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$H_3PW_{12}O_{40}$ supported on Cs modified mesoporous silica: catalytic activity in *n*-butane isomerisation and in situ FTIR study Comparison with microporous $Cs_xH_{3-x}PW_{12}O_{40}$

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Abstract

12-Tungstophosphoric acid, $H_3PW_{12}O_{40}$ (HPW), was supported over conventional mesoporous silica and MCM-41. The acidity of these supported materials and their catalytic activity in *n*-butane isomerisation were investigated. The differences in activity between these two series of supported HPW were ascribed to different HPW dispersion. Modification of the mesoporous silica and MCM-41 by treatment with cesium carbonate increased their catalytic activity. It was shown that the subsequent impregnation of the HPW resulted in the formation of the cesium salt ($Cs_3PW_{12}O_{40}$) supporting the HPW. An optimum of Cs:HPW ratio was observed, which was interpreted as due to a competition between dispersing the HPW on Cs salt formed and the acid site neutralisation by Cs^+ cation. The optimised catalyst, obtained by supporting HPW over Cs modified MCM-41, was found to be more active in the reaction of *n*-C_4 isomerisation than the conventional acidic Cs salt, $Cs_2HPW_{12}O_{40}$. Pyridine adsorption over supported HPW and microporous $Cs_2HPW_{12}O_{40}$ was investigated by in situ FTIR spectroscopy and compared to bulk HPW. Pyridine adsorption over bulk HPW lead to a peculiar spectrum ascribed to the formation of the bis-pyridinium species. Over supported HPW and microporous Cs salt, the classical spectra of the pyridinium species were observed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *n*-Butane isomerisation; Acidity; Heteropolyacids; Supported catalysts; Mesoporous silica; MCM-41; Cs modified silica and MCM; Brønsted sites

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1. Introduction

The *n*-paraffin isomerisation into branched hydrocarbons with higher octane number is an important process of the petrochemical industry. This transformation is favoured at low temperature, which is why strong solid acid catalysts are required such as Pt/chlorinated alumina. However, due to negative effects of chlorine on the environment, the search of environmentally friendly strong solid acids is justified. Heteropolyacids have been identified to be good candidates for this challenge due to their strong acidity [1]. Among them, 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ (HPW) has attracted most attention due to its highest acid strength in the series. Nevertheless, the main drawback of such materials for catalytic application is their low specific surface area. Therefore, for many catalytic applications, the dispersion of the heteropolycompound onto a high surface area carrier

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is necessary. For this purpose, two main approaches have been followed in the literature: the direct preparation of acidic porous salts or the dispersion of the heteropolyacid on classical supports.

The first approach concerns the acidic alkaline salts, abbreviated conventionally $M_xH_{3-x}PW_{12}O_{40}$ ($M = Cs^+$, K^+, Rb^+ or $NH_4{}^+$). Among them, the acidic Cs salt, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, was first reported by Misono and co-workers to be highly active in many acid-type reactions [2]. These salts, when prepared in aqueous solution by partial neutralisation of the proton of the heteropolyacid by alkaline cations and recovered from the mother solution by centrifugation, correspond to higher surface area solids with a global composition $M_xH_{3-x}PW_{12}O_{40}$, with x-value larger than 2 [3]. Unfortunately, via this method the protonic content and the textural features of the precipitated salt vary in a opposite way [3]. In terms of protonic surface density, the more acid catalyst corresponds to a composition near $Cs_2HPW_{12}O_{40}$ if prepared as described previously [3]. These porous acidic salts $M_xH_{3-x}PW_{12}O_{40}$ were shown to be composed of an acid phase dispersed on the microporous neutral salt $M_3PW_{12}O_{40}$ [4]. Recently, the characteristic features of their protonic sites were observed to be similar to those of the parent acid indicating that $Cs_3PW_{12}O_{40}$ is likely an ideal support for $H_3PW_{12}O_{40}$ [5].

The second approach, which was also the subject of extensive investigations, is the direct dispersion of the heteropolycompound on a conventional support such as silica [6–11], TiO_2, carbon, Al_2O_3 or ZrO_2 [12–15]. Because of its inertness towards the heteropolycompound structure, silica is probably the most suitable carrier for supporting heteropolyacids. However, even with silica support, it is not clear whether or not for low HPW loading, the heteropolyanion structure is preserved. Nevertheless, high activities were usually reported with supported HPW compared to that of the bulk acid ascribed to an enhanced dispersion of the HPW. Moreover, from published data, the second point which remains to be elucidated is, whether or not, the intrinsic acidity of the bulk HPW is maintained after dispersion on the carrier as in the case of acidic porous salts such as $Cs_2HPW_{12}O_{40}$.

More recently, alkaline modified silica was used to prepare supported HPW. Enhanced HPW dispersions and catalytic performances were reported by this way. This method of synthesis is intermediate between those described previously. It combines both the beneficial effect of the alkaline cation for the improvement of HPW dispersion and stability and the advantages linked to the use of a high surface area carrier with a controlled porosity. This approach, first described to our knowledge in 1997, was applied to acidic type reaction [16–18] and to redox transformation as well [19].

In the recent years, we have focused our efforts in improving and controlling the acidic properties of HPW based materials. The aim of the present work is to evaluate this new way of supporting $H_3PW_{12}O_{40}$ with respect to the more conventional microporous $Cs_2HPW_{12}O_{40}$ and to $H_3PW_{12}O_{40}$ dispersed on unmodified silica.

2. Experimental

2.1. Catalyst preparation

The preparation of bulk and porous heteropolyacids was carried out by conventional methods described elsewhere [3]. For the synthesis of supported HPW, two types of silica supports were used: a commercial mesoporous silica–gel, Grace Davison 432, with pore diameters ranging from 9 to 15 nm and a BET surface area of $304\,m^2\,g^{-1}$ (denoted hereafter SiO_2) and an ordered pure siliceous MCM-41 whose pore diameter is 2.8 nm (N_2 adsorption, BJH determination) and its BET surface area $988\,m^2\,g^{-1}$. This MCM-41 silica sample was prepared following a well known procedure [20].

