New insights into the encapsulation and stabilization of heteropolyacids inside the pore walls of mesostructured silica materials[†]

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A method of synthesizing stable and reactive modified mesoporous hybrid materials with intact heteropolyacid (HPA) Keggin units is reported. The materials were synthesized by a one-pot method using a mixture of structure directing agents (CTAB and Pluronic 123). The key to obtaining stable HPA containing materials was the sequential calcination and extraction steps, and the authors present a working hypothesis for this phenomenon. Studies of several other key factors concerning synthetic parameters are also reported. All materials were characterized by a wide variety of physical and spectroscopic methods at each step of the synthesis. The kinetics of the esterification of acetic acid by butanol mediated by several of the materials and relevant homogeneous acid catalysts showed that the HPA containing hybrid material was a highly effective catalyst.

1. Introduction

The diversity of known polyoxometalates (POMs) provides a broad spectrum of chemical properties in terms of morphology, polarity, oxidation potentials, acidity and solubility.1 Thus, one encounters polyoxometalates in very diverse settings (medicine, catalysis, material science).² In catalysis, polyoxometalate compounds have been extensively used as acid and oxidation catalysts in many reactions since their acid-base and redox properties can be tuned easily by simply changing polyanion chemical composition.^{2a,3} Their utility for industrial application has been limited, notably due to their tendency toward low surface area (1-10 m²/g). Considerable effort has been directed towards their heterogenization onto large surface area supports. In particular, periodic mesoporous silica materials have been used to take advantage of their uniform and narrow pore size distributions, highly ordered structure and high thermal stability.⁴

POM-functionalized ordered mesoporous materials have been obtained either by impregnation⁵ and/or by direct synthesis using sol-gel techniques.⁶ In such cases, the HPAs are not covalently connected to the silica surface, but are presumably held by weak interactions between surface silanols and the HPA acidic protons, and so some degradation of the modified materials by polar solvents may occur, including clustering by dissolution/ precipitation of HPAs on the outer surface of silica support, ^{5d} leaching of the active species and/or loss of mesoporous ordering in the material. 6a

Polyoxometalates immobilization by stronger chemical bonding was also reported using organically modified mesoporous silica.7 For example, an HPA was immobilized inside the channels of MCM-41 which had been modified by amine functional groups: the HPA was held through an ionic bond (anion, ammonium) and catalytic activity was shown to be equivalent to free HPA in solution. The strong ionic bond leads to higher stability for the catalyst in polar solvent media.7ª Transitionpolyoxometalates substituted of metal the type $[M^{II}(H_2O)PW_{11}O_{39}]^{5-}$ (M = Co, Zn), have also been chemically anchored to aminopropyl modified silica surfaces through dative bonding.^{7b} The open coordination site available to these metal clusters allows them to bind various functional ligands leading to the creation of solids containing highly dispersed clusters. More recently, polyoxometalate compounds were introduced onto periodic ordered mesoporous silica by covalent linkages.8 This interesting approach involves the co-condensation of TEOS (tetraethoxysilane) with Keggin-type monovacant polyoxometalate of the type $SiW_{11}O_{39}^{8-}$, in the presence of block copolymers. Covalent Si-O-W bonds were readily formed from the reaction of TEOS with the lacunary SiW₁₁ leading to the attachment of the POM to the mesopore walls as a "SiW11Si2" intermediate. The obtained hybrid materials exhibited higher stability in water-leaching experiments compared to impregnated samples suggesting that the nature of the link but also the strategy of synthesizing the material is important.

In this paper we wish to report our efforts to obtain stable and reactive modified mesoporous hybrid materials with intact heteropolyacid (HPA) Keggin units which are resistant to extraction. Different methods are reported, satisfactory results depending on a three step synthetic sequence: co-condensation of HPA and silica precursors, followed by calcination then extraction. The state of the solid structure and the integrity of the Keggin units were characterized at each major step of

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elaboration by several methods among the following: X-ray powder diffraction at small angles, elemental analysis, thermogravimetric analysis, infrared spectroscopy, diffuse reflectance UV-Visible spectroscopy, ³¹P NMR spectroscopy, nitrogen sorptions, and transmission electron microscopy (with EDX). The accessibility of the heteropolyacid groups was shown through a model catalytic esterification reaction.

