

Hybrid materials based on aluminum tungstophosphate or tungstosilicate as catalysts in anisole acylation

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Abstract

New hybrid materials were prepared by the immobilization of aluminum tungstophosphate or tungstosilicate in a polymeric blend formed by polyvinyl alcohol and polyethylene glycol by the freeze–thawing method. The salts retained the Keggin structure of the heteropolyanions during their synthesis and immobilization. Materials with spherical shape and a mean size of 2 μm were obtained, with an almost constant distribution of the salts along the sphere width. Besides, the immobilized salts presented very strong acid sites. The synthesized catalysts showed an excellent yield in anisole acylation with a catalytic activity higher than that of the catalyst obtained from AlCl_3 immobilized in the same polymeric matrix, related to a higher effectiveness in acylium ion formation of Keggin heteropolyanions with respect to chloride, due to their soft base nature. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Many heteropolycompounds with Keggin structure present high acidity. So, they can be used to catalyze interesting reactions. For example, they can be used to replace classical acids, such as sulfuric acid, with some advantages, such as a lower corrosion and a lower production of wastes, thus leading to eco-efficient processes.

The acidic properties of the salts of the heteropolyacids depend on the cation type, the constituent elements of the polyanion and their tertiary structure. The partial hydrolysis and the presence of inhomogeneities resulting from the synthesis also exert a marked influence. The salts of the Keggin acids can be classified into two groups [1]. The salts of small cations (classified as type A) are very soluble in water or polar organic solvents, possess a low specific surface area, and in general behave in many respects in a similar way to the parent acid. The salts of large cations (classified as type B) are insoluble in water, have high specific surface area and relatively high thermal stability.

A support that firmly immobilizes the type A salts will make it possible to carry out reactions in liquid phase, using the obtained materials as catalysts that can be easily separated from the reaction medium. In the case of the heteropolyacids (HPA), diverse supports have been tested, observing that the properties of the material as well as its catalytic behavior depend on the support, the HPA amount, and the pretreatment conditions, among other variables. Different solids such as active carbon, SiO_2 , or ZrO_2 are suitable supports [2].

Polymeric materials are a new type of support that can be used when the catalysts are employed in reactions carried out at relatively low temperatures, due to their instability at high temperature. Polyvinyl alcohol has been used in biotechnology to encapsulate enzymes or cells because it has a good tensile strength in dry conditions, though it has a high swelling index, and tends to be dissolved in water when it is not cross-linked. This may be a chemical or a physical cross-linking. It has been reported that PVA has good ability to form hydrogels by cross-linking with boric acid or formaldehyde [3]. Recently, the immobilization of *Lactobacillus kefir* in polyvinyl alcohol for the synthesis of hydrophobic quiral alcohols in organic solvents has been studied [4]. In the field of electrocatalysis, the use of polypyrrole, polythiophene, and polyaniline as heteropolyanion supports has been reported, the catalytically active species being introduced by electrochemical polymerization [5].

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The papers in which the immobilization of heteropolycompounds with Keggin structure is presented are scarce. Cui et al. [6] have reported the preparation of films of polyvinyl alcohol together with molybdotungstovanadogermanic acid, and studied their conductivity properties. Hasik et al. [7] have studied the catalytic behavior of tungstophosphoric acid supported on polyaniline for the decomposition of isopropanol. They have established that an HPA molecular dispersion is reached through a protonation reaction. Molybdophosphoric acid was also utilized to prepare HPA-polymer composite catalysts, using polyphenylene oxide, polyethersulfone, and polysulfone [8], which were tested as catalysts in the synthesis of *tert*-butanol in liquid phase, showing higher catalytic activity than the bulk acid. The same heteropolyacid was entrapped in polyvinyl alcohol cross-linked with succinic acid, and used as catalyst in the dehydration of α -pinene to obtain α -terpineol [9].

