Available online at www.sciencedirect.com

SCIENCE DIRECT®

Applied Catalysis A: General 270 (2004) 101–111

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

Vanadium-substituted Keggin heteropolycompounds as catalysts for ecofriendly liquid phase oxidation of 2,6-dimethylphenol to 2,6-dimethyl-1,4-benzoquinone

P. Villabrille[a], G. Romanelli[a,b], P. Vázquez[a,*], C. Cáceres[a]

[a] *Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J.J. Ronco" (CINDECA), UNLP-CONICET, 47 No. 257, B1900AJK La Plata, Buenos Aires, Argentina*

[b] *Laboratorio de Estudio de Compuestos Orgánicos (LADECOR), Departamento de Química, Facultad de Ciencias Exactas, UNLP, 47 y 115, 1900 La Plata, Buenos Aires, Argentina*

Received in revised form 22 April 2004; accepted 27 April 2004

Abstract

Molybdovanadophosphate heteropolycompounds, $H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$ and the corresponding Cs salts, were synthesized. The influence of thermal treatment on their Keggin primary structures and their acidic properties were studied. The presence of Keggin units and the V incorporation into these units were observed by TGA, DTA, DRS and FT-IR. $H_4PMo_{11}VO_{40}$ possesses an acid strength higher than that of the V-free sample and $H_9PMo_6V_6O_{40}$, at room temperature. Heating above 200 °C leads to considerable structural changes and acidity decrease. The Cs salts from $H_4PMo_{11}VO_{40}$ possesses stronger acidic sites than those from $H_9PMo_6V_6O_{40}$. Moreover when the Cs number increases, the acidic properties decrease. The salts with one, two, and three Cs are more unstable with temperature than the salt with 2.5 Cs. The specific surface area for the Cs salts depends on the temperature and Cs number. The prepared heteropolycompounds were used as catalysts for the liquid phase reaction of synthesis of 2,6-dimethyl-*p*-benzoquinone from 2,6-dimethylphenol, using hydrogen peroxide, with high yields. A selectivity to the *p*-benzoquinone of 79–59% was obtained when the reaction was catalyzed by Cs salts from the $H_4PMo_{11}VO_{40}$ acid.

Keywords: Keggin heteropolycompounds; Molybdovanadophosphate; Catalytic oxidation; 2,6-Dimethyl-1,4-quinone

1. Introduction

The design of practical catalysts at an atomic or molecular level has long been pursued, since precisely designed multifunctional catalysts are obviously desirable. However, catalyst design at this level is still a distant goal in many instances [1].

Currently there is considerable interest in exploiting both the structure of catalyst precursors and the multicenter active sites to facilitate catalysis by polyoxometalates [2]. It has been stressed that it is important to discover more reliable and efficient procedures before the exploration of possible new reactivity patterns [3]. Thus, it is very important to use fully characterized and more reliable catalyst precursors for catalytic reactions.

Polyoxometalates are well known as oxidation and acid catalysts in which the redox and acid-based properties can be tuned by variation of the structure type, the central heteroatom and addenda or transition-metal-substituted atoms. The catalytic function of the Keggin family has attracted much attention particularly because these compounds provide a good basis for the molecular design of mixed oxide catalysts and high capabilities in practical uses. The free acids are less stable than the salts but can be obtained in structurally better defined samples.

There are several large-scale industrial processes that use heteropolyoxometalates as oxidation and acid catalysts both in the solid state and in solution. Heteropoly catalysts are promising green catalysts since most of them are environment friendly.

The effect of vanadium substitution has already been the subject of studies in the literature. When molybdenum atoms of molybdophosphoric acid, $H_3PMo_{12}O_{40}$, are partly substituted by vanadium atoms, the acid strength diminishes

---

[*] Corresponding author. Tel.: +54-221-4210711; fax: +54-221-4254277.
E-mail address: vazquez@quimica.unlp.edu.ar (P. Vázquez).

0926-860X/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2004.04.028

along with its thermal stability. One quite intensively studied polyoxometalate is the molybdovanadophosphate of the Keggin structure, $H_5PMo_{10}V_2O_{40}$, known for its redox-type catalytic activity in oxydehydrogenation using molecular oxygen as oxidant [4]. $H_4PMo_{11}VO_{40}\cdot 32H_2O$ is another member of the family of heteropolyacid catalysts with fully hydrated Keggin anions in its room temperature form [5].

From the synthetic point of view, selectively site-substituted vanadium is not easy to achieve. The reaction of tri-lacunary species of Keggin and Dawson polyoxomolybdates with vanadates at different pH produced monovanadium-substituted Keggin species $(PMo_{11}VO_{40})^{4-}$ [2]. As is well known, partial substitution of vanadium for molybdenum, could be localized in two different positions: anionic (inside the heteropolyanion) and cationic (counter ions). Marchal-Roch et al. [6] have shown that both molecular and crystalline modifications of $(NH_4)_5(PMo_{11}V^{IV}O_{40})$ occur at high temperature. The cubic phase formed between 270 and 410 °C contains two different Keggin heteropolyanions and two different types of vanadium atoms. On the other hand, Ilkenhans et al. [5] have demonstrated that $H_4PMo_{11}VO_{40}$ may be either of the Keggin structure or of the inverse Keggin structure, a disorder modification with severe consequences for the packing of the anions within the crystal. In the latter case, vanadium could not be localized and does not lead to any discernible distortion of the anionic structure.

It was found that vanadium-containing polymolybdophosphates, in the form of tetra-*n*-butylammonium salts, efficiently catalyze the homogeneous low-temperature oxidations of saturated hydrocarbons with hydrogen peroxide [7]. Also, Seki et al. [8,9] have demonstrated that the catalytic oxidation of methane with hydrogen peroxide occurs on 11-molybdo-1-vanadophosphoric acid.

On the other hand, H_2O_2 is one of the oxidants frequently used in fine chemical synthesis, as an option to the conventional ones, since its use leads to a cleaner technology because it is easy to handle and its reaction produces only H_2O as by-product. Several researchers have utilized H_2O_2 as oxidant in the synthesis of *p*-benzoquinones. Minisci et al. [10] have reported the oxidation of dihydroxybenzenes by H_2O_2 in methanolic or aqueous solution of H_2SO_4, at room temperature in the presence of I_2 or HI as catalysts. A similar procedure has been utilized for the synthesis of *p*-quinones from 2,6-disubstituted phenols with high yields and selectivity, so this procedure is recommended as a valuable method also for industrial applications.

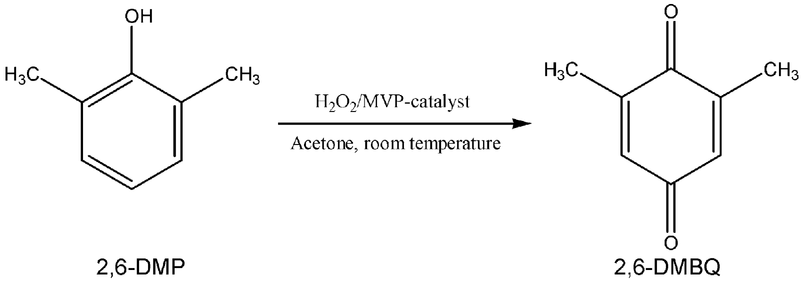
The system $H_2O_2/RuCl_3$ has been employed by Ito et al. [11] for the oxidation of 2,3,6-trimethylphenol to the corresponding *p*-benzoquinone with high yields. Acetic acid was used as solvent and the reaction was carried out at room temperature.

