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Borophosphate glasses: Synthesis, characterization and application as catalyst for bis(indolyl)methanes synthesis under greener conditions

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ABSTRACT

Glasses are a class of materials that have a multitude of uses and applications. In catalysis, they are frequently used as support materials. However, in this paper, we demonstrate that glass can be applied as an active material in catalysis. The glass was successfully applied as catalysts in bioactive bis(indolyl)methanes (BIMs) molecules with the capability to extend the reaction substrate to other *N*-heterocycle. Furthermore, we describe the synthesis and characterization of cheap and readily available borophosphate glass samples produced using a classical melt-quenching technique and their application as a catalyst. The main features of this glass-catalyzed reaction are high yields, recyclable catalyst, ease of scale-up to gram scale, and a solvent-free and metal-free approach.

1. Introduction

The development of greener catalysts for chemical process with simple raw materials and at low-cost processing technologies is a challenging. Currently, the metal nanoparticles show an extensive list of advantages if compared with bulk catalysis materials. Not only noble metals as Pt, Rh, Ru, Ir, Au, and Ag but also earth-abundant metals Mn, Fe, Co, Ni and Cu can be used for nanocatalysis synthesis. For example, metal nanoparticles applied for heterogeneous catalysis have been studied extensively due to the increase in their catalytic activity. [1] Despite their significant performance, the catalytic nanoparticle recycling, separation, thermal stability for high temperatures are recurrent drawbacks [1] [2]. Moreover, the atom/ion leaching of noble or earth-abundant metal can be noticed for several types of nanoparticles [3]. In this regard, our group is dealing now with the development of glasses with a specific task of producing catalyst materials for green chemistry.

Glass materials are a distinct group, frequently characterized by their lack of long-range order and the presence of a glass-transition temperature (T_g) [4]. At the basic science level, gaining a complete understanding of the nature of glasses and the development of appropriate theories are complex topics. Nevertheless, the engineering applications of glass materials worldwide are widespread. [5, 6] Commonly, silicate-based glasses are exploited due to their high refractive index, low thermal expansion coefficient, thermal shock resistance, high chemical durability and electrical resistivity [7, 8, 9]. The engineering of glass materials has enabled products ranging from simple commercial glassware for kitchens, laboratories or windows to technological devices tailored for optical applications, such as microscopes, telescopes and optical fibers, to be obtained [5]. Furthermore, laboratory glassware is recognized as inert and it has been extensively applied in chemical reactions because of this property.

The employment of glass materials as a catalyst in chemical reactions is practically an unexplored topic. Undoubtedly, the major application of glass is as a support material for catalysts, rather than as a catalytic material. Schmöger et al. [10] used Pd supported on porous glass to perform Suzuki and Heck reactions under aerobic conditions. Takahashi et al. [11] performed hydrogenation reactions over a nickel catalyst supported on porous glass prepared from borosilicate glass. Zolfagharinia et al. [9] applied immobilized sulfonic groups on glass waste as a catalyst in multicomponent reactions. Manna and Maiti [12] reported the application of multiple metal ions containing silicon-based glass ceramic material as a catalyst in the synthesis of pyridines without superficial and/or catalyst modification. Tupberg et al. [8]

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demonstrated the photocatalytic activity of zinc borophosphate glass, doped with the transition metal oxides TiO_2 and Cr_2O_3.

Although phosphate glass has the capacity to dissolve metal oxides at relatively low processing temperatures, [8, 13–16] the synthesis of a glass catalyst without transition metal ions is desirable for the development of greener chemical processes. Therefore, the use of glass materials as catalysts could represent an innovative approach to their application in heterogeneous reactions using organic synthesis.

In this context, several materials have been developed as solid catalysts in the condensation reaction between indoles and aldehydes to synthesize bis(indolyl)methanes (BIMs), using eco-friendly methodologies. Furthermore, this kind of catalyst has been shown to be an excellent alternative from the sustainability point of view, since they can be recycled [17–24] and can be employed in several solvent-free reactions. [25–29]. However, some of these catalysts have particular drawbacks that reduce their synthetic utility. These disadvantages include the use of transition metals, expensive materials, difficult preparation procedures, and long reaction times.

In recent years, different types of organic transformations have been performed with the application of metal- and solvent-free systems. Thus, in connection with our continued interest in the development of sustainable and greener chemical protocols [30] [31] [32] [33] [34] [35] [36], we describe herein the preparation of borophosphate glasses from cheap and readily available materials, in the absence of transition metals. The glasses obtained were then used directly as catalysts for the synthesis of BIMs and other related heterocyclic derivatives under solvent-free and metal-free conditions. In addition, the granulometry, recovery and reuse of the glass-catalyst were investigated.

2. Experimental

2.1. Glass synthesis and characterization

The glasses were fabricated using the (in mol%) NaH_2PO_4-H_3BO_3-Al_2O_3 glass template with NaH_2PO_4 and H_3BO_3 ratio set at 2, while Al_2O_3 was added to the matrix in proportions of 15% (30% Al^{3+}), 3% (6% Al^{3+}) or 0% (0% Al^{3+}). In a typical synthesis route, 5 g of the above-mentioned compounds were used after mixing them well using an agate mortar. The powder mixture was then transferred to a covered Pt/Au crucible and fused for 1 h at 1200 °*C* for the sample with 15% of Al_2O_3 and at 1050 °C for the samples with 3% and 0% of Al_2O_3. Boron-free glass samples were synthesized at 1050 °C with 3% of Al_2O_3 to elucidate the role of boron in glass catalysis. The glass samples were obtained by quenching them from the melt to room temperature in a graphite mould.

