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## 2-Methoxynaphthalene acylation using aluminum or copper salts of tungstophosphoric and tungstosilicic acids as catalysts

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### ABSTRACT

Aluminum or copper salts of the tungstophosphoric (TPA) and tungstosilicic (TSA) acids were synthesized. They present interesting characteristics as catalysts because they can have Lewis and/or Brønsted acidity. The salts were characterized by Fourier transform infrared (FT-IR) spectroscopy, measurement of the specific surface area BET, X-ray diffraction, differential scanning calorimetry (DSC) and estimation of the acidity by potentiometric titration with n-butylamine. The salts keep the Keggin structure of the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  and  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  heteropolyanions intact during the synthesis. The salts of TPA are thermally more stable than those of TSA. All the salts showed very strong acid sites by potentiometric titration, the acid strength and the number of acid sites being higher for the  $\text{Al}^{3+}$  salts. The salts also showed an excellent catalytic behavior in the reaction of 2-methoxynaphthalene acylation with acetic anhydride. The aluminum salts led to better yields, which are correlated with their higher acidity. Also, it was observed that the solvent nature has an effect on the attained conversion.

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### 1. Introduction

Many heteropolycompounds with Keggin structure have strong acidity, which leads to their use to catalyze reactions of great interest in the synthesis of organic compounds. They can be employed as replacement of conventional acids, such as e.g., sulphuric acid, with advantages such as lower corrosivity and low waste generation that make them suitable for eco-efficient processes.

The bulk heteropolyacids, such as the tungstophosphoric and tungstosilicic acids, lead to low catalytic yield in some acid reactions, mainly due to their low specific surface area. This disadvantage can be overcome by supporting the heteropolyacid on adequate porous solids [1] or using their salts with different cations.

The properties of the salts of Keggin heteropolyacids are sensitive to the cation type [2]. The salts of small cations (named A type) are soluble in water, have a low specific surface area and they generally behave similarly to the parent acid. In turn, the salts of large cations (named B type) are insoluble in water, have high specific surface area and relatively high thermal stability [3].

The salts of large cations gave excellent catalytic activity in diverse acid reactions [4–6]. However, the salts of the A type have been less utilized. Baba et al. [7] studied the generation of acidic sites in the  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  neutral salts of tungstophosphoric acid. Shimizu et al. [8,9] showed that polyvalent transition metal salts of

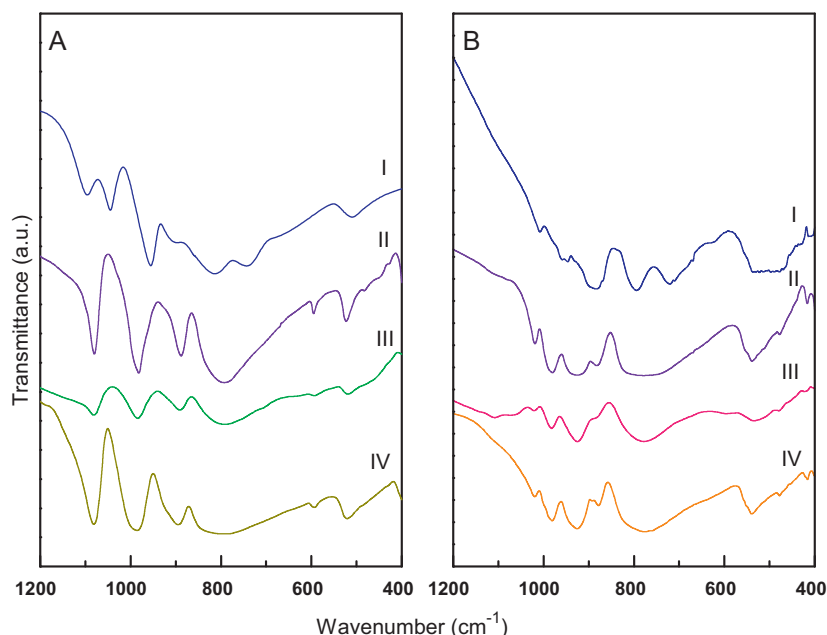
tungstophosphoric acid act as effective catalysts for Friedel–Crafts acylation of aromatics with carboxylic acids and alcohols.