Shimizu et al. [12] have concluded that the alkyl-substituted *p*-benzoquinones were easily synthesized by the oxidation of the corresponding phenols, with the H_2O_2/heteropolyacid (HPA) couple in acetic acid. So, the trimethyl-*p*-benzoquinones from 2,3,6-trimethylphenol or 2,3,5-trimethylphenol were obtained with high yields. Among the four kinds of heteropolyacids presented, $H_4P(Si)Mo(W)_{12}O_{40}$, phosphomolybdic acid (MPA) showed the highest activity. Besides, better yields of quinones were obtained in the reaction of disubstituted phenols than with monosubstituted ones.

Bryce-Smith and Gilbert [13] have found that 2,5- and 2,6-dimethylphenol can be oxidized efficiently to the corresponding *p*-benzoquinones with the system H_2O_2–AcOH (H_2SO_4).

It is important to emphasize that the quinone derivatives play an important role in biosystems and are useful intermediates of fine organic synthesis. For example, the 2,3,5-trimethyl-1,4-benzo-quinone is a key intermediate in the production of Vitamin E [14]. 2-methyl-1,4-naphtoquinone, Vitamin K3, constitutes an important additive in animal food, which is used commercially in large quantities. 2,6-dimethyl-1,4-benzoquinone is known to be the by-product in the numerous syntheses of compounds showing a physiological activity. For example, this quinone may be used for preparing trimethylbenzoquinone. It is also useful for preparing indophenol substituted maltose derivatives, which are used for the determination of the enzymatic activity of α-amilase.

The present work investigates the influence of the thermal treatment on the Keggin primary structure and the acidic properties of the molybdovanadophosphate heteropolycompounds for a better understanding of $H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$ and the corresponding Cs salts. The catalyst characterization was carried out by TGA/DTA, FT-IR, DRS, specific surface area, and the acidity was determined through potentiometric titration with *n*-butylamine. The catalytic activity of the molybdovanadophosphates (MVP) in the reaction of oxidation with H_2O_2 in liquid phase of the 2,6-dimethylphenol to 2,6-dimethyl-*p*-benzoquinone was determined.



2. Experimental

2.1. Catalyst preparation

$H_4PMo_{11}VO_{40}$ (M11PV1A) and $H_9PMo_6V_6O_{40}$ (M6-PV6A) were prepared by a hydrothermal synthesis method [15]. M11PV1A synthesis according to the following procedure is presented as example: a stoichiometric mixture of 0.98 g of phosphoric acid, 0.91 g of vanadium pentoxide and 14.4 g of molybdenum trioxide was suspended in 150 ml of distilled water. The mixture was stirred for 6 h at 80 °C. After cooling down to room temperature and removal of insoluble molybdates and vanadates, the heteropolyacid solution was evaporated and dried at 85 °C for 24 h. After that, orange crystals of M11PV1A were obtained.

Mixed proton-cesium and cesium salts, containing *x* cesium cations per heteropolyanion (where *x* is between 1 and 9) were prepared from M11PV1A and M6PV6A, named Cs*x*H4-*x*M11PV1 and Cs*x*H9-*x*M6PV6, respectively. A predetermined amount of the aqueous solution of CsCl (3 mol/l) was added slowly to the aqueous solution of HPA. The resulting precipitates were dried at room temperature for 24 h. The thermal stability was studied at different temperatures, in the range 100–400 °C.

2.2. Catalyst characterization

2.2.1. Textural properties

The specific surface area (S_{BET}) of solid samples was determined by nitrogen adsorption/desorption techniques using Micromeritics Accusorb 2100E equipment.

2.2.2. Diffuse reflectance spectroscopy

The solid samples were studied, in the range 200–600 nm, using UV-Vis Varian Super Scan 3 equipment, fitted with a diffuse reflectance chamber with an inner surface of $BaSO_4$. Samples were compacted in a Teflon sample holder to obtain a sample thickness of 2 mm.

2.2.3. Thermogravimetric and differential thermal analysis

The TG–DTA measurements of representative samples dried at 70 °C were carried out using Shimadzu DT 50 thermal analyzer. The TG–DTA experiments were performed under argon or nitrogen respectively, using 25–50 mg samples and a heating rate of 10 °C/min. Quartz cells were used as sample holders with α-Al_2O_3 as reference. The studied temperature range was 25–700 °C.

2.2.4. Fourier transform infrared spectroscopy

Bruker IFS 66 equipment, pellets with BrK, and a measuring range of 400–1500 cm^{-1} were used to obtain the FT-IR spectra of the solid samples.

2.2.5. Potentiometric titration

An amount of 0.05 ml of 0.1 N *n*-butylamine (Carlo Erba) in acetonitrile (J.T. Baker) was added to a known mass of solid (between 0.1 and 0.05 g) using acetonitrile as solvent, and stirred for 3 h. Later, the suspension was titrated with the same base at 0.05 ml/min. The electrode potential variation was measured with an Instrumentalia S.R.L. digital pHmeter, using a double junction electrode. The acidic properties of the samples measured by this technique enables the evaluation of the total number of acid sites and their acid strength. In order to interpret the results, it is suggested that the initial electrode potential (E) indicates the maximum acid strength of the surface sites, and the values (mequiv./g solid) where the plateau is reached, indicates the total number of acid sites. The acid strength of surface sites can be assigned according to the following ranges: very strong site, $E > 100$ mV; strong site, $0 < E < 100$ mV; weak site, $-100 < E < 0$ mV, and very weak site, $E < -100$ mV.

2.3. Catalytic test

The oxidation of 2,6-dimethylphenol was performed under vigorous stirring in a glass reactor at room temperature (15–20 °C). The reactions were performed by adding H_2O_2 250 volume (Analquim) in excess to a solution of 1 mmol of 2,6-dimethylphenol (Merck, this reactive was purified by sublimation at reduced pressure) and the catalyst (0.02 mmol) in acetone (5 ml, J. T. Baker). The reaction was followed by TLC (thin layer chromatography) until the initial phenol was consumed (1.5–48 h). TLC aluminium sheets (silica gel 60 F_{254} Merck) were used. The reaction mixture was diluted with 20 ml of distilled water and extracted twice with 10 ml of dichloromethane (J.T. Baker). The extract was dried over anhydrous sodium sulfate. The crude product was purified by chromatography on silica gel using a mixture of hexane–toluene (1:1) as eluent. The products were identified by comparison of the mass spectra of standard samples.

The selectivity of reaction was calculated as the molar ratio between the obtained amount of 2,6-dimethyl-1,4-benzoquinone and the total amount of 2,6-dimethylphenol. In all runs, the phenol conversion was 100%. The turnover frequency (TOF) was calculated as the moles of product per mole of catalysts per hour.