Two series of supported HPW samples were prepared. The first ones were obtained by direct incipient wetness impregnation of the silica support by a 12-phosphotungstic aqueous solution. The resulting samples are abbreviated as nH$_3$P/silica, n being P mol% (P:Si ratios of 1:100, 2:100, 3:100). The second series corresponds to HPW impregnated on Cs-modified silica supports. The Cs modified silicas were prepared by impregnation with a dilute Cs_2CO_3 aqueous solution using various Cs:Si molar ratios, followed by drying and calcination in air at 573K. Then the solids were impregnated with an aqueous HPW solution of the appropriate concentration. Finally, the resulting solids were dried and calcined at 573 K. These samples are abbreviated as: nH$_3$P/mCs-silica,

Table 1
Characteristics of supported HPW samples: composition, S_{BET} and HPW coverage (S_{HPW}/S_{SiO_2})

Support	Abbreviation	n[a]	m[b]	S_{SiO_2}[c] ($m^2\ g_{cat}^{-1}$)	S_{HPW}/S_{SiO_2}[d]	wt.% HPW[e]	S_{BET} ($m^2\ g^{-1}$)
SiO_2	SiO_2	0	0	304	0	0	304
	$H_3P/2Cs\text{-}SiO_2$	1	2	188	0.5	38.1	163
	$H_3P/Cs\text{-}SiO_2$	1	1	188	0.5	38.3	195
	$2H_3P/2Cs\text{-}SiO_2$	2	2	148	0.9	51.1	186
	$4H_3P/4Cs\text{-}SiO_2$	4	4	100	1.9	67.4	85
MCM-41	MCM	0	0	988	0	0	988
	H_3P/MCM	1	0	642	0.15	35.0	702
	$2H_3P$/MCM	2	0	472	0.3	51.8	463
	$3H_3P$/MCM	3	0	377	0.4	61.8	310
	H_3P/Cs-MCM	1	1	–	–	36.0	194
	$4H_3P$/4Cs-MCM	4	4	–	–	68.0	206
	$4H_3P$/8Cs-MCM	4	8	–	–	69.1	189
	$8H_3P$/8Cs-MCM	8	8	–	–	80.1	80

[a] n is P mol% (P:Si ratio × 100).

[b] m is Cs mol% (Cs:Si ratio × 100).

[c] Deduced from experimental total surface area assuming no modification of the silica surface.

[d] Assuming that one Keggin unit occupies $1.44 \times 10^{-18}\ m^2$.

[e] Deduced from the chemical analysis of W and Si contents.

where n is P mol% (P:Si ratio × 100) and m the Cs mol% (Cs:Si ratio × 100). The HPW loadings, deduced from the chemical analysis of Si and W elements, are ranging from 38 wt.% for H_3P/Cs-silica up to 80 wt.% for $8H_3P$/8Cs-silica. The two series of catalysts are listed in Table 1 together with their chemical composition, the total BET surface areas and calculated HPW coverage; S_{HPW}/S_{SiO_2}, assuming uniform HPW dispersion on the support and that one Keggin unit occupies $1.44 \times 10^{-18}\ m^2$.

2.2. Catalyst characterisation

Several parameters were investigated, as the textural features of the silica, the HPW and the Cs loadings. Supported materials were characterised by chemical analysis, X-ray diffraction (XRD), ^{31}P MAS-NMR, and N_2 adsorption isotherms. The acidic properties of supported HPW were characterised by in situ FTIR spectroscopy by means of pyridine adsorption and compared in detail to that of bulk HPW and microporous salts.

2.3. Catalytic testing

The n-butane isomerisation reaction was used as a test reaction. It was carried out in a differential flow microreactor under the following conditions: catalyst weight = 200 mg, $T_{reaction} = 473\ K$, 4.4% n-butane in N_2, total flow rate = $2.6\ l\ h^{-1}$. In some cases, the catalysts were pre-treated for 1 h at room temperature with a water saturated N_2 flow followed by a treatment at 473 K in nitrogen for 2 h. They will be designated with w as a subscript.

3. Results and discussion

3.1. Catalyst characterisation

3.1.1. X-ray diffraction study

XRD data indicate that the MCM-41 sample exhibits the ordered hexagonal structure characterised by an intense reflection peak at a d spacing of 3.8 nm. The intensity of this low angle reflection peak decreases progressively as the HPW loading increases (Fig. 1). After Cs impregnation, at a loading as high as 4 mol% (4Cs-MCM), the intensity of this low angle peak decreases strongly and more drastically after the HPW impregnation (Fig. 1). Cs and HPW loadings induce a drastic decrease of the intensity of the low angle reflection peak which may indicate a structural distortion of the MCM-41 or more simply a reduction of its long range order. At higher 2θ angle, the diffraction

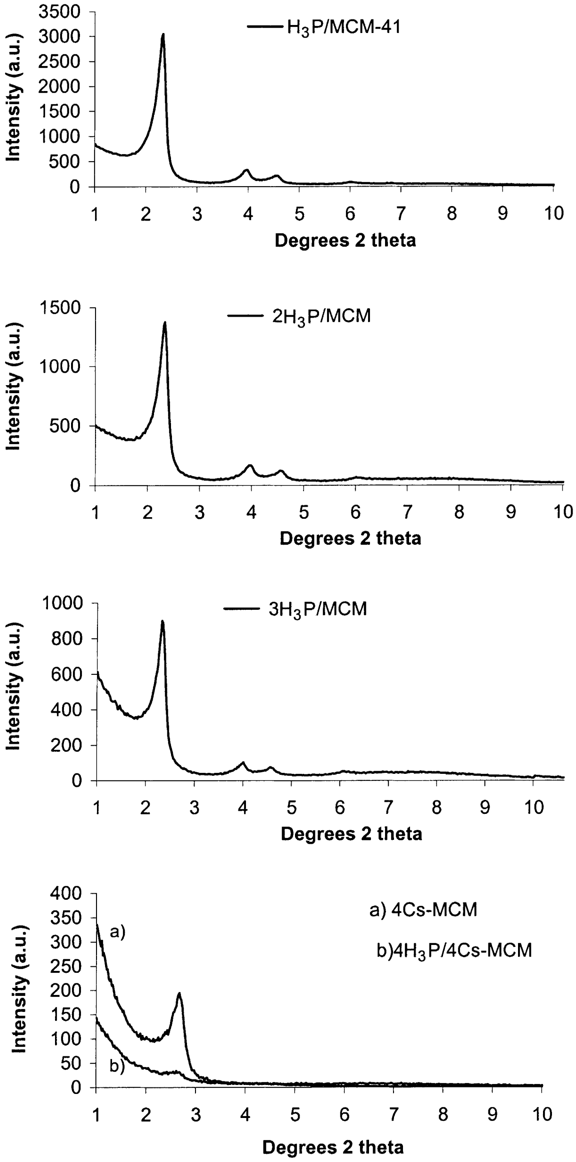

Fig. 1. XRD patterns, recorded at low angles, of nH$_3$P/MCM, 4Cs-MCM and 4H$_3$P/4Cs-MCM samples.

lines of bulk HPW were observed even for the lowest HPW loading (35 wt.% for H$_3$P/MCM) (Fig. 2). The XRD pattern of 4H$_3$P/4Cs-MCM exhibits also the lines of the cubic HPW structure. However, the peaks are broadened indicating a higher dispersion of the heteropolyanion. In addition, the unit cell parameters are near the values reported for the acidic cesium salts, 1.184 nm. Consequently, it seems reasonable to propose that such salts are formed at the silica surface.

