Supported heteropolycompounds as ecofriendly catalysts for 2,6-dimethylphenol oxidation to 2,6-dimethyl-1,4-benzoquinone

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Abstract

Supported catalysts were prepared by in situ deposition of the cesium salt of $H_4PMo_{11}VO_{40}$. Commercial silica was impregnated to incipient wetness with an aqueous solution of $CsNO_3$. The dried and calcined solid was then impregnated an aqueous solution of $H_4PMo_{11}VO_{40}$. Solids with 40% and 7% (w/w) of $Cs_3HPMo_{11}VO_{40}$ were obtained. To compare on behavior catalytic, a catalyst was prepared by silica impregnation with an aqueous solution of $H_4PMo_{11}VO_{40}$ (40%, w/w), using the incipient wetness technique. Impregnated silica particles showed a homogeneous distribution by scanning electron microscope (SEM). The Keggin structure was preserved for the salt in those catalysts according to the FT-IR and DRS characterization. The acidity of the solids with 40% and 7% (w/w) of $Cs_3HPMo_{11}VO_4$ was greater than that of the silica but lower than that of bulk salt. The catalysts were used in the oxidation of 2,6-dimethylphenol with aqueous hydrogen peroxide, in acetonitrile at 20 °C. The reaction was followed by UV–vis spectroscopy. The phenol conversion was 35% at 4 h for $H_4PMo_{11}VO_{40}/SiO_2$, 20% at 2 h and 29% at 135 h for 7% $Cs_3HPMo_{11}VO_4/SiO_2$, and 83% at 98 h for 40% $Cs_3HPMo_{11}VO_4/SiO_2$. The behavior of the latter was also studied by HPLC technique. Similar results were achieved with both techniques. The $Cs_3HPMo_{11}VO_4/SiO_2$ catalysts were almost totally insoluble in the reaction mixture.
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Keywords: Supported heteropolycompounds; Ecofriendly catalysts; 2,6-dimethylphenol oxidation; 2,6-dimethyl-1,4-benzoquinone

1. Introduction

One of the main objectives of innovations in processes is the development of new technologies, the so-called clean technologies [1]. The aims of these technologies are to obtain great sustainability and improve environmental conditions.

The industries related to fine chemicals, for example, the production of drugs, fall into the category of emergent industries. Therefore, the application of catalytic processes in these areas is relatively new. The essential factors that led this industrial sector to use the catalytic process were environmental control, the decrease of the costs of manufacture and the tendency toward chiral drugs. The substitution of stoichiometric processes by catalytic processes implies a great benefit for the costs as well as for the environment [2–4]. Catalytic oxidation is the most important technology for the conversion of hydrocarbon raw materials (alkanes, alkenes and aromatics) to industrial chemicals [5].

On the other hand, hydrogen peroxide is the technologically green oxidant by election [6], due to the innocuous nature of its by-product, water. In relation to this oxidant, in the last two decades, there has been a series of publications about the use of catalysts based on heteropolycompounds (HPC), among them there are several reviews [7–11]. The benefits derived from their intrinsic oxidant properties are reported in these papers and reactions in which these catalysts can potentially be used or that have been the subject of basic studies have been commented, for example by Kozhevnikov [9].

Vanadium-substituted heteropolycompounds are the most studied polyoxometalates due to their importance as catalysts for a variety of catalytic oxidation reactions. For example, hydroxylation of benzene, oxidation of toluene, nitrobenzene and norbornene [12] using aqueous hydrogen peroxide.

On the other hand, acidic cesium salts of the 1-vanado-11-molybdophosphoric acid have attracted much attention since the presence of vanadium increases the catalytic activity in

oxidation reactions, and cesium has been reported to increase both the stability and the reoxidation rate of the catalysts [13,14].

The effect of vanadium substitution in the heteropolycompounds was studied in previous works [15,16], where its influence on their redox and acidic properties was observed. The cesium salts of $H_4PMo_{11}VO_{40}$ are known as industrial catalysts for partial selective oxidation reactions [17]. The disadvantage of the acid cesium salts from heteropolyacids (HPA) is their insolubility, which makes the conventional aqueous impregnation impossible. Soled et al. [18] have presented a simple technique of in situ deposition of an acid cesium salt on silica. This technique consists in a first impregnation of dried and calcined silica with a solution of cesium nitrate and a second impregnation with a heteropolyacid solution.

