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Ionic liquid protected heteropoly acids for methanol dehydration

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ABSTRACT

We report herein the synthesis of an organic-inorganic hybrid composed by the ionic liquid protected Keggin structure, as a precursor for acid catalyst and its subsequent application in the methanol dehydration reaction. Special attention was paid to the thermal stability of the resulted hybrids as a function of the Keggin anion. The catalytic behaviour of these new materials are also studied and compared to the metal salt $Cs_2HPW_{12}O_{40}$. The prepared hybrids are less thermally stable than the metal salt, but their partial decomposition results in very active and selective catalysts for the dehydration of methanol to dimethyl ether.

1. Introduction

The popularity of the ionic liquids (IL) has attached a significant scientific interest in the last decade due to their unique properties; relatively wide electrochemically stable window, good electric conductivity, high ionic mobility, broad range of room temperature liquid compositions, negligible vapour pressure and excellent chemical and thermal stability [1,2]. Many of these materials have been applied in different fields of the material chemistry such as electrochemistry [3,4], organic synthesis [5], catalysis [2,5–10] and synthesis of nanostructured materials [11]. However, the use of the ionic liquid as an integral part of material is slightly studied.

The heteropoly acids (HPAs) and related polyoxymetalate compounds still provoke a huge interest in the scientific community. They are powerful acid and oxidizing catalysts but possess a fairly high thermal stability ranging from 350 to 450 °C depending on the type of the Keggin structure, being W- containing HPAs more stable than Mo containing acids [12]. Despite their valuable properties as catalysts for liquid-phase processes, their use as heterogeneous catalysts still needs improvement. Firstly, the HPAs have to be supported on mineral oxide in order to develop their specific surface and, depending on the application, their thermal stability. In addition, the application of the supported HPAs remains limited due to their sensitivity to the presence of water, which can produce an extensive and continuous leaching during the reaction on supported HPAs catalysts.

Here comes the idea of trying to improve the stability and to increase the lifetime of the Keggin structure by its protection with organic cation instead of supporting it on the mineral carrier [13]. Combining heteropoly acids with room temperature ionic liquids (RTILs) should ease the design of some interesting materials.

In addition, the acidity of the new materials, if exists, can be easily tested in the reaction of dehydration of methanol to dimethyl ether (DME), known to occur on acid type catalysts [14–16].

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

This study presents the preparation and characterization of ionic liquid protected phosphomolybdic ($PMo_{12}O_{40}{}^{3-}$) and phosphotungstic ($PW_{12}O_{40}{}^{3-}$) Keggin structure. For this purpose 1-butyl-3-methyl imidazolium methanesulfonate (Bmim) ionic liquid was used as a protecting cation. The resulted materials possess the known molecular structure of IL_3PA type. In this paper, the thermal stability and phase transformation under heating of such materials will be discussed.

2. Experimental

2.1. Synthesis

The halide free ionic liquid 1-butyl-3-methylimidazolium methanesulfonate was prepared by the method proposed by Cassol et al. [17]. The used reactants were methanesulfonyl chloride (Alfa

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Aesar), triethylamine (Alfa Aesar), 1-methylimidazole (Aldrich), n-butanol, dichloromethane, acetone and distilled water. The method goes first through the synthesis of the butyl methanesulfonate, as described below;

2.1.1. *Preparation of butyl methanesulfonate*

Methanesulfonyl chloride (61.1 g, 0.53 mol) was added slowly, under vigorous stirring, to a solution of *n*-butanol (39.4 g, 0.53 mol) and triethylamine (53.9 g, 0.53 mol) in dichloromethane (0.5 L). An external water–ice bath was used to control the reaction mixture temperature between 10 and 20 °C. After addition, stirring was continued for further 2 h at room temperature. Then, 200 mL of water was added and the aqueous phase containing the triethylammonium chloride by-product was separated. The organic phase was washed with water (200 mL) and dried with sodium carbonate. Finally, the solvent was evaporated and, after reduced pressure distillation, 55.14 g of a colorless liquid butyl methanesulfonate was obtained (73% yield).

