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Original Article

# Simple and low–cost transition metal-free borophosphate glass catalyst for aromatic alcohol oxidation by sodium hypochlorite

*Guilherme Felipe Lenz* [a,b], *Bruno Henrique Selinger* [b], *Rodrigo Sequinel* [b], *Fabiano Rosa da Silva* [b], *Danilo Manzani* [a], *Jorlandio Francisco Felix* [c,*], *Ricardo Schneider* [d,**]

[a] *Universidade de São Paulo—USP, Instituto de Química de São Carlos, São Carlos, SP, Brazil*
[b] *Universidade Federal do Paraná—UFPR, Departamento de Engenharias e Exatas, 85950-000, Palotina, PR, Brazil*
[c] *Universidade de Brasília—UnB, Instituto de Física—Núcleo de Física Aplicada, 70910-900, Brasília, DF, Brazil*
[d] *Universidade Tecnológica Federal do Paraná—UTFPR, Group of Polymers and Nanostructures, 85902-490, Toledo, PR, Brazil*

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ABSTRACT

The oxidation of primary and secondary alcohols to their respective aldehydes/ketones is one of the most important reactions in fine chemistry due to the industrial application of these products. Based on this, a large number of new catalysts and oxidants have been tested using this reaction as a catalytic model, mainly looking for a process that ensures high aldehyde selectivity. In this paper, we have used moisture stable borophosphate glass doped with 10 mol% $Al_2O_3$ as a heterogeneous catalyst in the oxidation of sodium hypochlorite, an effective, greener, and low-cost oxidant, using acetonitrile as solvent under mild conditions. The glass catalyst mass and the particle size were evaluated, as were the reaction temperature and oxidant amount, to determine the ideal reaction conditions where the conversions achieved 87.0 mol% for 1-phenylethanol to acetophenone and 79.4 mol% for benzyl alcohol to benzaldehyde, with benzaldehyde selectivity above 95%. Although sodium hypochlorite is a strong oxidant, benzaldehyde was the main product of the oxidation of benzyl alcohol due to the formation of a biphasic organic-aqueous system that protects the aldehyde from oxidation and allows the reaction to occur without the use of a phase transfer catalyst (PTC). HPLC analysis of both phases showed that alcohols, aldehyde, and ketone were mostly present in the organic phase (concentrations above 98.7%). During the reaction, a small amount of alcohol is transferred to the aqueous phase, where the oxidation took place. Once formed, the products are transferred back to the organic phase. ICP-OES analysis indicates that borophosphate glass acts in the reaction by partially releasing phosphate-based groups, reducing the pH of hypochlorite to 9. In this

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* Corresponding author.
** Corresponding author.

E-mail addresses: jorlandio@unb.br (J.F. Felix), rschneider@utfpr.edu.br (R. Schneider).

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sense, borophosphate glasses prove to be a simple and inexpensive alternative for the development of new catalysts.

## 1. Introduction

The oxidation of alcohols is considered a benchmark reaction for the development of new catalysts [1]. Besides this, the oxidation of primary and secondary alcohols to their respective aldehydes and ketones is a common laboratory procedure. These reactions traditionally employ toxic oxidants such as chromium VI salts (dichromate, chromic acid, and chromium trioxide), potassium permanganate [2,3], and pyridinium chlorochromate [4] that, although selective to aldehyde and ketones, generally require an excess to ensure better conversions. However, the procedure drawback is the generation of toxic waste [5]. At the same time, these reactions attract attention mainly because aldehydes and ketones are intermediates of many products used in fine chemistry [6]. The oxidation of benzyl alcohol to benzaldehyde is an important example since benzaldehyde is industrially the most important aromatic aldehyde and one of the main aromatic compounds used in the pharmaceutical, cosmetic, food, and perfumery industries [7–9].