The salts of the  $\text{Al}^{3+}$  or  $\text{Cu}^{2+}$  cations of the tungstophosphoric and tungstosilicic acids have interesting characteristics for their use as catalysts because they can present Lewis and/or Brønsted acidity. Firouzabadi et al. [10] have studied the effect of the nonhygroscopic  $\text{AlPW}_{12}\text{O}_{40}$  salt in the acylation of aromatic compounds with carboxylic acids, in the presence of trifluoroacetic anhydride.

The acylation is a very important method to obtain aromatic ketones, intermediates in the preparation of numerous chemical and pharmaceutical products [11]. The reaction is normally carried out with greater than stoichiometric amounts of Lewis acid catalysts, such as anhydrous metal halides  $\text{AlCl}_3$  or  $\text{ZnCl}_2$ , which have the disadvantage of generating a high volume of acid waste and metal salts when they are separated, and acid halides as acylating agent, which are expensive and pollutant reagents. Inorganic acids such as HF have also been used as catalysts [12], with the drawback of being toxic and corrosive. These are some of the reasons to find environmentally friendly solid catalysts, which can be used in catalytic amounts and be easily separated from the reaction medium.

There are some studies on the acylation of 2-methoxynaphthalene, employing different solids as catalyst, such as metal triflates [13], Nafion–silica composites [14], Al-MCM-41 mesoporous molecular sieves [15] and zeolites. Harvey et al. [16,17] studied this reaction over zeolite USY, H-beta and ZSM-12 and showed that in all the cases 1-acyl-2-methoxynaphthalene was obtained as the major product. In comparison to other zeolites,

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**Fig. 1.** (A) FT-IR spectra of  $\text{Na}_7\text{PW}_{11}\text{O}_{39}$  (I),  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (II), AITPA salt (III) and CuTPA (IV) salt. (B) FT-IR spectra of  $\text{Na}_8\text{SiW}_{11}\text{O}_{39}$  (I),  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  (II), AITSA salt (III) and CuTSA (IV) salt.

H-beta with narrower 12-ring channels and no super cages showed slightly increased selectivity for 6-acyl-2-methoxynaphthalene. During the acylation of 2-methoxynaphthalene with acetic anhydride the linear 6-acetyl-2-methoxynaphthalene (6-A-2MN) and the bulky 1-acetyl-2-methoxynaphthalene (1-A-2MN) can be formed. It was proposed that the more confined internal environment of H-beta restricts access to the 1-position of 2-methoxynaphthalene [17].

Fromentin et al. [18] studied the acylation of 2-methoxynaphthalene with acetic anhydride in liquid phase, using HBEA zeolite as catalyst, and observed the influence of the solvent on the velocity and the selectivity of the reaction. The importance of this reaction lies in the fact that 6-acetyl-2-methoxynaphthalene is an intermediary of the synthesis of the anti-inflammatory product naproxen [19]; nevertheless, 1-acetyl-2-methoxynaphthalene can be an interesting intermediary in phenylation reactions [20].

Based on previous work and continuing with our studies about the use of salts of heteropolyacids with Keggin structure, the results obtained in the acylation in liquid phase of 2-methoxynaphthalene with acetic anhydride, using  $\text{Al}^{3+}$  or  $\text{Cu}^{2+}$  salts of the tungstophosphoric and tungstosilicic acids as catalysts are presented, correlating the behavior with the properties of the salts, such as their acid characteristics, and also observing the effect of the nature of the solvent employed in the reaction.