Aluminum tungstophosphate (AITPA) or tungstosilicate (AITSA) can present interesting characteristics as catalysts since they can have Lewis and/or Brønsted acidity. To the best of our knowledge, their immobilization in polymeric materials to be used in acid reactions has not so far been reported in the literature. The objective of this work is the synthesis and characterization of these salts immobilized in a blend constituted by polyvinyl alcohol (PVA)–polyethylene glycol (PEG), and the study of their catalytic performance in an acid reaction. Due to the importance of acylation to synthesize aryl ketones, they were used as catalysts in the acylation of anisole with acetic anhydride as a test reaction, and their behavior was compared to that of AlCl_3 immobilized in the same polymeric matrix.

2. Experimental

2.1. Salt synthesis

The aluminum salts of the tungstophosphoric and tungstosilicic acids, named AITPA and AITSA, respectively, were prepared from aqueous solutions of the corresponding acids ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 21\text{H}_2\text{O}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$, Fluka p.a.), to which the required stoichiometric amount of the cation was added, employing $\text{Al}_2[\text{SO}_4]_3$ as cation source [10,11]. The resulting solution was stirred at room temperature for 60 min to assure a complete reaction. The salts were crystallized by evaporation till dryness in air at 70 °C, then they were washed with ethanol, and dried again at 70 °C.

2.2. Salt immobilization

To immobilize the salts, a solution of polyvinyl alcohol and polyethylene glycol, obtained by dissolution of PVA (Mallinckrodt) in a hot mixture of PEG (Mallinckrodt) in water, was used, stirring continuously till complete dissolution of PVA. Then the salt was added maintaining the stirring until a homogeneous mixture was obtained.

In order to obtain spherical particles of the catalyst, the solution was placed in a burette and was slowly poured into liquid nitrogen. The spheres were slowly thawed after nitrogen evaporation and, subsequently, they were dried at room

temperature for 24 h and then at 110 °C for 2 h. The samples were named $\text{AITPA}_{\text{PVA-PEG}}$ and $\text{AITSA}_{\text{PVA-PEG}}$. The amount of salt was fixed in order to obtain a concentration of 30% by weight in the final material.

The same procedure was applied for the preparation of a sample of AlCl_3 immobilized in PVA–PEG ($\text{Cl}_3\text{Al}_{\text{PVA-PEG}}$) and samples of the $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_4\text{SiW}_{12}\text{O}_{40}$ salts immobilized in the same matrix.

2.3. Physicochemical characterization

The specific surface area of the salts was estimated by the BET method from the adsorption–desorption isotherms of nitrogen at 77 K, using ASAP 2020 Micromeritics equipment. The sample was previously degassed at 100 °C for 1 h.

The X-ray diffraction (XRD) patterns of the bulk and immobilized salts were obtained with PW-1417 Philips equipment, using Cu $\text{K}\alpha$ radiation, Ni filter, 20 mA and 40 kV in the high voltage source, a scanning angle between 5 and 60° 2θ , and a scanning rate of 1°/min.

A Philips 505 scanning electron microscope was employed to obtain micrographs of the spheres of PEG-PVA containing aluminum tungstophosphate or tungstosilicate. The radial distribution of the salts in the spheres was determined using an energy dispersive X-ray analysis system (EDAX).

To obtain the Fourier transform infrared (FT-IR) spectra, IFS 66 Bruker equipment and pellets of the samples in KBr were utilized. The measurements were performed in the range 400–4000 cm^{-1} .

Two simultaneous thermal analysis, thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) study, were carried out using DT 50 Shimadzu equipment, in argon or nitrogen atmosphere, sample weight 25–50 mg, and heating rate 10 °C/min.

For the potentiometric titration, 0.05 g of solid were suspended in acetonitrile (90 ml) and stirred for 3 h. The suspension was titrated with a 0.05 N solution of *n*-butylamine in acetonitrile. The potential variation was measured with a Hanna 211 pH meter and a double junction electrode.