In this context, several works have sought catalysts and nanocatalysts [10,11] that increase the production of intermediate products, i.e. benzaldehyde [9]. Some of these new procedures have applied catalysts with or without an oxidant, highlighting the application of metallic nanoparticles, including, for instance, Au [6,12], Pt [13], Au-Pd [14], Ag [15]; Ag [8,16], Co [17], and Pd [18] in association with $O_2$; and Cu associated with hydrogen peroxide [19] or TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) [1,20]. The oxidant choice is also important, being suitable to the catalyst (e.g. Cu and TEMPO), as well as for the process as a whole, relatively stable and, if possible, having a low cost, as molecular oxygen, hydrogen peroxide, and sodium/calcium hypochlorite.

The application of sodium and calcium hypochlorite as an oxidant in organic synthesis was extensively reported in the 1980s. Stevens and co-workers applied “Swimming Pool Chlorine” (an inexpensive commercial sodium hypochlorite solution) to oxidize secondary alcohols to ketones [21] and diols/aldehydes to their respective ketones and methyl esters [22]. At the same time, calcium hypochlorite was applied to oxidize secondary methyl ethers into ketones [23], aldehydes to their corresponding carboxylic acids [24], secondary alcohols to ketones, primary alcohols to esters, and ethers to esters [25]. All these applications report hypochlorite as a versatile, effective, safer, and potential substitute for traditional chromium VI salts [3] and pyridine-based [4] oxidants in organic synthesis. Besides this, some alcohol oxidation using sodium hypochlorite has been recognized as environmentally benign and/or a greener process [26–30], when compared with that described by Stevens [21].

Germanophosphate glasses containing self-supported nickel-based nanoparticles as catalysts were recently described as a new protocol for benzyl alcohol oxidation using sodium hypochlorite as an oxidant [31]. In this study, good conversions were achieved (≈75 mol%), with high benzaldehyde selectivity (>99%), employing mild reaction conditions (20 °C, acetonitrile as solvent). In this sense, the glass acts as an active substrate for the synthesis of self-supported Ni-based catalysts. The employment of glass materials in catalysis is practically an unexplored topic [32], and the major application of this material is like a sort of support for catalysts [33–38].

However, Matzkeit et al. [32] reported the use of borophosphate glass as a catalyst for bioactive bis(indolyl)methanes molecules (BIMs) synthesis under solvent-free conditions, achieving high yields. Phosphate-based glass materials can be obtained from simple raw chemicals (e.g., $KH_2PO_4$, $P_2O_5$, $NaPO_3$, and $NaH_2PO_4$). Therefore, phosphate-based glasses could represent an unconventional method that moves towards the development of new heterogeneous catalysts.

In this sense, considering the relevance of the development of new catalysts and processes that look for chemical compounds of laboratory and industrial interest in an effective and selective way, and the use of less harmful chemical reagents, this work applied a simple and easy to produce borophosphate glass as a catalyst for the oxidation of benzyl alcohol and 1-phenylethanol by sodium hypochlorite 11 wt%, in an organic-aqueous biphasic system. To optimize the alcohol conversion and ensure good aldehyde selectivity, some experimental parameters of the reaction such as temperature, oxidant amount, catalyst mass and particle size, and reaction media were evaluated and monitored by High-Performance Liquid Chromatography (HPLC) analysis. HPLC analysis of both organic and aqueous phases was also used to propose the reaction mechanism. The glass catalyst was characterized by Raman spectroscopy, X-ray diffraction, density, and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

## 2. Experimental

### 2.1. *Glass production and characterization*

Borophosphate glass was prepared by melting-quenching technique [34,35] with high-purity reagents (Sigma–Aldrich®) using $NaH_2PO_4$, $H_3BO_3$, and $Al_2O_3$ as precursors. The $NaH_2PO_4/H_3BO_3$ molar proportion was set as 2 and $Al_2O_3$ was added in proportions of 0, 3, 5, 7, and 10 mol%. In a typical synthesis, 5 g of the aforementioned compounds in the predetermined proportions were weighted and homogenized in an agate mortar for 10 min, transferred to a covered Pt crucible, and then melted at 1050 °C in a resistive preheated oven for 1 h. The glass sample was obtained by quenching the molten mixture on a graphite mold at room temperature. Posteriorly, the glass was grounded in an agate mortar and sieved through a 150 to <400 mesh range, and stored under a vacuum desiccator until analysis.