## 2. Experimental

### 2.1. Catalyst preparation

The  $\text{Al}^{3+}$  or  $\text{Cu}^{2+}$  salts of the tungstophosphoric acid (TPA), which will be named AITPA and CuTPA, respectively, were synthesized by slowly adding, under vigorous stirring, aqueous solutions of  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{Cu}(\text{NO}_3)_2$  to an aqueous solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  in stoichiometric amount [21,22]. The solutions thus obtained were maintained under stirring at room temperature for 1 h. The salts were obtained by evaporating the solvent in air at  $70^\circ\text{C}$ , and then were washed with ethanol and dried again at  $100^\circ\text{C}$ . The same procedure was employed to obtain the salts of the tungstosilicic acid

(TSA), using  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ; the  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  salts will be named AITSA and CuTSA, respectively. The analysis by atomic absorption spectrometry of the salts gave a W:Al(Cu) molar ratio near to 12:1, 12:1.5, 12:1.33 and 12:2 for AITPA, CuTPA, AITSA and CuTSA, respectively.

### 2.2. Solid characterization

The specific surface area of the salts was estimated by the BET method from the nitrogen adsorption–desorption isotherms at  $-196^\circ\text{C}$ , using Micromeritics equipment, model ASAP 2020. Each sample was previously degassed at  $100^\circ\text{C}$  for 1 h.

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

The Fourier transform infrared (FT-IR) spectra were obtained utilizing Bruker IFS 66 equipment, and pellets of the samples in KBr, measuring in the range  $400$ – $4000\text{ cm}^{-1}$ .

The differential scanning calorimetry (DSC) measurements were carried out using Shimadzu DT 50 equipment in argon atmosphere, with a sample weight of  $25$ – $50\text{ mg}$ , and a heating rate of  $10^\circ\text{C}$  per min.

The obtained materials were potentiometrically titrated with the purpose of estimating their acidity. To this end,  $0.05\text{ g}$  of solid was suspended in  $90\text{ cm}^3$  of acetonitrile, and stirred for 3 h. The suspension was titrated with a  $0.05\text{ N}$  solution of n-butylamine in acetonitrile. The potential variation was measured with a Hanna 211 pHmeter, and a double junction electrode.

### 2.3. Acylation of 2-methoxynaphthalene with acetic anhydride

The activity of the AITPA, CuTPA, AITSA, and CuTSA salts in the acylation of 2-methoxynaphthalene (2MN) with acetic anhydride (AA) was measured. The reaction was carried out in a  $50\text{ cm}^3$  glass reactor equipped with a condenser, and magnetically stirred, at  $100^\circ\text{C}$ . The reaction was performed without solvent, employing AA in excess, and using a 2MN:catalyst molar ratio of 1:0.01. The progress of the reaction was followed, and the product analysis

was performed by gas chromatography, with Shimadzu GC-14B and Hewlett Packard 6890N GC chromatographs.

The measurements to study the solvent influence on the catalytic activity were carried out with the same reactor, employing 10 cm<sup>3</sup> of solvent, 5 mmol of AA, 2.5 mmol of 2MN, and 0.025 mmol of catalyst (AA:2MN:catalyst molar ratio of 2:1:0.01).

The conversion was expressed as the ratio of converted to initial 2MN.

### 3. Results and discussion

The textural characterization of the Al<sup>3+</sup> or Cu<sup>2+</sup> salts synthesized from TPA and TSA, employing Al<sub>2</sub>[SO<sub>4</sub>]<sub>3</sub> or Cu[NO<sub>3</sub>]<sub>2</sub>, showed that the specific surface area, estimated by the BET method, was in all the cases lower than 10 m<sup>2</sup>/g. These salts of Keggin heteropolyacids can be classified as type A salts, according to the literature [4].

