



An efficient catalytic route for the preparation of silyl ethers using alumina-supported heteropolyoxometalates

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ABSTRACT

In the present work the phenol trimethylsilylation with hexamethyldisilazane using molybdophosphovanadates supported on commercial alumina cylinders as catalysts was studied. These catalysts were prepared by incipient wetness impregnation also including Fe and Cu as cations, which can be present as bulk heteropolyacids or in the previously impregnated support. These solids were characterized by several techniques such as diffuse reflectance spectroscopy, Fourier transformed infrared spectroscopy, optical and scanning electron microscopies, and X-ray diffraction, among others.

The catalytic test was performed under different reaction conditions in order to know the performance of the synthesized catalysts. The method shows high conversion of phenol under heterogeneous conditions. Phenol trimethylsilyl ether formation was obtained using hexamethyldisilazane as acylating agent and toluene as reaction solvent, with different reuses. In addition, they are environmentally friendly materials. The $\text{H}_2\text{PMo}_{11}\text{VCuO}_{40}$ supported on alumina showed higher activity in the tested reaction.

Finally, various alcohols and phenols were silylated to trimethylsilyl ethers, under mild conditions, and excellent yields were obtained.

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1. Introduction

Heteropolyacid (HPA) compounds with Keggin structure are polynuclear complexes principally constituted by molybdenum or tungsten as polyatoms, and phosphorus and silicon as central atoms or heteroatoms. They operate either as multielectron oxidants or strong acids, with an acid strength higher than that of classic acids. They are used as industrial catalysts for several liquid-phase reactions [1–6]. They are very important for industries related to fine chemistry, such as flavors, pharmaceuticals and food industries. HPAs are important compounds used as catalysts for industrial synthetic processes [7], such as alkylation [8]. Catalytic processes based on HPAs have many advantages over liquid acid catalysis. They are noncorrosive, cheap and environmentally friendly, presenting fewer disposal problems. Their reuse is possible and their separation from liquid products is easier than for homogeneous catalysts [7].

We have reported a range of heteropolycompounds with Keggin, Wells–Dawson and Preyssler structure types for performing

catalytic acidic reactions such as tetrahydropyranylation of phenols and alcohols [9–12], synthesis of coumarins [13], acylals [14], dihydropyrimidinones [15], flavones, chromones [16], ethyl β -arylaminoacronates [17], among others [18,19]. It was found that vanadium-containing polymolybdophosphates catalyze the oxidation of different substrates such as phenols [20] and sulfides [21], using aqueous hydrogen peroxide as clean oxidant.

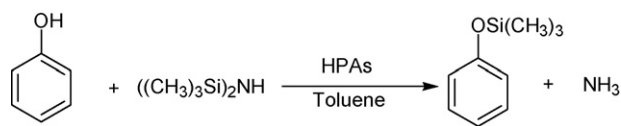
Protection of the functional organic group is an important process in multistep synthesis. The most important uses of trimethylsilyl groups in organic synthesis are for the protection of hydroxyl groups of alcohols, phenols and carboxylic acids. The trimethylsilyl group is one of the most important and widely used groups for protecting the hydroxyl function. This group is often used in analytical chemistry to prepare silyl ethers as volatile derivatives of alcohols and phenols [22]. Silyl ethers have general stability for most nonacidic reagents and high solubility in nonpolar solvent [23].

Several methods have been reported for the silylation of the hydroxyl group, including the reaction of alcohols with trimethylsilyl halides in the presence of the stoichiometric amount of a base such as imidazole [24], 4-(N,N-dimethylamino)pyridine [25], N,N-diisopropylethylamine [26], lithium sulfide [27], and nonionic super base catalyst [28] with trimethylsilyl triflate, which is more reactive than the chloride, with allylsilanes in the presence of a catalytic amount of p-toluenesulfonic acid, with iodine, with

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Scheme 1.

trifluoromethane sulfonic acid, and with $\text{Sc}(\text{OTf})_3$ [23]. However, some of these methods have frequently suffered from drawbacks such as lack of reactivity or the difficulty in removing the amine salt derived from the reactions of by-produced acid and co-bases during the silylation reaction [28].

On the other hand, hexamethyldisilazane (HMDS) is a cheap, commercially available, and stable compound that can be used for the preparation of trimethylsilyl ethers from hydroxyl compounds. Recently, Mojtahedi et al. [29] reported an efficient solvent-free method for the preparation of silyl ethers in the presence of no additive using ultrasound to promote the protection reactions. Its handling does not require special precautions, and the workup is not time-consuming, because the only by-product of the reaction is ammonia, which is easily removed from the reaction medium [23]. Even though the handling of this reagent is easy, the low silylation power of HMDS is the main drawback to its application; therefore there are a variety of catalysts for achieving this reagent [30–45].

In relation to the HPA used by our group, the heteropolyacid, where one molybdenum atom of the molybdophosphoric acid was substituted by one vanadium atom, was synthesized and doped with Cu or Fe from their respective oxides using the hydrothermal synthesis method [46]. The changes observed indicate V inclusion in the primary structure of the heteropolyanion and that Cu or Fe do not substitute into the primary structure, they occupy positions in the secondary structure. High yields were achieved under mild conditions of reaction (room temperature, acetone as solvent) when those catalysts were used in the conversion of 2,6-dimethylphenol to 2,6-dimethyl-1,4-benzoquinone using aqueous hydrogen peroxide as oxidizing agent [46].

For the above-mentioned reason the present work investigates the catalytic properties of supported molybdophosphovanadates (MPV), $\text{HPMo}_{11}\text{VFeO}_{40}$ and $\text{H}_2\text{PMo}_{11}\text{VCuO}_{40}$, with Keggin structure, on alumina cylinders. The catalyst characterization was carried out by optical and electronic microscopies, FT-IR, DRS, XRD, and acidic properties were determined through potentiometric titration with *n*-butylamine. The catalytic activity of those solids in the silylation of phenols and alcohols in the presence of HMDS was determined (Scheme 1).

