $H_{1.3}Cs_{1.7}\,M.n$ (M for mild). The one prepared by wet impregnation will be designated as $H_{1.3}Cs_{1.7}$ imp. The "classical acidic" salt prepared by precipitation, abbreviated Cs_2HP was prepared by adding the stoichiometric amount of an aqueous solution (5 M) of cesium chloride to a 0.1 M aqueous solution of $H_3PW_{12}O_{40}$. The proton content deduced both from chemical analysis and from TGA was equal to 1.1 H per Keggin unit.

2.2. Characterisations

Porosity and surface area determinations were performed using a laboratory-made automated equipment for N_2 adsorption measurements at liquid-nitrogen temperature. The samples were degassed, prior to measurement, under vacuum at 473 K for 2 h, the heating temperature rate was 3 $K\,min^{-1}$. The analysis of the experimental points included the determination of: (1) BET surface area; (2) the pore size distribution in the microporosity range using the MP method and the t-plot which allow the estimation of the equivalent microporous surface; the thickness equation of Harkins and Jura was employed as reference isotherm [20]; (3) the mesopore size distribution deduced from the desorption branch of the isotherm using the Kelvin equation and the procedure given by Roberts.

Thermogravimetric analyses were carried out under N_2 flow in a Setaram 92-12 TGA-DTA apparatus with a heating rate of 5 $K\,min^{-1}$ up to 1023 K. TGA curves exhibit several losses of water. Below 523 K the weight losses can be ascribed either to water of crystallisation or physisorbed water, and the further one between 523 and 750 K to the departure of the "constitutional" water; that is to say, the release of the protons bound to the anion. This weight loss, occurring between 523 and 750 K, is considered as the deprotonation step of the heteropoly acid. For the bulk acid $H_3PW_{12}O_{40}$, the constitutional water equals 1.5 H_2O, which fits well with the three protons per Keggin unit. In a previous work [15] we have already shown that for the acidic Cs salts the proton contents deduced in this way and given by the chemical analysis of the Cs and W content are in good agreement. Consequently, the deprotonation step in TG experiments can be considered as a measurement of the H^+ content of the different samples. The exotherms near 861 K for the mixtures and 873 K for the pure acid form characterise the destruction of the acid and the crystallisation of its constituent oxides.

X-ray diffraction patterns were obtained at room temperature with a Siemens diffractometer using Cu Kα radiation.

2.3. Catalytic properties

The reaction studied was n-butane isomerisation at 473 K, a reaction which requires strong acid sites. The samples were pretreated before reaction at 473 K under nitrogen flow (1.5 $dm^3\,h^{-1}$) for 2 h. One used a flow microreactor with 100–200 mg of catalyst, a gas feed composition of n-butane/N_2 = 4.5/95.5 and a flow rate of 1.2 $dm^3\,h^{-1}$ (reaction gases were analysed by on-line GC). The reactor incorporated two independent lines: one for the pretreatment stream and another one for the n-butane/N_2 stream. During the pretreatment process, the composition of the n-butane feed was stabilised and analysed. The pretreatment stream was replaced by the stabilised butane/N_2 stream at the beginning of the reaction by means of a four-way valve. The first analysis was performed after 4 min and was considered as the initial activity.

3. Experimental results and discussion

3.1. Influence of the catalyst proton contents

Samples with various proton contents were prepared by grinding Cs_3P and $H_3P{\cdot}21H_2O$ at the desired stoichiometry for 5 min. They correspond to the abbreviation H_xCs_{3-x} 5.21. The samples were prepared in order to correspond to the final x values: 0.5, 1, 1.5, 2 and 2.5.

3.1.1. Proton content measured by thermogravimetry

We usually check the proton content of HPA by thermogravimetric analysis, since we have shown in a previous work [15] that the proton content drawn from TGA was in good agreement with the value deduced from the chemical analysis (W and Cs contents). The thermogravimetric curves presented in figure 1 evidence the evolution of several discrete weight losses for the series of samples. The last weight loss, which occurs between 623 and 823 K, is ascribed to the deprotonation step and is taken as a measurement of the H content. The first ones which occur below 573 K can reasonably fit with the departure of crystallisation water and/or physisorbed water. Table 1 summarises the measured H contents together with the expected x value, drawn from the synthesis stoichiometry. As expected the proton content calculated from TGA is in agreement with the synthesis stoichiometry. The exothermal peaks were observed at the same temperature. They are ascribed to the crystallization of the constitutive oxides consecutive of the destruction of the Keggin unit of the acid part of the samples.