In addition, it is important to emphasize that quinone derivatives play a key role in the biosystems and that they are useful intermediaries in the synthesis of fine chemical compounds. For example, 2,3,5-trimethyl-1,4-benzoquinone is an intermediary in the production of vitamin E [19]. Kholdeeva et al. [20] reported the 2,3,6-trimethylphenol oxidation to the corresponding quinone with aqueous hydrogen peroxide.

The objective of this work is to study the Keggin type heteropolycompounds supported on silica as catalysts for a clean liquid phase oxidation of 2,6-dimethylphenol to 2,6-dimethyl-1,4-benzoquinone using aqueous hydrogen peroxide as oxidant (Scheme 1).

2. Experimental

2.1. Synthesis of catalysts

The $H_4PMo_{11}VO_{40}$ (M11PV1) heteropolyacid was synthesized by a hydrothermal synthesis method [16]. 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 M11PV1 were obtained.

A supported catalyst was prepared by in situ deposition of a cesium salt of M11PV1. The silica (S) used as support was a commercial one, Rali-Chemie AG AF 125, with a surface area of 253 m^2/g and a pore volume of 2.6 cm^3/g. Firstly, the solid

was impregnated to incipient wetness with an aqueous solution of $CsNO_3$ (99.8% AlfaAesar). It was dried to 60 °C for 24 h and calcined in air to 200 °C for 4 h. Then, the solid was impregnated by a similar technique with an aqueous solution of M11PV1, and thermally treated in a similar way. The catalysts obtained were 40% (w/w) of $Cs_3HPMo_{11}VO_{40}/SiO_2$ (40% Cs3M11PV1/S) and 7% (w/w) of $Cs_3HPMo_{11}VO_{40}/SiO_2$ (7% Cs3M11PV1/S).

On the other hand, silica was impregnated to incipient wetness with an aqueous solution of M11PV1. A catalyst with 40% (w/w) of $H_4PMo_{11}VO_{40}/SiO_2$ (40% M11PV1/S) was obtained.

2.2. Characterization of catalysts

The catalysts were characterized by a Philips 505 scanning electron microscope (SEM) using an accelerating voltage of 15 eV. The samples were stuck as powder on a graphited band and coated with graphite.

Fourier transform infrared spectroscopy (FT-IR) spectra of solid samples were recorded using a Bruker IFS 66 spectrometer, with pellets in KBr and a measuring range of 400–1500 cm^{-1}.

The solid samples were also studied by diffuse reflectance spectroscopy (DRS) in the range 200–450 nm, using UV–vis Varian Super Scan 3 equipment, fitted with a diffuse reflectance chamber with $BaSO_4$ inner surface.

X-ray diffraction (XRD) patterns of solid samples were recorded. To obtain these graphs, a Philips PW-1390 device with built-in recorder was used. Conditions were as follows: Cu Kα radiation; Ni filter; 20 mA; 40 kV in the high voltage source; scanning angle (2θ) from 5° to 60° and scanning rate of 1°/min.
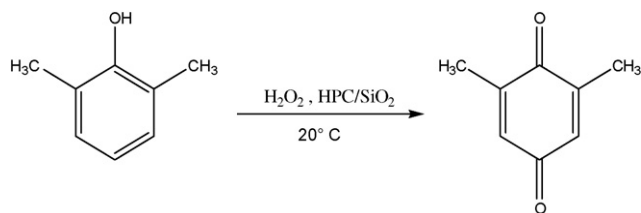
Textural properties of the solid samples were determined by nitrogen adsorption/desorption techniques using Micromeritics Accusorb 2100E equipment.

The acidity of the catalysts was determined by potentiometric titration with a solution of *n*-butylamine in acetonitrile (0.05 N). The electrode potential variation was measured with an Instrumentalia S.R.L. digital pH meter, using a double junction electrode.

2.3. Oxidation of 2,6-dimethylphenol

The oxidation of 2,6-dimethylphenol (2,6-DMP) was performed under vigorous stirring in a glass reactor at 20 °C. The reactions were carried out by adding H_2O_2 70% (Analquim) in excess (1 ml) to a mixture of 1 mmol of 2,6-DMP (Aldrich) in acetonitrile (5 ml, J.T. Baker) and the catalyst (0.02 mmol).