2. Materials and methodology

2.1. Catalyst preparation

2.1.1. Synthesis of catalyst

$\text{HPMo}_{11}\text{VFeO}_{40}$ (FeMoVP) and $\text{H}_2\text{PMo}_{11}\text{VCuO}_{40}$ (CuMoVP) (specific surface area of the heteropolyacid with Keggin structure, range from 3 to $10\text{ m}^2/\text{g}$) were prepared by a hydrothermal synthesis method [10,20].

Table 1
Nomenclature of catalysts.

Support	Precursor First-step impregnation	Precursor Second-step impregnation	Nomenclature Supported catalyst
Alumina (Al)	MoVP	–	AlHPA
Alumina (Al)	CuMoVP (HPA)	–	AlCuHPA
Alumina (Al)	FeMoVP (HPA)	–	AlFeHPA
Alumina (Al)	Cu acetate (AcCu)	$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (HPA)	AlAcCuHPA

2.1.2. Synthesis of supported catalysts

Commercial alumina (Akzo) (specific surface area, $282\text{ m}^2/\text{g}$; mean pore diameter, 4.2 nm; pore volume, $0.58\text{ cm}^3/\text{g}$) as cylinders was used as support. The support was used without further treatment. The supported catalysts were obtained by incipient wet impregnation of both MPV using ethanol as solvent. The concentration of the impregnation solution was 120 g Mo/l MPV solution. A third catalyst was prepared to compare the catalytic activity of Mo and V together ($\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, MoVP) in relation to Cu in another structure such as copper acetate. Cu cations from ethanolic acetate solutions (the Cu concentration in mol is the same as the amount of Cu in MPV) were impregnated on alumina and then, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ was impregnated on the doped supports with Cu cations. Finally, MoVP was synthesized to compare it with other catalysts. Then, the solids were dried at room temperature. Finally, the catalysts were thermally treated at $200\text{ }^\circ\text{C}$ for 6 h. The used nomenclature is shown in Table 1.

2.2. Catalyst characterization

2.2.1. Diffuse reflectance spectroscopy (DRS)

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.

2.2.2. Fourier transformed infrared spectroscopy (FT-IR)

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

2.2.3. Optical and scanning electron microscopies

The optical observations were made with AxioTech Zeiss equipment, with Donpisha 3CCD camera, and digital imaging. The SEM analysis was carried out with a scanning electron microscope Philips 515, with energy dispersive analyzer (EDAX-Phoenix).

2.2.4. XRD analyses

Power XRD patterns were recorded on the same samples that had been analyzed by FT-IR. The equipment used was a Phillips PW-1732 with built-in recorder, using Cu $\text{K}\alpha$ radiation, nickel filter, 20 mA and 40 kV in the high-voltage source, and scanning angle between 5° and 60° of 2θ at a scanning rate of 1° per min.

2.2.5. Potentiometric titration

0.05 ml of *n*-butylamine (0.1 N), in acetonitrile, 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 enable the evaluation of the 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 (meq/g

solid), where the plateau is reached, indicate 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

2.3.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by spectroscopy data (^1H NMR). The NMR spectra were recorded on a 200 MHz Bruker Advance spectrometer. The NMR spectra were measured in CDCl_3 relative to TMS (0.00 ppm). Reactions were monitored by thin layer chromatography (TLC) analyses.

2.3.2. General procedure: supported MPV-catalyzed silylation of phenols and alcohols in the presence of HDMS

To a mixture of the substrate (1 mmol) and catalyst (100 mg) in toluene (3 ml), HMDS (0.7 mmol) was added dropwise. In relation to the leaching with toluene, the HPA amount removed from the catalysts was less than 0.1% the initial content. This result corroborates the insolubility of HPA in toluene when it is impregnated on alumina supports.

Then, the mixture was stirred at the experiment temperature for the specified time. The reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and washed twice with toluene, 3 ml. The filtrate and the washing liquids were combined, and the obtained phase was washed with 1 M NaOH solution (5 ml). Then it was dried over anhydrous sodium sulfate, filtered and concentrated in vacuo. The residue was subjected to short-column flash chromatography, eluting the product with 1:1 hexane–toluene mixtures. The products were identified by ^1H NMR. The yield was calculated as mol% of obtained product to mol of starting substrate.

^1H NMR (CDCl_3 , 200 MHz) trimethylphenoxy silane: $\delta = 7.30$ (t, 2H, J, 8 Hz), (7.04 t, 1H, J, 7.2 Hz), 6.92 (d, 2H, J, 7.8 Hz), 0.35 (s, 9H) ppm.

3. Results and discussion

3.1. Catalyst characterization

The DRS provided additional information about the substitution of ions into the Keggin units [47]. The charge transfer absorption spectra of most nonreduced polyanions appear in the 200–500 nm regions and consist of bands that 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. The spectra (figure not shown in this publication [46]) show that the inclusion of one or more V atoms in the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (MPA) results in a significant red shift in the absorption edge. Such change in the band assigned to oxygen bonds–molybdenum transfers indicates a possible weakening of such bonds due to the presence of one V atom in the Keggin unit. For Cu or Fe, the samples do not show significant differences. This suggests that Cu (Fe) cations do not modify the absorption properties of V–Mo Keggin unit [46].

In relation to FT-IR, the main characteristic features of bulk MPA are observed at 1064 ($\text{P}-\text{O}_a$), 964 ($\text{Mo}-\text{O}_d$), 871 ($\text{Mo}-\text{O}_b-\text{Mo}$), and 784 ($\text{Mo}-\text{O}_c-\text{Mo}$) cm^{-1} . The oxygen atoms in the primary Keggin structure fall into four classes of symmetric-equivalent oxygen: $\text{P}-\text{O}_a-(\text{Mo})_3$ oxygen atom common to the PO_4 tetrahedron and to a trimetallic group, $\text{Mo}-\text{O}_b-\text{Mo}$, connecting two Mo_3O_{13} units by corner sharing; $\text{Mo}-\text{O}_c-\text{Mo}$, connecting two MoO_6 units by edge