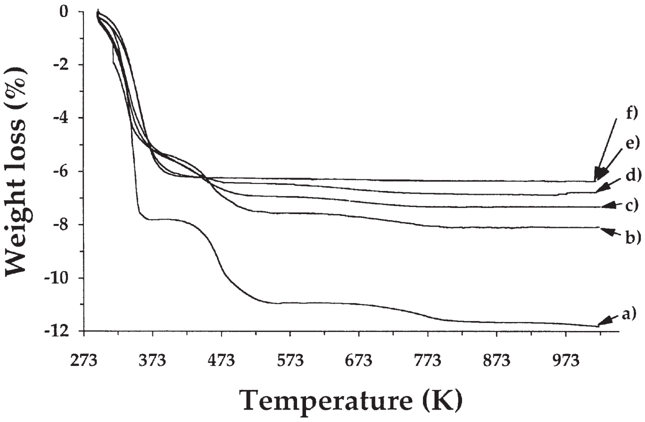


Figure 1. Thermogravimetric curves of H_xCs_{3-x} 5.21 samples versus the temperature. (a) $x = 3$, (b) $x = 2.2$, (c) $x = 1.7$, (d) $x = 1.0$, (e) $x = 0.5$, (f) $x = 0$.

Table 1
H content (x) of the samples H_xCs_{3-x} 5.21.

H content per Keggin unit		Temperature of the exothermal peak (K)
Expected[a]	Measured[b]	
3 (ground bulk acid)	3	867
2.0	2.2	865
1.5	1.8	863
1.0	1.1	863
0.5	0.5	broad peak around 860
0 (ground neutral Cs_3P)	0	–

[a] Drawn from the synthesis stoichiometry.
[b] Measured by thermogravimetry.

3.1.2. Structural features

Firstly, it was informative to follow the structural evolutions of the bulk acid $H_3P{\cdot}21H_2O$ and of the neutral salt Cs_3P after the grinding procedure. The XRD spectra reported in figure 2 show marked differences after $H_3P{\cdot}21H_2O$ grinding: the XRD pattern presented the diffraction lines of the two lower hydrates: $H_3P{\cdot}6H_2O$ characterised by its cubic structure and $H_3P{\cdot}13H_2O$ which crystallised in a triclinic system. It was not surprising to observe that the grinding process results in a dehydration, since some local heating may have occurred due to frictions.

On the other hand, in the case of the porous Cs_3P, its crystallographic structure was preserved after grinding. However, one notices only a slight decrease of the crystallinity of the porous salt after grinding (figure 3).

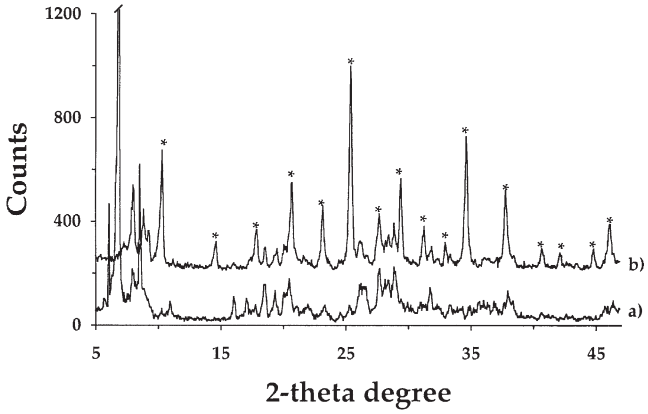


Figure 2. XRD patterns of $H_3P{\cdot}21H_2O$ sample (a) before and (b) after grinding. *Peaks of $H_3P{\cdot}6H_2O$ cubic structure.