2. Experimental

2.1 Materials

Tetraethoxysilane (TEOS), poly- (ethylene oxide)–poly-(propylene oxide)–poly(ethylene oxide) block copolymer (Pluronic 123, MW: 5000) and phosphomolybdic acid, $H_3PMo_{12}O_{40} \cdot xH_2O$, were purchased from Aldrich Chemicals and used without further purification. Cetyltrimethylammonium bromide and tungstophosphoric acid, $H_3PW_{12}O_{40} \cdot xH_2O$, were obtained from Acros.

2.2 One pot synthesis of $H_3PW_{12}O_{40}$ modified SBA-15 type silica using a mixed surfactant system

The general approach for the synthesis of HPA modified hybrid materials involves the polymerization of a silica precursor in the presence of heteropolyacid using a mixture of non-ionic (Pluronic 123) and ionic (CTAB) structure directing agents. Composition for 4 g Pluronic 123: 125 g HCl (1.9 M); 8.16 g TEOS (0.0392 mol); 2.3 g H₃PW₁₂O₄₀ (8 10⁻⁴ mol); 0.2 g CTAB (5.5 10^{-4} mol). In a typical procedure, tetraethoxysilane (TEOS), aqueous acid (HCl) and templates were combined and allowed to react at 40 °C for 30 minutes (prehydrolysis reaction). The phosphotungstic acid, solubilized in a minimum of water, was then introduced dropwise. The temperature was maintained at 40 °C for 20 hours followed by ageing during 24 hours at 100 °C. The solid was recovered by filtration, washed with water and dried at 70 °C (as-made solid, 2). The templates were removed quantitatively from the as-made material by calcination (2-C) followed by extraction with methanol (2-CE). For comparison, blank materials (without H₃PW₁₂O₄₀) were prepared according to the same procedure and are referred to as 1 and 1-CE for the as-made and calcined/extracted solids, respectively.

2.3 Characterization

Low-angle X-ray powder diffraction (XRD) data were acquired on a Bruker D5005 diffractometer using Cu K α monochromatic radiation ($\lambda = 1.054184$ Å). Nitrogen adsorption–desorption isotherms at 77 K were measured using a Micromeritics ASAP 2010M physisorption analyzer. The samples were evacuated at 180 °C for 24 h before the measurements. Specific surface areas were calculated following the BET procedure. Pore size distribution was obtained by using the BJH pore analysis applied to the desorption branch of the nitrogen adsorption/–desorption isotherm. Infrared spectra were recorded from KBr pellets using a Mattson 3000 IRFT spectrometer. Liquid UV-vis spectra were recorded using a Vector 550 Bruker spectrometer. Solid UV-vis and near infrared spectra were recorded from aluminium cells with Suprasil 300 quartz windows, using a PerkinElmer Lambda 950 and PE Winlab software. A Netzsch thermoanalyser STA 409PC was used for simultaneous thermal analysis combining thermogravimetric (TGA) and differential thermoanalysis (DTA) at a heating rate of 10 °C min⁻¹ in air from 25–1000 °C. ³¹P MAS NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 121.51 MHz with a classical 4 mm probehead allowing spinning rates up to 10 kHz. The spectra were obtained by direct irradiation of phosphorus and proton decoupling. In all cases it was checked that there was a sufficient delay between the scans allowing a full relaxation of the nuclei. Depending of the amount of phosphorus in the samples and the nature of the samples between 100 and 10 000 scans were accumulated. The chemical shifts are given relative to external 85% H₃PO₄. Liquid NMR spectra were recorded on a Bruker AC-300 spectrometer and referenced as following: ¹H (300 MHz), internal SiMe₄ at $\delta = 0.00$ ppm, ¹³C (75 MHz), internal CDCl₃ at $\delta = 77.2$ ppm, and ³¹P (121 MHz), external 85% H₃PO₄ at $\delta =$ 0.00 ppm. Metal determinations were performed by ICP-OES (Activa Jobin Yvon) spectroscopy from a solution obtained by treatment of the solid catalyst with a mixture of HF, HNO₃ and H₂SO₄ in a Teflon reactor at 150 °C. High resolution transmission electron microscopy (HRTEM) was performed with a 200 kV JEOL 2010 microscope, with a point to point resolution of 0.195 nm (spherical aberration coefficient Cs = 0.5 mm). This instrument was equipped with an EDS X-ray analyzer LINK-ISIS. The preparation of the sample was performed by dispersing the catalyst powder within an EPON resin. Very thin slices (20-40 nm) were obtained by ultramicrotomy of the sample. The Ultramicrotome is a Leica Ultra cut UCT equipped with a diamond knife. The slices are then recovered on a microscopy copper grid (3.05 mm; 200 mesh) previously coated with a holeycarbon film. The Raman spectra were achieved on powders at room temperature with a LabRAM HR spectrometer (Jobin Yvon) equipped with a CCD detector. The emission line at 514.53 nm from an Ar⁺ ion laser (Spectra Physics) was focused on the sample under the microscope, the analyzing spot being ~ 1 µm. Time of acquisition was varied according to the intensity of the Raman scattering. The spectral resolution was about 2 cm⁻¹. Homogeneity of the samples was checked focusing the laser beam on various points.