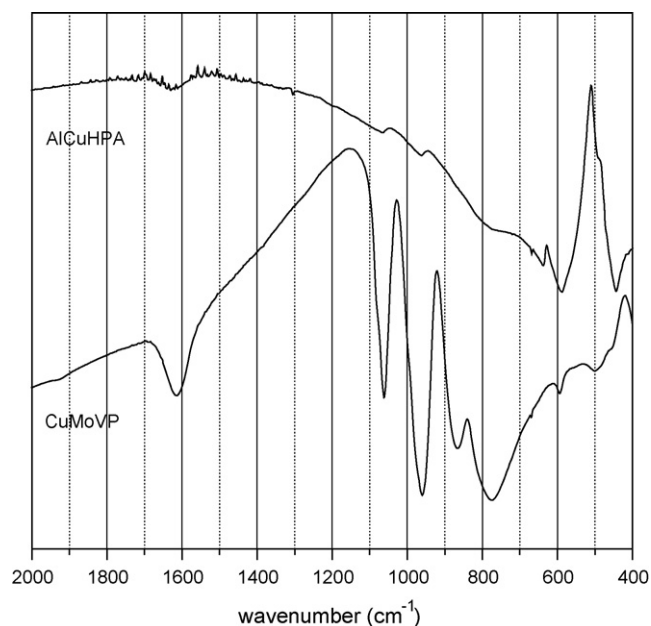


Fig. 1. FT-IR spectra of AlCuHPA sample.

sharing and terminal O_d-Mo . The characteristic stretches associated with MPV, especially CuMoVP, are presented in Fig. 1. In this spectrum, the $\text{P}-\text{O}_a$ and $\text{Mo}-\text{O}_d$ bands were shifted as compared to MPA bands. The $\text{P}-\text{O}_a$ band was negatively shifted 1 cm^{-1} , and for the $\text{Mo}-\text{O}_d$ band, the shift was 4 cm^{-1} . 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 [48]. 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 $\text{Mo}-\text{O}_d$ stretching frequencies and a possible splitting of the $\text{P}-\text{O}_a$ band, depending on the Me nature [48]. This splitting can be considered as an indirect evaluation of the strength of the $\text{Me}-\text{O}_a$ interaction. The stronger $\text{Me}-\text{O}_a$ interaction corresponds to weaker $\Delta\nu$. In accordance with these results, Bielanski et al. [49] have observed slight negative shifts of $\text{P}-\text{O}_a$ (9 and 10 cm^{-1}) and $\text{Mo}-\text{O}_d$ 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 $\text{Mo}-\text{O}_b-\text{Mo}$ mode [50]. Then, the behavior observed in Fig. 1 indicates that V has indeed been incorporated into the Keggin units, and Cu^{2+} is introduced by the proton into the secondary Keggin structure. The spectra of bulk and supported FeMoVP is not shown because it is very similar to the spectra of CuMoVP, both bulk and supported on alumina. In addition, the behavior of this HPA is comparable to that of CuMoVP [46]. In addition, the AlCuHPA spectrum is shown in Fig. 1. In this spectrum it can be observed that the shoulders coincide with the main bands of CuMoPVA.

The characteristics of XRD patterns of supported catalysts (not shown in this work) are similar to alumina, so neither the diffraction lines of HPA nor those of other related crystalline phases were detected. From previous [51–55] and present results it can be inferred that the HPA is deposited as separate entities on alumina. This will be corroborated by other techniques for the characterization of supported catalysts.

As regards the acidic properties, the acidity of the heteropolyanions is Brönsted in nature. The potentiometric curves of bulk and supported MPV are shown in Fig. 2. The titration of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$

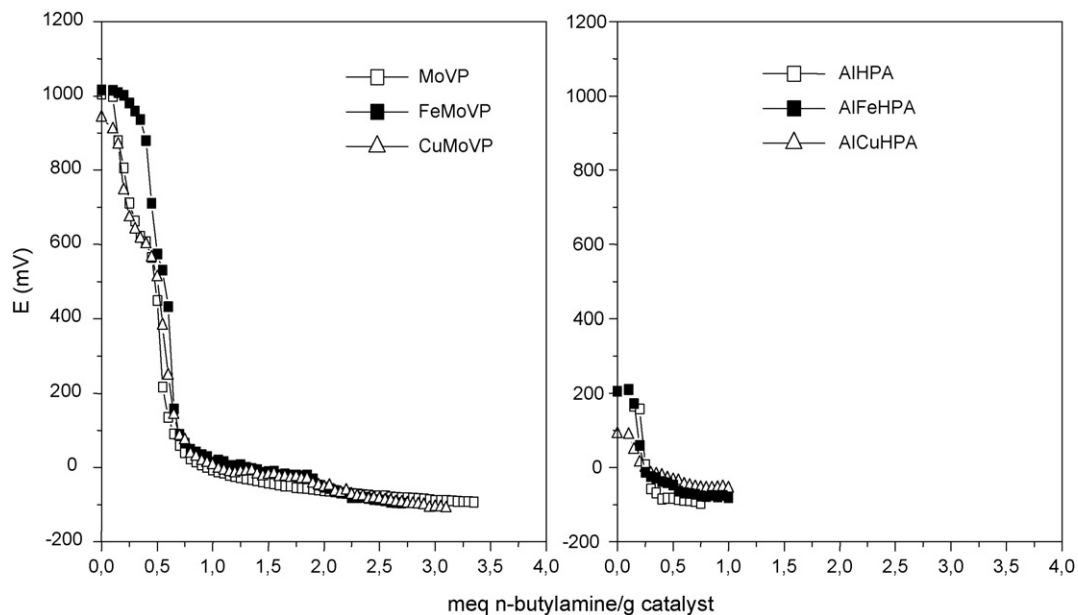


Fig. 2. Potentiometric titration curves for bulk and alumina-supported HPA.