The FT-IR spectra of the AlTPA and CuTPA salts dried at 100 °C were compared to the bulk tungstophosphoric acid spectrum (Fig. 1A II). It presented bands at 1081, 982, 888, 793, 595, and 524 cm<sup>-1</sup>, in agreement with the values reported in the literature [23]. The first five bands are assigned to the stretching vibrations of the P–O<sub>a</sub>, W–O<sub>d</sub>, W–O<sub>b</sub>–W, and W–O<sub>c</sub>–W bonds, and to the deformation of the O<sub>a</sub>–P–O<sub>a</sub> bond, respectively. The subscripts indicate oxygens binding W and P (a), or bridging different WO<sub>6</sub> octahedra sharing corners (b) or edges (c), and terminal oxygens (d) that are only bonded to one W atom. The FT-IR of the Al<sup>3+</sup> or Cu<sup>2+</sup> salts showed the characteristic bands of the [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anion. However, the band assigned to the stretching vibration of the W–O<sub>d</sub> bond is slightly broadened, as the result of the splitting into two components. For the CuTPA salt (Fig. 1A IV), the maxima of the peaks are placed at 991 and 981 cm<sup>-1</sup>. The occurrence of the new component is the result of the interaction between the [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anion and the Al<sup>3+</sup> or Cu<sup>2+</sup> cations, as was observed for the cesium and potassium salts [6,24]. Besides, a widening of the band assigned to the stretching vibration of the P–O<sub>a</sub> bond was observed in the spectrum of the AlTPA salt (Fig. 1A III), which can be due to the presence of [SO<sub>4</sub>]<sup>2-</sup> residues.

With regard to the FT-IR spectra of the TSA salts (Fig. 1B), features similar to those of bulk TSA were observed. The characteristic bands of bulk tungstosilicic acid were placed at 1019, 982, 926, 884, 778 and 541 cm<sup>-1</sup> (Fig. 1B II), in agreement with those referred to in the literature [23] for this heteropolyacid. The first band is not assigned, while the others are ascribed to the stretching vibrations of the W–O<sub>d</sub>, Si–O<sub>a</sub>, W–O<sub>b</sub>–W, and W–O<sub>c</sub>–W bonds, and to the deformation O<sub>a</sub>–Si–O<sub>a</sub> + W–O–W. However, in the spectra of the CuTSA salt, the band at 982 cm<sup>-1</sup> (stretching of the terminal W–O<sub>d</sub> bond) presented a slight broadening and a shoulder at 999 cm<sup>-1</sup>. On the other hand, the band at 884 cm<sup>-1</sup> (bridged W–O<sub>b</sub>–W bond) showed a shoulder at 892 cm<sup>-1</sup>. These effects can appear as a result of the interaction between the [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> anion and the cations, similarly to the TPA salts.

During the synthesis of the salts, a partial transformation of the [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> and [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> anions into the [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> and [SiW<sub>11</sub>O<sub>39</sub>]<sup>8-</sup> lacunar phases could be produced; however, by comparing the spectra of the samples with those corresponding to the lacunar phases (Fig. 1A I and B I), it was not detected that such transformation had taken place. The obtained results let us establish that the primary Keggin structure remains intact.

Through characterization by XRD, it was observed that the diffraction pattern of the aluminum salt of TPA (Fig. 2A II) presents similar characteristics to that of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O (Fig. 2A I), with a slight shift in the peak position. The H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O hexahydrated acid presents a body-centered cubic (bcc) structure. The displacement in the peak location can be due to the size differ-

**Table 1**

Acylation of 2MN with AA: conversion and product distribution<sup>a</sup>.

Sample	2MN conversion (%)	Product distribution (%)		
		1-A-2MN	6-A-2MN	Other <sup>b</sup>
AlTPA	99	98	2	–
AlTSA	97	97	2	1
CuTPA	85	96	1	3
CuTSA	71	96	1	3

<sup>a</sup> Reaction conditions: time: 65 min, temperature: 100 °C.

<sup>b</sup> Other: 8-A-2MN and β-naphthol.

ence between the Al<sup>3+</sup> and [H<sub>5</sub>O<sub>2</sub>]<sup>+</sup> cations, as was reported for diverse salts in the literature, where the variations in the lattice parameters have been attributed to such difference [25]. Instead, the diffraction pattern of the Cu<sup>2+</sup> salt (Fig. 2A III) only presented some of the peaks observed in the pattern corresponding to the Al<sup>3+</sup> salt. Due to the low crystallinity of the obtained copper salt, it was not possible to establish to which type of crystalline structure it belongs.