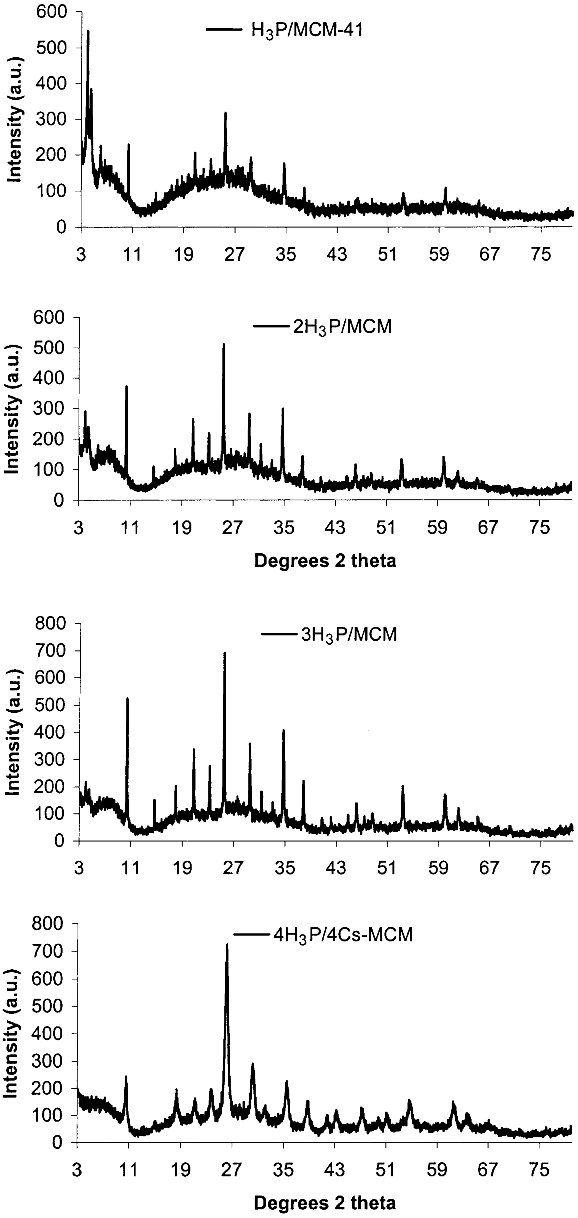

Fig. 2. XRD patterns recorded from 3 to 80° (2θ) of nH$_3$P/MCM and 4H$_3$P/4Cs-MCM samples.

3.1.2. ^{31}P MAS-NMR study

^{31}P MAS-NMR spectra of nH$_3$P/MCM-41 with increasing HPW loadings show a main peak at

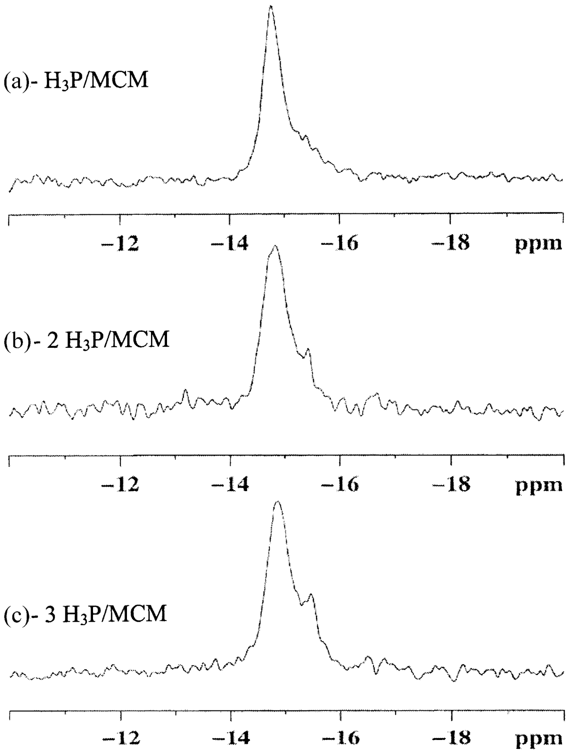

Fig. 3. ^{31}P MAS-NMR spectra of nH$_3$P/MCM samples.

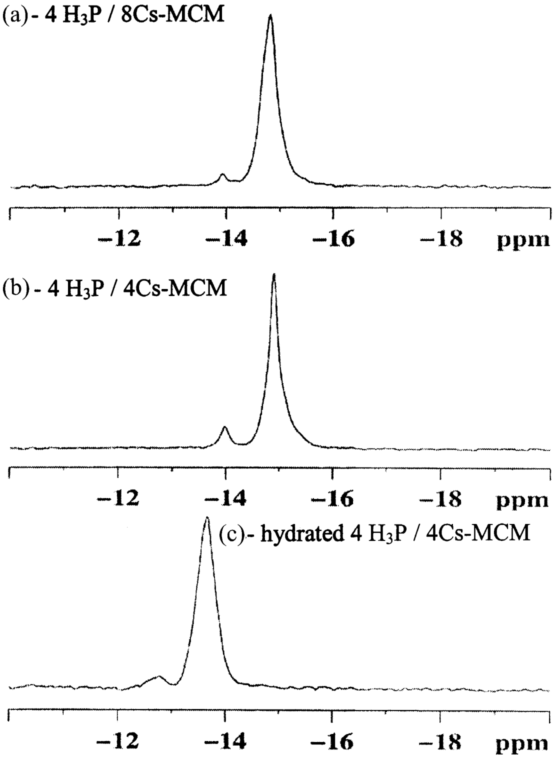

Fig. 4. ^{31}P MAS-NMR spectra of 4H$_3$P/8Cs-MCM, 4H$_3$P/4Cs-MCM and hydrated 4H$_3$P/4Cs-MCM samples.

−14.8 ppm and a shoulder at −15.5 ppm (Fig. 3). The relative intensity of the shoulder at −15.5 ppm increases progressively with the HPW loading. It is well known that the ^{31}P NMR chemical shift of HPW is very sensitive to its hydration level. A chemical shift of −15.5 ppm is characteristic of its hydrated form. Dehydrated bulk HPW shows a low field shift of ^{31}P NMR peak indicating local structural changes of the Keggin anion [21].