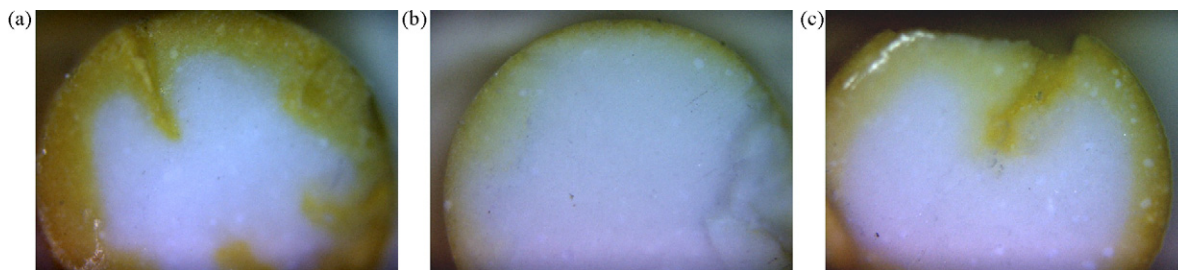


Fig. 3. Optical micrographs of the supported HPA: (a) AlAcCuHPA; (b) AlCuHPA; (c) AlFeHPA.

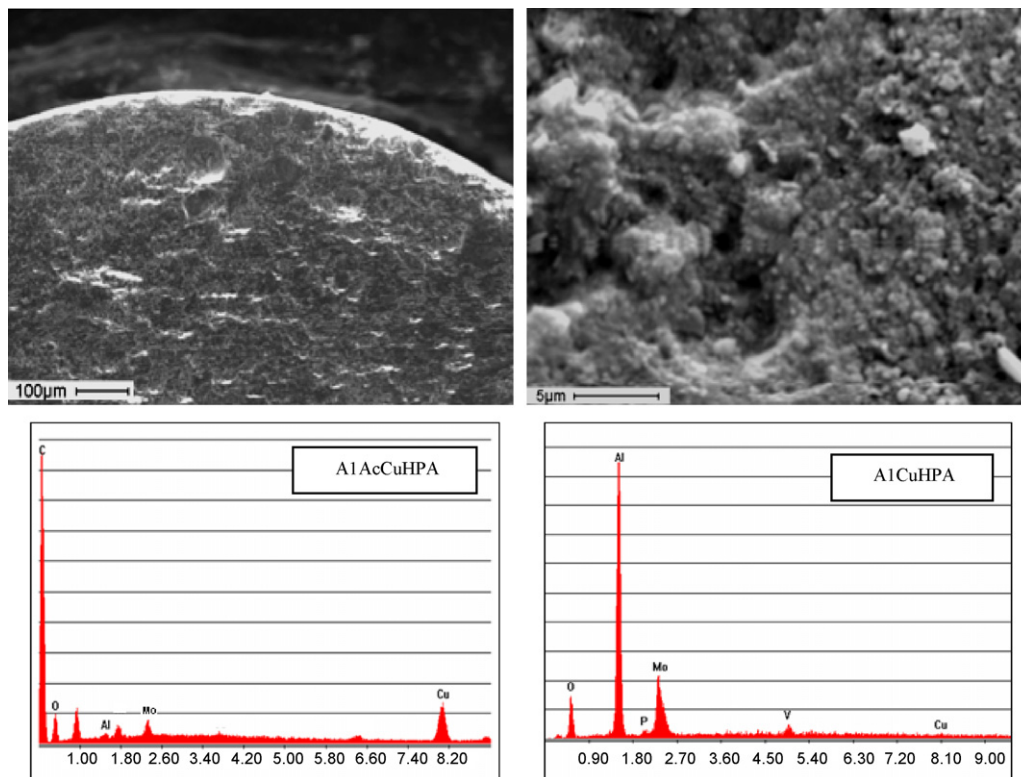


Fig. 4. SEM photographs and EDAX superficial analyses of AlAcCuHPA catalyst.

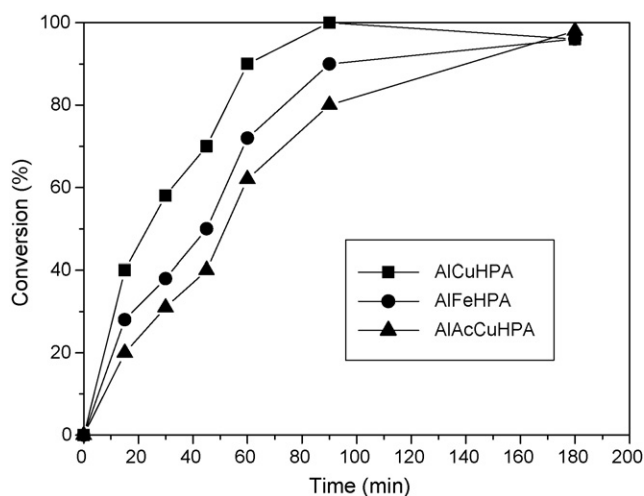


Fig. 5. Phenol trimethylsilylation conversion, with HMDS, using MVP supported on alumina.

(MoVP), bulk and supported on alumina, is presented as an example and for its comparison with other heteropolycompounds. At room temperature, MoVP 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. The replacement of one Mo^{6+} by V^{5+} modifies the Keggin structure as was shown before. 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. When Fe^{3+} or Cu^{2+} are introduced into the secondary structure as proton replacement, the acid strength is 1113 and 941 mV, respectively. In two cases, the number of acidic sites is similar. When CuMoVP and

FeMoV are supported, their acidity decreases to 89 and 208 mV, respectively. In all cases, the number of sites is reduced from 3 to 1 meq *n*-butylamine/g catalyst. This decrease in acid strength as well as the number of sites could be due to a strong interaction between the precursor and support. Based on previous experiences (not published) Akzo alumina has acidic properties and this is represented by its isoelectric point (4.2); perhaps this property is the most remarkable in the behavior reported for supported catalysts.

The optical micrographs of AlAcCuHPA, AlCuHPA and AlFeHPA are shown in Fig. 3; the magnification used, in all cases, was 50 \times . The AlAcCuHPA corresponds to the only sample prepared by comparison with CuMoVP. This solid was impregnated with Cu^{2+} acetate ethanolic solution, dried and then newly impregnated with CuMoVP. It is worth pointing out that S_{BET} of alumina is 282 m^2/g as compared between two precursors, MPV and AcCu, respectively. The specific surface area of the supported catalysts was 50–80 m^2/g lower than that of alumina due to pore blockage, in accordance with different previous studies [51–55].