2.4 Catalytic tests

Protocol. The liquid phase esterification of acetic acid with n-butanol was chosen as a model reaction to evaluate the performance of our hybrid materials. The catalytic reaction was carried out in a two-necked flask under nitrogen. The reaction mixture was composed of acetic acid (5.24 g, 0.087 mol), n-butanol (7.29 g, 0.098 mol), nonane (0.80 g, 6.23 10^{-3} mol) and toluene (4.9 ml). When a strong acid catalyst was added the amount was adjusted to give 7.85×10^{-6} mol based on $H_3PW_{12}O_{40}$ (100 mg for **2-CE** and 22.6 mg for molecular $H_3PW_{12}O_{40}$). In the case of the silica blank, 100 mg of **1-CE** was used. The reactor was placed in a preheated oil bath at 80 °C.

Analysis. The reaction was monitored by taking aliquots (0.2 ml) periodically (30 minutes), which were diluted with toluene (\sim 1 ml) and analyzed on a Varian CP-3800 gas chromatograph equipped with a flame ionization detector, a Varian CP-8400 autosampler and a CP-Sil5CB capillary column (30 m, 0.32 mm

internal diameter, 0.25 μ m film thickness). Nitrogen was used as gas carrier. Conversion and yield were determined by GC based on relative area of the GC-signals referred to an internal standard (nonane) calibrated to the corresponding pure compounds.

3. Results and discussion

The overall objective of the project was the production of an HPA containing catalytic material with the following criteria: high surface area materials in which stable, intact Keggin units have been integrated without significant changes in reactivity compared to the HPA in solution. Thus, one must balance the need for a robust link to the surface with the avoidance of profound changes in the chemical nature of the HPA. In order to better understand each step of the synthesis, a high level of characterisation was required throughout involving both molecular level techniques (variously NMR, Raman, UV-Vis) and bulk properties (XRD, TGA, BET). Finally, the materials were tested as catalysts, with the sole objective of demonstrating that the active HPA species was fully accessible.

3.1 Mixed surfactant templating approach for the one pot synthesis of H₃PW₁₂O₄₀ modified SBA-15 type silica

Given the failure of post-synthetic methods to provide stable modified materials, we chose to pursue direct synthetic or onepot-approaches to our objective. The basic SBA-15 protocol chosen involves the polycondensation of a silica precursor, typically tetraethoxysilane (TEOS), in the presence of a nonionic structure directing agent (SDA, Pluronic 123).9,4c As has been shown elsewhere, superior results, in terms of mesoscopic order, for organically modified SBA-15 silica were obtained by first allowing polycondensation of TEOS for a fixed period before introduction of the organic moiety.¹⁰ It has also been reported that the use of an ionic SDA, cetyltrimethylammonium bromide (CTAB) favors stronger HPA/support interactions, but attempts to use pure CTAB leads to HPA precipitation from the synthetic mixture.¹¹ We postulated that addition of smaller quantities of CTAB to a synthesis based on Pluronic 123 as SDA might ameliorate HPA inclusion without leading to precipitation and without disrupting the ordering of the micelles.

Thus, the polycondensation of TEOS in the presence of a mixture of non-ionic (Pluronic 123) and ionic (CTAB) structure directing agents was carried out in aqueous HCl at 40 °C for 30 minutes before dropwise addition of phosphotungstic acid, $H_3PW_{12}O_{40}$ (aq). The temperature was maintained at 40 °C for 20 hours followed by ageing at 100 °C. The solid was recovered by filtration, washed with water and dried at 70 °C. The two-template method was performed without addition of HPA (blank material 1) and was reproduced with the addition of different HPAs (based on tungsten and molybdenum) at various theoretical loadings. One example of a stable material in which $H_3PW_{12}O_{40}$ was incorporated by direct synthesis, **2**, serves as the basis for most of the other materials in this report.