The oxidation of 2,6-DMP was followed in time by means of UV–vis spectroscopy. The mixture was centrifuged and samples of 0.1 ml were obtained. They were diluted with distilled water, first dilution 1/100 (concentrated sample) and second dilution 1/25 (diluted sample). Their UV–vis spectra were registered in the range 200–450 nm, 50 nm/min and slit beam width between 0.7 and 1.0 using a Varian Super Scan 3 equipment.

Scheme 1. Oxidation reaction of 2,6-dimethylphenol to 2,6-dimetylbenzoquinone with aqueous H_2O_2 at 20 °C.
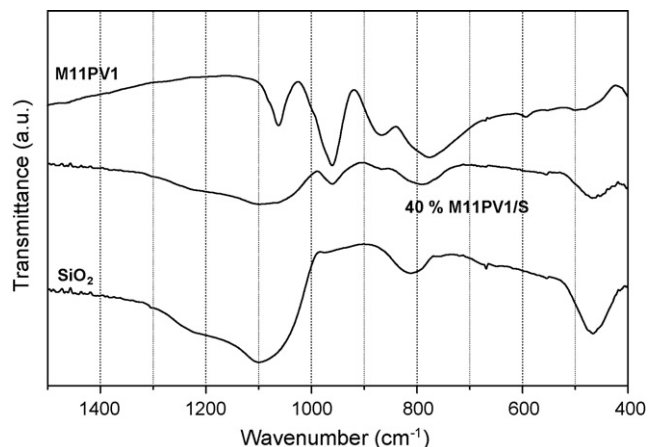
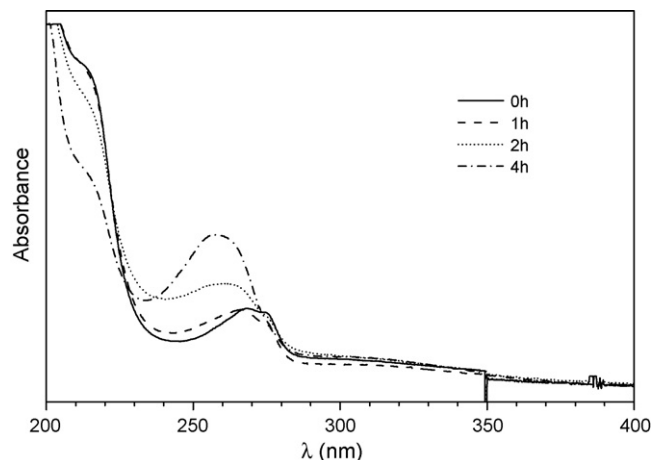Fig. 1. FT-IR spectra of silica, M11PV1 and 40% M11PV1/S samples.

Fig. 3. UV–vis spectra of diluted reaction samples in function of time, using 40% M11PV1/S as catalyst.

On the other hand, the spectra of reactant and product were carried out. Their absorption maxima were 213 nm for 2,6-DMP and 257 nm for 2,6-dimethyl-1,4-benzoquinone (2,6-DMBQ). Then, the respective calibration curves were obtained with acetonitrile/H_2O_2 solutions as reference. The absorbance values of the diluted samples at 257 and 213 nm at different reaction times were determined, the 2,6-DMP concentration was then calculated. The 2,6-DMP percentage conversion values were obtained as the percentage ratio between the 2,6-DMP concentration decrease and the initial 2,6-DMP concentration.

In particular, when 40% Cs3M11PV1/S catalyst was used, the oxidation of 2,6-DMP was followed in time by means of HPLC.

KNK-500-A equipment with a Supelcosil LC-18 column (25 cm × 4.6 mm × 5 μm) and UV–vis detector was used. The operating conditions were 45% (v/v) acetonitrile as mobile phase, flow of 1 ml/min and lambda (λ) of 213 nm.

To obtain 2,6-DMP calibration curve, solutions of this substrate were prepared. The 2,6-DMP conversion values were calculated as above-mentioned. Two experiments for 2,6-DMP catalytic oxidation were carried out, in one of them reaction solution samples of 0.1 ml were obtained in the range 0–29 h of reaction and they were diluted with distillate water (1/250) and analyzed by HPLC. The other experiment was carried out in similar way but taking out the catalyst of the reaction solution after 6 h.