2.1.2. *Preparation of 1-butyl-3-methylimidazolium methanesulfonate*

Butyl methanesulfonate (55.14 g, 0.36 mol) was mixed with 1-methylimidazole (29.74 g, 0.36 mol) and the reaction mixture was kept at room temperature by means of an external water bath. After 24 h, one crystal of 1-butyl-3-methyl imidazolium methanesulfonate (Fluka) was added and the crystallization reaction was allowed to proceed at room temperature for 120 h. Recrystallization was performed twice using acetone as solvent (120 mL; from reflux temperature to freezer temperature overnight). After vacuum drying, 77.4 g of colorless and very hygroscopic crystals of 1-butyl-3-methylimidazolium methanesulfonate were obtained (95% yield).

The HPAs were synthesized as proposed by Wu [18], by mixing in appropriate amounts Na_2MoO_4 or Na_2WO_4 respectively with H_3PO_4 in the presence of HCl. The hybrid salt with IL_3PA molecular structure was synthesized according to Ranga Rao et al. [19]. In a typical synthesis, an aqueous solution of the IL in slight excess was added dropwise to heteropoly acid aqueous solution and the rapid formation of precipitate was observed. The obtained salt was then filtered and dried at room temperature.

2.2. *Characterizations*

TGA experiments were performed on SDTQ60 thermobalance from 30 to 900 °C with heating rate of 10 °C min^{-1} in constant air flow of 50 mL min^{-1}.

X-ray diffraction (XRD) analysis was performed in a high temperature camera Anton Paar HTK 1200 coupled with an X'Pert Pro Philips diffractometer, equipped with X'Celerator detector with an opening of 2.18° step of 0.05° and an equivalent time acquisition of 30 s. The diffractograms were taken every 50 °C in the range of 25–500° C, from 5° to 50° in flow of synthetic air.

TPO was performed in a U-shaped quartz reactor under oxygen flow (21% in He) from 25 °C to 400 °C with heating rate of 10 °C min^{-1}. All the products were followed by mass spectrometry in Balzers Omnistar Bentchop equipment.

2.3. *Catalytic reaction*

Prior the reaction, activation was carried out at 400 °C for 1 h in the reaction flow (methanol and air). After the activation procedure the temperature was decreased to the temperature of dehydration reaction (275 °C). Both, activation and reaction were carried out in a vertical tubular quartz reactor housed in an electrical oven at atmospheric pressure using 50 mg of sample for every experiment. Methanol was supplied with a syringe pusher at a flow rate of 0.234 mL min^{-1}, vaporized and fed in air flow (21.5 mL min^{-1}). The products were monitored by an on-line GC equipped with FID detector and DB-1 column.

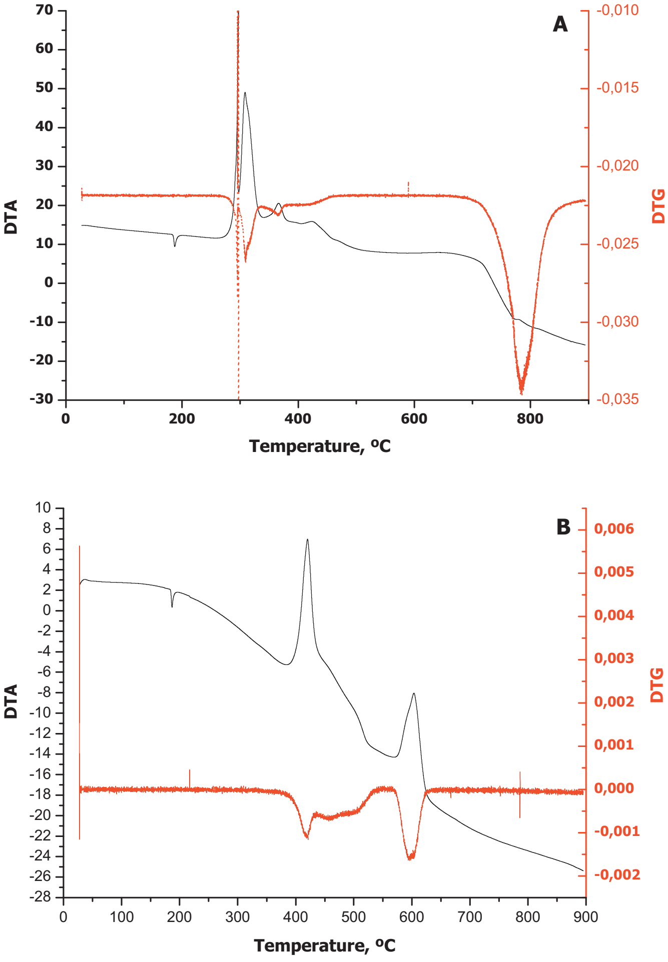

Fig. 1. TGA curves of A) $Bmim_3PMo_{12}O_{40}$ and B) $Bmim_3PW_{12}O_{40}$.