A similar behavior was observed for the salts synthesized from TSA (Fig. 2B). These salts presented low crystallinity and their diffraction patterns only showed some of the characteristic peaks of the cubic structure of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O or H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>. Vakulenko et al. [26] have reported the same type of behavior for the Na<sup>+</sup> or K<sup>+</sup> soluble salts, contrary the high crystallinity displayed by the Rb<sup>+</sup> or Cs<sup>+</sup> insoluble salts of TSA [26,27].

The DSC diagrams of the AlTPA and CuTPA salts presented endothermic peaks below 250 °C, which indicate the loss of physisorbed or crystallization water molecules, and an exothermic peak whose maximum is placed at 603 °C for the aluminum salt, and at 563 °C for the copper salt, due to the salt decomposition (Fig. 3A). The decomposition temperature of the aluminum salt is similar to that of TPA, which is placed at 600 °C, while the copper salt presented a lower thermal stability.

The DSC diagrams of the AlTSA and CuTSA salts (Fig. 3B) showed similar characteristics to those found for the salts of TPA. Endothermic peaks associated with water removal below 250 °C, and an exothermic peak assigned to the thermal decomposition of the salts, were observed. In this case, the decomposition occurred at slightly lower temperature, 549 °C for the CuTSA salt and at 536 °C for the AlTSA salt, as a result of the lower thermal stability of TSA, whose decomposition temperature is placed at 534 °C. It was observed that the thermal stability of these salts is lower than that reported in the literature for the cesium or rubidium salts of TSA, that present maxima near or above 700 °C, respectively [26,27].

By potentiometric titration with n-butylamine it is possible to estimate the strength of the acid sites present in the salts and the number of acid sites present in the salts. The initial electrode potential (*E<sub>i</sub>*) indicates the maximum strength of the acid sites and the value from which the plateau is obtained (meq amine/g salt) could be used to carry out a comparison of total number of acid sites (*N<sub>as</sub>*) of different samples.

The maximum strength of the acid sites, which can be classified according to the following scale *E<sub>i</sub>*: *E<sub>i</sub>* > 100 mV (very strong sites), 0 < *E<sub>i</sub>* < 100 mV (strong sites), –100 < *E<sub>i</sub>* < 0 mV (weak sites), and *E<sub>i</sub>* < –100 mV (very weak sites) [28].

The potentiometric titration with n-butylamine indicated that the salts have very strong acid sites and, besides, that the AlTPA and AlTSA salts present acid sites with higher acid strength, being *E<sub>i</sub>* = 642 and 585 mV, respectively. The CuTPA salt showed a maximum acid strength rather lower (*E<sub>i</sub>* = 574 mV), while the CuTSA salt presented the lowest value (*E<sub>i</sub>* = 395 mV). It was determined by this technique that the AlTPA and AlTSA salts present a total number of acid sites (*N<sub>as</sub>*) higher than that corresponding to the copper samples. Additionally, *N<sub>as</sub>* decrease in the