3. Results and discussion

3.1. Characterization of M11PV1A and M6PV6A acids

3.1.1. TGA–DTA analysis

The primary structure is the structure of the heteropolyanion itself. In this work the primary and secondary structure of the heteropolyacids with Keggin structure is explored. The primary unit is composed of a central heteroatom, usually P or Si, contained in an oxygen tetrahedron. This central tetrahedron is surrounded by 12 corner-sharing octahedrons, each containing a transition metal ion, such as Mo or W.

$H_3PMo_{12}O_{40}$ possesses three acidic protons associated with each Keggin anion. The substitution of one Mo^{6+} ion

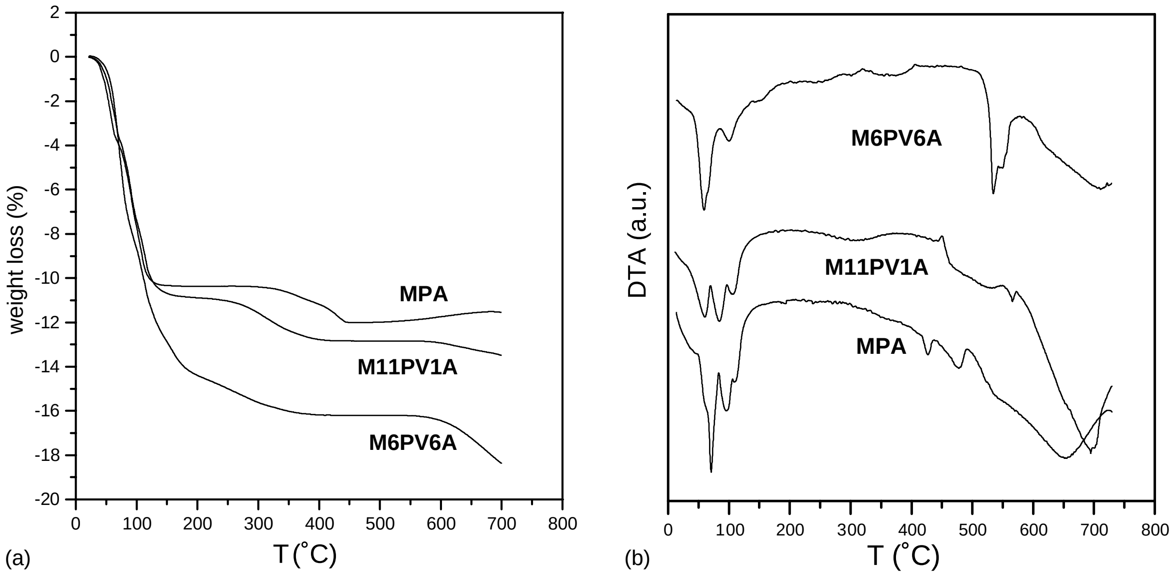


Fig. 1. TGA (a) DTA (b) of $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$.

by a V^{5+} ion in a Keggin anion requires an additional charge-balancing proton. TGA and DTA results for MPA, M11PV1A, and M6PV6A are presented in Fig. 1a and b.

Between 40 and 125 °C, DTA shows that all the water molecules do not play the same role. In this temperature range, endothermic peaks due to the presence of water molecules interacting in different ways were observed (Fig. 1b). Some of them within clusters, such as H_3O^+ or $H_5O_2{}^+$, are more tightly bound in the crystal structure. HPA possess crystallization water that binds the close Keggin units in the secondary structure by forming water bridges.

The weight loss between 40 and 125 °C observed in the TGA analyses indicates that MPA, M11PV1A and M6PV6A are hydrated with 12 molecules of water (Fig. 1a).

Bardin and Davis [16] have shown that the number of protons per Keggin unit could be determined by measuring the amount of water evolved during thermal decomposition of the acid. The weight loss, between 125 and 400 °C, corresponds to the decomposition of the Keggin units and to the evolution of protonic water, the so-called constitution water. The experimental results allow establishing that MPA, M11PV1A and M6PV6A possess three, four and nine protons in agreement with the theoretical values.

Above ~450 °C, it is observed by DTA that the HPAs decompose in a mixture of oxides as will be discussed later.

TGA and DTA results provide some evidence for the presence of Keggin units, but other techniques are necessary, such as FT-IR and DRS, for an accurate identification of the structure.

3.1.2. DRS and FT-IR

The DRS provided additional information about the substitution of ions into the Keggin units [17]. The charge transfer absorption spectra of most non-reduced polyanions appear in the 200–500 nm region and consist of bands which may be ascribed to oxygen-to-metal transfers. The tetrahedral Mo exhibits two absorption bands at 220 and 260 nm, whereas Mo in octahedral coordination presents, in addition to those bands, another band at a higher wavelength. Fig. 2 shows that the inclusion of one or more V atoms in the MPA results in a significant red shift in the absorption edge.

The main characteristic features of bulk MPA in FT-IR are observed at 1064 cm^{-1} (P–O_a), 964 cm^{-1} (Mo–O_d), 871 cm^{-1} (Mo–O_b–Mo), and 784 cm^{-1} (Mo–O_c–Mo) (see Fig. 3). The oxygen atoms in the primary Keggin structure fall into four classes of symmetric-equivalent oxygen: P–O_a–$(Mo)_3$ oxygen atom common to the PO_4 tetrahedron and to a trimetallic group, Mo–O_b–Mo, connecting two Mo_3O_{13} units by corner sharing; Mo–O_c–Mo, connecting two MoO_6 units by edge sharing and terminal O_d–Mo.

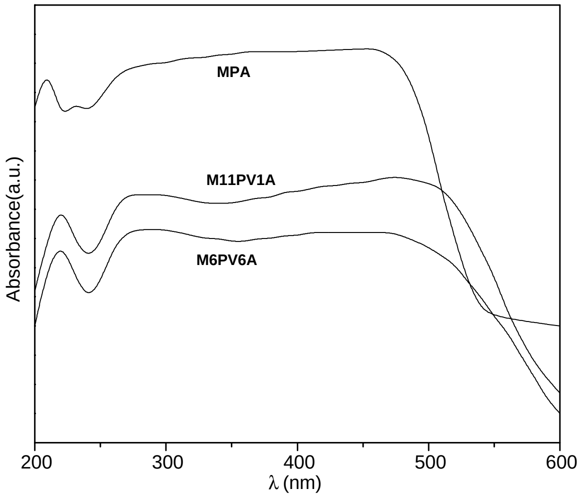


Fig. 2. DRS spectra of $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$ at room temperature.

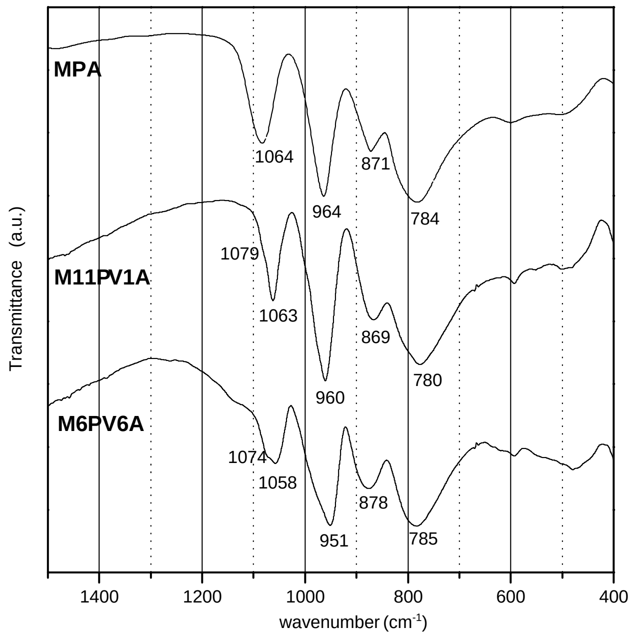


Fig. 3. FT-IR spectra of $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$ at room temperature.