2.4. Catalytic evaluation

The activity of the catalysts in the anisole acylation with acetic anhydride was measured. The reaction was carried out in a Pyrex[®] glass reactor of 50 ml equipped with a condenser, and the reagents were magnetically stirred at 100 °C. An anisole:acetic anhydride:aluminum salt molar ratio of 10:3:0.01 was utilized. The evolution of the reaction was followed by gas chromatography using dodecane as internal reference.

3. Results and discussion

The specific surface area calculated by the BET method of both aluminum tungstophosphate and tungstosilicate, synthesized employing $\text{Al}_2[\text{SO}_4]_3$, was lower than 10 m^2/g . As was mentioned above, these AITPA and AITSA salts are classified as Type A [11].

The FT-IR spectrum of TPA dried at 70 °C presents bands at 1081, 982, 888, 793, 595, and 524 cm^{-1} , in accordance with those reported in the literature for the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ acid [12]. The first five bands are assigned to the P–Oa, W–Od, W–Ob–W, W–Oc–W stretchings, and to Oa–P–Oa deformation, respectively. The subscripts correspond to oxygens binding W and P (a), or bridging different WO_6 octahedra that share corners (b) or edges (c), and terminal oxygens and (d) bonded to only one W atom.

The FT-IR spectrum of bulk TSA, presents bands at 1019, 982, 926, 884, 778, and 541 cm^{-1} , which coincide with those referred to in literature [12] for this heteropolyacid. Such bands are present in the spectrum of the AITSA salt dried at 70 °C (Fig. 1a), although the band placed at 982 cm^{-1} (stretching of the W–Od terminal bond) has a slight broadening, and a shoulder at 999 cm^{-1} . In addition, the band at 884 cm^{-1} (W–O–W bridged bond) shows a shoulder at 892 cm^{-1} . These effects can appear as a result of the interaction between the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anion and the Al^{3+} cations. A transformation of the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anion into the $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ lacunar species was not detected.

A similar behavior was found for the AITPA salt. The FT-IR diagram of the AITPA salt dried at 70 °C presents the characteristic bands of the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion (Fig. 1d). However, the band assigned to the W–Od stretching is broadened, as a result of the splitting into two components. The appearance of a new component is a result of the interaction between the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion and the Al^{3+} cations. A transformation of the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ species into the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ lacunar phase during the synthesis of the salts was not detected for this salt either.

In the FT-IR spectra of the immobilized AITSA_{PVA-PEG} (Fig. 1b) and AITPA_{PVA-PEG} (Fig. 1e) salts the characteristic bands of the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anions, respectively, appear overlapped to those of the support (Fig. 1c). By this technique, it is possible to establish that undegraded Keggin anions are present when the aluminum tungstophosphate or tungstosilicate are immobilized in PVA–PEG, without the presence of the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ or $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ lacunar phases.

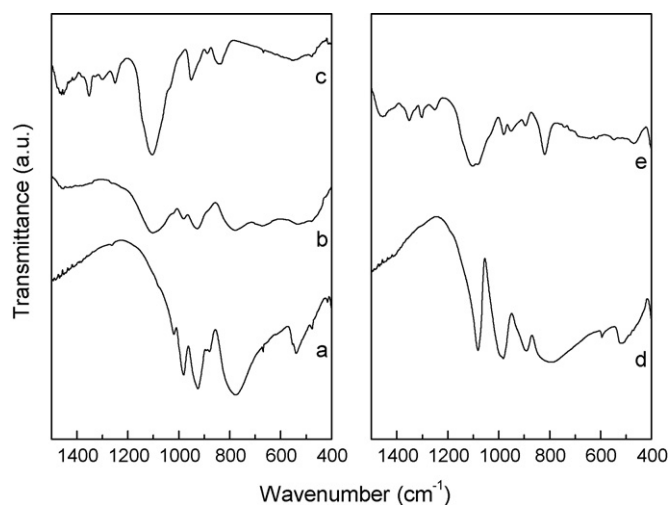


Fig. 1. FT-IR spectra of AITSA (a), AITSA_{PVA-PEG} (b), PVA–PEG (c), AITPA (d), and AITPA_{PVA-PEG} (e) samples.