The glass density (ρ) was measured with the bulk glass samples by the Archimedes method using a density module mounted on a Mettler Toledo ME240/M analytical balance and ethanol as immersion solvent.

The total content of aluminum, boron, sodium, and phosphorus on borophosphate glasses was determined by ICP-OES using a Thermo Scientific® iCap 6000 Series Spectrometer. The ICP solutions were prepared in triplicate with 100 mg of sample 100-time diluted by ultrapure 1% (v/v) $HNO_3$ aqueous solution in an ultrasonic bath. The analytical standard curves (0.1–10 mg $L^{-1}$) were prepared using a multi-element standard solution (Fluka®) diluted by the aforementioned solvent. All samples were prepared in plastic materials to avoid borosilicate glass interference. Emission lines used for quantification in axial view: Al 396.152 nm; B 249.678 nm; Na 589.592 nm, and P 185.942 nm [35].

Raman spectrum of the glass sample was recorded using a micro-Raman Renishaw InVia®, laser power 8 mW, 633 nm excitation wavelength, and CCD (Charge Coupled Device) detector. The powder glass sample was measured without any additional treatment. Deconvolution analysis of the Raman spectrum was carried out by Voigt functions using the Fityk program (version 1.3.1).

The amorphous nature of the borophosphate glass powders was assessed by X-ray powder diffraction (XRD) measurements, using a Rigaku SmartLab SE Diffractometer equipped with the Cu Kα radiation ($\lambda = 1.5418$ Å), and at angles between 15° and 80° ($\theta - 2\theta$).

### 2.2. *Benzyl alcohol and 1-phenylethanol oxidation by NaOCl*

First of all, the concentration of the NaOCl solution was determined as 11 wt% by iodometric titrimetric analysis (Supplementary Information, Section 2).

Benzyl alcohol (BnOH) and 1-phenylethanol (BnEtOH) oxidations were conducted using NaOCl 11 wt% as oxidant and acetonitrile (ACN) as a solvent, based on our previous paper [32]. Initially, the reaction parameters oxidant and catalyst amount, temperature, and catalyst mesh were tested to optimize the reaction conditions, as reported in Table 1. All reactions were carried out under constant stirring. Thus, the glass catalyst was first dispersed in 10 mL ACN for 2 min, followed by the addition of 0.75 mmol of the aforementioned alcohols. The oxidant, NaOCl, was added in 4 equal portions (total amount tested divided by 4) in the beginning and within 30, 60, and 90 min of the reaction, being the reaction time adjusted according to the optimization of reaction conditions [28].

**Table 1 – Parameters tested to optimize the reaction conditions of BnOH and BnEtOH glass-catalysed oxidation by NaOCl.**

| Parameter | Evaluated |
|---|---|
| NaOCl amount mmols (mL) | 1.6 (1); 3.2 (2); 4.8 (3); and 6.4 (4) |
| Temperature (°C) | 20, 30, and 50 |
| Catalyst amount (mg) | 0; 25; 50; 75; 100; 125, and 150 |
| Particle size (mesh) | 150-200; 200–250; 250–325; 325–400; <400 |

After the evaluation of oxidant amount, temperature, catalyst mass, and particle size, the standard reaction conditions applied for additional tests (Supplementary Material), the effect of pH, and catalyst reuse were: 75 mg and 100 mg glass-catalyst for benzyl alcohol and 1-phenylethanol reactions, respectively, first dispersed in 10 mL ACN for 2 min, followed by the addition of 0.75 mmol of the alcohols. NaOCl was added in 4 equal portions of 1 mL (total 4 mL, 6.4 mmol) in the beginning and for 30, 60, and 90 min. The reactions were carried out under constant stirring at 50 °C for 3 or 5 h.

For catalyst reuse, the reaction media, containing the catalyst, was centrifuged at 3400 rpm for 10 min. The sedimented catalyst was separated from the liquid, washed with 5 mL of absolute ethanol, and the mixture centrifuged at 3400 rpm for 5 min. This procedure was repeated 3 times. Then, the freshly washed catalyst was dried at 80 °C for 4 h and reused.