The characteristic stretches associated with the Keggin structures of M11PV1A and M6PV6A are presented in Fig. 3. In these spectra the P–O_a and Mo–O_d bands were shifted compared to MPA. The P–O_a band was negatively shifted 1 cm^{-1} in M11PV1A and 5 cm^{-1} in M6PV6A. For the Mo–O_d band, the shift was 4 and 13 cm^{-1}, for M11PV1A and M6PV6A, respectively. Additionally, a splitting of the P–O_a band to 1079 and 1074 cm^{-1} was observed.

Previous investigations discussed the vibrational spectra of Keggin compounds as a function of the nature of the metal (Me) introduced, considered as a perturbing element [18]. The typical patterns of Keggin structure are modified as follows: the introduction of a Me, other than Mo in the structure, induces a decrease in the Mo–O_d stretching frequencies and a possible splitting of the P–O_a band, depending on the Me nature [18]. This splitting can be considered as an indirect evaluation of the strength of the Me–O_a interaction. The weaker ΔV the stronger the Me–O_a interaction. In accordance with these results, Bielanski et al. [19] have observed slight negative shifts of P–O_a (9 and 10 cm^{-1}), and Mo–O_d bands when V is incorporated into the Keggin structure. Other effects can be evidenced by vibrational spectrometry such as, H bonding through the water molecules and/or the hydroxonium ions H_3O^+ or $H_5O_2{}^+$, and electrostatic anion–anion interactions. The former effect induces a frequency decrease and the latter a frequency increase for the Mo–O_b–Mo mode [18,20]. Then, the behavior observed in Fig. 3 indicates that V has indeed been incorporated into the Keggin units.

3.1.3. Potentiometric titration with n-butylamine

Acid and basic functions of a solid are not properly defined thermodynamically. The acid strength of a solid is defined as the ability of the surface to convert an adsorbed neutral base into its conjugated acid. If the reactions proceeds by means of proton transfer from the surfaces to the adsorbate, the acid strength is expressed by the Hammett acidity function, H_o [21]. According to an indicator test, $H_3PW_{12}O_{40}$ has a Hammett acidity function less than −8.2 and it has even been suggested to be a superacid. A superacid is an acid with a strength greater than that of 100% sulfuric acid with a value of $H_o = -12$ [21]. The use of an indicator test such as the Hammett acidity is considered a reference method, but this method is difficult to apply to colored solids, especially if they are weak acids. For these cases, a potentiometric method was developed. The method is based on the observation that the potential difference is mainly determined by the acidic environment that is around the electrode membrane. The measured electrode potential is an indicator of the superficial acidic properties of dispersed solid particles. Three different solvents to disperse the solid for potentiometric titration, benzene, acetonitrile and iso-octane, have been used by Cid and Pecchi [22]. In our case, toluene was tested and the results were not reproducible. Then acetonitrile was used as solvent.

An aliphatic amine, such as *n*-butylamine with a constant of basic dissociation of approximately 10^{-6} allows the potentiometric titration of a strong acid in dissolution.

The complementary nature of these potentiometric titrations suggests that the variations in measured potential difference are due to the inherent surface heterogeneity and not to the surface induction effect of previously absorbed *n*-butylamine during the stabilizing period (3 h).

The acidity of the HPA is BrØnsted in nature. At room temperature (r.t.), the M11PV1A sample presents very strong sites, with a maximum acid strength, corresponding to an initial electrode potential of 978 mV, higher than that obtained for the V-free sample (MPA), 600 mV (Fig. 4a). The replacement of one Mo^{6+} by V^{5+} modifies the Keggin structure as was shown before (see Fig. 3). There is a weakness of the V–O_a interaction and the protons reside mainly in the bridging water moieties forming $H_5O_2{}^+$. This modification changes the charges of different oxygen atoms of Keggin primary structure, mainly O_b, and could be related to a higher acid strength of a new proton [18].

The acid strength of the M6PV6A sample decreases considerably (355 mV) and the value of the plateau indicates the lowest number of acid sites shown by the heteropolyacids studied. In this case, the high number of V in the primary structure induced a high number of protons, whereas the total high charge of the Keggin anion promoted a higher interaction with protons. This behavior deeply decreases the M6PV6A acidity.

3.1.4. Temperature influence on HPA acidity

Previous studies about the temperature influence on the acidic properties of bulk MPA [23] demonstrated that the

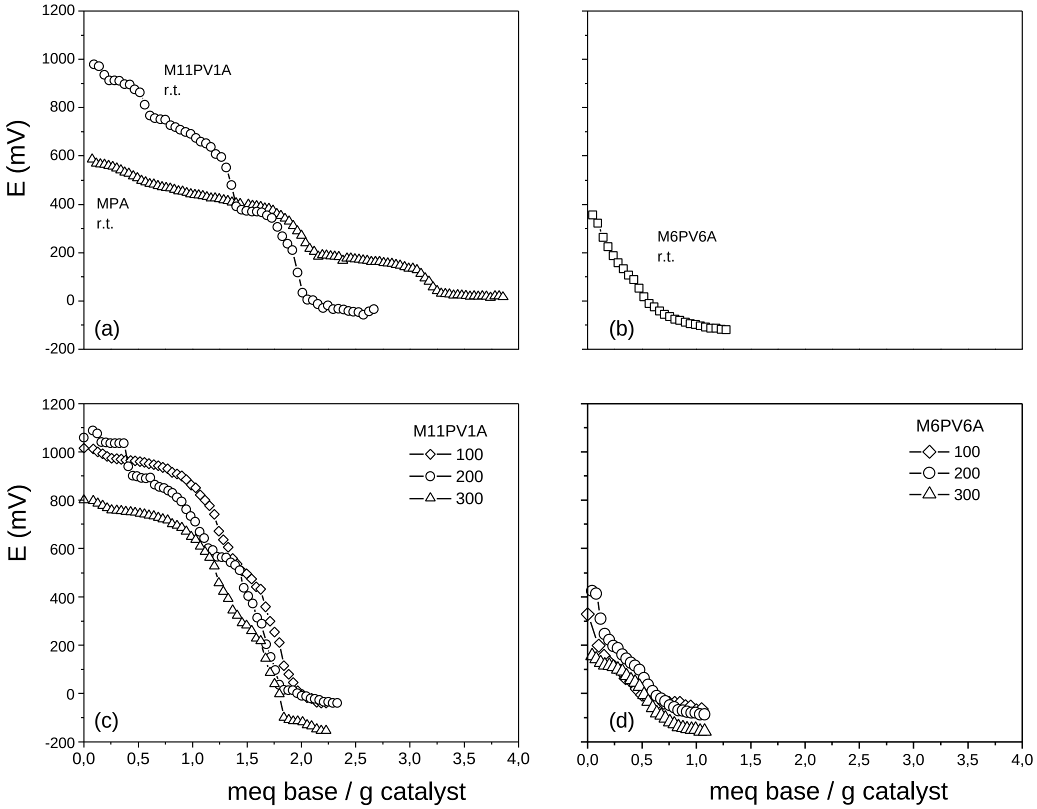


Fig. 4. Potentiometric titration curves of: (a) $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$ at room temperature; (b) $H_9PMo_6V_6O_{40}$ at room temperature; (c) $H_4PMo_{11}VO_{40}$; (d) $H_9PMo_6V_6O_{40}$ at different calcination temperatures.