By means of the freeze–thawing method spheres of PVA–PEG were obtained, with a mean size of 2 μm , in which the aluminum tungstophosphate or tungstosilicate are included. Their micrographs (Fig. 2) showed a sponge-like structure conformed by a network of cross-linked channels. According to the microanalysis performed by EDAX, the tungsten and aluminum content along the diameter of the spheres is practically uniform.

The XRD diagrams of the AITPA_{PVA-PEG} and AITSA_{PVA-PEG} samples are similar to that obtained for the spheres prepared from only PVA–PEG. They do not present any of the diffraction lines of the aluminum tungstophosphate or tungstosilicate, as a result of a high dispersion in the polymeric matrix.

The DSC diagram of the aluminum tungstophosphate, AITPA, (Fig. 3a) and that of the aluminum tungstosilicate, AITSA, (Fig. 3d) show a group of endothermic peaks below 250 °C and an exothermic peak with a maximum at 603 and

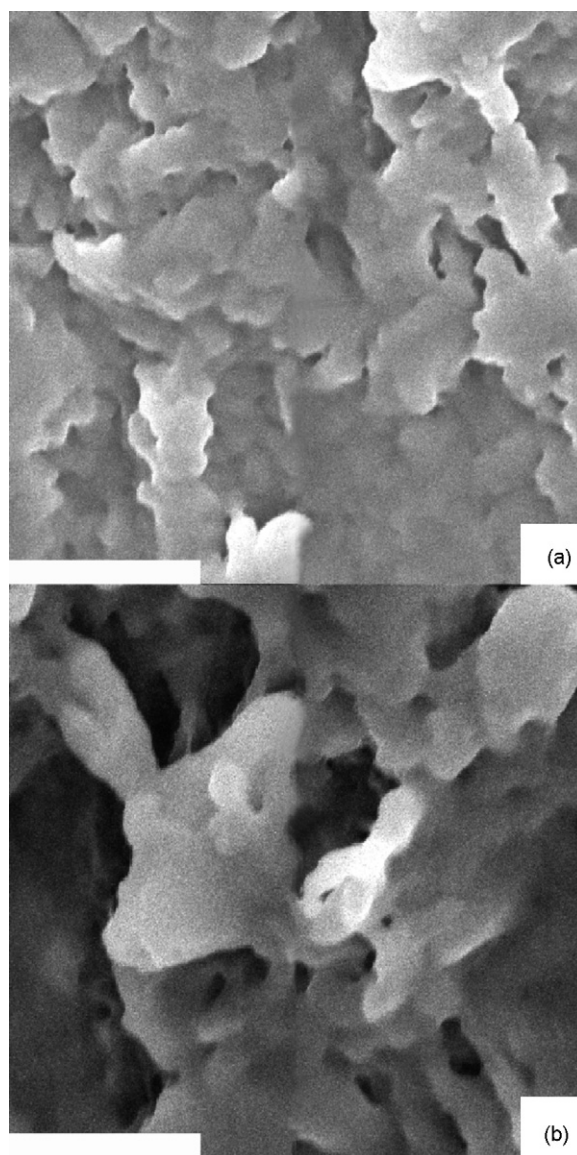


Fig. 2. Secondary electron micrograph of AITPA_{PVA-PEG} sample, bar size 20 μm (a) and 10 μm (b).