3. Results and discussion

The SEM mapping of different elements in the particles of the silica supported catalyst shows a homogeneous distribution of Cs, V, Mo and P inside silica particles according to the percentage atomic ratios expected.

The FT-IR spectrum of the supported catalyst prepared from M11PV1 shows that the Keggin structure of the heteropolyacid was preserved on silica after impregnation (Fig. 1). In the same way, the presence of undegraded Keggin structure was observed in the FT-IR spectra of the catalysts obtained by in situ
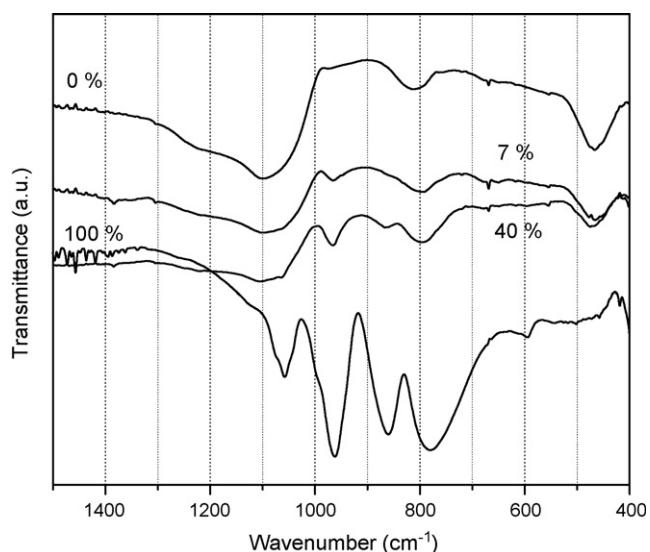

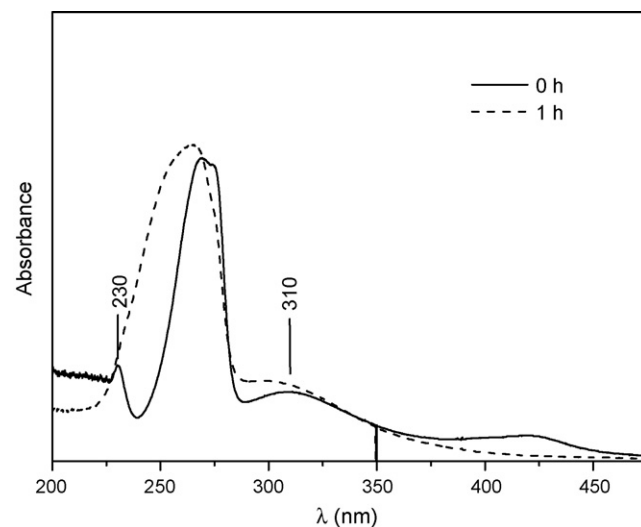Fig. 2. FT-IR spectra of $Cs_3HPMo_{11}VO_{40}$ on silica at different concentrations.

Fig. 4. UV–vis spectra of concentrated reaction samples in function of time with 40% M11PV1/S as catalyst.
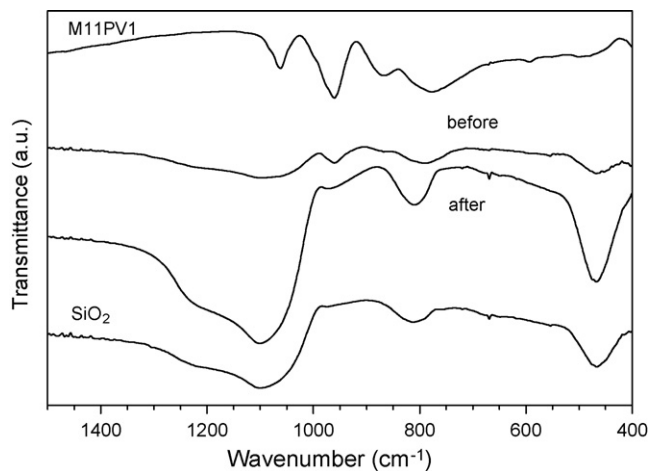
Fig. 5. FT-IR spectra of 40% M11PV1/S catalyst, before and after using it in the reaction.

deposition of Cs3M11PV1 salt on silica (Fig. 2). These results were corroborated by DRS.