acid strength increases when the calcination temperature goes up to 200 °C and decreases at higher temperatures. In addition, the degree of hydration strongly influences the acidity of bulk acid. Fig. 4c and d shows potentiometric curves for M11PV1A and M6PV6A, which were calcined at 100, 200, and 300 °C. For both compounds, at 200 °C, the acid strength is higher than the values at r.t. and at 100 °C, because in this temperature range the protons are hydrated and during the process of dehydration there are changes in the proton environment.

On the other hand, Mioc et al. have shown [24] that heating above 200 °C leads to considerable structural changes and to a reduction in the unit cell dimensions, with the result that acidic properties decrease.

Fig. 5 presents the FT-IR spectra of M11PV1A and M6PV6A at room and at higher temperatures (200–400 °C). From structural aspects, the dehydration progressively “undresses” the hydrated protons and weakens the H bonding, and a rearrangement of the packing is induced by the removal of water molecules [18]. The anhydrous acid may consists of an almost isotropic distribution of protonated Keggin units in the framework. The protons would be localized on the most highly charged oxygen atoms (O_b), so a decrease in the intensity of the Mo–O_b–Mo band (near 900 cm^{-1}) would be expected (Fig. 5). Above 200 °C, the spectra also show the disappearance of the 1072 cm^{-1} shoulder. The acidic properties decrease as well, according to the results obtained by potentiometric titration shown in Fig. 4.

In our case, at temperatures close to 300 °C for M11PV1A and M6PV1A, MoO_3 formation did not occur as indicated by the FT-IR spectra. During calcination the heating rate is very important. This observation proves that the thermal stability of HPA is not only determined by its thermodynamics but also by the kinetics of the structural disintegration and reorganization processes [25].

A treatment at 400 °C leads to a deep modification related to a partial degradation of the polyanion.

3.2. Characterization of Cs salts from M11PV1A and M6PV6A

The secondary structure of HPA is the three-dimensional arrangement consisting of polyanions, counter cations, and additional molecules. The secondary structures are flexible to different extents depending on the counter cation and the structure of the polyanion. The tertiary structure of HPA represents the manner in which the secondary structure assembles into solid particles and relates to properties such as particle size, surface area, and pore structure [1]. This explains the great importance of Cs salts. The incorporation of Cs in the Keggin structure increases the surface area and modifies the structure and the acidic properties of the compound.

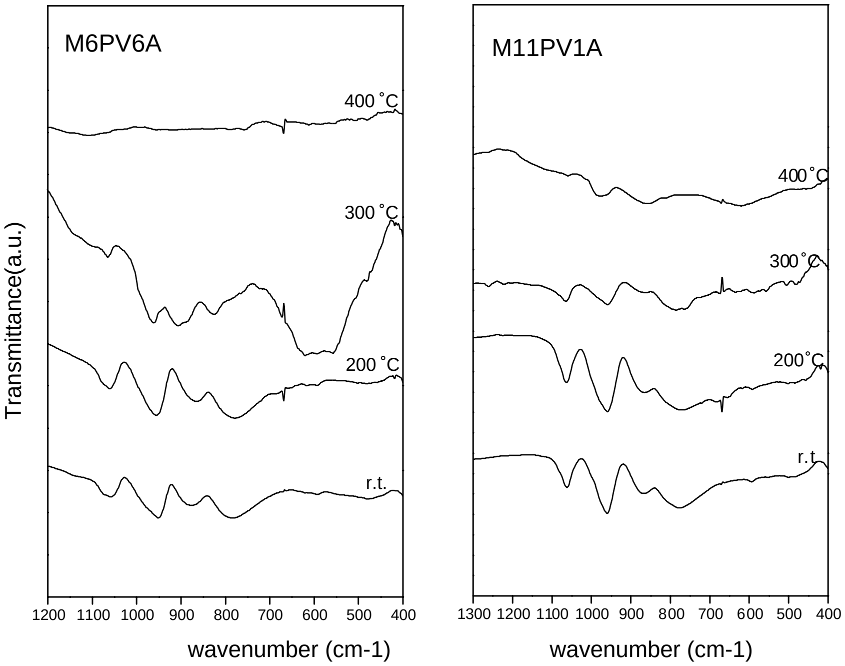


Fig. 5. FT-IR spectra of $H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$ at different calcination temperatures.

3.2.1. Potentiometric titration with n-butylamine

The acidity of the salts was measured by potentiometric titration and the acid strength at r.t. is shown in Fig. 6. The salts from M11PV1A present stronger acidic sites than those from M6PV6A. This behavior may be attributed to the higher acidity of the HPA with one V atom and also due to the lower amount of hydration water of M6PV6A salts. This amount was determined by TG analysis. The results suggested that the electrostatic potential around the primary Keggin structure is strongly influenced by the hydration water, possibly by the network of H-bonding. When the Cs number increases, the H-bonding decreases, which leads to a decrease in the acidic properties.

Fig. 7 presents the potentiometric curves of Cs1H3M11PV1, Cs2H2M11PV1, Cs2.5H1.5M11PV1, and Cs3HM11PV1, at r.t. and thermally treated at 200 °C. This figure shows that the substitution of one H by Cs in M11PV1A (CsH3M11PV1) gives the highest acidity at r.t. On the other hand, the salts calcined at 200 °C present higher acidity than the sample at r.t., as mentioned above for the case of the M11PV1A acid.

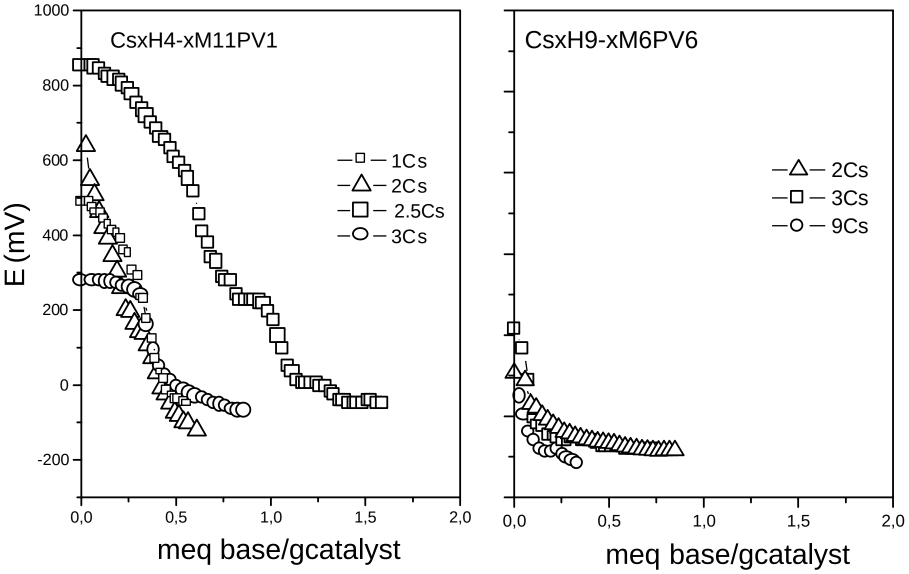


Fig. 6. Potentiometric titration curves of Cs salts of $H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$, with different Cs number.