3. Results

3.1. *Thermogravimetric analysis (TGA)*

The thermal stability of the obtained hybrids has been studied by thermogravimetric analysis (TGA) in the presence of O_2. The results are presented in Fig. 1.

The hybrid material based on phosphomolybdic acid (Fig. 1A) exhibits low thermal stability and starts to decompose at 300 °C in air. The organic part is lost by 3 successive steps up to 450 °C, indicated by the DTG curve accompanied by a heat release visible in the DTA curves. In the 450–700 °C temperature range, the obtained phase remains stable. At 730 °C the hybrid exhibits a single mass loss and heat consumption due to the sublimation of the molybdenum oxide in the presence of oxygen [20].

It is well known, that the thermal stability of the HPAs follows the trend W > Mo and P > Si [21]. One could expect that the phosphotungstic based hybrid will decompose at higher temperatures compared to the phosphomolybdic one, which was confirmed by TGA experiments. The W-based hybrid starts to decompose at 400 °C in only two delayed steps of organics combustion resulting in a final weight loss of around 15 wt.% (Fig. 1B).

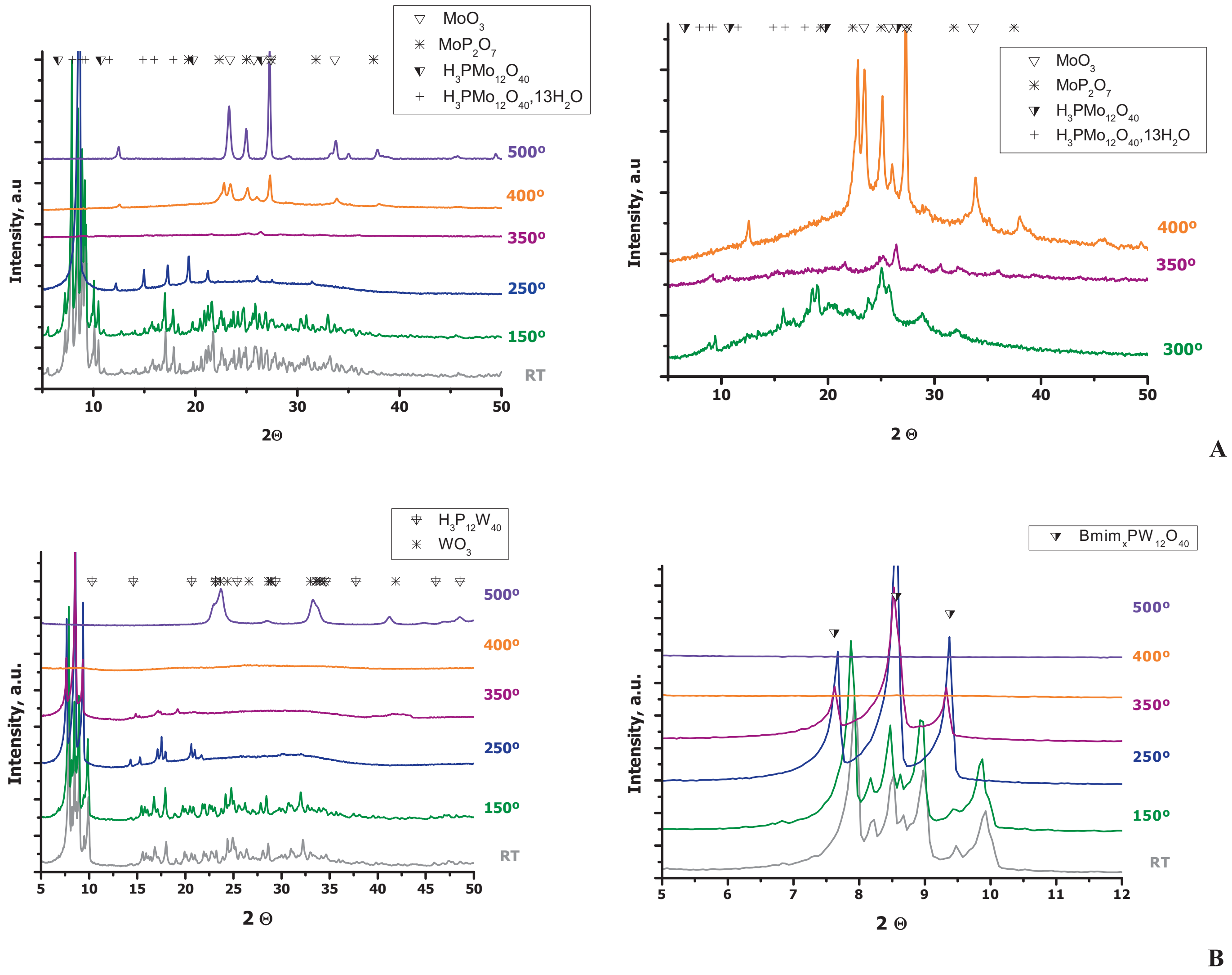

Fig. 2. XRDiffractograms as a function of temperature of A) $Bmim_3PMo_{12}O_{40}$ (first line) and B) $Bmim_3PW_{12}O_{40}$ (second line).

3.2. X-ray diffraction study

In order to study in more details the phase formation and distribution in both hybrids, a XRD study as a function of the temperature was undertaken. The XRD patterns of the materials, $Bmim_3PMo_{12}O_{40}$ and $Bmim_3PW_{12}O_{40}$ were measured in situ in flowing air from room temperature to 500 °C at every 50 °C (Fig. 2).