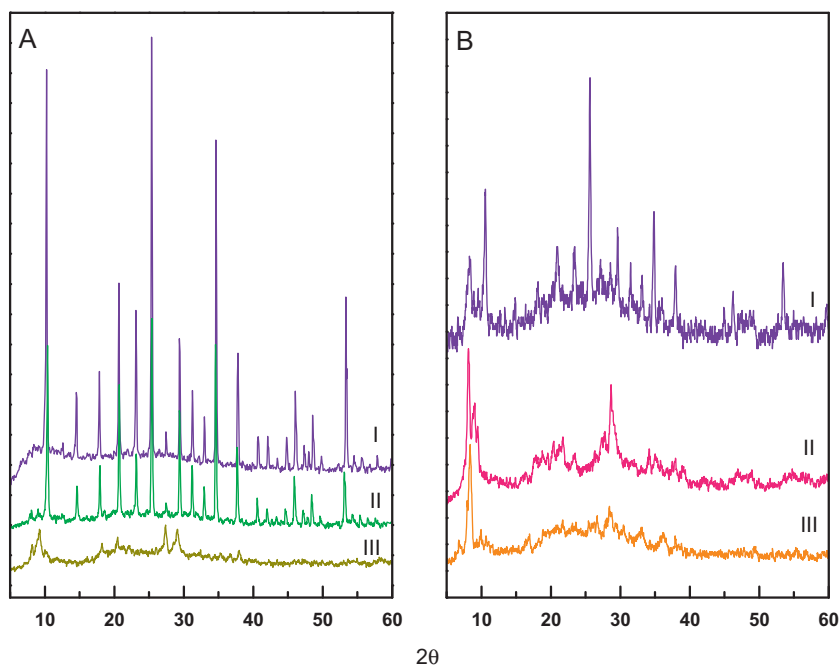
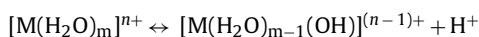


Fig. 2. (A) XRD patterns of bulk H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O (I), AITPA salt (II), and CuTPA salt (III). (B) XRD patterns of bulk H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O (I), AITSA salt (II), and CuTSA salt (III).

following order AITPA (0.11 meq/g)  $\approx$  AITSA (0.10 meq/g) > CuTPA (0.08 meq/g) > CuTSA (0.07 meq/g).

The acid sites can be of Brønsted and/or Lewis type. The presence of both types of sites was put in evidence in the AlPW<sub>12</sub>O<sub>40</sub> and Cu<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub> salts by IR spectroscopy, adsorbing pyridine or NH<sub>3</sub> as probe molecule [7]. It was also proposed that, for the neutral salts of TPA or TSA, the Brønsted acidity is due to H<sup>+</sup> generated by dissociation of water molecules coordinated to the metallic cation, according to the following reaction:



The catalytic activity of the AITPA, AITSA, CuTPA and CuTSA salts was evaluated in the reaction of 2MN acylation with acetic anhydride. The maximum values of 2MN conversion obtained were, in all cases, equal to or higher than 95% (Fig. 4). However, when the aluminum salts are employed, these conversion values were reached at a significantly lower time.

The proposed mechanism for the acylation implies the formation of an adsorbed acylium ion by interaction of the acylating agent with Brønsted or Lewis acid centers. The better performance of the AITPA and AITSA catalysts can be related to a higher capacity in the formation of the acylating ion. If it is taken into account that the Al<sup>3+</sup> cation has a value of absolute hardness higher than that of the