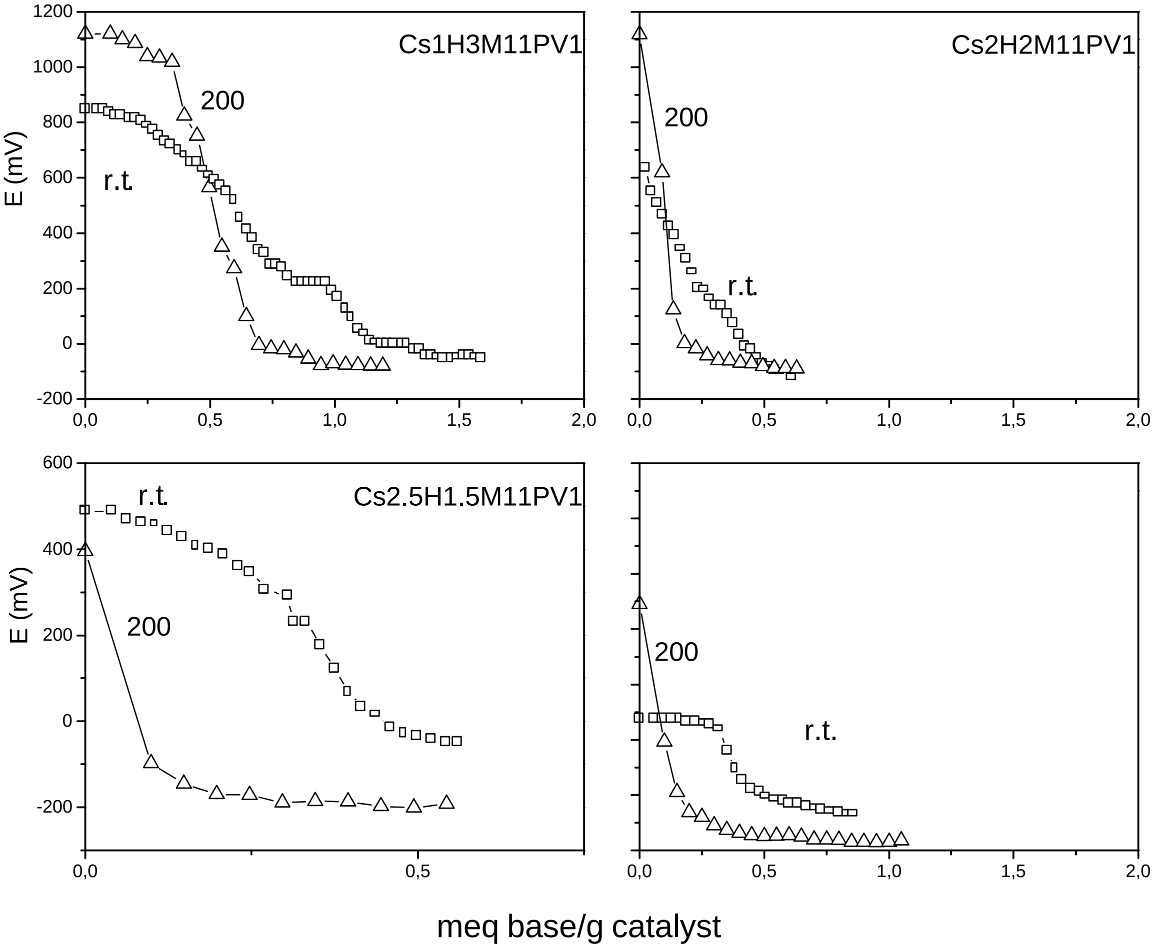


Fig. 7. Potentiometric titration curves of Cs salts of $H_4PMo_{11}VO_{40}$ at room temperature and 200 °C.

3.2.2. *FT-IR*

Fig. 8 shows the FT-IR spectra of Cs salts from M11PV1A at different calcination temperatures. In all cases, the FT-IR spectra present the characteristic feature of M11PV1A up to 200 °C. At 300 °C, the FT-IR spectra of Cs1H3M11PV1, Cs2H2M11PV1, and Cs3HM11PV1 salts present a band at 1037 cm^{-1}. The enhancement of the intensity of this band is likely to be induced by the oxometallo framework surrounding the PO_4 tetrahedron [18]. This is consistent with the progressive formation of other species, which implies the instability of $PMo_{11}V$, with a release of vanadium from the structure. These results coincide with the loss of acidity of Cs salts above 300 °C.

At temperatures higher than 300 °C, the mixtures of MPA and salts from M11PV1A undergo a deep transformation through irreversible decomposition.

3.2.3. *Specific surface area*

The specific surface area of Cs salts from M11PV1A at different calcination temperatures are shown in Table 1. At room temperature and at 100 °C, the S_{BET} increases when the Cs number increases. At 300 °C the S_{BET} diminishes considerably. It is interesting to note that the specific surface area of M11PV1A is 13.8 m^2/g and that of Cs1H3M11PV1 is 73.5 m^2/g at r.t., with similar acidic properties (Figs. 4 and 7).

The value of 64.3 m^2/g for Cs2.5H1.5M11PV1, at 300 °C, is in agreement with the FT-IR spectra since at this temperature the salt does not present the band at 1037 cm^{-1}. This result indicates that the Keggin structure could be intact, with different number of protons by protonic water, at a temperature as high as 400 °C.