The unconverted BnOH, BnEtOH, and the oxidation products benzaldehyde (BnCHO), benzoic acid (BnCOOH), and acetophenone (BnCOCH) were determined using HPLC (Thermo Scientific ® Ultimate 3000). The separation was performed at 30 °C using an octadecylsilane C18 column (Ace ltd.®), a flow rate of 1 mL $min^{-1}$ in gradient elution, with the mobile phase composed of the mixture of acidified water (0.01% v/v phosphoric acid, pH 2.75 ± 0.05) and acetonitrile (ACN, J.T. Baker® HPLC grade): initial 30% ACN → to 60% ACN in 10 min, keeping this condition until 15 min. The detection was made by a diode-array detector (DAD) at 210 nm. Aliquots of the reaction media were collected at the beginning, during, and at the end of the reaction, diluted 10 times with the mobile phase, and filtered in a 0.22 μm hydrophilic PVDF syringe filter [31]. Analytical standards (Sigma Aldrich®, Supelco®) were used as a reference for sample concentration determination.

To verify the distribution of compounds (mmol) in the biphasic formed phases, the organic reaction media was centrifuged (3400 rpm, 6 min), and a fraction of both organic and aqueous phases were collected for HPLC analysis.

The selectivity, linear range, quantification limit, precision, and accuracy of the HPLC method were previously tested to ensure the correct determination of the reaction compounds. BnOH and BnEtOH conversions (C), product yields (Y), and BnCHO selectivity (S) were calculated, respectively, according to Eqs. (1)–(3). n refers to the number of mmol calculated for each compound.

$$C_{alcohol}\,(mol\%) = \frac{n\ alcohol_{initial} - n\ alcohol_{time}}{n\ alcohol_{initial}}\, x\ 100 \tag{1}$$

$$Y_{product}\,(mol\%) = \frac{n\ product_{time}}{n\ product_{theoretical}}\, x\ 100 \tag{2}$$

$$S_{BnCHO}(\%) = \frac{n\ BnCHO_{end}}{\sum n_{end} BnCHO,\ \ BnCOOH}\, x\ 100 \tag{3}$$

All pH measurements were performed by an MS Tecnopon® digital pHmether previously calibrated with standard solutions (pH 4–10). pH adjustment, when needed, was made with HCl 10 wt% and NaOH 10 wt% solutions.

## 3. Results and discussion

### 3.1. Glass-catalyst characterization

Table 2 shows the molar composition of P, Na, B, and Al as their respective oxides, determined by ICP-OES [35], for borophosphate glass doped with 10 mol% $Al_2O_3$ used as a catalyst for benzyl alcohol and 1-phenylethanol oxidation by NaOCl.

Figure S1 shows the x-ray diffraction patterns for a borophosphate glass series with an increase of $Al_2O_3$ content from 0 to 10 mol%. The absence of crystallization peaks and the presence of the broad amorphous regions (halo) indicate the glassy characteristic of the materials. Moisture-resistant borophosphate glasses (molar ratio P/B = 2) can be obtained with the addition of $Al_2O_3$ (10 mol%) at a relatively low fusion temperature (e.g., 1050 °C) [32,35]. The successive addition of $Al^{3+}$ ions reduces the moisture absorption of borophosphate glasses and increases the glass transition temperature ($T_g$). However, concentrations above 12.5 mol% $Al_2O_3$ crystallize when fused at 1050 °C [35].

The addition of $Al_2O_3$ improves the chemical resistance of borophosphate glasses due to the depolymerization of the phosphate network and the formation of P–O–Al bonds [35,39]. The depolymerization of phosphate glass structure can be observed through Raman spectroscopy, Fig. 1. The band at ≈ 330 $cm^{-1}$ is associated with symmetric stretching of the O–P–O bond in metaphosphate structures ($Q^2$, based on $Q^n$ terminology, where n represents the number of bridging oxygen that links one tetrahedron to another) [35,39–41]. Borophosphate B–O–P band is observed at ≈ 630 $cm^{-1}$ [41], and the symmetric stretching of P–O–P at ≈ 700 $cm^{-1}$ [32,35,40,42]. With the addition of 10 mol% $Al_2O_3$, Al–O–Al bending modes can be noticed at ≈ 540 $cm^{-1}$ [32,35].