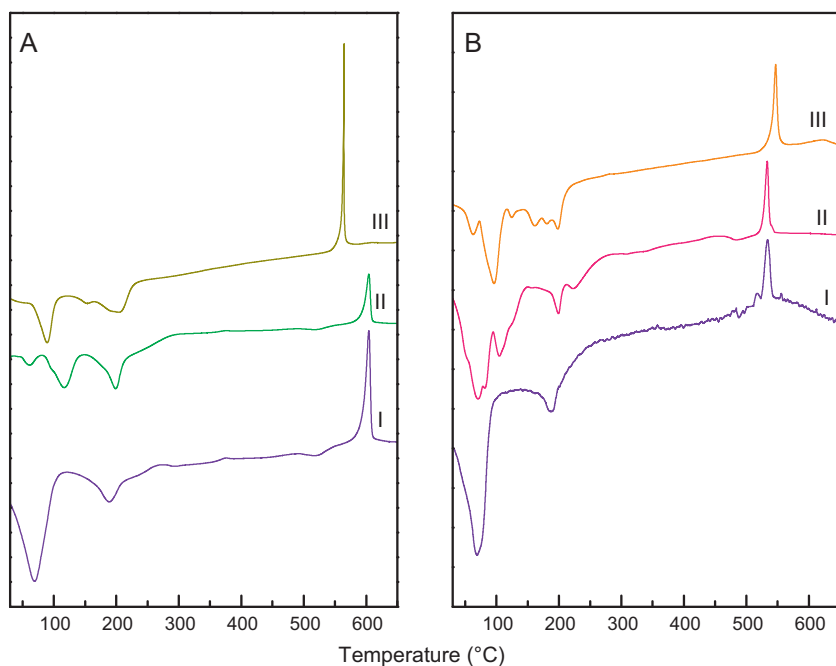


Fig. 3. (A) DSC diagrams of TPA (I), AITPA salt (II), and CuTPA salt (III). (B) DSC diagrams of TSA (I), AITSA salt (II), and CuTSA salt (III).

**Table 2**  
Acylation of 2MN with AA: effect of the solvent nature on the conversion and product distribution<sup>a</sup>.

Sample	Solvent	DN <sup>b</sup> (kcal/mol)	2MN conversion (%)	Product distribution (%)		
				1-A-2MN	6-A-2MN	Other <sup>c</sup>
AlTPA	1,2-Dichloroethane	0	59	100	–	–
	Nitrobenzene	4.4	54	98	2	–
	1,4-Dioxane	14.8	47	99	1	–
	Ethyl acetate	17.1	40	99	1	–
CuTPA	1,2-Dichloroethane	0	41	98	1	1
	Nitrobenzene	4.4	33	97	2	1
	1,4-Dioxane	14.8	24	97	1	2
	Ethyl acetate	17.1	15	97	1	2

<sup>a</sup> Reaction conditions: time: 90 min, temperature: 75 °C.<sup>b</sup> DN: donor number.<sup>c</sup> Other: 8-A-2MN and  $\beta$ -naphthol.

$\text{Cu}^{2+}$  cation, the latter is less effective to induce the formation of the acylium ion, explaining the observed behavior [29].

The acylation of 2MN generally occurs in the position 1, which is kinetically favored. In all the assays, the principal product is 1-acetyl-2-methoxynaphthalene (1-A-2MN), obtained with a selectivity higher than 96% (Table 1), together with 6-acetyl-2-methoxynaphthalene (6-A-2MN), traces of 8-acetyl-2-methoxynaphthalene (8-A-2MN) and  $\beta$ -naphthol, which result from 2MN hydrolysis.

In the classical acylation reactions, the solvent used commonly has an influence both on the achieved conversion and the selectivity, depending on the solvent capacity to form complexes with the acylating agent [30].

The studies about the influence of the solvent type were performed employing the aluminum and copper salts with higher catalytic activity (AlTPA and CuTPA). The conversion values and the product distribution are shown in Table 2.

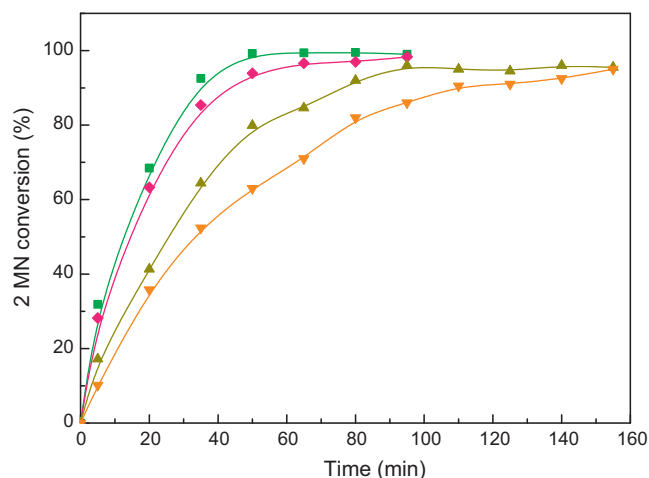
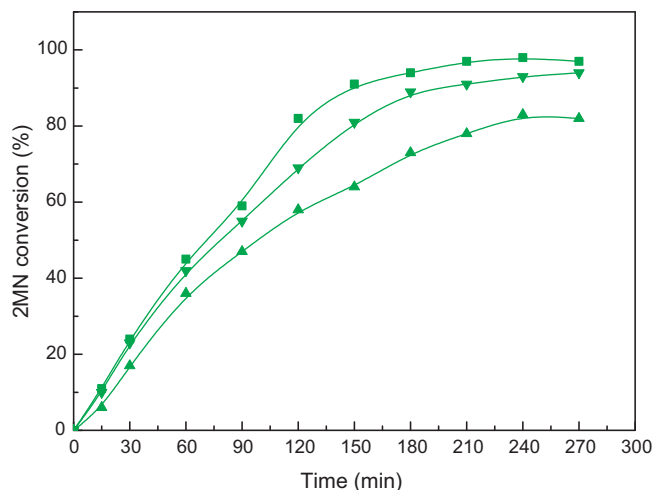
It was observed that the conversion decreased with the increase of the donor number (DN, defined as the  $-\Delta H$  value for the formation of the adduct 1:1 between the  $\text{SbCl}_5$  and an electron donor solvent in a dilute solution in 1,2-dichloroethane). The decrease seems more marked for the CuTPA sample. The stronger donor solvents (higher DN) interact more strongly with the acylating electrophilic species formed on the catalyst, negatively modifying the electrophilic power of the acylating species, thus reducing the conversion attained. The beneficial effect of employing weak donor solvents has been put in evidence in the synthesis of aromatic ketones [31].