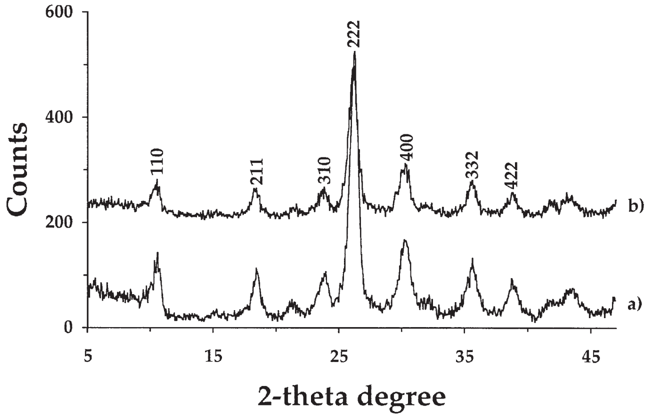


Figure 3. XRD patterns of Cs_3P sample (a) before and (b) after grinding.

XRD patterns of the mixed catalysts prepared by grinding: H_xCs_{3-x} 5.21 ($x = 0.5$, 1.5 or 2) are shown in figure 4. All patterns are quite similar to that of the Cs_3P sample and one can observe the absence of the diffraction lines ascribed to one of the different H_3P hydrates. These results give proof of the high dispersion of the acid phase. However, for the sample prepared with the highest H_3P/Cs_3P ratio, a loss of crystallinity appeared together with a variation in the cell parameters and the increase of the relative intensity of the (110) diffraction peak. The relative intensity of this plane was the highest for $H_3P{\cdot}6H_2O$. The cell parameter values reported in table 2 show no drastic changes for $x < 1.5$. For $x \geqslant 1.5$, the cell parameter values increased up to the cell parameter of $H_3P{\cdot}6H_2O$ (1.216 nm). These data suggest that a solid solution phase could be formed for samples prepared with the highest H_3P/Cs_3P ratio values ($x \geqslant 1.5$). However, it is worthwhile noting that the samples prepared with high acid content ($x \geqslant 1.5$) have less crystallinity.

In the case of acidic cesium salts prepared by precipitation from aqueous solution and separated by centrifugation, all samples presented the cubic phase with the same unit cell ($a_0 = 1.184$ nm). Nevertheless, it was shown that with this method of preparation the proton content was limited to $H/P = 1$ [15]. This is probably the reason why we did not observe a similar evolution of the cell parameters. These results seem to indicate that the formation of solid solution between H_3P and Cs_3P could be possible for samples with low Cs/P ratio ($\leqslant 1.5$).

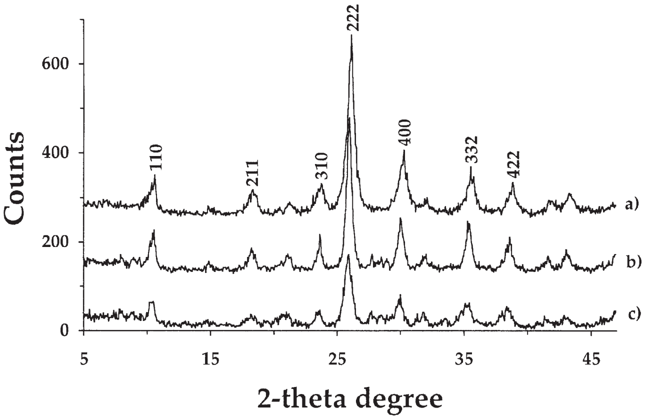


Figure 4. XRD patterns of H_xCs_{3-x} 5.21 sample after grinding. (a) $x = 0.5$, (b) $x = 1.5$, (c) $x = 2$.

Table 2
Cell parameters of H_xCs_{3-x} 5.21 from XRD patterns.

x values	0	0.5	1	1.3	1.5	2	3
a_0 (nm)	1.182	1.181	1.184	1.184	1.187	1.193	1.216

3.1.3. Textural features

The BET surface area measurement data are presented in table 3. As one could expect, the Cs_3P sample exhibited a high surface area (160 $m^2\,g^{-1}$) compared to its parent acid form H_3P (7 $m^2\,g^{-1}$). Moreover, some porosity modifications, which we analysed using the MP method and the t-plot curves from the N_2 isotherms, were observed. One may distinguish between mesoporosity ($\varnothing > 2.0$ nm), microporosity (0.6 nm $< \varnothing <$ 2.0 nm) and ultramicroporosity ($\varnothing < 0.6$ nm) in these solids (table 3).

