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Influence of the ionic liquid presence on the selective oxidation of glucose over molybdenum based catalysts

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ABSTRACT

Two different approaches are proposed in this work in order to study the influence of the ionic liquid presence in the reaction of glucose oxidation by H₂O₂ in mild conditions. The ionic liquids are applied either as a solvent by using homogeneous Mo based catalyst, [Mo(O)(O₂)₂(H₂O)_n] complex, or by using it as an integral part of a heterogeneous catalyst, organic inorganic hybrids based on Mo Keggin structure. Both catalytic strategies resulted in acceptable glucose transformation degrees but lead to different oxidation products depending on the role of the ionic liquid. The hybrid approach restrains the number of the received products being the most selective one. A detailed study of the effect of the hybrid nature and reaction conditions is proposed in the second part of this study.

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1. Introduction

The efficient transformations of polysaccharides into valuable compounds, such as fuels and important intermediate chemicals is a relevant topic nowadays and has attracted the attention of the scientific community [1–4]. The glucose, the monomer of cellulose, constitutes the most abundant and available monosaccharide and its transformations into furan derivatives like HMF (hydroxymethyl furfural) [5], FDCA (Furan dicarboxylic acid) [6], DFF (2,5 diformylfuran) [7] or sugar acids (aldonic and aldaric acids) is being widely investigated in the last years [8–10]. Within added-value chemicals issued from glucose, the gluconic acid, obtained via oxidation of the glucose aldehyde group is in versatile use in pharmaceutical, chemical, food, beverage and textile industries, either as additive, as chelating agent for cleaning purposes or for the extraction of metal traces in solutions [11]. Its current production is carried out via enzymatic process, in presence of glucose oxidase. However, this methods presents several drawbacks such as need of high amounts of expensive enzyme, its irreversible deactivation, the exhaustive control of process parameters (such as pH and temperature), the need of several pre-reaction purification processes in order to remove impurities and the long reaction times to obtain

acceptable yields [12]. All this disadvantages stimulates the pursuit for new efficient, environmental friendly catalysts and processes to improve carbohydrate conversion and, therefore, biomass exploitation.

The production of gluconic acid has been studied over catalysts of different nature, including enzymatic [13] and heterogeneous, based on platinum [14,15] and, more recently, on gold [16,17]. Recently, a group of compounds, the as called ionic liquids (ILs), showed great potential in carbohydrate chemistry either as catalyst or as a solvent. The ILs are compounds consisting in ions with melting points below 100 °C whose principal advantages could be resumed in high ionic mobility, good electric conductivity, low vapor pressure and good thermal and chemical stability [18,19]. Most commonly used ILs are composed by quaternary ammonium salts or cyclic amine salts [20]. They have already found its application in catalysis as a solvents [21–24] in electrochemistry [25] and organic synthesis, however, the use of the ionic liquid as a part of hybrid catalyst is barely studied [20,26–30].

On the other hand the polyoxometalates, well-known catalytically active compounds were also considered as a potential glucose transformation catalysts [20]. In particular, the Keggin-type polyoxometalates, classified as anionic metal-oxygen clusters of the early transition metals, appear as a good candidates for carbohydrate conversion [31–33]. Properties like strong Brønsted acidity, fast multi-electron transfer, high proton mobility, high solubility in various solvents and resistance to hydrolytic and oxidative degradations in solutions converts these compounds in versatile

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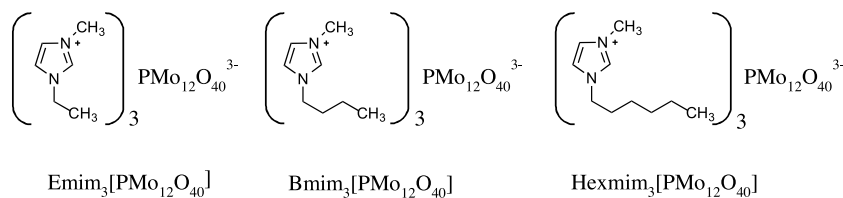


Fig. 1. Structure of IL/ $\text{PMo}_{12}\text{O}_{40}$ hybrids used as catalytic System 2.