The X-ray diffraction (XRD) powder pattern of the "as-made" material, **2**, showed three clear peaks in the 20-range of 0.6 to 3°, characteristic of hexagonally ordered mesophases, with a d(100) spacing of 98 Å (see Fig. 1, left, and Table 1). Analogous results were obtained for the blank material **1** (Table 1). In the case of **2**, the presence of H₃PW₁₂O₄₀ was indicated by elemental analysis (Table 1, W 12.8 \pm 0.05%_{wt}, P 0.2 \pm 0.05%_{wt}, W/P = 11 \pm 2.5) and the structural integrity of the HPA Keggin unit was confirmed by the presence of a single, very sharp peak at -15.3 ppm in the MAS ³¹P NMR spectrum (Fig. 1, right).

3.2 Template removal methods and HPA Keggin unit stability

The removal of the SDA from the pores while maintaining the ordering of the mesostructure is a key issue to address particularly for direct synthesis. In this study, both of the generally cited methods, extraction of the template and calcination led to quantitative removal of the SDA resulting in highly ordered, SDA free materials (2-E and 2-C, respectively). The extraction was performed by the soxhlet method using methanol (16 hours). The calcination was performed overnight under a flow of air at 500 °C. Extraction of the templates was confirmed by TGA and by infrared spectroscopy. In the case of the as-made material 2, a 22.7% weight loss was observed between 80 to 160 °C in the TGA, whereas in the 2-E and 2-C materials, no notable weight loss was observed above 80 °C (see ESI Fig. S1[†]). Furthermore, the v(CH) bands in the infrared spectrum of 2 were not at all present in the infrared spectra of 2-E and 2-C (see ESI Fig. S2[†]). The X-ray diffractograms of 2-E and 2-C (see Fig. 2, left, (a) and (b)



Fig. 1 XRD pattern (left) and MAS ³¹P NMR (right) of 2.

Table 1 Physical and textural properties of SBA-15 type silica materials containing $H_3PW_{12}O_{40}$

			Structural and textural properties							
Sample	Si(%wt)	W(% _{wt})	d ₁₀₀ ^{<i>a</i>} /Å	Wall thickness ^b /Å	$S\mu^{c}\!/m^{2}g^{-1}$	$V\mu^d/cm^3g^{-1}$	V_p^{e}/cm^3g^{-1}	$\mathbf{D}_{\mathbf{p}}^{f}/\mathbf{\mathring{A}}$	S_{BET}/m^2g^{-1}	
1			98		_					
1-CE			94	53.9	64.7	0.022	1.00	54.4	831	
2	14	12.8	98							
2-E	35.2	0.14	102	44.6	231.5	0.094	0.94	73.5	740	
2-C	26.1	23.6	92	39.2	133.5	0.057	0.452	67	305	
2-CE	25.8	17.3	96	43.1	152.5	0.068	0.53	67.5	428	

^{*a*} d(100) spacing (the error is estimated as 3 Å). ^{*b*} Calculated by $a_0 - pore$ size with $a_0 = 2d(100)/\sqrt{3}$. ^{*c*} Micropore surface determined using the *t*-plot method. ^{*d*} Micropore volume determined using the *t*-plot method. ^{*e*} Total pore volume at P/P₀ = 0.980. ^{*f*} Pore size from desorption branch applying the BJH pore analysis.



Fig. 2 XRD pattern (left) and MAS ³¹P NMR (right) of (a) 2-E; (b) 2-C; and (c) 2-CE.

respectively, and Table 1) indicate that the long range mesostructural order is maintained in all of the materials.

The effect of SDA removal by these methods on the HPA Keggin unit, as determined by ³¹P MAS NMR, appeared catastrophic, at least at first glance. When the SDA was removed by soxhlet extraction using methanol, **2-E**, no resonance peak between -200 and +200 ppm appeared (Fig. 2, right, spectrum a), suggesting that all of the HPA had been extracted along with the templates. This observation was confirmed by microanalysis where only traces of tungsten were found (Table 1, $0.14\%_{wt}$ for **2-E** vs. 12.8%_{wt} for **2**).