Firstly, we observed that the BET surface area of the samples decreased with increasing H content but, more importantly, that vigorous grinding resulted in a decrease in surface area, for instance, by almost a factor two for the $H_{1.3}Cs_{1.7}$ ground samples. For comparison, Cs_3P lost only 5% of its BET surface area *after grinding*, due principally to a decrease of mesoporosity. The theoretical surface area of the samples, calculated from their chemical composition and the surface area values of Cs_3P and H_3P before the grinding, are also reported in table 3. All the theoretical values are higher than the measured ones. The data presented in table 3 seems to indicate that the BET surface area decrease is due mainly to micropore blockage and not to the collapse of the texture through the grinding. For ground solids with a high acid content, the microporosity contribution seems mainly reduced with regard to the mesoporosity. However, no general trend between the changes in different porosity types and Cs content could be clearly established.

Table 3
Textural features of H_xCs_{3-x} 5.21.

Sample	S_{BET} ($m^2\,g^{-1}$)	S calculated[a] ($m^2\,g^{-1}$)	S_{meso} ($\varnothing > 1.8$ nm)	S_{micro} ($\varnothing = 0.6$–1.8 nm)	S_{micro} ($\varnothing < 0.6$ nm)
H_3Cs_0 0.21	7	–	–	–	–
H_3Cs_0 5.21	7	–	–	–	–
$H_2Cs_{1.0}$ 5.21	43	56	28	6	9
$H_{1.5}Cs_{1.5}$ 5.21	65	83	22	34	9
$H_{1.3}Cs_{1.7}$ 5.21	63	95	19	39	5
$H_1Cs_{2.0}$ 5.21	43	111	16	13	14
$H_{0.5}Cs_{2.5}$ 5.21	147	139	10	101	36
H_0Cs_3 5.0	151	–	19	99	37
H_0Cs_3 0.0	160	–	46	77	33

[a] Calculated from the S_{BET} of Cs_3P and H_3P and the chemical composition of the samples.

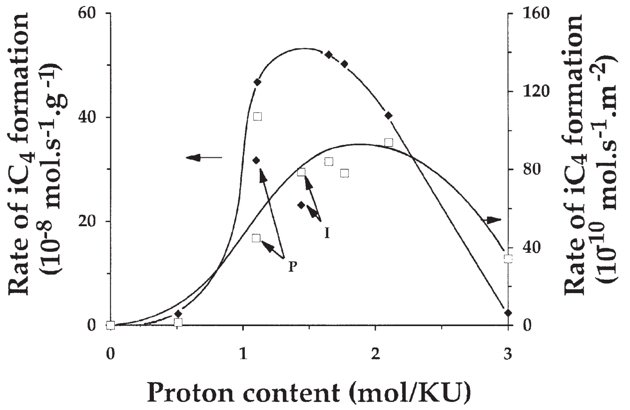


Figure 5. Catalytic activity of H_xCs_{3-x} 5.21 in n-butane isomerisation at 473 K. Pretreatment conditions: 2 h at 473 K under N_2 flow rate of 1.2 $dm^3\,h^{-1}$. Reaction conditions: m(catalyst) $= 0.1$–0.2 g, n-butane/N_2 $= 4.5/95.5$, total flow rate $= 1.2$ $dm^3\,h^{-1}$. I: activities of the sample prepared by wet impregnation; P: activities of the sample prepared by precipitation.