At room temperature, both samples exhibit the typical structure of HPAs organic hybrids with molecular structure proposed by Ranga Rao et al. [19,22]. However, at high temperature in the presence of air, the stability of the hybrids strongly depends on the nature of the parent acid. At temperatures higher than 250 °C, the structure of $Bmim_3PMo_{12}O_{40}$ is no longer available and products from the decomposition of the phosphomolybdic acid start to appear in the following order; $H_3PMo_{12}O_{40}\cdot 13H_2O$ (JCPDS# 01-075-1588) completely dehydrated $H_3PMo_{12}O_{40}$ (JCPDS# 01-070-1705), molybdenum phosphate MoP_2O_7 (JCPDS# 00-039-0026) and molybdenum oxide MoO_3 (JCPDS# 00-001-0706). At 500 °C, MoO_3 was the only phase detected. In the 250–300 °C temperature range the diffraction pattern shows a slightly amorphous character caused by the presence of the dehydrated phosphomolybdic acid [23]. The detailed distribution of all obtained phases as a function of the temperature for both hybrids is presented in Table 1.

The hybrid originated from $H_3PW_{12}O_{40}$ maintained the original structure up to 200 °C and then starts to change. Probably, a part of the ionic liquid is removed and the hybrid converts to a new structure very similar to the initial one (Fig. 2. right hand image), denoted in the table as an organic deficient hybrid, $Bmim_xPW_{12}O_{40}$. This structure is stable till 400 °C where the material structure

Table 1
Detected crystal phases at different temperatures.

Temperature (°C)	Phases ($Bmim_3$ $PMo_{12}O_{40}$)	Phases ($Bmim_3$ $PW_{12}O_{40}$)
RT	$Bmim_3$ $PMo_{12}O_{40}$	$Bmim_3$ $PW_{12}O_{40}$
50	$Bmim_3$ $PMo_{12}O_{40}$	$Bmim_3$ $PW_{12}O_{40}$
100	$Bmim_3$ $PMo_{12}O_{40}$	$Bmim_3$ $PW_{12}O_{40}$
150	$Bmim_3$ $PMo_{12}O_{40}$	$Bmim_3$ $PW_{12}O_{40}$
200	$Bmim_3$ $PMo_{12}O_{40}$	$Bmim_x$ $PW_{12}O_{40}$
250	$H_3PMo_{12}O_{40} + 10MoO_3\cdot H_3PO_4\cdot 24H_2O$	$Bmim_x$ $PW_{12}O_{40}$
300	$H_3PMo_{12}O_{40} + 10MoO_3\cdot H_3PO_4\cdot 24H_2O$	$Bmim_x$ $PW_{12}O_{40}$
350	$H_3PMo_{12}O_{40} + 10MoO_3\cdot H_3PO_4\cdot 24H_2O$	$Bmim_x$ $PW_{12}O_{40}$
400	$+MoP_2O_7$	amorphous*
450	$MoP_2O_7 + MoO_3$	amorphous*
500	MoO_3	$+WO_3$
550	MoO_3	WO_3
600	MoO_3	WO_3