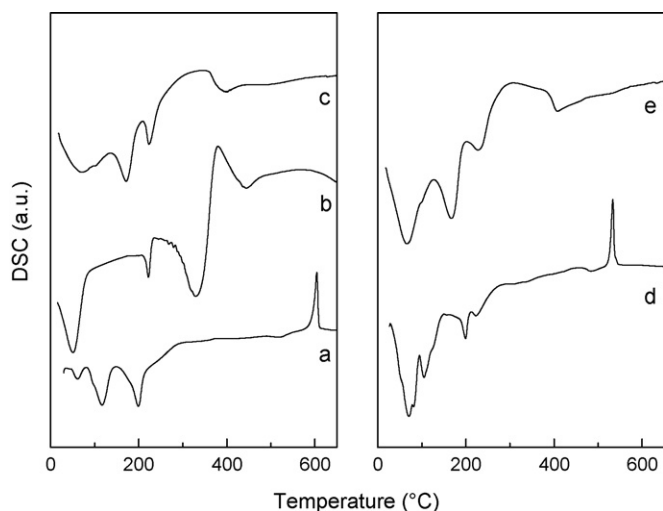


Fig. 3. DSC diagram of AITPA (a), PVA-PEG (b), AITPA_{PVA-PEG} (c), AITSA (d), and AITSA_{PVA-PEG} (e) samples.

536 °C, respectively. The endothermic peaks are assigned to the removal of physisorbed or crystallization water molecules, whereas the exothermic peak is due to the decomposition of the Keggin anion.

The DSC diagram of the PVA-PEG blend (Fig. 3b) utilized to immobilize the salts presents four endothermic peaks at 51, 222, 330, and 444 °C. The first two peaks are associated with the loss of water and other volatile compounds (aldehydes, ketones, and ethers), while those placed above 240 °C are assigned to the removal of alkanes, alkenes, and other unsaturated hydrocarbons, resulting from the thermal degradation of PVA and PEG [13]. From TGA, it was estimated that the amount of physisorbed water is about 11% of the total weight of the PVA-PEG matrix, and that the matrix is almost completely degraded at temperatures near 500 °C (weight loss higher than 95%).

With regard to the immobilized aluminum tungstophosphate, AITPA_{PVA-PEG}, the DSC diagram (Fig. 3c) presents the endothermic peaks associated with the elimination of water, aldehydes, ketones and ethers below 300 °C, and only the higher temperature endothermic peak associated with the removal of alkanes, alkenes, and unsaturated hydrocarbons. The absence of the exothermic peak assigned to the decomposition of the anion lets us infer that the stability of the salt increases when it is incorporated into PVA-PEG. However, we do not rule out the possibility that the exothermic peak could be masked by the decomposition of the polymeric support. The same behavior was found for the immobilized aluminum tungstosilicate AITSA_{PVA-PEG} (Fig. 3e).

By titration with *n*-butylamine, it is possible to determine the strength and the number of acid sites present in the salts. It is considered that the initial electrode potential (Ei) indicates the maximum strength of the acid sites and the value from which the plateau is obtained (meq amine/g salt) indicates the total number of acid sites that the titrated solid presents. The strength of the acid site can be classified according to the following scale: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ mV (weak sites), and $E_i < 100$ mV (very weak sites) [14].

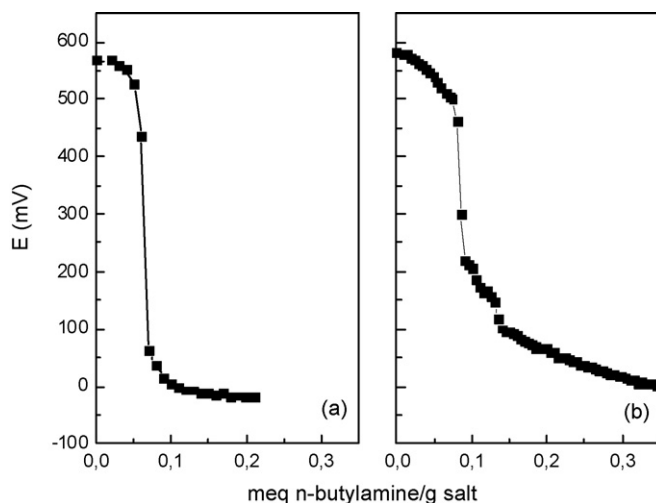
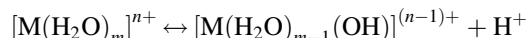


Fig. 4. Potentiometric titration curves of AITPA_{PVA-PEG} (a) and AITSA_{PVA-PEG} (b) samples.