Consequently, it seems reasonable to ascribe the shoulder at −15.5 ppm to hydrated HPW crystallites weakly bonded to the support while the main peak at −14.8 ppm could correspond to heteropolyanions showing a slight distortion with respect to bulk hydrated HPW. Since the materials were analysed in an equivalently hydrated form, this distortion of the Keggin unit should result from the interaction with the silica support and/or the presence of different states of hydration generated also by the presence of the support. The spectra of HPW supported on Cs-modified MCM-41 show a principal sharp resonance line at −14.8 ppm and a smaller one at −13.9 ppm (Fig. 4). The intensity of this former peak decreases when the Cs content increases. The chemical shift of the dominant peak at −14.8 ppm is in agreement with the ^{31}P NMR chemical shift measured on the neutral salt $Cs_3PW_{12}O_{40}$ [21]. The small peak at −13.9 ppm is presumably related to the presence of the acid phase without Cs^+ as countercation since its intensity is reduced when higher Cs loading are used. However, this non-exchanged acid phase could be immobilised in a partially dehydrated state.

3.1.3. Textural features

The textural features were drawn from N_2 adsorption–desorption isotherms. Commercial silica loaded with increasing amounts of HPW shows mainly a decrease of its adsorption capacity, resulting in lower BET surface area values. The isotherms are

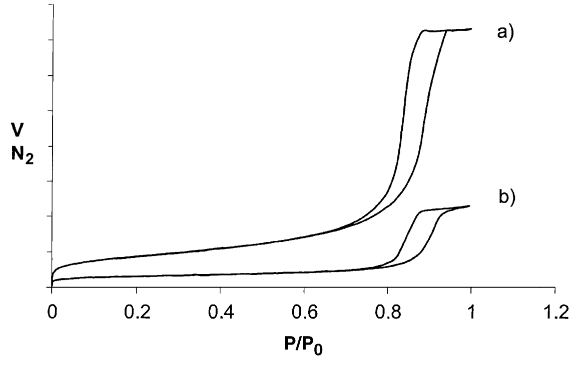

Fig. 5. N_2 isotherms of (a) initial commercial silica SiO_2 (b) $4H_3P/4Cs\text{-}SiO_2$ samples.

of IV type according to IUPAC classification, given by mesoporous materials (Fig. 5). The BET surface values fall down to 85 $m^2\,g^{-1}$ for $4H_3P/4Cs\text{-}SiO_2$ (Table 1). However, if we consider the high HPW loading in mass and refer the surface area per gram of silica alone, we get only small changes in surface area values (column 5 in Table 1). In addition, the isotherm shape and the hysteresis loop remain almost unchanged indicating that the pore/shape was not changed by the HPW, i.e. that the heteropolyanions were either introduced in the porosity, filling progressively the pores and/or being deposited on the external surface of the silica particles.

N_2 isotherms performed on MCM-41 samples give a reversible type IV isotherm and the pore diameter calculated from BJH method equal 2.8 nm, against 3.8 nm from the *d* spacing from XRD, as shown above. We are of the opinion that the 2.8 nm from BJH method is more realistic. Unlike commercial silica, the mesopores filling by N_2 at 77 K takes place reversibly over a short range of P/P_0 (Fig. 6). The samples with increasing amounts of HPW on MCM-41 evidenced a progressive clogging of the regular mesoporous structure (Fig. 6). The step in the isotherm branch, near $P/P_0 = 0.35$, which indicates the occurrence of capillary condensation in the regular mesopores, is progressively reduced as the H_3P content increases. These data indicate that the pore dimension of the MCM-41 (2.8 nm) does not allow the penetration of the heteropolyanion (≈1.2 nm) into the regular pores of the carrier. More likely, the heteropolyanions may stick on the surface of the MCM-41 particles and not in the pores. For HPW dispersed on Cs modified silica, this phenomenon is more pronounced. Cs and HPW impregnation might have disrupted the long range order of the MCM-41 as indicated by the XRD data resulting in its decreased adsorption capacity. However, high external surface areas were measured even for the highest HPW loading, 189 and 80 $m^2\,g^{-1}$ for $4H_3P/8Cs$-MCM and $8H_3P/8Cs$-MCM, respectively.

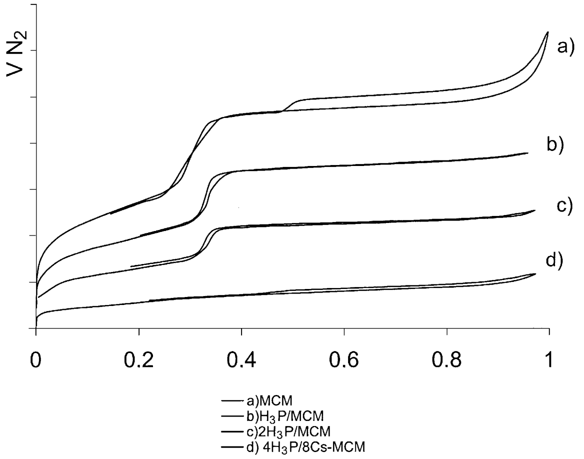

Fig. 6. N_2 isotherms of MCM-41, nH_3P/MCM-41 and $4H_3P/4Cs$-MCM samples.

3.2. In situ FTIR study

The IR spectra of the various catalysts were investigated in order to collect information on the structural features of the supported HPW in order to assess the nature of the interaction of the HPW with the support, on one hand, and to probe the acid properties of the material, on the other hand. To achieve this goal, two different techniques were used:

(i) a suspension of the material in water was sprayed over a silicium wafer and dried;
(ii) the material was pressed into self supported wafer in the usual way.

The former technique produced higher quality spectra in the Keggin unit domain, while the latter produced improved spectra in the high frequency domain, particularly for the adsorption of surface species as pyridine.