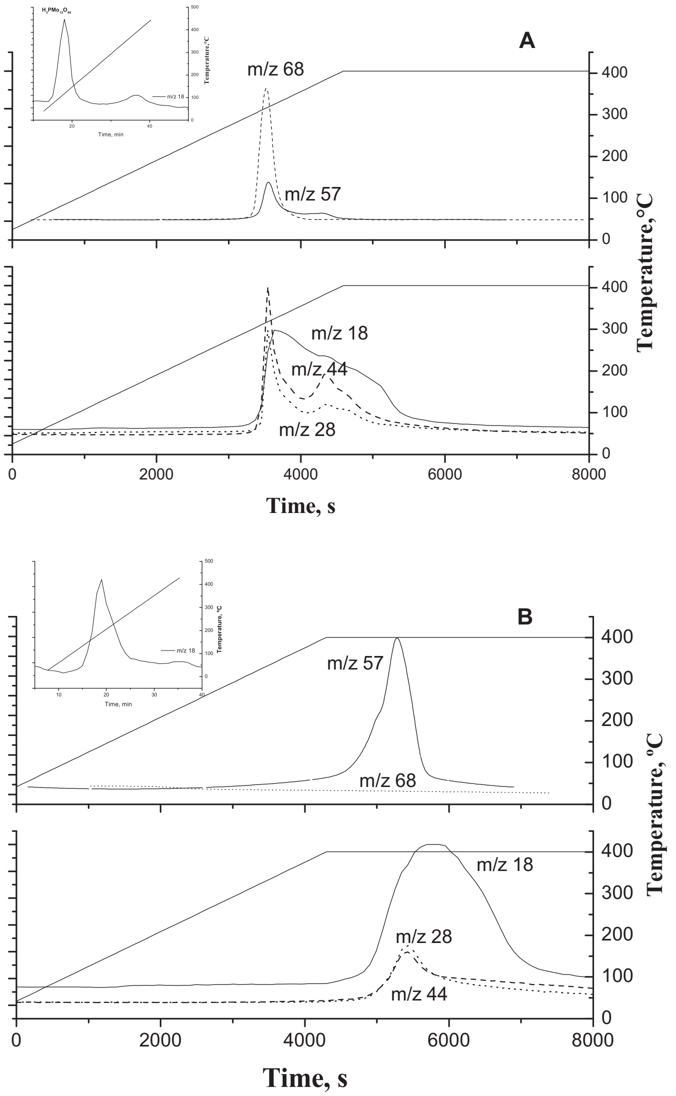

Fig. 3. Temperature programmed oxidation of A) $Bmim_3PMo_{12}O_{40}$ and B) $Bmim_3PW_{12}O_{40}$.

reorganizes through hydrated phosphotungstic acid (JCPDS# 00-050-0654) and then becomes amorphous. It has been reported elsewhere, that the HPAs could become amorphous when anhydrous acid is obtained at temperatures close to 400 °C [14]. The WO_3 (JCPDS# 00-032-1395) appears at 500 °C as a minor phase and remains the only one present at 600 °C.

3.3. Temperature programmed oxidation (TPO)

In order to find out what happened with the ionic liquid during the activation period prior the reaction a TPO study coupled with qualitative MS analysis was carried out. The results are presented in Fig. 3.