When (a) and (b) sample micrographs are compared, AlAcCuHPA shows a most important penetration for both precursors. For AlCuHPA, the micrograph presents a thin yellow-orange shell of alumina cylinder. Perhaps, this difference is due to the impregnation of bulk CuMoVP in only one step. This behavior is very similar to sample (c) (AlFeHPA) and the acidic properties could be comparable for this reason. This distribution is similar too because Mo strongly interacts with surface alumina, and the diffusion process is mainly inhibited for that Mo property. In addition, this methodology is cheap in relation to the other two-step impregnation.

Finally, in Fig. 4, SEM micrographs are shown together with superficial analysis of the samples. The morphological aspect of all samples is similar, therefore only the AlAcCuHPA sample is presented in the figure. The superficial analysis of samples conducted by EDAX shows that in AlAcCuHPA the support (alumina) is barely noticed, while in the other samples it is more superficially exposed; this is consistent with that observed by optical microscopy in relation to a layer impregnated by the catalyst and probably due

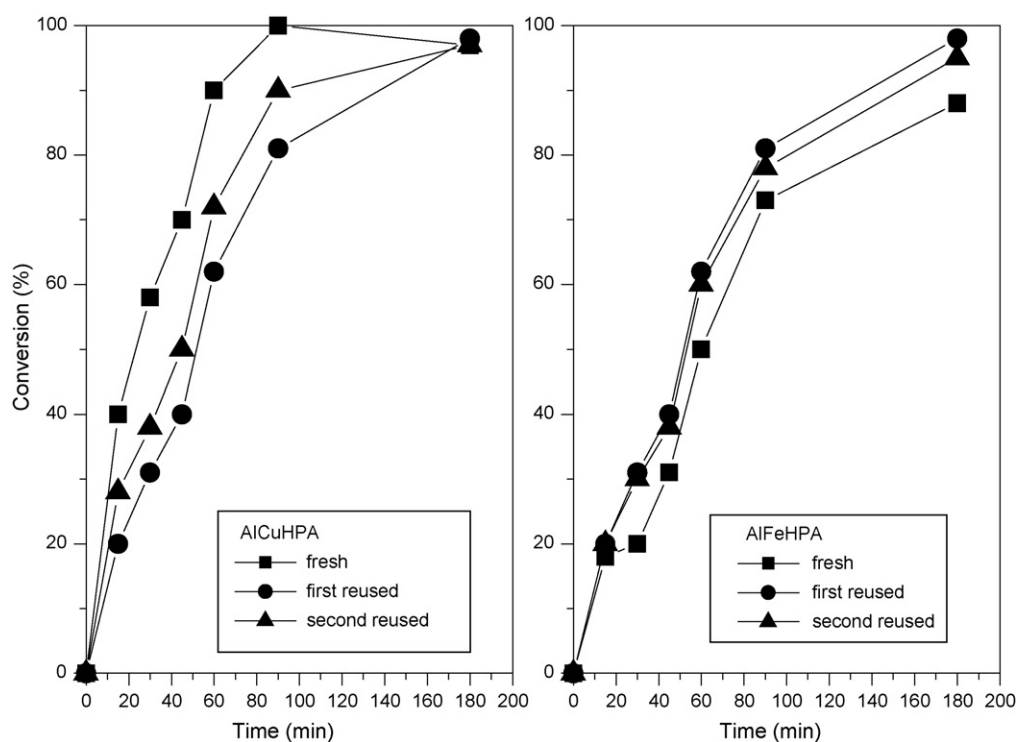


Fig. 6. Reuse of AlCuHPA and AlFeHPA catalysts in the studied reaction.

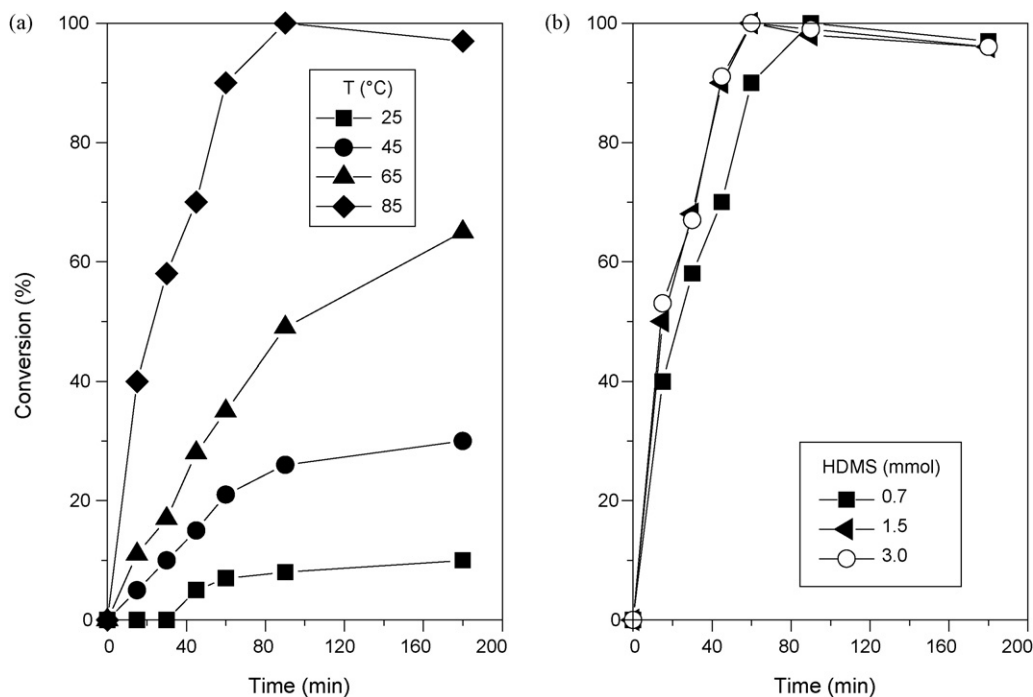


Fig. 7. Influence of temperature (a) and amount of acylating agent (b) on phenol conversion using AlCuHPA as catalyst.

to the two-step impregnation. In the superficial analysis of AlCuHPA, the C detected is due to used Cu acetate.