The potentiometric titration with *n*-butylamine indicated that the AITPA_{PVA-PEG} and AITSA_{PVA-PEG} samples present acid sites with similar acid strength, with $E_i = 570$ and 580 mV, respectively (Fig. 4). This strength is considerably higher than that of the sites present in the PVA-PEG matrix used for the immobilization ($E_i = -63$ mV).

It was determined by this technique that the immobilized aluminum tungstosilicate AITSA_{PVA-PEG} presents a total number of acid sites slightly higher than that of the AITPA_{PVA-PEG} sample. These sites can be Brønsted and/or Lewis type. The presence of both types of sites has been shown in the $Al_{0.5}PW_{12}O_{40}$ and $Cu_{1.5}PW_{12}O_{40}$ salts by IR spectroscopy, adsorbing pyridine or NH_3 as probe molecule [1]. It has also been proposed that, for the neutral salts of TPA or TSA, the Brønsted type acidity is due to the formation of H^+ by dissociation of water molecules coordinated to the metallic cation, according to the following reaction:



The catalytic activity of the immobilized aluminum tungstophosphate and tungstosilicate, AITPA_{PVA-PEG} and AITSA_{PVA-PEG}, in the anisole acylation with acetic anhydride is shown in Table 1. The main product of the reaction was *p*-methoxyacetophenone (*p*-MAP), obtained with selectivity higher than 90%, together with *o*-methoxyacetophenone (*o*-MAP). Only the formation of monoacylated products was detected.

The specific catalytic activity (SCA), expressed as moles of product formed per mole of aluminum, for the AITPA_{PVA-PEG}

Table 1
Specific catalytic activity in anisole acylation

Sample	AITPA _{PVA-PEG}	AITSA _{PVA-PEG}	AlCl ₃ PVA-PEG
SCA	178.4	114.3	96.3

SCA (specific catalytic activity): moles of product formed per mole of Al^{3+} in the catalyst. Reaction time: 30 min.

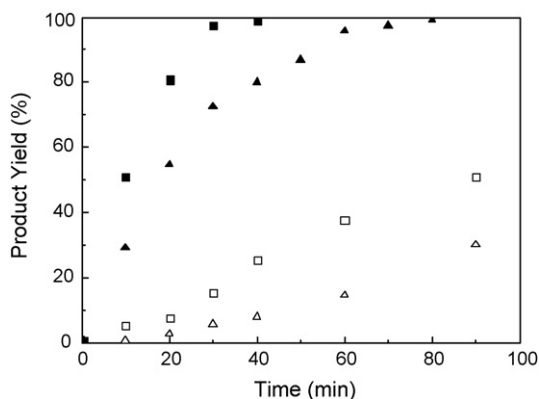


Fig. 5. Yield as a function of time for AITPA_{PVA-PEG} (■), AITSA_{PVA-PEG} (▲), and Cs₃PW₁₂O₄₀ (□) and Cs₄SiW₁₂O₄₀ (△) salts immobilized in PVA-PEG.

sample, is higher than that corresponding to AITSA_{PVA-PEG}. It is interesting to note that the values of SCA of both catalysts are higher than that obtained employing AlCl₃ immobilized in PVA-PEG. This result can be explained taking into account the proposed mechanism for acylation, which implies the formation of an adsorbed acylium ion by the interaction of an acylating agent with Brønsted or Lewis acid centers [15,16]. The better performance of the AITPA_{PVA-PEG} and AITSA_{PVA-PEG} catalysts with respect to AlCl₃_{PVA-PEG} is attributed to the fact that the [PW₁₂O₄₀]³⁻ and [SiW₁₂O₄₀]⁴⁻ anions are more effective in the formation of the acylium ion. This effectiveness is related to the character of soft base that polyoxoanions possess, which becomes significant when the reactions take place in liquid phase [1].