The phosphomolybdic acid based hybrid starts to decompose at temperatures close to 300 °C showing a lower thermal stability than the $Bmim_3PW_{12}O_{40}$. The later appears to be stable at the activation temperature for 30 min and then starts to decompose. It is interesting to emphasize, that the two hybrids do not lead to the same oxidation products. In addition to the signals corresponding to CO, CO_2 and H_2O (*m*/*z* 28, 44 and 18, respectively) the signals of unsubstituted imidazolium (*m*/*z* 68) and butyl radical (*m*/*z* 57) are observed in the MS spectra of the evolved products. The presence of both *m*/*z* signals at 57 and 68 for $Bmim_3PMo_{12}O_{40}$ suggests the presence of acid centres able to break the butyl–imidazolium bond. However, the presence of only the butyl signals in the $Bmim_3PW_{12}O_{40}$ case suggests strong bonding between the imidazolium cation and the Keggin structure at this temperature in this solid. This was further confirmed by the lower quantity of oxidation products (CO, CO_2 and H_2O) detected when compared to the amounts obtained from the phosphomolybdic hybrid.

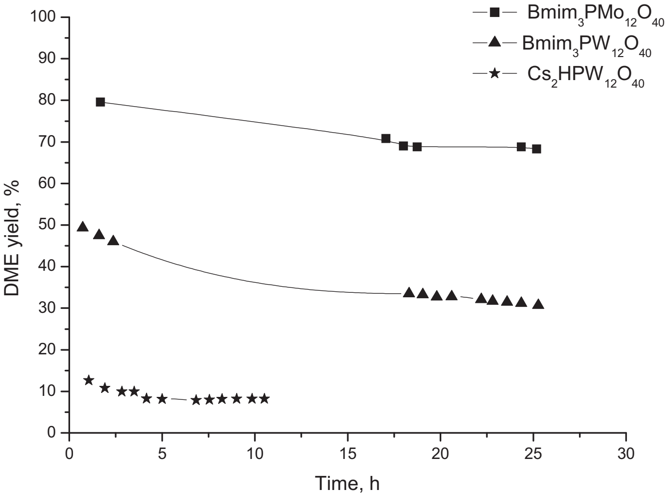

Fig. 4. DME yield for the prepared samples.

3.4. Methanol dehydration

The results for methanol dehydration are presented in Fig. 4 as dimethyl ether yield versus time.

The selectivity to dimethyl ether (DME) is close to 100% at 275 °C for both hybrids. However, the hybrid based on phosphomolybdic acid presents higher activity. By comparing the catalytic activity of the different hybrids with the one achieved over water insoluble $Cs_2HPW_{12}O_{40}$ acidic metal salt of HPAs, the effect of the ionic liquid on the catalytic activity is studied. The acid metal salt of the phosphotungstic acid ($Cs_2HPW_{12}O_{40}$) presents low activity to methanol dehydration, which confirms that the obtained hybrids could be very interesting for further investigation as acid catalyst precursors.

Another interesting fact is that at the temperature of activation (400 °C) in the reaction flow, methanol is fully converted to CO_2 over both hybrids. The hybrids become oxidizing catalysts in the reaction

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + H_2O$$

4. Discussion

4.1. $Bmim_3PMo_{12}O_{40}$

From the TGA results, it can be deduced that the presence of oxygen promotes the combustion of the ionic liquid. However, the stability of the material in a broad range of temperatures (450–700 °C) suggests that a stationary phase is rapidly obtained. The fast transformation of the mixed oxide products of the secondary Keggin structure decomposition takes place, thus leading to the formation of stable α-MoO_3 phase, which, in the presence of oxygen, suffers sublimation at high temperatures. It can be concluded that the presence of oxygen promotes the formation of MoO_3 and once formed, it starts to catalyze the organic part oxidation. The ionic liquid removal occurs in three successive steps,

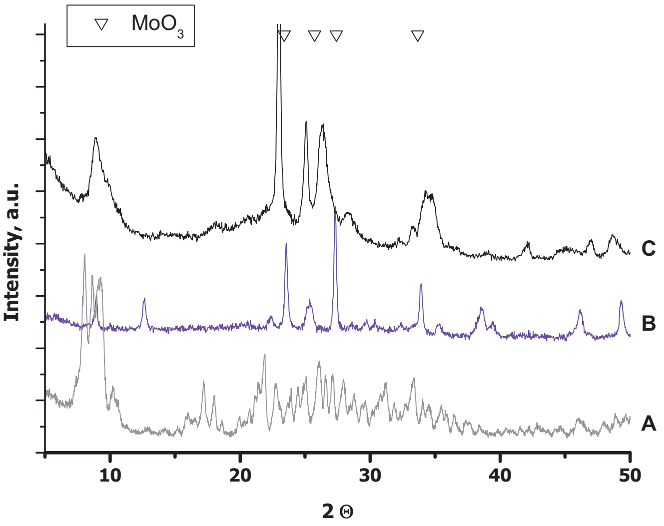

Fig. 5. XRD patterns of the Bmim$_3$ PMo$_{12}$O$_{40}$ A) before B) after the reaction and C) of the parent acid after the oxidation treatment.