The results for SDA removal by calcination, **2-C**, were less absolute. The tungsten microanalysis (Table 1) showed no significant loss of tungsten in the material.¹² However, in the ³¹P MAS NMR spectrum, a very broad and intense series of resonances between 10 and -30 ppm surrounded the central, fine peak at -15 ppm of **2-C** (Fig. 2, right, spectrum b). Other analogous materials prepared in this series (differing HPA, different loading) showed only the broad resonances with no such fine central peak whatsoever (see ESI Fig. S3†). Clearly, calcination leads to significant, even quantitative breakdown of the highly symmetric HPA Keggin unit of **2**.

In the context of a leaching study, **2-C** was submitted to soxhlet extraction with methanol. To our initial surprise, this treatment led to the reformation of the Keggin unit and a stable

HPA modified material, 2-CE. Evidence for the Keggin unit reconstruction is found in the ³¹P MAS NMR of 2-CE (Fig. 2, right, spectrum c) where the only resonance observed was the fine peak at -15 ppm corresponding to the hydrated HPA molecular moiety.13 Microanalysis showed a small decrease of the tungsten loading (17.3%_{wt} for 2-CE vs. 23.6%_{wt} for 2-C) which could be due to the loss of HPA and/or to the partial filling of the mesoporous material by the alcohol, but certainly not the total elimination of the HPA moiety as was observed for extraction without calcination, 2-E. The X-ray diffractograms of 2-CE showed long range mesostructural ordering, although some loss of order with respect to 2-C and 2-E was indicated by the diminished peak intensity (Fig. 2, left, diffractogram c). Furthermore, the characteristic peaks of the HPA in the 3° to 80° (2 θ scale) region of the diffractograms were absent, indicating that the HPA was homogeneously dispersed over the solid (see ESI, Fig. S4[†]).

The TEM/EDX study of the surface of 2-CE showed well ordered long range ordering of the material and, most importantly, that tungsten was uniformly present over most of the ordered surface. Some "dark" pores showed high tungsten content, presumably plugged by the aggregation of many HPA units (see ESI Fig. S5†).

The textural data derived from the BET analysis of nitrogen adsorption and desorption experiments are presented in Table 1. The materials exhibit type IV isotherms characteristic of mesoporous solids, with large pore diameters (55–75 Å, see ESI Fig. S6–S8† for graphical data). It is interesting to note that while the material which was synthesized in the absence of HPA, **1-CE**, had little microporosity (specific microporous volume of 0.022 cm³ g⁻¹ and microporous surface area of 64.7 m² g⁻¹), the materials prepared in the presence of HPA, **2-E** and **2-CE**, had significant microporous nature (0.094 cm³ g⁻¹ and 231.5 m² g⁻¹; 0.068 cm³ g⁻¹ and 152.5 m² g⁻¹ respectively). Also note that **2-E**, the solid in which all of the HPA has been removed, has significantly more microporous volume and surface than the HPA containing **2-CE**.

Thus, material **2-CE** appears to conform to the structural criteria of the synthetic project. The ³¹P MAS NMR and the diffuse reflectance UV-Vis and infrared spectroscopies (ESI Fig. S9 and Fig. S10† respectively) would seem to indicate that chemical properties of the HPA inclusions may be similar to the free acid. Before confirming the accessibility and chemical activity of the modified material by catalytic benchmarking, a brief discussion of several side studies is presented.

3.3 Investigation of synthesis conditions

Influence of the concentration of CTAB. As mentioned above, the materials **2** are based on a synthetic procedure in which the SDA mixture is Pluronic/CTAB in a 1 : 0.8 molar ratio. The logic

behind this approach was based on previous authors' hypotheses that such mixed micelles with ionic surfactants is an easy way to change the surface charge distribution (at the surface of the micelle) and may lead to stronger interactions between the template and the inorganic precursor.¹⁴ We hypothesized that we could pre-organize the highly polar HPA at the surface of the micelle in an analogous manner.