On the other hand, the higher specific catalytic activity of the AITPA_{PVA-PEG} sample with respect to that shown by AITSA_{PVA-PEG} can be attributed to the higher effectiveness of the [PW₁₂O₄₀]³⁻ anion in the formation of the acylium ion. In order to show this effect, the acylation reaction was carried out using the samples obtained by immobilizing, in the same polymeric matrix, the Cs₃PW₁₂O₄₀ and Cs₄SiW₁₂O₄₀ salts, which contain the Cs⁺ cation, a Lewis acid much weaker than the Al³⁺ cation [17]. The yield obtained in anisole acylation as a function of time is presented in Fig. 5, together with the values corresponding to the immobilized aluminum salts of the heteropolyacids. It is thus shown that the replacement of the cation leads to an important decrease in activity, and the higher effectiveness of the [PW₁₂O₄₀]³⁻ compared to [SiW₁₂O₄₀]⁴⁻ anion is clearly observed.

The new synthesized polymer-supported heteropolysalts led to excellent yields, higher than 90%, in short times, using an anisole:acetic anhydride:aluminum salt molar ratio of 10:3:0.01 at 100 °C. Their catalytic performance was similar or better than those reported using other HPA-based catalysts (see e.g. [18–20]). However, it must be pointed out that these works were performed in different reaction conditions.

The activity of the catalysts decreases with their reuse if they are not adequately treated. The activity can be completely restored if the catalyst is treated with dichloromethane for 2 h in a Soxhlet extractor (Fig. 6). When the used catalyst is only

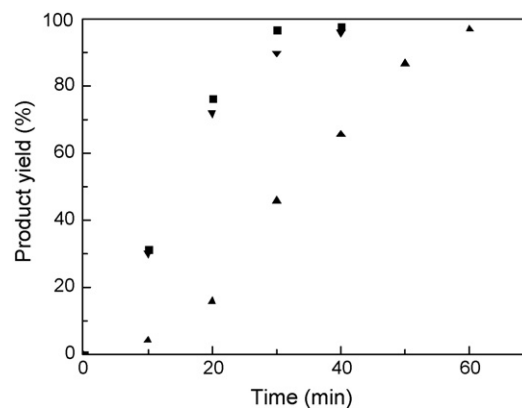


Fig. 6. Yield as a function of time for the fresh (■), washed (▲), and extracted (▼) AITPA_{PVA-PEG} catalyst.

washed with dichloromethane at 20 °C, the activity decreases and a higher time is required to obtain the maximum conversion of the substrate. The analysis of the extract showed that the used catalyst retains *p*-MAP and anisole. According to the literature, the acylation of aromatic compounds employing heterogeneous catalysts diminishes due to the product adsorption on the catalyst surface, which inhibits substrate adsorption [21,22].

On the other hand, it was confirmed that there was not a detectable migration of AITPA or AITSA to the organic phase during the reaction. In order to study this possible effect a test was performed, in which the AITPA_{PVA-PEG} (or AITSA_{PVA-PEG}) catalyst was filtered after heating it at reflux in anisole. Neither tungsten nor aluminum was detected in the solution by atomic absorption spectrometry, and no conversion was observed after addition of acetic anhydride to the solution at the reaction temperature.

4. Conclusions

It has been demonstrated that aluminum tungstophosphate and tungstosilicate, immobilized in a polymeric matrix constituted by polyethylene glycol and polyvinyl alcohol by the freeze–thawing method, retain their Keggin primary structure and present very strong acid sites.

The use of these materials as catalysts in the anisole acylation led to higher yields than that obtained with a catalyst prepared from AlCl₃ by the same procedure. It can be considered that this result is related to the greater effectiveness in acylium ion formation of the Keggin anions with respect to chloride.

This type of catalyst can be utilized in acid reactions carried out in liquid phase at relatively low temperatures, without an appreciable loss of the catalytically active species, to replace the homogeneous catalysts conventionally employed.

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