starting by butyl–imidazolium bond breaking suggesting the presence of acidic active centres able to break the C–N bond. All the characterization methods confirm that the only phase originated from this hybrid is MoO$_3$. Hence, in the conditions of activation (400 °C), when only the MoO$_3$ is present, the hybrid give rise oxidizing catalyst converting methanol to CO$_2$, but at the temperature of the dehydration reaction (275 °C) becomes acidic. At the temperature of the dehydration reaction, the phase composition could be influenced by the water formation. It was reported [15] that in the presence of water the phosphomolybdic acid treated at 400 °C transforms from the mixture of phosphorus oxide, α and β MoO$_3$ into a mixture of PMo$_{12}$H and α-MoO$_3$. Hence, the presence of water limits the collapse of the Keggin structure thus leading to quasi equilibrium and acid catalyst able to dehydrate methanol. That fact could explain the high activity of this hybrid in the dehydration reaction, which if only MoO$_3$ is present should convert to an oxidizing reaction and it is not the case. In addition a change of the catalyst colour is observed going from yellowish (colour of the initial hybrid) through blue (oxide/hydroxide species of mixed valence known as molybdenum blues) to greenish at the end of the reaction (probably of the mixture of MoO$_3$ and PMo$_{12}$H units). However, the diffraction pattern of the catalyst after reaction shows only the presence of MoO$_3$ (Fig. 5).

The key parameter for this hybrid is probably its tendency to form the β-form MoO$_3$ which hinders the textural evolution, and its capability to react with the water vapour in the presence of phosphoric oxide, as reported elsewhere [24]. This renders this hybrid a very good precursor for the highly active catalyst in the dehydration of methanol.

4.2. Bmim$_3$ PW$_{12}$O$_{40}$

The TGA curves for the phosphotungstic acid originated hybrid show two steps of organics removal from the hybrid, the second one at high temperature (600 °C), which suggests that in the reaction conditions, the organic part still exists as an intermediate phase. The initial temperature of the decomposition is 100 °C higher than that of the phosphomolybdic hybrid. In addition, the diffraction patterns study as a function of the temperature reveals that the hybrid looses part of the ionic liquid protection converting itself into an organic deficient hybrid. Based on the TPO results, one could suggest that the organic deficient hybrid consists of the Keggin anion and methyl-imidazolium cation which suggests that this hybrid is able to break only the butyl–imidazolium bond. At the temperature of the activation, the obtained products appear to be amorphous caused by the presence of free dehydrated phosphotungstic acid.

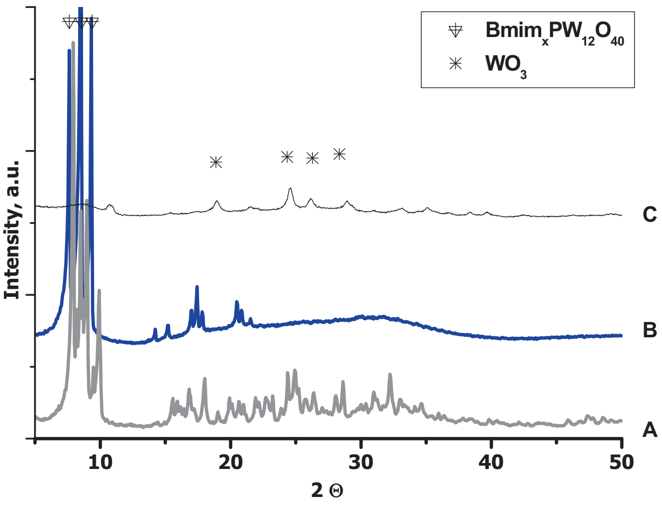

Fig. 6. XRD patterns of the Bmim$_3$ PW$_{12}$O$_{40}$ A) before B) after the reaction and C) of the parent acid after the oxidation treatment.