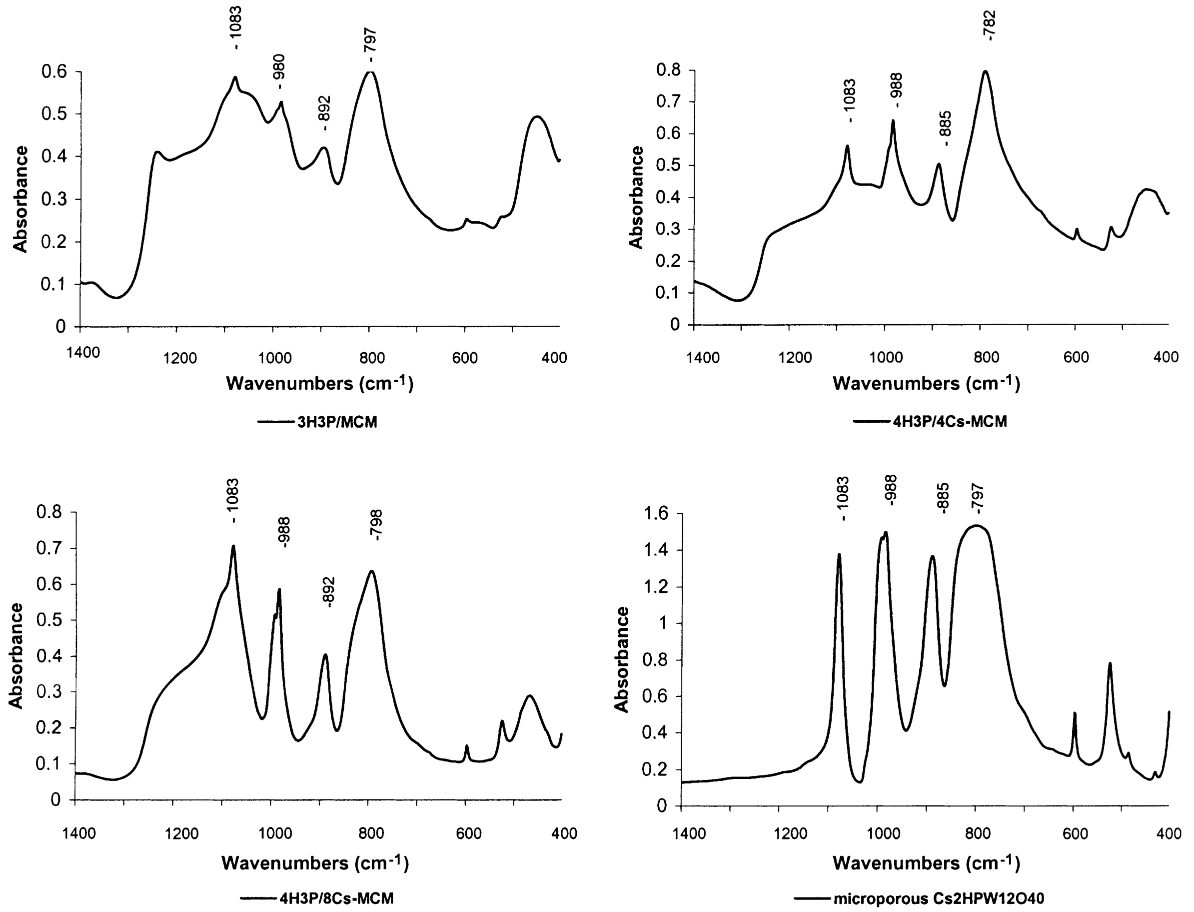

Fig. 7. In situ FTIR spectra of HPW supported on MCM-41 or Cs-MCM-41 and the microporous acid salt $Cs_2HPW_{12}O_{40}$ samples. Spectra recorded at 293 K after treatment under vacuum at 293 K for 30 min.

The absorption bands related to the Keggin unit are those which may indicate the conservation of the integrity of the parent structure together with the occurrence of an interaction of the HPW (or acid salt) with the support.

The spectrum of the HPW supported over unmodified MCM-41 is shown Fig. 7. The Keggin unit absorption domain is partially obscured by the absorption originating from the MCM-41 network. However, all the usual bands of the heteropolyanion are present and experience a general high frequency shift and broadening [5]. This is in agreement with ^{31}P NMR results which also show that ^{31}P has experienced a significant shift from that of hydrated HPW. In addition to the Keggin unit fingerprint, ν_{OH} are observed at 3747 and 3502 cm^{-1} due to both OH groups from the MCM-41 and HPW (Fig. 8). More interestingly, δ_{OH} dual absorption is clearly seen at 1700 and 1642 cm^{-1}, respectively, due to protonated water, presumably $H_5O_2{}^+$, generated by HPW, and water physisorbed onto MCM-41. The presence of the δ_{OH} at 1700 cm^{-1} is a clear evidence that the supported HPW has retained, at least, part of its acidic properties. However, pyridine adsorption investigated using IR spectroscopy shows differences compared to bulk HPW. Indeed, as shown in Fig. 9, the spectrum recorded over $3H_3P$/MCM, after pyridine adsorption and evacuation at 423 K, revealed a single 19 b vibration mode absorption at 1540 cm^{-1}. This result is at variance with what is observed over bulk HPW (Fig. 9b): a dual 19 b

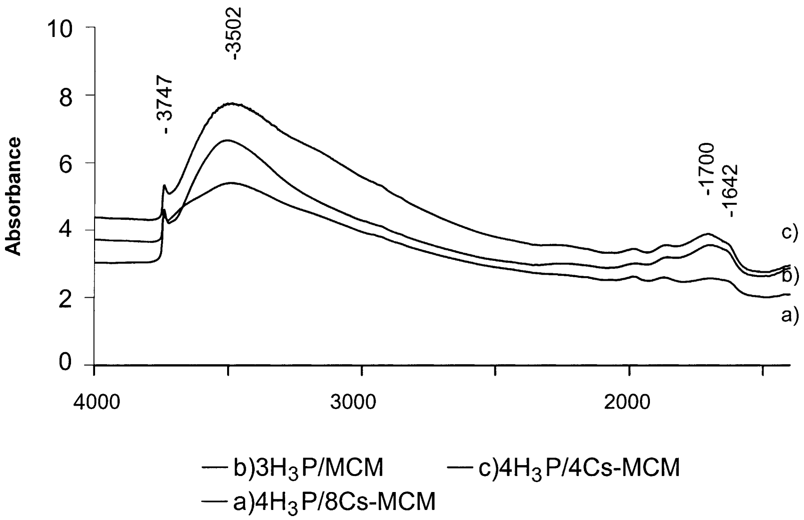

Fig. 8. In situ FTIR spectra of MCM or Cs-MCM supported HPW samples recorded at 293 K after treatment under vacuum at 293 K for 30 min.

vibration mode at 1531 and 1542 cm^{-1} is observed. Through adsorption of gaseous pyridine over bulk HPW, bulk pyridinium salt is formed with the well defined structure associating two pyridine molecules [22]. Over supported HPW, a surface pyridinium ion was formed very much like on other acid surfaces such as silica–alumina, zeolites ... This suggests an important modification of the HPW structure originated from dispersion and/or interaction with the support.