The X-ray diffraction pattern of the 40% M11PV1/S catalyst is similar to the silica diffraction pattern; no characteristic diffraction lines of a crystalline structure were observed. These and the above-mentioned results from FT-IR allow supposing that the heteropolyacid is very well dispersed on silica, so its crystalline structure could not be detected.

For the catalyst prepared by in situ deposition of Cs3M11PV1 (40%) the X-ray diffraction pattern shows the Cs3M11PV1 cesium salt diffraction lines. This means that the impregnated salt on silica was preserved almost without degradation, as was also observed by FT-IR. However, other diffraction lines were observed for 7% Cs3M11PV1/S. Then, it is possible to suppose that there was an interaction between the salt and the silica during the impregnation of the low loading catalyst, which produced the partial degradation of the Keggin structure.

The nitrogen adsorption and desorption isotherms obtained for the supported catalysts were typical of porous materials

with mesopores and a wide pore size distribution. The BET specific surface area, the pore size, and the total pore volume of silica decrease with in situ impregnation of the cesium salt of the M11PV1 heteropolyacid.

The acidity order was determined by potentiometric titration as follows: Cs3M11PV1 $\gg$ 40% Cs3M11PV1/S > 7% Cs3M11PV1/S > S.

The 40% M11PV1/S catalyst was used in the oxidation of 2,6-DMP in acetonitrile at room temperature. The reaction was followed by UV–vis spectroscopy. The 2,6-DMP conversion came up to 35% after 4 h of reaction. The registered spectra are shown in Fig. 3.

In the UV–vis spectra of the concentrated reaction samples (Fig. 4) two bands at 230 and 310 nm were also observed, they belong to the M11PV1 heteropolyacid. Then, leaching of the catalyst in the reaction media is evidenced.

During the test, the 0 h sample changes its color from orange to green and turns to orange again after addition of H_2O_2. Probably, a Mo (VI) amount of the orange catalyst is reduced to Mo (V) (blue, "heteropolyblue") when it is added to acetonitrile/2,6-DMP solution and the color turns to green. Then, the solution turns to orange again when H_2O_2 is added; Mo (V) is oxidized to Mo (VI).

On the other hand, the FT-IR spectra of fresh and used 40% M11PV1/S catalysts were compared (Fig. 5). Probably, some leaching or decomposition of the supported catalyst could have occurred during the reaction, since the characteristic bands of M11PV1 were not observed in the used catalyst spectrum.

The 7% Cs3M11PV1/S catalyst was also studied by UV–vis spectroscopy during the catalytic oxidation of 2,6-DMP with aqueous hydrogen peroxide. The spectra obtained for diluted and concentrated samples of reaction solution are shown in Fig. 6a and b, respectively. A comparison of these results with those corresponding to 40% M11PV1/S showed a clear difference related to catalyst leaching in the reaction media. The 7% Cs3M11PV1/S catalyst results more stable than the 40% M11PV1/S catalyst. No Keggin heteropolyanion bands were observed in the UV–vis spectrum of the initial
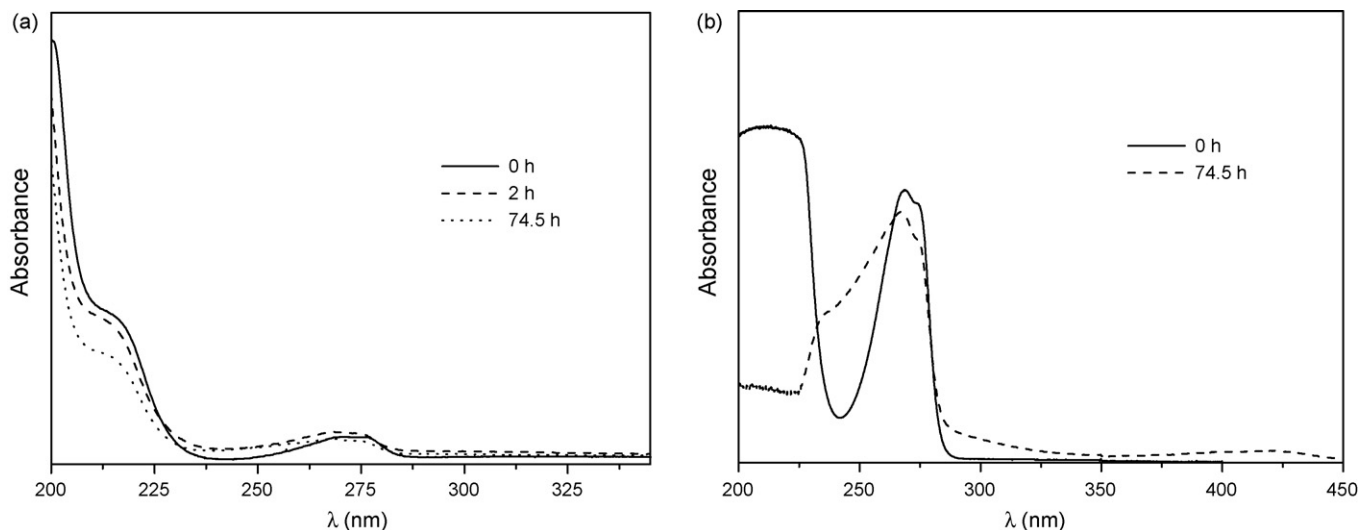