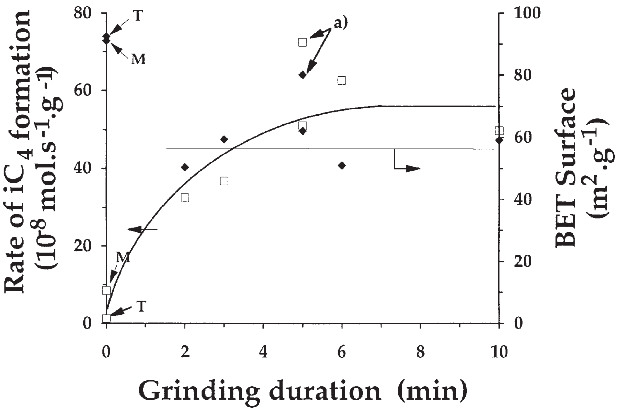


Figure 6. Catalytic activity in n-butane isomerisation and BET surface area of $H_{1.3}Cs_{1.7}$ t.21 versus the grinding duration (t). Pretreatment conditions: 2 h at 473 K under N_2 flow rate of 1.5 $dm^3\,h^{-1}$. Reaction conditions: m(catalyst) $= 0.1$–0.2 g, n-butane/N_2 $= 4.5/95.5$, total flow rate $= 1.2$ $dm^3\,h^{-1}$. a): grinding using 3.55 g of sample instead of 2 g; M: activities and S_{BET} of the sample prepared through mild mixing; T: theoretical values calculated from the activities and the S_{BET} of Cs_3P and H_3P before grinding.

Table 4
Deactivation factors calculated for H_xCs_{3-x} 5.21 in n-butane isomerisation performed at 473 K.

x values	0	0.5	1	1.3	1.5	2	3
R_1[a] (%)	0	17.6	47	47	69	82	−14[b]

[a] R_1 (%) $= 100 \times$ (rate at 4 min − rate at 130 min)/rate at 4 min.
[b] An initial activation step was initialy observed with $H_3PW_{12}O_{40}$ if pretreated at 473 K [21].

3.1.4. Catalytic activity measured in n-butane isomerisation at 473 K

The catalytic activities of the samples Cs_xH_{3-x} 5.21 as a function of the proton content x are presented in figure 5. Since rapid deactivation was observed for all samples, all catalytic activities reported in figure 6 are given after 4 min of time on stream. The selectivity was ca. 90% in isobutane and the remaining products were mainly propane and pentanes. These catalytic data are given as per gramme (specific rates) and per m^2 (intrinsic rates), since the number of protons accessible to the reactant molecules is not known. However, a clear conclusion may be drawn, it appears that the initial catalytic activity is very much enhanced by grinding when compared with the activity of the two starting materials: Cs_3P and H_3P. The catalytic activity measurement supported the previous physico-chemical characterisations indicating the good dispersion of the acid on the higher area Cs_3P salt.

We have tried to quantify the extent of deactivation by means of a deactivation coefficient (R (%) $= 100 \times$ (rate at 4 min − rate at 130 min)/rate at 4 min). The values are reported in table 4. Rate of deactivation was shown to be dependent on the proton density of the catalyst, with the most rapid deactivation observed for the solid with the highest protonic density. A “classical” Cs salt such as Cs_2HP, prepared by precipitation, is characterised by a deactivation coefficient of 68 under the same conditions of reaction. This simple estimation of the deactivation extent demonstrates that the solids prepared by grinding are as stable as those prepared by precipitation, although being more active.

3.2. Influence of the grinding procedure

In order to evaluate the general effect of the grinding procedure, we have chosen to investigate in detail the ef-