However, as reported by Rocchiccioli-Deltcheff et al. [24], the production of water during the reaction can play an essential role on the reactivity. In the temperature range where the thermal pretreatment produces an anhydrous acid, the water produced during the catalytic reaction allows a steady state where the anhydrous HPA and the 13-hydrate coexist. The resulted phase is probably responsible of the acidic character and activity in the dehydration reaction. Kozhevnikov et al. [25] also reports that the proton sites in solid HPAs are strongly dependent on the hydration degree: the less hydrated the compounds, the more trapped the protons. However, the phosphotungstic hybrid shows lower catalytic activity compared to the phosphomolybdic hybrid despite of the fact that the phosphotungstic acid should present higher acid strength [21]. The XRD patterns (Fig. 6) of the hybrid after the reaction show the presence of the organic deficient hybrid, which could explain the lower activity due to the presence of the ionic liquid protection layer.

A comparison of the catalytic activity of the both hybrids to the Cs$_2$HPW$_{12}$O$_{40}$ in the same conditions was made. However, the metal salt, thermally more stable, presents low catalytic activity for the dehydration of methanol, which helps us to conclude that probably the intact Keggin anions are not the active species for this reaction.

4.3. Comparison of the thermal stability of the hybrids to the parent acids

In order to compare the stability of the hybrids to those of the original acids, the later were submitted to the oxidation treatment, in the same conditions (from RT to 400 °C, heating rate of 10° min^{-1}). For H$_3$PMo$_{12}$O$_{40}$ only the signals corresponding to H$_2$O (m/z = 18) were observed. Two water loss processes can be distinguished in the temperature range between 50–200 °C, one major loss corresponding to the physicsorbed water and the loss of the H$_2$O molecules of the primary acid structure, and the second at around 370 °C corresponding to the Keggin structure decomposition (Fig. 3A inset). For the H$_3$PW$_{12}$O$_{40}$ acid, again two H$_2$O losses are detected, one major at higher temperature compared to the H$_3$PMo$_{12}$O$_{40}$ in the 150–200 °C temperature range and the second one observed during the isotherm period at 400 °C (Fig. 3 inset B).

The XRD patterns of the solids, after the oxidation treatment show that the $H_3PMo_{12}O_{40}$ acid loses a part of Keggin structure water molecules and turns into a mixture of dehydrated acid and MoP_2O_7 (Fig. 5C). In the case of the corresponding hybrid, low or inexistent protection was observed. However, the presence of the organic part forces in first place the combustion of the organic molecule and then the acid loses water at temperatures around 300 °C, as shown from the TPO experiments. It should be noted that the combustion of the organic part for this hybrid is accelerated by the first appearence of MoO_3.

The $H_3PW_{12}O_{40}$ seems to present better thermal stability compared to the $H_3PMo_{12}O_{40}$. The XRD pattern after the treatment shows the presence of a mixture of the original dehydrated acid and WO_3 (figure 6 C). The corresponding hybrid however shows better stability and in the conditions of the reaction, does not convert into WO_3 or other oxidation products of the $H_3PW_{12}O_{40}$. The hybrid oxidation goes through organic part partial oxidation resulting directly into catalyst - organic deficient hybrid.

5. Conclusions

In summary, as shown above the thermal stability of the hybrids do not differ a lot from the stability of the initial acids, except in the order of water removal and Keggin structure decomposition. Even if many catalytic reactions are performed at relatively high temperatures (often > 350 °C) and it is necessary to use a catalyst that is stable under these thermal conditions, the partial decomposition of the hybrids in the activation procedure could conduct to precursor of catalytically active species. However the conditions of the activation have to be optimized in order to reveal the truly potential of the hybrids.

The partial decomposition of the hybrids results in an active and more important very selective catalyst for the dehydration of methanol to dimethyl ether.

It should be noted that the nature of the ionic liquids plays as well an important role in the acid protection; the preliminary study of 1(3-carboxipropyl) 3-methyl imidazolium protection of the Keggin structure shows a very different results which are now object of detailed study.

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