To confirm the importance of this approach, materials were also prepared using more CTAB (the same mass of Pluronic, 1 : 1.6 molar Pluronic/CTAB ratio) and using only Pluronic. The XRD study of these two materials (Fig. 3, bottom) shows that mesoscopic ordering was present throughout (as-made, calcined, and calcined-extracted stages) for these two templating methods. The ³¹P MAS NMR spectra of the calcined-extracted materials (Fig. 3, top, spectra c) show that the Keggin unit was not fully restored (compared to Fig. 2c, right). In the absence of CTAB, the central Keggin unit peak at 15.3 ppm was surrounded by a very broad and intense resonance band, and in the case of the higher CTAB concentration, no central peak at all was observed. The very clean results obtained for the 1 : 0.8 molar ratio mixed template appear to be near optimal.

Influence of the prehydrolysis reaction time. As mentioned above, previous authors have indicated that the incorporation of HPA to the synthesis is facilitated by allowing some

400 mg of CTAB



Absence of CTAB





Fig. 3 XRD pattern (bottom) and MAS ³¹P NMR (top) of $H_3PW_{12}O_{40}$ modified SBA-15 type silica in the absence (left) and in the presence (right) of CTAB: (a) as-made; (b) a after calcination; and (c) b after extraction.



Fig. 4 MAS ³¹P NMR (left) and XRD pattern (right) of $H_3PW_{12}O_{40}$ modified SBA-15 type silica after simultaneous introduction of TEOS and tungstophosphoric acid: (a) as-made; (b) a after calcination; and (c) b after extraction.

polymerisation of the silica precursor (TEOS) before introduction of the functionalised silica precursors. The present study confirms a similar effect in the case of HPA inclusion in the synthetic protocol. When TEOS and HPA were simultaneously added to the aqueous solution of the mixed SDA templates, an ordered solid was obtained which includes the HPA in its intact Keggin unit. (Fig 4, bottom left). Mesoscopic order was maintained throughout the calcination and extraction, but again the restoral of the Keggin unit in the extracted-calcined product was far from complete (Fig. 4, top left).

Applicability of the synthetic method to various HPAs. Initial feasibility studies were performed on other heteropolyacids, namely $H_3PMo_{12}O_{40}$ and $Na_3PW_{12}O_{40}$. Encouraging results in terms of mesoscopic order and Keggin unit restoration were obtained (see Fig. 5 and 6) and further studies into the optimisation of the synthesis and the applications of these materials are underway. It is also interesting to note the failure of the mixed addenda phosphovanadomolybdic acid $H_4PVMo_{11}O_{40}$ in this protocol. Again, little restructuring of the Keggin unit was observed in the calcined-extracted material, but significantly, elemental analyses indicated the total absence of vanadium after calcination. Clearly, the vanadium was irreversibly extracted from the polyanion framework upon thermal treatment.¹⁵

3.4 Demonstration of the accessibility of the HPA sites

To establish that the stabilization of the HPA in the walls of the material does not inhibit its catalytic properties, a series of catalytic experiments were undertaken using a catalytic benchmark reaction, the esterification of acetic acid by n-butanol. The basic protocol and kinetic analysis of Sepulveda and coworkers were used to determine the observed second order rate constant for the reaction.¹⁶ If the heteropolyacid sites are accessible, the catalytic reaction rate should be superior to a blank system (no catalyst, unmodified SBA-15...).

Rate constants were determined by fitting experimental data to the kinetic model described by Sepulveda. The basic second order rate law was tested:

$$-\frac{d[A]}{dt} = k[A][B]$$

where [A] is the concentration of acetic acid, [B] is the concentration of butanol and *t* is time of reaction. The units are chosen such that the rate constant *k* is expressed in ml mol⁻¹ h⁻¹. The integration of this equation leads to the expression:

$$[A]kt = \frac{1}{1-M} \ln\left(\frac{M(1-\chi_A)}{M-\chi_A}\right)$$



Fig. 5 XRD pattern (right) and MAS ³¹P NMR (left) of $H_3PMo_{12}O_{40}$ modified SBA-15 type silica: (a) as-made; (b) a after calcination; and (c) b after extraction (Mo $6.73\%_{wt}$).



Fig. 6 XRD pattern (right) and MAS ³¹P NMR (left) of $Na_3PW_{12}O_{40}$ modified SBA-15 type silica: (a) as-made; (b) a after calcination; and (c) b after extraction (W 6.75%_{wt}; Na 0.57%_{wt}).

where M is the ratio of the initial concentrations of acetic acid and butanol:

$$M = \frac{[A_0]}{[B_0]}$$

and χ_A is the conversion of acetic acid:

$$\chi_A = \frac{[A]_0 - [A]}{[A]_0}$$

The experimental data is plotted in the form of "kt" vs. time, and thus the slope of the plot is equal to the observed rate

constant. Given that the acid catalysts were added such that the ratio of substrate to strong acid was equal for those runs, and that other relevant parameters were constant (reactant ratios, temperature, solvent, *etc.*) these rate constants can be compared in a meaningful manner.