The band at ≈ 930 $cm^{-1}$ (inset graph, Fig. 1) is associated with isolated orthophosphate groups ($Q^0$) and asymmetric stretching of P–O–P in $Q^2$ structures [35,40]. The main effect of $Al^{3+}$ addition to the borophosphate glass network is the depolymerization process, e.g. the reduction of metaphosphate structures ($Q^2$) and the increase of pyrophosphate groups ($Q^1$). This effect can be observed in the 1000–1250 $cm^{-1}$ region of the Raman spectrum: pyrophosphate band $\nu_s$ P–O occurs at ≈ 1030 $cm^{-1}$ [41], whilst metaphosphate band $\nu_s$ $PO_2$ occurs at ≈ 1100 $cm^{-1}$ [41], and both overlap to form a single band with a maximum at 1070 $cm^{-1}$, as highlighted in the inset graph of Fig. 1. The asymmetric stretching $\nu_{as}$ $PO_2$ occurs at ≈ 1235 $cm^{-1}$ [35,41].

The density of borophosphate glass rises with $Al_2O_3$ addition up to 7.5 mol% $Al_2O_3$ and decreases with further addition of $Al_2O_3$ (10 mol%) (Fig. 2). The variations in density indicate that aluminum addition changes the O/P ratios determined from the ICP-OES analysis: for glasses with $Al_2O_3$ amount below 7.5 mol%, O/P < 3.5, and metaphosphate structures are predominant ($Q^2$). On the other hand, 10 mol% $Al_2O_3$ borophosphate glass has O/P > 3.6, and pyrophosphate groups are predominant [43,44]. These variations in O/P ratios also change the predominant Al groups. In glasses with O/P < 3.5, the $Al_2O_3$ addition tends to replace P–O–P and $PO^-Na^+$ bonds by cross-linked POAl(6)-phosphate chains, increasing the glass density, for instance. However, further aluminum additions change O/P > 3.5, with the replacement of POAl(6) groups for more open POAl(4) structures, reducing the glass density [43,44].

**Table 2 – Molar glass composition determined by ICP-OES.**

| Sample | Composition (mol%) | | | |
|---|---|---|---|---|
| | $P_2O_5$ | $Na_2O$ | $B_2O_3$ | $Al_2O_3$ |
| Borophosphate glass | 37.7 | 34.3 | 17.6 | 10.4 |

### 3.2. Benzyl alcohol and 1-phenylethanol oxidation evaluation

The oxidation of benzyl alcohol (primary alcohol) and 1-phenylethanol (secondary alcohol) to benzaldehyde and acetophenone, respectively, were carried out using acetonitrile as the solvent, NaClO as oxidant, and borophosphate glass (10 mol% $Al_2O_3$) as the catalyst. After the addition of NaOCl to the reaction, a biphasic organic-aqueous system was formed, and its role is properly discussed in section 3.2.1. The reaction conditions were optimized to determine the best alcohol conversion and aldehyde selectivity.

Sodium hypochlorite was added to the reaction at 20 °C [31] varying its amount between 1.6 mmol (1 mL) and 6.4 mmol (4 mL). Fig. 3 shows the effect of oxidant over alcohol oxidation. When added 1.6 and 3.2 mmol (oxidant: alcohol molar ratio 2.1:1 and 4.2:1, respectively) in both reactions, BnOH (Fig. 3(a)) and BnEtOH (Fig. 3(b)) achieved a constant conversion, indicating that the oxidant is the limiting reactant. Increasing the NaClO amount to 4.8 and 6.4 mmol (oxidant: alcohol molar ratio 6.4:1 and 8.5:1, respectively), the conversions rise for both reactions. Applying 6.4 mmol (4 mL) of NaClO, BnOH conversion after 10 h of reaction was 58.0 mol% (Fig. 3(a))) and BnEtOH conversion was 70.4 mol% (Fig. 3(b)). Thus, 6.4 mmol of NaClO was set as the standard amount for further reactions.