When MCM-41 material was treated with Cs^+ and subsequently impregnated with HPW to achieve Cs:P molar ratio of 2:1 or 1:2, the IR spectrum exhibited a Keggin unit pattern almost identical with that of the acid salt for the highest Cs loading (Fig. 7). Therefore, this result reinforces the idea that the acid has reacted with Cs^+ cation to form a cesium salt deposited on the surface of MCM with a very loose interaction, if any.

At this stage it is not clear whether the excess acid part is dispersed over the neutral salt, as it was established earlier in the absence of a support, or interacting directly with the MCM surface. Since the interaction of the acid with the MCM is only witnessed by a small high frequency shift of the W–O vibration, it seems more reasonable to assume that the acid part is dispersed on the salt via epitaxial growth of the excess acid over the salt formed by the early neutralisation of the added acid. The acidity of such supported materials is again in line with the formation of the corresponding acid salt as may be seen from the δ_{OH} vibration which exhibited a dual adsorption at 1700 and 1642 cm^{-1} (Fig. 8).

The intensity ratio of the high frequency δ_{OH} absorption is within the reciprocal of the corresponding Cs:P ratio, the higher the Cs content, the lower the intensity of the band at 1700 cm^{-1} taken as a reference. This is an indication that the non-stoichiometric supported salt contains acid sites strong enough to protonate water molecules to form the $H_5O_2{}^+$ complex proportionally to the residual protons.

Pyridine adsorption as monitored by IR confirmed the Brønsted acidic character of the supported non-stoichiometric salts (Fig. 9). It is also noteworthy to mention that the pyridinium ions are similar in structure to conventional surface pyridinium ions observed on other surfaces by contrast to their structure in bulk pyridinium salt of HPW, again indicating a high dispersion of the HPW over Cs-MCM or most probably over the corresponding cesium salt. Note also that over the conventional microporous acidic salt, $Cs_2HPW_{12}O_{40}$, only surface pyridinium ions are observed in agreement with the fact that these materials can be considered as an acid phase dispersed on the microporous $C_3PW_{12}O_{40}$ [4].

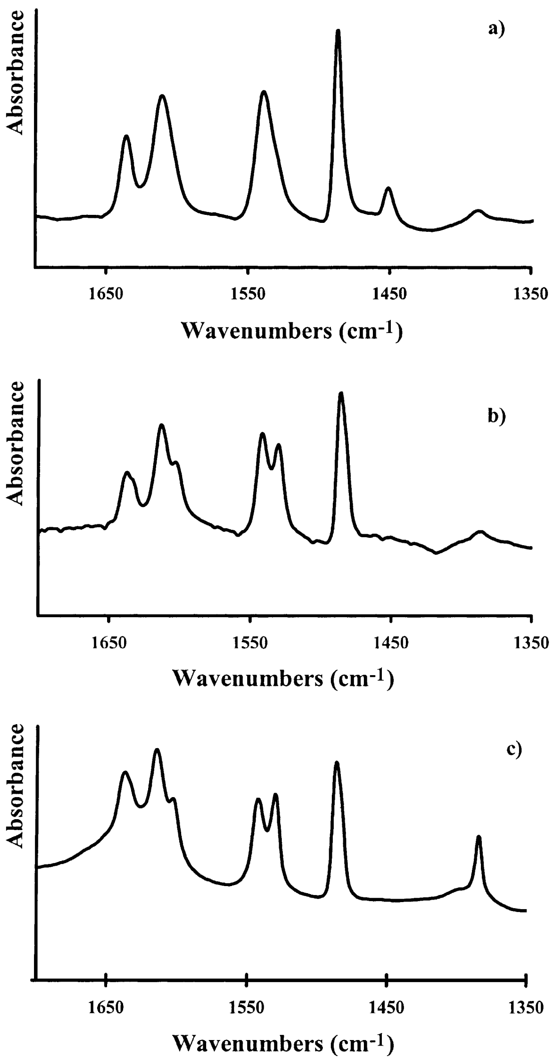

Fig. 9. Adsorption of pyridine evacuated at 423 K over HPW materials pre-treated at 473 K. (a) $3H_3P/MCM$; (b) bulk HPW; (c) IR spectrum of bulk pyridinium salt.

3.3. Catalytic activity in n-C_4 isomerisation reaction

3.3.1. Influence of the silica nature

Table 2 shows the effect of the nature of the silica support on the initial rate of *i*-C_4 formation. It is worthwhile to mention that the initial activity of HPW supported on Cs-modified MCM-41 is always higher than that of HPW supported on Cs-modified commercial silica in spite of similar HPW loadings and surface area values. As described previously, the main difference between the two types of catalysts is the site of the HPW grafting. The regularity of the MCM-41 pore system coupled with their relative small dimension (2.8 nm) leads to the adsorption of the heteropolyanions on the external surface of the particles rather than in the pores.

To generate highly active catalysts, it was reasonable to expect that the penetration of the heteropolyanions inside the porosity might favour their dispersion and consequently catalytic activity. The present results are in favour of an enhanced accessibility to the heteropolyacids using MCM with respect to the other mesoporous silica with larger pores. Surprisingly, the entrance of the 2.8 nm pores of the MCM does not allow the penetration of the heteropolyanions, but leads, nevertheless, to a larger external active surface, presumably by favouring HPW dispersion on the external surface.

3.3.2. Influence of Cs^+ cation

To examine the influence of the Cs^+ cation, the initial catalytic activity of $4H_3P/4Cs\text{-}MCM_w$ and $3H_3P/MCM_w$ are compared in Table 3. These samples were chosen due to their nearly equal H^+ content assuming the formation of acidic cesium salts at the silica surface. As shown in Table 3, the initial activity

Table 2
Initial rate of *i*-C_4 formation for H_3P/Cs-silica samples

Catalysts	*i*-C_4 formation rate (10^{-7} mol h^{-1} g^{-1})	S_{BET} ($m^2\,g^{-1}$)	*i*-C_4 formation rate (10^{-7} mol h^{-1} g_{HPW}^{-1})
$H_3P/Cs\text{-}SiO_{2w}$	0.75	195	2.0
$H_3P/Cs\text{-}MCM_w$	2.9	194	8.1
$4H_3P/4Cs\text{-}SiO_{2w}$	2.5	85	3.7
$4H_3P/4Cs\text{-}MCM_w$	4.7	206	6.9

Conditions: $m_{cat} = 0.2$ g; total flow rate = 2.6 l h^{-1}; n-C_4: 4.4% in N_2; $T_{reaction} = 473$ K; catalyst pre-treatment: hydration at ambient temperature followed by flushing with N_2 for 2 h at 473 K.