Four systems were tested in which all parameters except the presence and identity of the catalytic adduct were kept constant: **2-CE**, molecular $H_3PW_{12}O_{40}$, an SBA-15 having no added HPA, and no acid adduct. In the first two cases, where strong acid catalysts were used, the substrate/acid molar ratio was maintained at ~11 000.¹⁷ In all cases, the observed data



Fig. 7 Esterification of acetic acid by n-butanol: conversion of acetic acid versus time (left) and rate constant determination (right).

Table 2 Esterification of acetic acid by n-butanol

	Catalyst	Conversion ^{<i>a</i>} at $t = 6 h$	Second order rate constant ^{b} /ml mol ⁻¹ h ⁻¹
Homogeneous catalyst	$H_{3}PW_{12}O_{40}$	24%	16
Heterogeneous catalysts	HPA@SBA-15-CE	49%	49
Blank	Silica blank	13%	6.6
	No catalyst	14%	7.7

^{*a*} Conversions based on unreacted acetic acid were determined by GC. ^{*b*} Determined at 80 °C by fitting experimental data to the kinetic model described by Sepulveda *et al.* Applied Catalysis A: General 2005, **288**, 18.



Scheme 1 Sketch of proposed interpretation of data.

(concentration of acetic acid followed by GC) exhibit an excellent fit to the second order kinetic model and thus the second order rate constants could be determined (see Fig. 7 and Table 2).

The second order rate constant determined at 80 °C for **2-CE** (49 ml mol⁻¹ h⁻¹) was more than three times higher than that determined for the molecular $H_3PW_{12}O_{40}$ (16 ml mol⁻¹ h⁻¹) and 6–7 times higher than the SBA-15 only and the no catalyst blank reactions (6.6, and 7.4 ml mol⁻¹ h⁻¹ respectively).

Clearly, the HPA moiety of **2-CE** was accessible to reactants and active, the primary objective of this series of experiments. The factors leading to this enhancement of the activity of the solid supported catalyst with respect to the homogeneous system (enhanced acidity, confinement ...) as well as the stability of the solid with respect to leaching are under further study.

3.5 Proposed rationalisation of observations

At this stage, the reasons behind the reconstruction of the Keggin unit into a stably fixed and reactive form have not been demonstrated, but we believe that our working hypothesis merits mention in this report. The proposed explanation, represented in Scheme 1, is based on two key hypotheses, each of which warrants further study.

Firstly, we propose that when the HPA is introduced, it takes up a position at the periphery of the micelle creating surface microporocity by molecular imprinting. Thus, after polymerisation of TEOS, some of the HPA is at the center of micropores in the interior walls of the as-made material (Scheme 1, upper left). The extraction protocol, if performed at this step, leads to total elimination of the HPA from these micropores (Scheme 1, lower left).

The second key hypothesis is that calcination leads to some restructuring of the surface which inhibits extraction. One possibility would be that calcination has reduced the size of the entrance of the micropore host of the, now thermally degraded, HPA moiety (Scheme 1, top center). When the methanol extraction of the calcined material is performed, that part of the degraded HPA which was on the surface is eliminated. However, the surface restructuration inhibits the extraction of the HPA in the micropores, and methanol-mediated reformation of the Keggin structure takes place in the solid.¹⁸ Thus, the final material contains trapped, structurally intact and accessible HPA moieties at the surface of the channels of the mesoporous silica (Scheme 1, top right).

4. Conclusion

In summary, new, stable and reactive HPA modified mesoporous hybrid materials have been obtained by one-pot synthesis in the presence of HPA and two template molecules, one ionic and one non-ionic, together. Template removal by calcination–extraction sequence was essential to yield stable materials with intact Keggin unit. The catalytic results showed that not only the sites were accessible, but also that the catalytic activity of the new material was three times that of the homogeneous HPA system. Further work is currently underway to demonstrate the structural factors leading to the stabilization of the HPA unit during template removal and to extend the scope of this new synthetic method to multifunctional catalyst design.

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