3.3. *Catalytic activity*

The 2,6-dimethylphenol oxidation results, using H_2O_2 as oxidant and M11PV1A, M6PV6A and their Cs

Table 1
S_{BET} (m^2/g) values of M11PV1A and the Cs salts

Samples	r.t.	100 °C	300 °C
M11PV1A	13.8	15.5	6.5
Cs1H3M11PV1	73.5	61.8	16.0
Cs2H2M11PV1	75.5	59.9	32.1
Cs2.5H1.5M11PV1	108.5	102.8	64.3
Cs3H1M11PV1	152.7	154.9	15.6

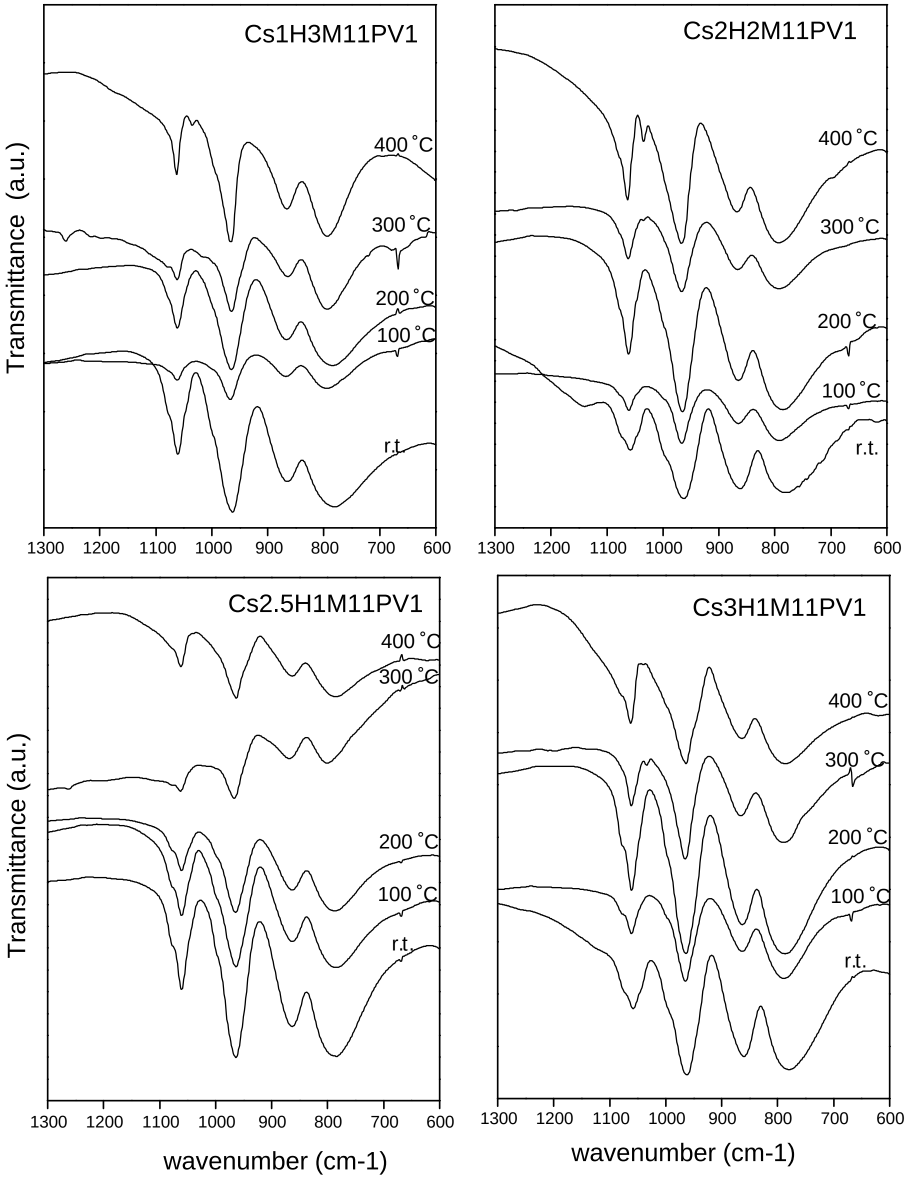


Fig. 8. FT-IR spectra of Cs salts of $H_4PMo_{11}VO_{40}$ at different calcination temperatures.

salts as catalysts, are summarized in Table 2. A high yield of 2,6-dimethyl-*p*-benzoquinone was obtained and 2,6-dimethyl-3-hydroxy-*p*-benzoquinone was observed as by-product. No product was formed in the reactor in the absence of a catalyst (entry 11). The conversion was 100% in all cases, although the necessary reaction time increased with the number of Cs and V atoms in the catalyst.

The selectivity to 2,6-dimethyl-*p*-benzoquinone and the estimated turnover frequency (TOF) values, when the M11PV1A acid was used as catalyst (entry 1), were similar to the values observed for the reaction catalyzed by its Cs salts with one Cs atom (entry 2). Catalytic activity, however, decreased with the increase in Cs number in the salt from 1 to 3 (entries 2–5). So, the reaction time increased from 1, 5 to 7 h, the selectivity to *p*-benzoquinone decreased from 79 to 59% and the TOF from 26 to 4 moles product/mole catalysts h.

These results indicate that the selectivity to *p*-benzoquinone using a very insoluble catalyst in the reaction medium as Cs3H1M11PV1, was 59%. When this catalyst is used, though the reaction rate is low, the very important advantages of the heterogeneous liquid phase reactions were obtained. Among other advantages, the catalyst is easily separable by filtration.

The increase in the catalytic activity for the Cs salt series Cs3 to Cs1 can be related to the increasing number of defects in the crystal structure of the salts. According to Mestl et al. [26], the structures of cesium salts of molybdovanadophosphoric acid Cs_xA, $A = H_{4-x}PMo_{11}VO_{40} \cdot nH_2O$ with $x =$ 1–4, are derived from the crystal structure of Cs_3A by the

Table 2
Oxidation of DMP over M11PV1A, M6PV6A and their Cs salts as catalysts[a]

Entry	Catalysts	Reaction time (h)	C[b] (%)	S[c] (%)	TOF[d]	MAS[e] (mV)
1	M11PV1A	1.5	100	85	25	978
2	Cs1H3M11PV1	1.5	100	79	26	850
3	Cs2H2M11PV1	2	100	67	18	638
4	Cs2.5H1.5M11PV1	4	100	64	8	488
5	Cs3H1M11PV1	7	100	59	4	278
6	M6PV6A	1.5	100	77	17	355
7	Cs2H7M6PV6	48	100	39	0.4	106
8	Cs3H6M6PV6	48	100	57	0.6	213
9	MPA	1.5	Traces	Traces	–	600
10	Cs2.5H0.5M12P	48	Traces	Traces	–	432
11	No catalyst	72	No	–	–	–

[a] Reaction conditions: 1 mmol 2,6-dimethylphenol, 5 ml acetone, 0.02 mmol catalysts, 22 mmol H_2O_2 (250 volume), 20 °C, stir.
[b] Conversion (C) of 2,6-dimethylphenol.
[c] Selectivity (S) to 2,6-dimethyl-1,4-benzoquinone.
[d] Turnover frequency (number of moles of product formed per mole of catalyst per hour).
[e] Maximun acid strength.

introduction of statistically distributed defects into the cation or anion sublattice depending on the Cs stoichiometry. Only the structure of Cs_3A does not contain any structural defects. Cs_3A is also the salt with the highest BET surface area. On the other hand, the maximum acid strength also decreased when the Cs number in the salt was changed from 1 to 3.

The effect of substituting one Mo atom by one V atom (entries 1 and 9 for acids, 4 and 10 for salts) was very important for improving the catalytic activity of the heteropolycompound. Then the redox property of V was also proved in agreement with the redox potential values reported in the bibliography, 0.52 V for $H_3PMo_{12}O_{40}$ [27] and 0.65 V for $H_4PMo_{11}VO_{40}$ [28].

On the other hand, the TOF values for the corresponding quinone, when the heteropolycompounds with six V atoms (entries 6–8) were used as catalysts, were lower than those obtained for the heteropolycatalysts with one V atom (entries 1, 3, and 5). The maximum acid strength also decreased when the number of V atoms in the heteropolycatalysts increased.