Fig. 6. UV–vis spectra in function of time of diluted (a) and concentrated (b) reaction samples using 7% M11PV1/S as catalyst.
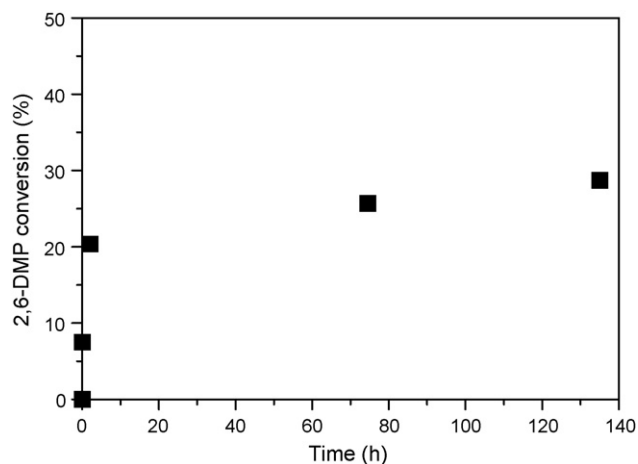
Fig. 7. Conversion in function of time for the 2,6-DMP oxidation with aqueous H_2O_2 using 7% Cs3M11PV1/S.

Fig. 9. UV–vis spectrum derivatives of the reaction mixture using 40% Cs3M11PV1/S as catalyst.

concentrated reaction solution (0 h sample), although a small band of the catalyst begins to develop at 300 nm in the spectrum of the 74.5 h sample (Fig. 6b). Fig. 7 shows that the 2,6-DMP conversion is approximately constant for 2 h of reaction when the low loading supported catalyst is used. This catalyst allows obtaining 20% and 29% of reactive conversion after 2 and 135 h of reaction, respectively.

On the other hand, the performance of the 40% Cs3M11PV1/S catalyst in the above-mentioned reaction was studied by UV–vis spectroscopy. Fig. 8 shows the reaction solution spectra corresponding to different reaction times. The conversion resulted in 83% for 98 h of reaction. Consequently, this catalyst was much more active than the low loading one.

For this test, the derivatives of UV–vis spectra of the reaction sample are presented in Fig. 9. It is corroborated that there are practically no changes in the derivative at 98 h of reaction. This indicates that the reaction at 98 h was almost completed [21].
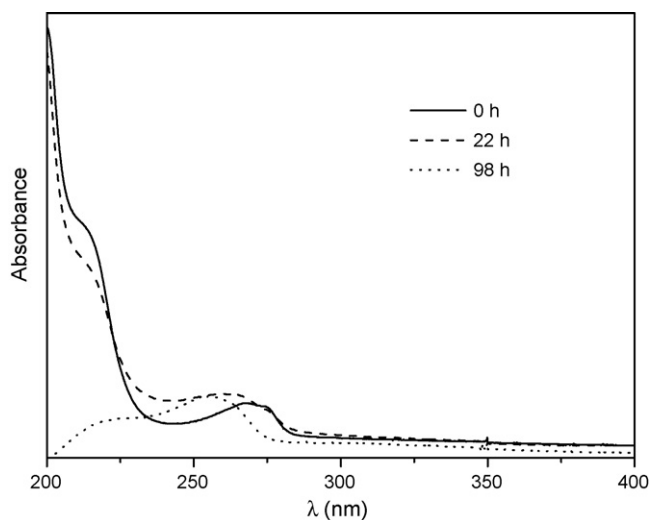
In the UV–vis spectra of the concentrated sample of the reaction solution a band at 306 nm is observed for 98 h of reaction (Fig. 10). This band of the Keggin heteropolyanion begins to appear for the 22 h sample spectra and it results more pronounced at the 98 h sample spectra. It could be suggested that the catalyst was practically not leaching in the reaction media during 22 h.