3.2. Catalytic activity

Primarily as a model reaction, silylation of phenol with HMDS was performed in the presence of MVP supported on alumina (AlCuHPA, AlFeHPA and AlAcCuHPA), in toluene, at 85 °C. The reaction yields very low conversions (15%) in the absence of a catalyst for 120 min, but when MVP is added, the times are reduced consid-

erably and the conversion increases to values close to 100% (Fig. 5). For 90 min of reaction, using AlCuHPA, a conversion of 100% is observed, with 100% selectivity to silyl ether. For the same time, AlAcCuHPA presents a conversion of 78% with similar selectivity. In both cases, the cation is Cu^{2+} but with a different impregnation technique on alumina cylinders; this behavior could be due to a major surface presence of AlCuHPA (Fig. 3). For the AlFeHPA catalyst, a conversion of 90% is observed at 90 min. It is possible to say that since AlCuHPA and AlFeHPA show a similar distribution on the alumina surface and comparable acidic properties because due

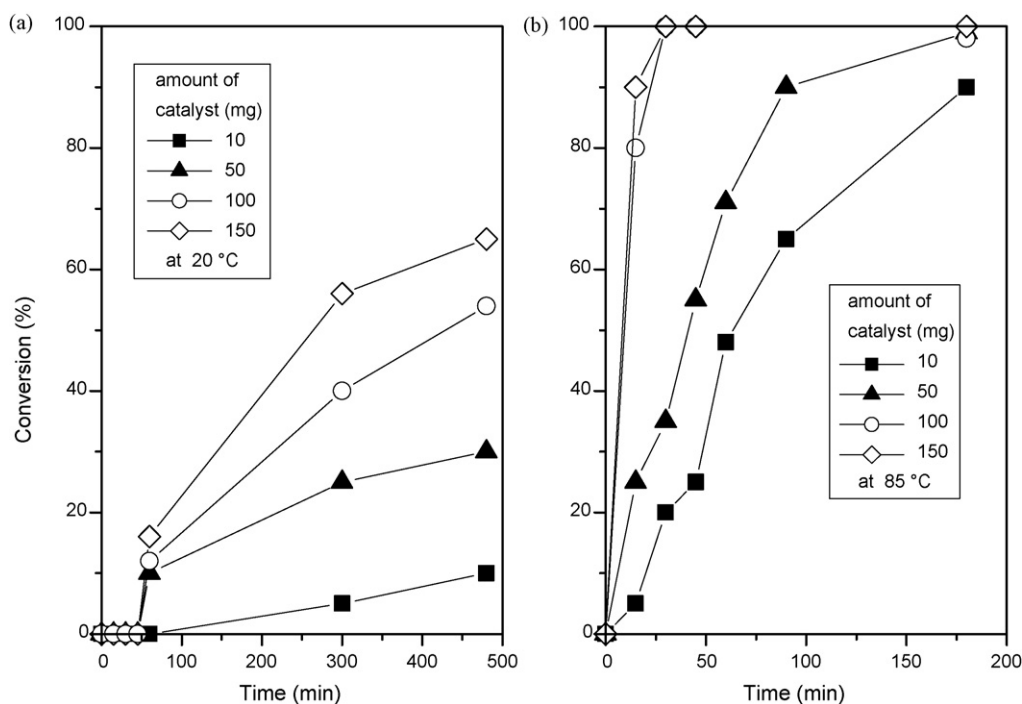


Fig. 8. Effect of AlCuHPA amount, at 20 °C (a) and 85 °C (b) for the phenol trimethylsilylation.

to their acid strengths, they can be classified as very strong sites, $E > 100$ mV, see experimental section the conversions are very close. In order to compare the strong acidity of HPA, traditional catalysts such as H_2SO_4 and TsOH were tested; the results obtained were lower than HPA in reaction system. It is important to indicate that Hammett acidity is considered as a reference method to classified strong acidity, but it is difficult to apply to colored solids, especially if they are weak acids. For these cases, a potentiometric method was developed; the measured potential difference is mainly determined by the acidic environment around the electrode membrane. The measured electrode potential is an indicator of the bulk acidic properties of the dispersed solid particles. The use of an aliphatic amine such as *n*-butylamine, whose basic dissociation constant is approximately 10^{-6} , allows carrying out a potentiometric titration of a strong acid, which is applicable to these systems. For this reason this type of titration was used for HPAs, fundamentally because of their colored system in bulk or supported phase.

On the other hand, when the time increases (180 min), AlCuHPA decreases its conversion and the other two catalysts used enlarge their conversions. AlAcCuHPA presents this behavior perhaps because of its distribution on bulk cylinders, since longer time helps the diffusion process.

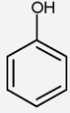
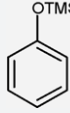
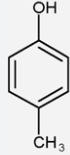
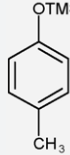
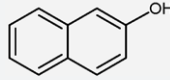
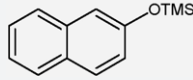
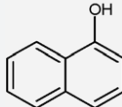
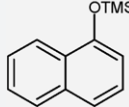
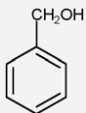
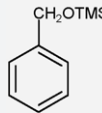
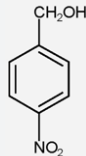
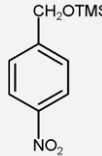
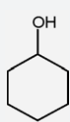
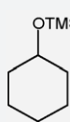
Due to the need to obtain catalysts for green processes, the use of catalysts that can be recycled is required for reducing the catalytic cost, among other reasons. When the reaction was completed, the insoluble catalyst was filtered, dried under vacuum ($20^\circ C$) and reused. These results of reused AlCuHPA and AlFeHPA catalysts are shown in Fig. 6. For AlCuHPA, the conversions obtained for 2 cycles, at 90 min, were 80% and 90%, respectively. But at 180 min, the first and second reuses gave 97% and 98%. In the case of AlFeHPA catalyst, at 180 min, the conversion obtained was 98% and 95%, respectively, for both reuses. This different conversion with respect to the fresh catalyst (85%) could be due to a better distribution of the active phase on the alumina surface after two contacts with the solvent under the reaction conditions.

In addition to investigating the behavior of supported MVP on alumina, the effect of temperature, amount of HMDS and amount of catalysts, for different reaction temperatures, were studied. In order to carry out these tests the AlCuHPA catalyst was used.