The solvent type used can also have an influence on the product distribution obtained, according to its ability to form complexes with the acylating agent. It has been reported that the acylation mainly occurs in the position 6 when nitrobenzene is employed, while the position 1 is favored when carbon disulfide is used [30].

In our study the product distribution is almost independent of the solvent type and the nature of the catalyst employed. The influence of the catalyst nature on the selectivity has been interpreted in terms of the shape selectivity for HBEA, FAU, MFI and MOR zeolites [18,16,32].

The activity of the catalysts progressively declines with the successive uses if they are not properly treated. When the AlTPA catalyst is leached with 1,2-dichloroethane at 20 °C after each use, and dried at 100 °C, the activity decreases, and a higher time to obtain the maximum conversion is needed. Instead, the conversion can be nearly recovered if the catalyst is treated with 1,2-dichloroethane for 4 h in a Soxhlet extractor (Fig. 5).

The extract analysis showed the presence of 2-MN and 1-A-2MN, which were retained by the catalyst. According to the literature, the acylation of aromatic compounds employing solid catalysts decreases in the re-use due to product adsorption on the catalyst surface, which inhibits the substrate adsorption, as has been reported for anisole acylation [31,33,34], and a similar conclusion was reached here for the acylation of 2-methoxynaphthalene with acetic anhydride.

**Fig. 4.** 2MN conversion as a function of time for the AlTPA (■), AlTSA (◆), CuTPA (▲) and CuTSA (▼) salts.**Fig. 5.** 2MN conversion as a function of time for the fresh (■), leached (▲) and extracted (▼) AlTPA catalyst.

#### 4. Conclusions

The aluminum or copper tungstophosphates and tungstosilicates maintain the Keggin structure of the corresponding heteropolyanion intact during their synthesis. The salts of the tungstophosphoric acid are thermally more stable than those of tungstosilicic acid, in accordance with the lower thermal stability of the latter acid. The aluminum salts of both heteropolyacids have a stronger acid strength and a higher number of acid sites than those of the copper salts.

The synthesized salts are an excellent alternative to the classical catalysts for their use in the acylation reaction of 2-methoxynaphthalene with acetic anhydride, as the salts led to very good conversion, with 1-acetyl-2-methoxynaphthalene as the main product. The best yields were obtained with the aluminum salts, in line with their higher acidity. The nature of the solvent employed in the reaction must be taken into account because it has an effect on the conversion, the weak donor solvents being more suitable. The prepared catalysts can be reused with only a slight decrease in the conversion if they are appropriately treated, since product adsorption on the catalyst surface inhibits substrate adsorption.

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