Differential thermal analysis (DTA) measurements were performed using a Perkin Elmer thermal analyzer (model STA6000). The measurements were conducted under nitrogen atmosphere at a heating rate of 10 °C/min^{-1} in the range of 100 °C and 850 °C.

The chemical resistance against relative humidity (RH(%)) was monitored as a function of the aluminium content. Powdered samples (325 mesh) were placed in a sealed chamber with controlled relative humidity (saturated NaCl solution, ≈75% at 25 °*C*) and the mass was monitored for 24 h. The Raman measurements have been performed using the Renishaw InVia micro-Raman System equipped with CCD camera and 514.5 nm argon laser line as an excitation source. Deconvolution of the Raman spectra was performed by Fityk program (version 1.3.1). XRD patterns were recorded using the Bruker D2 Phaser Diffractome ter equipped with the CuK_α radiation (λ = 1.5418 Å). The diffraction patterns were obtained at angles between 10° and 80° ($\theta - 2\theta$).

2.2. Synthesis of bis(indolyl)methanes

Borophosphate glass (20 mg), indole or compound **4** (0.50 mmol) and aldehyde (0.30 mmol) were placed in a test tube and stirred at 70 °C for the time indicated in Table 2. The organic compounds were then directly extracted with ethyl acetate (3 × 5 mL), dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel using an appropriate mixture of hexane and ethyl acetate as the eluent. The identity and purity of the products were confirmed by ^{1}H NMR, ^{13}C NMR and melting points and all spectral data were in perfect agreement with those reported in the literature (see Supplementary Information). A control reaction was performed with indole (0.50 mmol) and aldehyde (0.30 mmol) and an ordinary crushed glass ((≈75% SiO_2, 15% Na_2O e 10% CaO, < 325 μm) provided by NanoGlass Reverse Logistics Company (Toledo, Paraná, Brazil).

2.3. Reuse of glass catalyst

The recyclability of the glass catalyst was investigated. After complete extraction of the organic phase of the reaction, the borophosphate glass/catalyst was washed with ethyl acetate (3 × 5 mL), and then dried in an oven at 100 °C for 30 min. The dried solid catalyst was reused in subsequent reactions under solvent-free conditions, at 70 °*C* for 2.5 h.

3. Results and discussion

3.1. Glass characterization

The increase in the content of Al^{3+} ions considerably enhanced the glass resistance in the presence of moisture (Fig. 1), which is attributed to the replacement of humidity-sensitive P-O-P bonds by strong Al-O-P covalent bonds. [16–37] In the case of the borophosphate glass with 30% of aluminium ions, when exposed to an atmosphere with high relative humidity its mass did not increase, indicating that there is no water absorption. On the other hand, when the concentration of aluminium ions was 0% or 6%, the chemical stability of the glass sample was reduced and the mass increase reached ≈64% (0% Al^{3+}) after 24 h of exposure.

Fig. 2 shows the results of the Raman analysis of the synthesized borophosphate glass samples. The Raman spectrum is mainly composed of two broad bands located below and above of ≈820 cm^{-1}. The most intense band is located between 820 cm^{-1} and 1350 cm^{-1}. This region, when decomposed, is comprised of the complex overlapping of the stretching PO_2, PO_3 and P-O-P groups and it is strongly affected by the addition of Al^{3+} ions. The specific Raman peaks were fitted with a series of Voigts line shapes (Fig. 3). Fig. 3(A) shows the deconvoluted Raman spectrum for the sample without Al^{3+} ions. The main broad

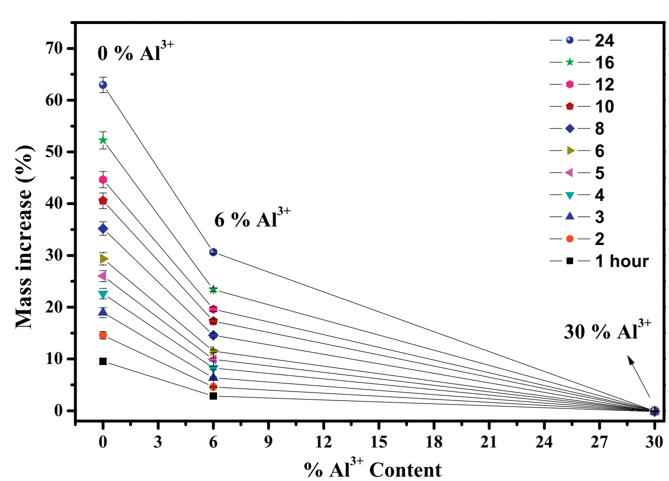

Fig. 1. Water absorption behavior for borophosphate glasses with different content of Al^{3+} ions under relative humidity of 75%.