In Fig. 7a, phenol conversion versus reaction time at different temperatures, 25, 45, 65 and $85^\circ C$, respectively, is presented when 100 mg of AlCuHPA is used. For $25^\circ C$, the reaction begins the phenol conversion at about 50 min, for the same time at $45^\circ C$, the conversion is 20%. When the reaction temperature increases from 65 to $85^\circ C$, the conversions take values of 60%, in both cases, for 180 and 40 min, respectively. This behavior of the used catalyst could be due to the increase of the contact between active phases and the reagent when the temperature increases.

In Fig. 7b, the conversion of phenol versus time, at different HMDS concentration (0.7, 1.5 and 3 mmol), is presented. The results show that AlCuHPA catalyst conversion of around 50% is attained after 30 min, at $85^\circ C$, using 1.5 mmol of HMDS. Similar conversion is attained after 30 min, at $85^\circ C$, using 3 mmol of silylating agent. In any case, it was possible to obtain similar conversions for low temperatures, using 100 mg of catalyst. From this result it is evident that the amount of active phase and reagent is very important to obtain conversions near to 100%. Then, conversion of phenol versus time with different amounts of catalyst, 10, 50, 100 and 150 mg, are shown when AlCuHPA is used. These runs were performed at 20 and $85^\circ C$, respectively, and are presented in Fig. 8a and b. After a 300-min reaction time, at $20^\circ C$, the conversion around 55% is attained when 150 mg of catalyst was used. This value is approximately close to 5% for 10 mg. When a similar study was carried out at $85^\circ C$, for the same amounts of catalysts, the conversions obtained were 100 and 50% for a reaction time five times shorter.

Table 2
Trimethylsilylation of phenols and alcohols^a.

Entry	Substrate	Products	Time (h)	Yields (%) ^b
1			1.5	100
2			1.5	98
3			2	96
4			1.5	99
5			1	95
6			1	93
7			2	99

^a Products were characterized by their 1H NMR spectra. Reaction conditions: substrate 1 mmol, HMDS 0.7 mmol, toluene 3 ml, AlCuHPA catalyst 100 mg, $85^\circ C$, stirring.

^b Isolated yield.

As an example, the results that were extended to other starting phenols and alcohols are shown in Table 2. In all the reactions, the evolution of ammonia gas was observed. We were also able to isolate all catalyst from the reaction mixture and reuse it for a similar reaction without observable loss of its catalytic activity.

As a result of the assays performed and informed in this research, in Fig. 6 we propose a catalytic cycle for the esterification of cinnamic acids with phenols using PWMO as catalyst. The cycle begins with the protonation of the carboxylic oxygen of the cinnamic acid caused by the HPA; this interaction generates a carbocation in the carboxylic carbon atom that is later attacked by a phenol molecule acting as nucleophile. The instability of the generated ion promotes the proton transfer and consequent water molecule elimination, generating a new cation that finally deprotonates, giving the aryl cinnamate and recovering the catalyst.

According to [7], tungstophosphoric acid effectively activates hexamethyldisilazane for the selective silylation of primary, secondary, tertiary and phenolic hydroxyl groups under solvent-free conditions at 55 – $60^\circ C$. It is clear that the objective in both studies is very different in relation to reaction conditions; the active

phase is similar but sites to reaction have different neighbors, such as Mo–V–Fe or Mo–V–Cu; in any case the Brønsted acidity of this supported catalyst could present a reaction mechanism similar to that proposed by Firouzabadi et al. [7].

4. Conclusions

In conclusion, supported molybdophosphovanadates, which can be prepared simply from commercially available and relatively cheap starting materials, are an efficient, thermally stable and recoverable catalyst for the silylation of phenols and alcohols in toluene at ambient temperature. The present protocol provides a novel, efficient and recyclable methodology for the preparation of trimethylsilyl ethers in high yields with an easy workup procedure; the catalyst can be recovered and reused over several reaction cycles without considerable loss of reactivity. Moreover, this methodology introduces a practical and viable green technology for the silylation of phenols and alcohols. We are currently exploring further applications of this solid to other types of functional group transformation in our laboratories.