The reaction using NaOCl as oxidant tends to be strongly affected by temperature, and the addition of this compound leads to an exothermic process, requiring, in some cases, the reactions to be carried out in ice baths or under mild temperatures [21,22,45]. For instance, Mombarg et al. [46] have reported that 2,3-butanediol oxidation by NaClO catalyzed by $NiSO_4 \cdot 6H_2O$ was slow in temperatures above 20 °C, whereas an exothermic reaction occurs at 30 °C. However, the formation of the organic-aqueous biphasic system allows us to investigate the effect of ambient to 50 °C over the alcohol conversion. In this sense, Fig. 4 shows the effect of temperature on BnOH and BnEtOH oxidation at 20, 30, and 50 °C. The increase of the temperature from 20 to 30 and 50 °C provides higher conversions. At 50 °C, the maximum conversion of BnOH (77.2 mol%, Fig. 4 (a)) and BnEtOH (75.7 mol%, Fig. 4 (b)) were achieved after 5 h. Thus, the temperature rise to 50 °C allows a reduction of reaction time by half without loss in alcohol conversion.

Fig. 5 shows the effect of catalyst mass on the reaction, where the glass catalyst plays a fundamental role mainly in

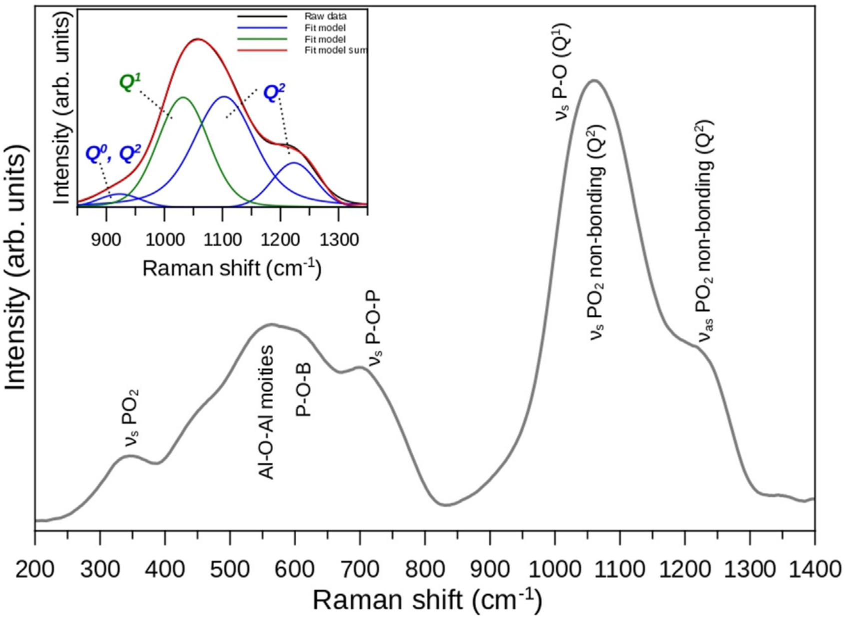


**Fig. 1 – Raman spectrum of 10 mol% $Al_2O_3$ borophosphate glass-catalyst. The inset graph shows the deconvolution of 850–1350 cm$^{-1}$ region highlighting $Q^1$ and $Q^2$ phosphate groups.**

BnOH oxidation. Without the glass catalyst, conversions reached only 12.4 mol% for BnOH (Fig. 5(a)) and 0.6 mol% for BnEtOH (Fig. 5(b)). Nevertheless, for BnOH oxidation, the increase of glass mass from 25 mg to 75 mg results in conversions between 72.7 and 78.5 mol%. Additional mass, 100 mg, does not result in higher conversions. On the other hand, BnEtOH conversion showed to be more affected by glass-catalyst mass (Fig. 5(b)). The increase from 25 mg to 75 mg of glass-catalyst led to conversions between 56.2 and 80.3 mol%. For further mass increases (100–150 mg), the conversion levels are between 85 and 87 mol%. These low conversions achieved in uncatalyzed reactions indicate that the glass catalyst and the biphasic organic-aqueous system play an important role in the process, even being NaOCl readily active in the oxidation of primary and secondary alcohols in other reports [5,21,22,45].