Table 3
Initial rate of i-C_4 formation on $4H_3P/m$Cs-MCM and $3H_3P$/MCM

Catalysts	i-C_4 formation rate (10^{-7} mol h^{-1} g^{-1})	i-C_4 formation rate (10^{-7} mol h^{-1} g_{HPW}^{-1})
$4H_3P/8Cs$-MCM_w	2.0	2.9
$4H_3P/4Cs$-MCM_w	4.7	6.9
$3H_3P/MCM_w$	1.8	2.9

Conditions: $m_{cat} = 0.2$ g; total flow rate = 2.6 l h^{-1}; n-C_4: 4.4% in N_2; $T_{reaction} = 473$ K; catalyst pre-treatment: hydration at ambient temperature followed by flushing with N_2 for 2 h at 473 K.

of $4H_3P/4Cs$-MCM_w is more than twice that of $3H_3P/MCM_w$ in spite of a lower BET surface area value (206 against 310 m^2 g^{-1}, respectively). Therefore, the higher activity of HPW supported on Cs-modified MCM can be ascribed only to the presence of Cs^+ cation. These catalytic results clearly indicate that the acid properties of HPW dispersed over Cs treated silica are enhanced compared to that for HPW supported over unmodified silica. These catalytic data are in agreement with the previous ^{31}P NMR and FTIR results which have shown that the Cs^+ cations prevent the Keggin structure distortion caused by strong interaction with the carrier surface in the absence of cationic centres. Paradoxically, Cs^+ cations should contribute to the acidity enhancement by this way. Note that the HPW peaks in XRD patterns (Fig. 2) are broader when Cs is present, indicating a better dispersion of HPW species.

To clarify the role of the Cs^+ cation, the catalytic activities of $4H_3P/8Cs$-MCM_w and $4H_3P/4Cs$-MCM_w are reported in Table 3. These two catalysts have about the same HPW loading but differ by their molar Cs:P ratio (1 or 2). A clear relationship between the initial activities and their H^+ content appears: the initial activity of $4H_3P/4Cs$-MCM is more than twice that of $4H_3P/8Cs$-MCM. This result suggests strongly that the Cs^+ cation dispersed on the silica support is effectively in the position of countercation relative to the Keggin anion. These catalytic results show that if the presence of Cs^+ cations is beneficial for the catalytic activity, their concentration is to be optimised with respect to the HPW loading, presumably avoiding the over neutralisation of the protonic sites of the supported HPW, while favouring HPW dispersion.

3.3.3. *Effects of HPW loading*

The catalytic activity of H_3P/MCM with increasing HPW amount (1, 2 and 4 mol%) is reported in Table 4 together with that of the bulk HPW. One can observe that the specific activity of MCM-41 supported HPW varies slightly with HPW loading, whatever the activity is referred per gram catalyst or gram HPW and is definitely higher than for bulk HPW, which is due to HPW dispersion. Higher HPW loading did not increase the initial activity and the catalyst decay was more pronounced which may be linked to a higher protonic density coupled to an unfavourable texture.

Table 4
Initial rate of i-C_4 formation on nH_3P/MCM and bulk H_3P

Catalysts	i-C_4 formation rate (10^{-7} mol h^{-1} g^{-1})	i-C_4 formation rate (10^{-7} mol h^{-1} g_{HPW}^{-1})
H_3P/MCM	1.3	3.7
$2H_3P$/MCM	1.7	3.3
$3H_3P$/MCM	1.6	2.6
Bulk H_3P	0.95	0.95

Conditions: $m_{cat} = 0.2$g; total flow rate = 2.6 l h^{-1}; n-C_4: 4.4% in N_2; $T_{reaction} = 473$ K; catalyst pre-treatment: flushing with N_2 for 2 h at 473 K.

Tables 5 and 6 show the catalytic activity of the two Cs-modified silica supports loaded with different HPW amounts. On the commercial mesoporous silica

Table 5
Initial rate of i-C_4 formation on nH_3P/mCs-SiO_2

Catalysts	i-C_4 formation rate (10^{-7} mol h^{-1} g^{-1})	i-C_4 formation rate (10^{-7} mol h^{-1} g_{HPW}^{-1})
H_3P/Cs-SiO_{2w}	0.75	2.0
$2H_3P/2Cs$-SiO_{2w}	1.9	3.7
$4H_3P/4Cs$-SiO_{2w}	2.4	3.6

Conditions: $m_{cat} = 0.2$ g; total flow rate = 2.6 l h^{-1}; n-C_4: 4.4% in N_2; $T_{reaction} = 473$ K; catalyst pre-treatment: hydration at ambient temperature followed by flushing with N_2 for 2 h at 473 K.

Table 6
Initial rate of i-C_4 formation on nH_3P/mCs-MCM

Catalysts	i-C_4 formation rate (10^{-7} mol h^{-1} g^{-1})	i-C_4 formation rate (10^{-7} mol h^{-1} g_{HPW}^{-1})
H_3P/Cs-MCM_w	2.9	8.1
$4H_3P/4Cs$-MCM_w	4.7	6.9
$8H_3P/8Cs$-MCM_w	3.5	4.4

Conditions: $m_{cat} = 0.2$ g; total flow rate = 2.6 l h^{-1}; n-C_4: 4.4% in N_2; $T_{reaction} = 473$ K; catalyst pre-treatment: hydration at ambient temperature followed by flushing with N_2 for 2 h at 473 K.

(Table 5), the initial activity increases progressively with the HPW loading. Using MCM-41 as a support, a maximum catalytic conversion was obtained for intermediate HPW and Cs loadings if expressed per gram catalyst and decreased regularly if expressed per gram HPW, all catalysts being initially more active than for mesoporous silica.

3.3.4. Influence of water pre-treatment

Most of the catalytic results described above have been obtained over hydrated supported catalysts. Such catalysts were designated as follows $n\mathrm{H_3P/MCM_w}$ or $n\mathrm{H_3P/SiO_{2w}}$ instead of $n\mathrm{H_3P/MCM}$ or $n\mathrm{H_3P/SiO_2}$ in absence of water in the pre-treatment flow.

The effect of such treatment on the activity of the HPW supported on the commercial silica is shown in Fig. 10. Hydration pre-treatment has a beneficial effect on the stability of the catalyst and little effect on the initial activity. This effect is not dependent on the $\mathrm{Cs^+}$ amount. On HPW/MCM samples, only slight modifications were observed (Fig. 11).