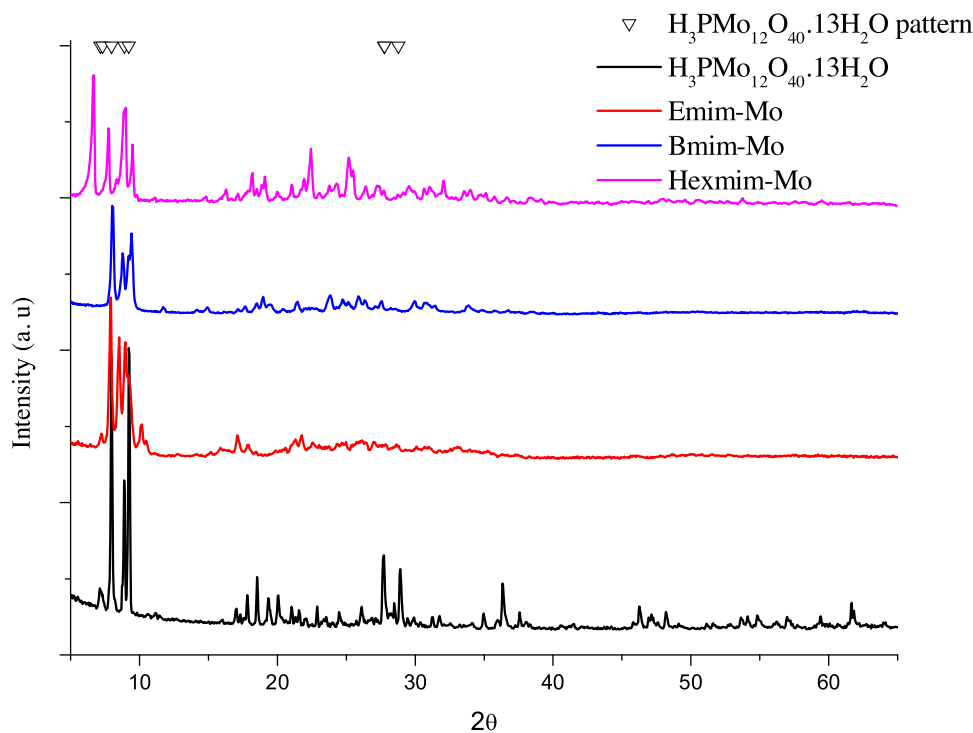


Fig. 2. XRD diffractograms of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ (JCPDS #01-075-1588) and its hybrids.

materials for using in catalysis [34]. Furthermore, their properties can be tuned by varying the composition and the counter cations [31,35,36]. The proton compensated polyoxometalates, known as heteropoly acids (HPA) however cannot be used in liquid-phase reactions with polar solvents due to their solubility and impossibility for recuperation. However, the substitution of protons with another organic or inorganic cations results in insoluble materials and, therefore, useful in heterogeneously catalyzed liquid-phase reactions [31]. Additionally, the substitution of all the protons with organic cations could result in a new class of organic-inorganic hybrid materials which takes advantages on both inorganic (strength, thermal stability and chemical resistance) and organic part (lightness, flexibility and versatility) features. Perfect example of organic cations which could be applied in the hybrid are those of ionic liquids (ILs) [20,37–39].

In this context, the main goal of this work is to study the influence of the IL on the catalytic performance of Mo based compounds. The ionic liquids are evaluated either as a solvent (*System 1*) or as integral part of the catalyst (*System 2*) in the liquid-phase oxidation of glucose with hydrogen peroxide as oxidant. In *system 1*, 1-butyl-3-methylimidazolium hexafluorophosphate (Bmim) PF_6 ionic liquid is used as solvent and $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{H}_2\text{O})_n]$ complex as catalyst. In *system 2*, three different hybrids based on phosphomolybdic acid ($\text{PMo}_{12}\text{O}_{40}^{3-}$) and three IL cations, 1-ethyl-3-methylimidazolium (Emim), 1-butyl-3-methylimidazolium (Bmim) and 1-hexyl-3-methylimidazolium (Hexmim), are used as catalysts in aqueous solution.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of oxodiperoxomolybdenum complex (*System 1*)

Solution of the aqua complex of oxodiperoxomolybdenum, $[\text{Mo}(\text{O})(\text{O}_2)_2(\text{H}_2\text{O})_n]$ (henceforth $[\text{MoO}_5]$) was prepared as follows. A suspension of MoO_3 (Sigma Aldrich, 3.617 g, 25 mmol) in 40 mL 30% aqueous hydrogen peroxide (VWR) was heated at 50 °C with continuous stirring overnight after which complete dissolution of the molybdenum resulting in a clear yellow solution was observed. At this point the solution was cooled to 0 °C and several drops of hydrogen peroxide were added and the solution was then made up to 100 mL and stored in a sealed volumetric flask at 4 °C. Occasional venting of this solution is advised upon prolonged storage due to the accumulation of pressure following catalytic decomposition of hydrogen peroxide. A solution of $[\text{MoO}_5]$ with concentration 0.25 M is thus obtained.

2.1.2. Synthesis of heteropolyacid and hybrids (*System 2*)

Phosphomolybdic acid was prepared as reported in the literature [40] by using $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ (Sigma Aldrich), H_3PO_4 (85%) (Panreac), HCl (37%) (VWR), diethyl ether (Panreac), HNO_3 (65%) (VWR) and distilled water.

For the $\text{Emim}_3[\text{PMo}_{12}\text{O}_{40}]$ (from this point forward Emim-Mo) synthesis [30], appropriate quantities of prepared $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (0.9 g) and 1-ethyl-3-methylimidazolium methanesulfonate (Alfa

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