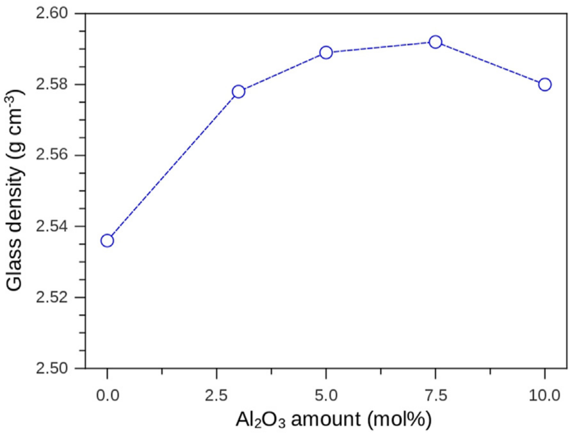
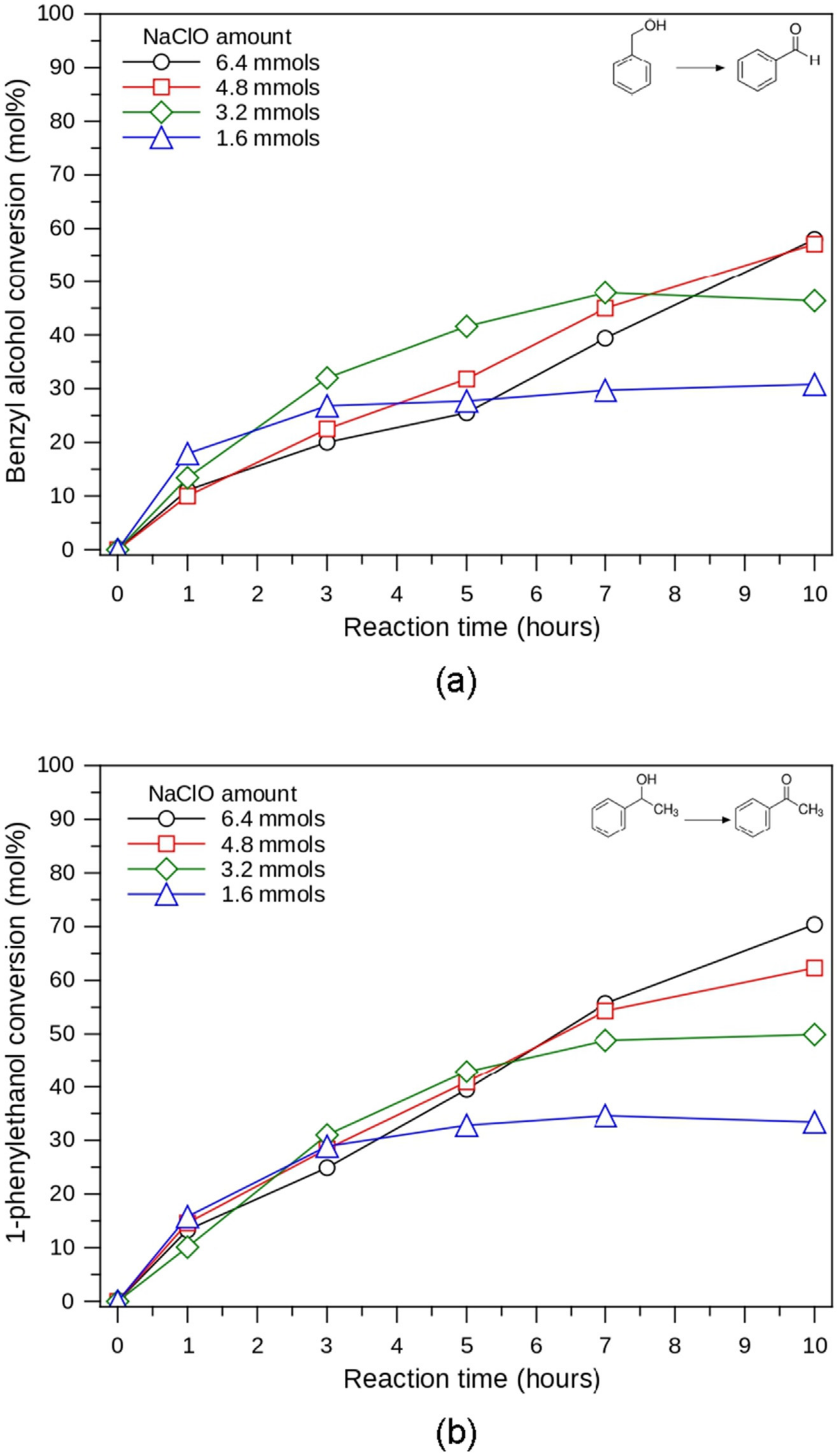