The FT-IR spectra of fresh and used 40% Cs3M11PV1/S catalyst in the reaction mentioned above are shown in Fig. 11. The characteristic bands of the Keggin heteropolyanion were present in both cases. The leaching of this catalyst during the reaction was not significant. Therefore it also results more stable than the 40% M11PV1/S catalyst in the operating conditions used.

The oxidation reaction of 2,6-DMP using 40% Cs3M11PV1/S as catalyst and acetonitrile as solvent was also studied by HPLC. The chromatograms obtained after 29 h of reaction indicated that 2,6-DMBQ was the only product formed. Taking into account this result, the conversion to 2,6-DMBQ in

Fig. 8. UV–vis spectra in function of time of diluted reaction samples using 40% Cs3M11PV1/S as catalyst.

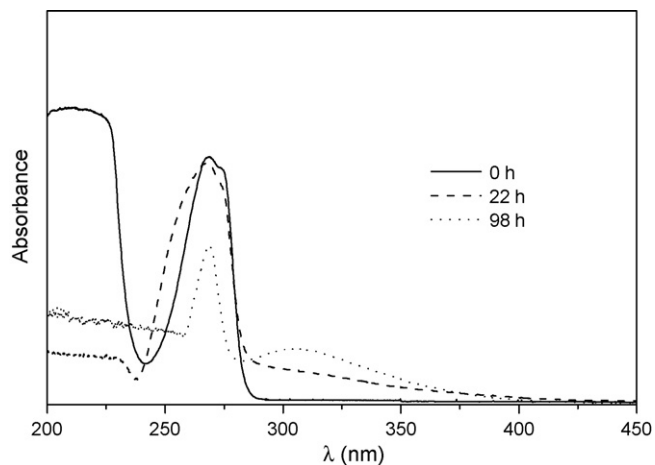Fig. 10. UV–vis spectra of concentrated reaction samples using 40% Cs3M11PV1/S as catalyst in function of time.

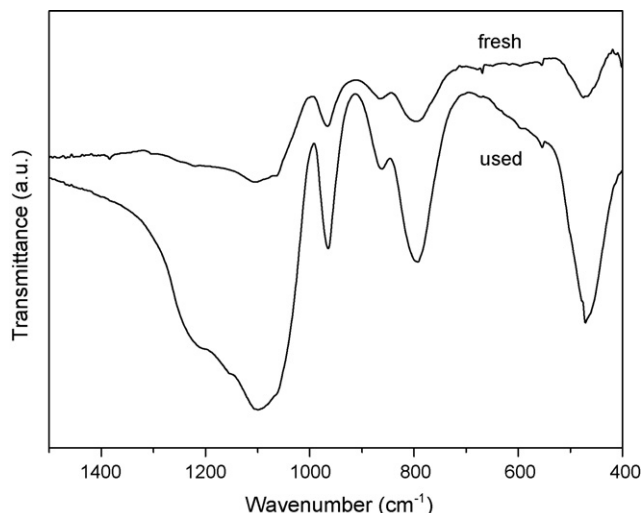Fig. 11. FT-IR spectra of fresh and used 40% Cs3M11PV1/S catalyst in the liquid phase oxidation of 2,6-DMP.

Fig. 13. 2,6-DMP concentration (a) during the 40% Cs3M11PV1/S catalyzed reaction and (b) after taking off the catalyst from the reaction, at different reaction times.

function of reaction time (Fig. 12) was calculated from the 2,6-DMP concentration decrease determined by HPLC (Fig. 13, curve a). Fig. 12 shows that the conversion to 2,6-DMBQ reaches a value of 79% at 29 h of reaction.