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References

- [1] Y. Ono, in: J.M. Thomas, K.I. Zamaraev (Eds.), *Perspectives in Catalysis*, Blackwell, London, 1992, p. 341.
- [2] Y. Izumi, K. Urabe, M. Onaka, *Zeolites, Clay and Heteropolyacids in Organic Reactions*, Kodansha, Tokyo-VCH, New York, 1992, p. 99.
- [3] T. Okujara, N. Mizuno, M. Misono, *Appl. Catal. A: Gen.* 222 (2001) 63.
- [4] I.V. Kozhevnikov, *Appl. Catal. A: Gen.* 256 (2004) 3.
- [5] M. Misono, *Catal. Rev. Sci. Eng.* 29 (1997) 269.
- [6] G. Davis, *Angew. Chem. Int. Ed.* 41 (2002) 858.
- [7] H. Firouzabadi, N. Iranpoor, K. Amani, F. Nowrouzi, *J. Chem. Soc.* 1 (2002) 2601.
- [8] Y. Izumi, R. Hasebe, K. Urabe, *J. Catal.* 84 (1983) 402.
- [9] G. Romanelli, P. Vázquez, L. Pizzio, C. Cáceres, M. Blanco, *J. Autino, Synth. Commun.* 33 (2003) 1359.
- [10] G. Romanelli, P. Vázquez, N. Quaranta, L. Pizzio, J.C. Autino, C. Cáceres, M. Blanco, *Appl. Catal. A: Gen.* (2004) 163.
- [11] G. Romanelli, J. Autino, M. Blanco, L. Pizzio, *Appl. Catal. A: Gen.* 295 (2005) 209.
- [12] G. Romanelli, G. Baronetti, H. Thomas, J. Autino, *Tetrahedron Lett.* 43 (2002) 7589.
- [13] G. Romanelli, D. Bennardi, D. Ruiz, G. Baronetti, H. Thomas, J. Autino, *Tetrahedron Lett.* 45 (2004) 8935.
- [14] G. Romanelli, H. Thomas, G. Baronetti, H. Thomas, *Tetrahedron Lett.* 44 (2003) 1301.
- [15] G. Romanelli, G. Sathicq, G. Baronetti, H. Thomas, J. Autino, *Synth. Commun.* (2007).
- [16] D. Bennardi, G. Romanelli, J. Jios, P. Vázquez, C. Cáceres, J. Autino, *Herocyclic Commun.* 13 (2007) 77.
- [17] L. Pizzio, G. Romanelli, P. Vázquez, J. Autino, C. Cáceres, M. Blanco, *Appl. Catal.* 308 (2006) 153.
- [18] D.M. Ruiz, G.P. Romanelli, P.G. Vazquez, H.J. Thomas, J. Autino, *ABC-6 International Congress*, Genova (Italy), 2009.
- [19] D.M. Ruiz, G.P. Romanelli, P.G. Vázquez, J. Autino, 15^o Congresso Brasileiro de Catálise-5^o Congresso de Catálise do MERCOSUL, Buzios (Brasil), 2009.
- [20] P. Villabril, G. Romanelli, P. Vázquez, C. Cáceres, *Appl. Catal.: Gen.* 270 (2004) 101.
- [21] G. Romanelli, P. Vázquez, P. Tundo, *Synlett* (2005) 75.
- [22] N. Azizi, M. Saidi, *Organometallics* 23 (2004) 1457, and references cited therein.
- [23] D. Zareyee, B. Karimi, *Tetrahedron Lett.* 48 (2007) 1277.
- [24] E. Corey, A. Venkateswarlu, *J. Am. Chem. Soc.* 94 (1972) 6190.
- [25] S. Chaudhary, O. Hernández, *Tetrahedron Lett.* 20 (1979) 99.
- [26] L. Lombardo, *Tetrahedron Lett.* 25 (1984) 227.
- [27] G. Olah, B. Gupta, S. Narang, R. Malhorta, *J. Org. Chem.* 44 (1979) 4272.
- [28] J. Aispurúa, C. Palomo, *Tetrahedron Lett.* 26 (1985) 475.
- [29] M. Mojtahedi, M. Abaee, V. Vahid, A. Zolfaghari, *Ultrason. Sonochem.* 14 (2007) 596.
- [30] H. Shaterian, F. Shahrekipoor, M. Ghashang, *J. Mol. Catal.* 272 (2007) 142.
- [31] A. Khazaei, M. Zolfigol, A. Rostami, A. Choghamarani, *Catal. Commun.* 8 (2007) 543.
- [32] T. Jim, Y. Li, T. Sun, T. Li, *J. Chem. Res.* (2002) 456.
- [33] T. Tillu, V. Jadhav, H. Borate, R. Wakharkar, *Arkivoc* (2004) 83.
- [34] H. Firouzabadi, N. Iranpoor, S. Sobhani, S. Ghassamipour, *Synthesis* (2005) 595, and references cited therein.
- [35] B. Karini, B. Golshani, *J. Org. Chem.* 65 (2000) 7228.
- [36] B. Akhlaghinia, M. Asadi, E. Safaee, M. Heydarpoor, *Phosphorus Sulfur Silicon* 179 (2004) 2099.
- [37] B. Akhlaghinia, S. Tavakoli, *Synthesis* (2005) 1775.
- [38] F. Shirini, E. Mollarazi, *Catal. Commun.* 8 (2007) 1393.
- [39] F. Shirini, M. Zolfigol, K. Mohammadi, *Phosphorus Sulfur* 178 (2003) 1567.
- [40] R. Ghorbani-Vaghei, M. Zolfigol, M. Chegeny, H. Veisi, *Tetrahedron Lett.* 47 (2006) 4505.
- [41] A. Khazaei, M. Zolfigol, Z. Tanbakouchian, M. Shiri, K. Niknam, J. Saien, *Catal. Commun.* 8 (2007) 917.
- [42] H.R. Shaterian, R. Doostmohammadi, M. Ghashang, *Chin. J. Chem.* 26 (9) (2008) 1709.
- [43] X. He, E. Hurley, B.C. Noll, K.W. Henderson, *Organometallics* 27 (13) (2008) 3094.
- [44] M.M. Mojtahedi, M. Saeed, V. AbaeeHamidi, A. Zolfaghari, *Ultrason. Sonochem.* 14 (5) (2007) 596.
- [45] N. Azizi, R. Yousefi, M. Saidi, *J. Organomet. Chem.* 691 (2006) 817.
- [46] P. Villabril, G. Romanelli, L. Gassa, P. Vazquez, C. Cáceres, *Appl. Catal. A: Gen.* 324 (2007) 69.
- [47] B. Bardin, R. Davis, *Appl. Catal. A: Gen.* 185 (1999) 283.
- [48] C. Rocchiccioli-Deltcheff, M. Fournier, *J. Chem. Soc., Faraday Trans.* 87 (1991) 3913.
- [49] A. Bielanski, L. Malecka, L. Kubelkova, *J. Chem. Soc., Faraday Trans.* 85 (1989) 2847.
- [50] C. Rocchiccioli-Deltcheff, R. Thouvenot, R. Franck, *Spectrochim. Acta, Part A* 32 (1976) 587.
- [51] M. Castillo, P. Vázquez, M. Blanco, C. Cáceres, *J. Chem. Soc., Faraday Trans.* 92 (17) (1996) 3239.
- [52] L. Pizzio, P. Vázquez, G. González, M. Blanco, C. Cáceres, H. Thomas, in: G. Froment, et al. (Eds.), *Studies in Surface Science and Catalysis*, vol. 106, 535, Elsevier, 1997.
- [53] P. Vázquez, M. Blanco, C. Cáceres, *Catal. Lett.* 60 (1999) 205.
- [54] A. Rives, E. Payen, R. Hubaut, P. Vázquez, L. Pizzio, C. Cáceres, M. Blanco, *Catal. Lett.* 71 (2001) 193.
- [55] G. Romanelli, P. Vázquez, L. Pizzio, N. Quaranta, J. Autino, M. Blanco, C. Cáceres, *Appl. Catal. A: Gen.* 261 (2004) 163.