Results in Fig. 11 show that when Cs-MCM was employed as a support, water pre-treatment induced mainly an increase of the initial activity. The fact that rehydration of $\mathrm{4H_3P/4Cs\text{-}MCM}$ enhanced the initial activity may be explained by the contribution of two phenomena:

- A likely enhancement of the HPW dispersion. As a matter of fact in a previous work [23], it was shown that the mobility of HPW over $\mathrm{Cs_3PW_{12}O_{40}}$ support was increased under wet conditions.
- The hydration of the supported HPW to its maximum level may produce an increase of the number of protonic sites assuming that the supported HPW were initially immobilised on the MCM support in a partially dehydrated state.

To elucidate the effect of such pre-treatments, $^{31}\mathrm{P}$ MAS-NMR analyses were realised on wet and dry samples. The dry catalyst $\mathrm{4H_3P/4Cs\text{-}MCM}$ exhibits two distinct sharp resonance peaks: the main one at −14.9 ppm, characteristic of the symmetrical Keggin anion $\mathrm{Cs_3PW_{12}O_{40}}$ and a smaller one at −13.9 ppm which can be attributed to HPW in interaction with the $\mathrm{Cs_3PW_{12}O_{40}}$ salt. Upon exposure to water vapour, the two resonance lines were shifted by 1 ppm towards higher field and the two lines were broadened (Fig. 4). These two modifications may result from a

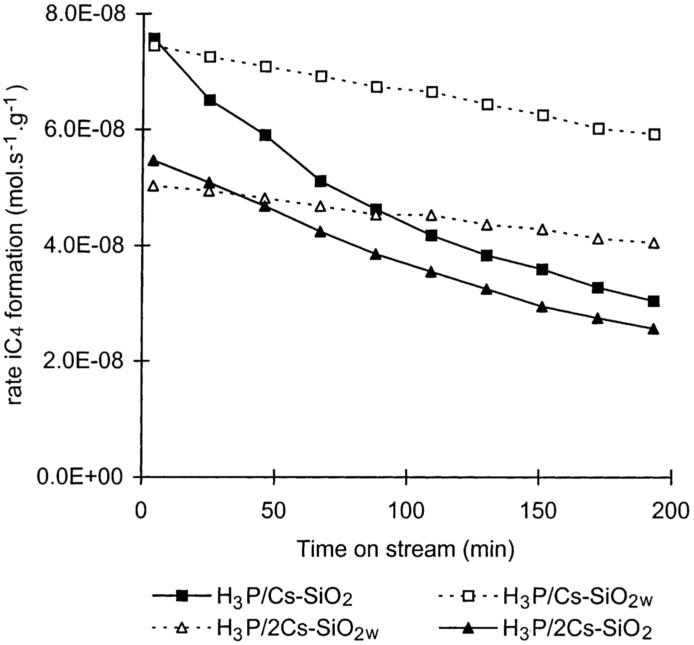

Fig. 10. Influence of water treatment on the activity of $\mathrm{H_3P/Cs\text{-}SiO_2}$ and $\mathrm{H_3P/2Cs\text{-}SiO_2}$ in n-$\mathrm{C_4}$ isomerisation reaction at 473 K.

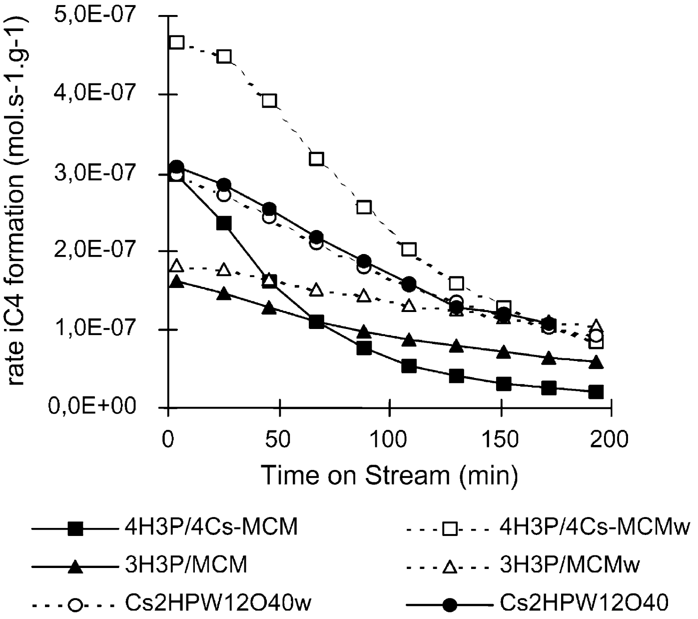

Fig. 11. Influence of water treatment on the activity of $3H_3P$/MCM, $4H_3P$/4Cs-MCM and microporous $Cs_2HPW_{12}O_{40}$ samples in n-C_4 isomerisation reaction at 473 K.

strengthening of the interaction of the HPW with the silica support which may be due in turn to an improved HPW dispersion. These NMR results support our earlier assumption that the water pre-treatment could favour the HPW dispersion onto the silica support [23].

The catalytic activity of pure microporous $Cs_2HPW_{12}O_{40}$ is also reported in Fig. 11 for comparison. Unlike supported HPW, this material is almost insensitive to the wet pre-treatment. Furthermore, data in Fig. 11 demonstrate that the optimised $4H_3P/4Cs\text{-}MCM_w$ exhibits a higher initial specific activity than microporous $Cs_2HPW_{12}O_{40}$.

4. Conclusions

MCM-41 was shown to provide a better support for HPW than a conventional mesoporous silica, on the basis of n-C_4 isomerisation reaction activity. This was assigned to a better dispersion of the HPW species, particularly on the external surface. In addition, it has been shown that the dispersion of HPW over unmodified MCM-41 does not enhance significantly the activity of the resulting material compared to the bulk acid in the reaction of n-C_4 isomerisation.

Improved HPW dispersion and catalytic activity was achieved upon treated MCM-41 with cesium cations even though some structural disruption of the MCM-41 framework was observed. The dispersion was shown to occur via formation of a cesium salt serving subsequently as an anchor site to additional HPW. In other words, it is concluded that the dispersion of the HPW over MCM-41 is favoured by increasing the cesium content, i.e. the number of anchor sites. However, the Cs:P ratio needs to be optimised to prevent the total neutralisation of the Brønsted sites.

Pyridine adsorption, monitored by IR spectroscopy, confirmed the presence of acid Brønsted sites with formation of conventional superficial pyridinium species on HPW dispersed on MCM, mesoporous silica, Cs-MCM and microporous $Cs_2HPW_{12}O_{40}$. The formation of bis-pyridinium species was only observed and is characteristic of the bulk HPW. Protonated water clusters were identified on the supported HPW showing that these Brønsted sites are able to protonate water molecule.

Finally, water treatment prior to the catalytic reaction was also shown to improve the activity which was assigned to additional dispersion of HPW.

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