Following the objective of checking the truly heterogeneity of the reaction, a test using the 40% Cs3M11PV1/S catalyst was performed. The catalyst was taken out of reaction solution after 6 h. Then, the 2,6-DMP concentration was determined in the solution. These results are shown in Fig. 13, curve b. It can be observed that the 2,6-DMP concentration was practically constant from 6 to 29 h of reaction. However, in Fig. 13, curve a, it is shown that the 2,6-DMP concentration changes considerably in the presence of the catalyst during the same period of time. This indicates that the catalyst was practically not leaching.
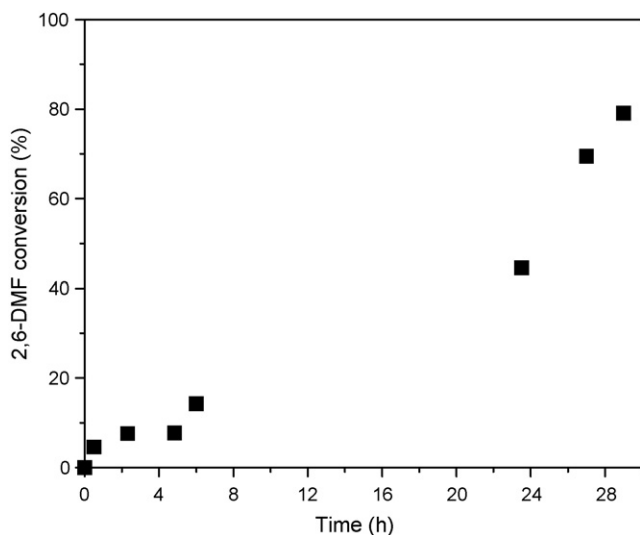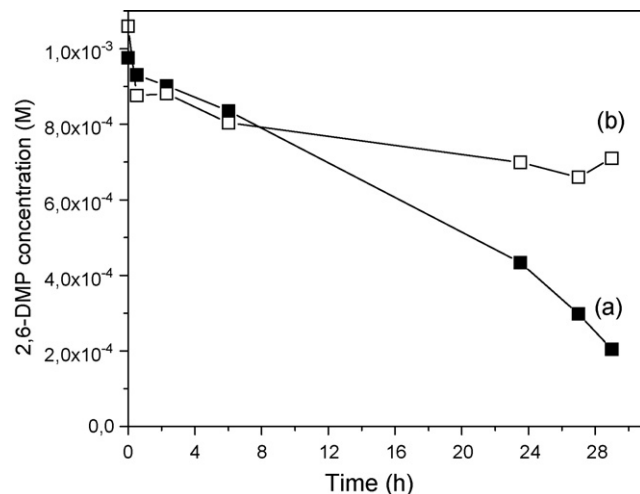

Fig. 12. Conversion of 2,6-DMP in function of time for its oxidation with aqueous H_2O_2 using 40% Cs3M11PV1/S as catalysts.

4. Conclusions

The catalysts prepared by impregnation of silica with vanadium and molybdenum heteropolycompounds preserved an undegraded Keggin structure, except in the case of the 7% Cs3M11PV1/S catalyst in which many of the heteropolycompound are degraded due to interaction with the support. All of them were used in the oxidation reaction of 2,6-DMP. The catalyst obtained by incipient wetness impregnation with the M11PV1 heteropolyacid on silica showed leaching in the reaction media.

The 7% Cs3M11PV1/S catalyst resulted more stable with respect to leaching in the reaction media. The conversion of 2,6-DMP reached a value of 20% at 2 h and increased only up to 29% at 135 h.

The 40% Cs3M11PV1/S catalyst was more active than the low content ones. The 2,6-DMP conversion was 83% for 98 h of reaction. It is worth mentioning that this catalyst was not practically solubilized in the reaction media during 22 h. Therefore, it was more stable, under the operating conditions used, than the supported catalyst of the M11PV1 with the same content of Keggin phase. It was observed that the only product present was 2,6-DMBQ until 29 h of reaction.

In another experiment, it was demonstrated that the 40% Cs3M11PV1/S catalyst had almost not leached, and that the reaction was heterogeneous. The catalyst was taken out of the reaction media at 6 h and the determination of 2,6-DMP concentration was followed in time. The obtained results showed that the 2,6-DMP concentration did not practically change from 6 to 29 h of reaction. However, 2,6-DMP concentration considerably changed in the presence of the catalyst in this period.

In short, silica supported catalysts of heteropolycompounds with high conversion to 2,6-DMBQ and insoluble in the reaction media were prepared.

Acknowledgments

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