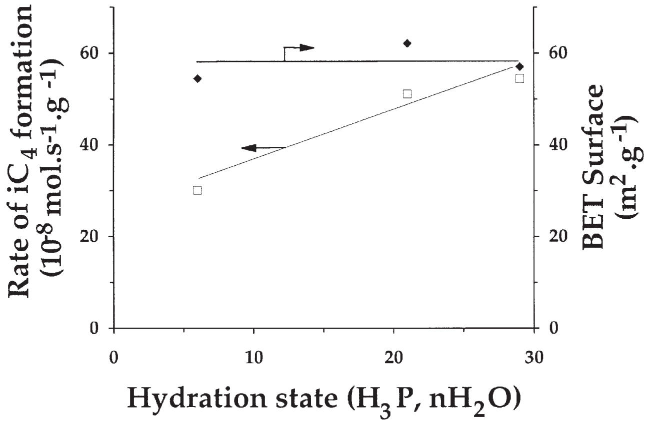


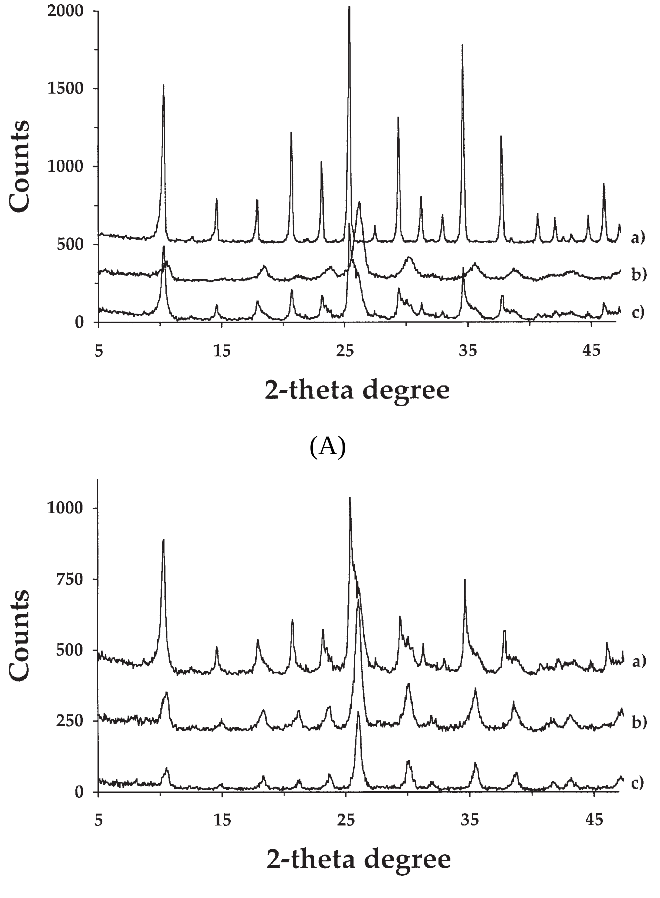
Figure 7. Catalytic activities in n-butane isomerisation and BET surface area of $H_{1.3}Cs_{1.7}$ 5.n samples versus the hydration state of $H_3P(n)$.

fect of the grinding duration on catalytic performances and physico-chemical properties. The grinding duration was shown to have an effect on activity (figure 6). An optimum in activity was reached when the solids were ground for more than 6 min. The BET surface area values for different grinding durations are reported also in figure 6, and vary between 50 and 63 $m^2 g^{-1}$. The BET surface area values were not seen to vary linearly with the grinding extent.

A sample prepared through mild mixing, $H_{1.3}Cs_{1.7}$ M.21, was also seen to present a higher activity than a theoretical value calculated from the activity of H_3P and Cs_3P (figure 6). This result indicates that, even through mild mixing, a dispersion of the acid phase occurs.

All the materials prepared in this work were obtained after the grinding of a total amount of 2 g of solid. An additional $H_{1.3}Cs_{1.7}$ 5.21 sample was prepared through grinding a total amount of 3.55 g of solid precursors. In this case, an improvement in the measured activity for n-butane isomerisation was observed. The rate of iC_4 formation after 4 min of time on stream reached the value of 72×10^{-8} mol s^{-1} g^{-1}. This improvement may be due to its higher BET surface area (80 $m^2 g^{-1}$) instead of 63 $m^2 g^{-1}$ obtained if only 2 g of precursors were ground.

This data shows that the grinding procedure has an effect on catalyst behavior. However, it appears that the improvement of the catalytic performances is somewhat arbitrary and requires an optimisation of the grinding equipment–grinding procedure system.



(A)

(B)

Figure 8. (A) XRD patterns of (a) $H_3P\cdot6H_2O$, (b) Cs_3P, (c) $H_{1.3}Cs_{1.7}$ 5.6. (B) XRD patterns of (a) $H_{1.3}Cs_{1.7}$ 5.6, (b) $H_{1.3}Cs_{1.7}$ 5.21, (c) $H_{1.3}Cs_{1.7}$ 5.30.