Therefore, it could be assumed that the high yield to 2,6-dimethyl-*p*-benzoquinone from 2,6-dimethylphenol resulted from both factors, the oxidative ability and the acidic properties of the heteropolycompounds. The oxidation of 2,6-dimethylphenol using hydrogen peroxide and catalyzed by HPA is influenced by the replacement of a Mo atom by vanadium species, which are more active in a redox process. On the other hand, the Brønsted acidity may have some influence since the protons could be involved in the mechanism of the oxidation reaction [9].

4. Conclusions

$H_4PMo_{11}VO_{40}$ and $H_9PMo_6V_6O_{40}$ were synthesized from binary oxides using the hydrothermal synthesis method. Mixed proton-cesium and cesium salts, containing *x* cesium cations per heteropolyanion (where *x* is between 1 and 9) were synthesized from both acids. The catalysts were characterized by TGA/DTA, FT-IR, DRS, S_{BET}, and acidity measurements. The presence of Keggin units and the V incorporation into the Keggin units were observed. The mono-substituted vanadium acid, $H_4PMo_{11}VO_{40}$, possesses an acid strength higher than the V-free sample and $H_9PMo_6V_6O_{40}$, at room temperature. Heating above 200 °C leads to a considerable structural changes and to a reduction of unit cell dimensions. As a consequence, the acidic properties decrease. A treatment at 400 °C leads to a deep modification related to the partial degradation of the polyanion. The Cs salts from $H_4PMo_{11}VO_{40}$ possess stronger acidic sites than those from $H_9PMo_6V_6O_{40}$. Moreover when the Cs number increases, the acidic properties decrease. The salts calcined at 200 °C present higher acidity than the sample at r.t.. At 300 °C, the salts with one, two, and three Cs are unstable and simple vanadates are formed. At temperatures higher than 300 °C, the salts from $H_4PMo_{11}VO_{40}$ undergo a deep transformation through irreversible decomposition. The Keggin structure of the 2.5 Cs salt could be intact, with different number of protons as protonic water, at a temperature as high as 400 °C. The specific surface area for the Cs salts at r.t. and at 100 °C increases when the Cs number increases. At 300 °C the S_{BET} diminishes considerably.

The vanadium-substituted Keggin heteropolyacids and their Cs salts prepared in this work were used as catalysts for the liquid phase reaction of synthesis of 2,6-dimethyl-*p*-benzoquinone from 2,6-dimethylphenol, using hydrogen peroxide. High yields were achieved under mild conditions of reaction (room temperature, acetone as solvent). A value of selectivity to *p*-benzoquinone of 79–59% was obtained when the reaction was catalyzed by Cs salts from the $H_4PMo_{11}VO_{40}$ acid.

These results are very important since it is well known that many kinds of quinone derivatives play prominent roles in biosystems.

Therefore, this study shows the preparation and characterization of new catalysts for liquid phase oxidation reactions. These reactions are more important for industries related to fine chemicals such as pharmaceuticals, flavors and food industries, among others, with the advantages that they are environment friendly.

Acknowledgements

The authors thank Dr. Laura Briand for her valuable comments, L. Osiglio, G. Valle and N. Bernava for their experimental contribution and to project X224 of UNLP for the financial support.

References

[1] M. Misono, Chem. Commun. 13 (2001) 1141.

[2] K. Nomiya, S. Matsuoka, T. Hasegawa, Y. Nemoto, J. Mol. Catal. A: Chem. 156 (2000) 143.

[3] X. Wei, R. Bachman, M. Pope, J. Am. Chem. Soc. 120 (1998) 10248.

[4] A. Khenkin, R. Neumann, A. Sorokin, A. Tuel, Catal. Lett. 63 (1999) 189.

[5] Th. Ilkenhans, B. Herzog, Th. Braun, R. Schlogl, J. Catal. 153 (1995) 275.

[6] C. Marchal-Roch, N. Laronze, N. Guillou, A. Teze, G. Hervé, Appl. Catal. A: Gen. 203 (2000) 143.

[7] G. Süss-Fink, L. Gonzalez, G.B. Shul'pin, Appl. Catal. A: Gen. 217 (2001) 111.

[8] Y. Seki, N. Mizuno, M. Misono, Appl. Catal. A: Gen. 194 (2000) 13.

[9] Y. Seki, J. Seok Min, M. Misono, N. Mizuno, J. Phys. Chem. B 1044 (2000) 5940.

[10] F. Minisci, A. Citterio, E. Vismara, F. Fontana, S. De Bernardinie, J. Org. Chem. 54 (1989) 728.

[11] S. Ito, K. Aihara, M. Matsumoto, Tetrahedron Lett. 24 (1983) 5249.

[12] M. Shimizu, H. Orita, T. Hayakawa, K. Takehira, Tetrahedron Lett. 30 (1989) 471.

[13] D. Bryce-Smith, A. Gilbert, J. Chem. Soc. (1964) 873.

[14] A. Kholdeeva, N.N. Trukhan, M.P. Vanina, V.N. Romannikov, V.N. Parmon, J. Mrowiec-Bialon, A.B. Jarzebski, Catal. Today 2717 (2002) 1.

[15] F. Kern, St. Ruf, G. Emig, Appl. Catal. A: Gen. 150 (1997) 143.

[16] B. Bardin, R. Davis, Top. Catal. 6 (1998) 77.

[17] B. Bardin, R. Davis, Appl. Catal. A: Gen. 185 (1999) 283.

[18] C. Rocchiccioli-Deltcheff, M. Fournier, J. Chem. Soc. Faraday Trans. 87 (1991) 3913.

[19] A. Bielanski, L. Malecka, L. Kubelkova, J. Chem. Soc. Faraday Trans. 85 (1989) 2847.

[20] C. Rocchiccioli-Deltcheff, R. Thouvenot, R. Frannck, Spectrochim. Acta A 32 (1976) 587.

[21] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.

[22] R. Cid, G. Pecchi, Appl. Catal. 14 (1985) 15.

[23] L. Pizzio, P. Vázquez, M. Blanco, C. Cáceres, in: Proceedings of the XVII Simposio Iberoamericano de Catálisis, Portugal, 2000, p. 563.

[24] J. Mioc, R. Dimitrijevic, M. Davidovic, Z. Nedic, M. Mitrovic, Ph. Colomban, J. Mater. Sci. 29 (1994) 3705.

[25] G. Mestl, T. Ilkenhans, D. Spielbauer, M. Dieterle, O. Timpe, J. Krohnert, F. Jentoft, H. Knozinger, R. Schlogl, Appl. Catal. A: Gen. 210 (2001) 13.

[26] G. Mestl, S. Berndt, H. Sauer, G. Weinberg, D. Herein, R. Schlögl, in: Proceedings of the Fourth European Congress on Catalysis EUROPA-CAT IV, Italy, 1999, p. 499.

[27] K. Eguchi, T. Seiyama, N. Yamasoe, S. Katsuki, J. Catal. 111 (1988) 336.

[28] T. Murtha, US Patent 4 507 507 (1985).