3.3. *Influence of the hydration state of the bulk acid used for the grinding*

Following the previous results, which show that the catalytic activity was dependent on the H_3P dispersion on the porous Cs_3P, we investigated the effect of the starting H_3P hydration state. Three different hydrates were used for this investigation: $H_3P\cdot6H_2O$, $H_3P\cdot21H_2O$ and $H_3P\cdot30H_2O$. The resulting catalysts are abbreviated as follows: $H_{1.3}Cs_{1.7}$ 5.6, $H_{1.3}Cs_{1.7}$ 5.21, $H_{1.3}Cs_{1.7}$ 5.30. The results reported in figure 7 indicate clearly that there is an improvement of catalytic activity with increase of the acid hydration state, even though the surface area remained about unchanged.

The XRD spectra of the three solids, reported in figure 8, are very informative: the XRD spectrum of $H_{1.3}Cs_{1.7}$ 5.6 exhibits dissymmetric peaks, which are likely the result of the superposition of the patterns of both Cs_3P and $H_3P\cdot6H_2O$ (figure 8(A)). Both solids crystallised in a cubic structure but exhibit different cell parameters: 1.184 and 1.216 nm, respectively. On the other hand, the XRD spectra of $H_{1.3}Cs_{1.7}$ 5.21 and $H_{1.3}Cs_{1.7}$ 5.30 are quite similar to that of the primary Cs_3P (see figure 8(B)). These data evidence the good dispersion of H_3P on the isostructural support Cs_3P: the H_3P dispersion being enhanced by the hydration level of the starting H_3P, water molecules favoring the species mobility.

3.4. *Comparison with acidic salts prepared by precipitation in aqueous solution or by wet impregnation of the stoichiometric salt $Cs_3PW_{12}O_{40}$*

The catalytic activities of the Cs_2HP sample prepared by the classical method of precipitation in aqueous solution and $H_{1.3}Cs_{1.7}$ prepared by wet impregnation were also investigated for comparison (figure 5) (abbreviated, respectively, P and I). These two catalysts are seen to be less active. This is certainly due to the following reasons: the precipitated sample exhibits an equivalent BET surface area but certainly a lower dispersion state of the acid. The impregnated sample has a lower BET surface area but a dispersion similar to that of the ground samples and its intrinsic activity is comparable.

4. Conclusions

The reported results show that a vigorous grinding of mechanical mixtures of the acid H_3P and its Cs_3P salt led to particularly efficient catalysts for the n-butane isomerisation reaction. It is shown that such a grinding dispersed the low surface area acid on top of the Cs_3P salt. We postulated previously that the H_3P acid was trapped in the pores of Cs_3P during the precipitation of the Cs salts [4,15]. In the present preparation the relative amount of protons in the Cs salt can be varied over the whole composition range, while it was not possible directly by precipitation followed by centrifugation and drying, since a maximum of $H/P = 1$ was obtained. However, if the precipitation was not followed by a separation of the precipitates from the mother solutions, the entire range of composition (H/P = 3–0) can be obtained by a wet method. Such a procedure was described by Misono et al. [14] and leads to solids with high BET surface area only for the higher H density ($H/P > 1$).

Comparison with a supported catalyst formed directly by wet impregnation of a neutral salt $M_3PW_{12}O_{40}$ shows that grinding results in more active catalysts. Higher BET surface area associated with a good dispersion of the acid phase could explain such a high activity of the acidic salts prepared by grinding. Catalysts with high BET surface area, high H quantities ($H/P > 1$) and with a good acid dispersion (as desmonstrated by the XRD patterns) can then be obtained if hydrated acids are used for the grinding.

Activity measurements and XRD patterns showed the marked role of the crystallisation water in the dispersion ability of the acid phase. One can emphasise also the importance of the grinding procedure, linked evidently with the equipment used for the grinding and with the more or less hydrated starting material.

Our results can also explain some discrepancies observed in the literature where a total range of proton/Cs contents could be obtained after precipitation, but without filtration to eliminate the excess solution. Our opinion is that in such cases one presumably has a deposit of acid on the top of the Cs_3P salt from the solution after evacuation of the water solvent, as for an impregnation procedure. The advantage of our procedure is that the largest surface area material available was used as a support even though the grinding decreased it by a factor of two, which resulted in a better dispersion of the acid. It also allows us to prepare samples with a proton/Cs ratio in the whole range of chemical compositions with a relatively high BET surface area. For these solids, strong enhancement of catalytic activity was obtained when H content was higher than 0.5 per Keggin unit and was optimum in the range of $1 < x < 2$.

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