**Fig. 2 – Glass density for borophosphate glass series doped with a crescent amount of $Al_2O_3$ (0–10 mol%).**

At least, the glass-catalyst particle size effect in the reaction was evaluated. The previous evaluations for oxidant, temperature, and catalyst mass were carried out with glass particle sizes between 325 and 400 (Tyler) (44–37 μm). As a general trend, the reduction of particle size of the catalyst or the use of nanocatalysts tends to increase the surface area and, consequently, the conversion [38,47,48]. So, the glass catalyst sieved with a lower Tyler scale (higher glass particle, 150–325 mesh range) results in reduced yields (67–72 mol% for benzyl alcohol and 68–70 mol% for 1-phenylethanol), whereas higher Tyler sieves (325–400 and <400 mesh) rise the conversion, Fig. 6. However, the lowest particle glass catalyst (<400 mesh) shows an opposite behavior with a reduced conversion (72.3 mol% for benzyl alcohol and 77.1 mol% for 1-phenylethanol) in relation to the 400–325 range (higher glass particle size, 78.2 mol% for benzyl alcohol and 85.6 mol% for 1-phenylethanol) due to its agglomeration and adhesion to the reaction vessel.

### 3.2.1. *Proposed mechanism*

The “salting-out” [49] or “sugaring-out” [50,51] is a well-established analytical procedure used to extract organic solutes from water [49], allowing its quantitative analysis [52]. The process is characterized by the formation of a biphasic organic-aqueous system when a salt is added to a water-acetonitrile mixture, for instance. Thus, the addition of aqueous NaClO 1.6 mmol mL$^{-1}$ to acetonitrile results in a biphasic organic-aqueous system [31]. The catalyzed reaction proceeds in the aqueous phase and the oxidized products are transferred to the organic phase. At the end of the procedure, the reaction system was centrifuged to separate the organic from the aqueous phase and to determine the concentration of the reactants and products, Table 3. Benzyl alcohol and benzaldehyde are present mainly in the organic phase, whereas benzoic acid was only observed in the aqueous phase



(a)

(b)

**Fig. 3 – Effect of NaClO amount on benzyl alcohol (a) and 1-phenylethanol (b) oxidation catalyzed by borophosphate glass. Reaction temperature: 20 °C, catalyst amount: 100 mg, *catalyst mesh 325–400*, under stirring.**

in a small amount. The maximum percentage of BnOH mmols present in the aqueous phase related to the organic phase was 1.3%, whilst for BnCHO it was 0.5%. The same pattern occurs with BnEtOH and BnCOCH, where the maximum percentage of BnEtOH mmols present in the aqueous phase was 0.5% related to the organic phase, whilst for BnCOCH it was 0.2%.

Acetophenone is the only expected product of 1-phenylethanol oxidation (secondary alcohol), whilst two products can be obtained by benzyl alcohol oxidation—benzaldehyde and benzoic acid. Benzaldehyde is one of the most important aromatic molecules applied in the cosmetic, perfumery, food, and pharmaceutical industries [8]. Thus, the development of selective routes for aldehyde

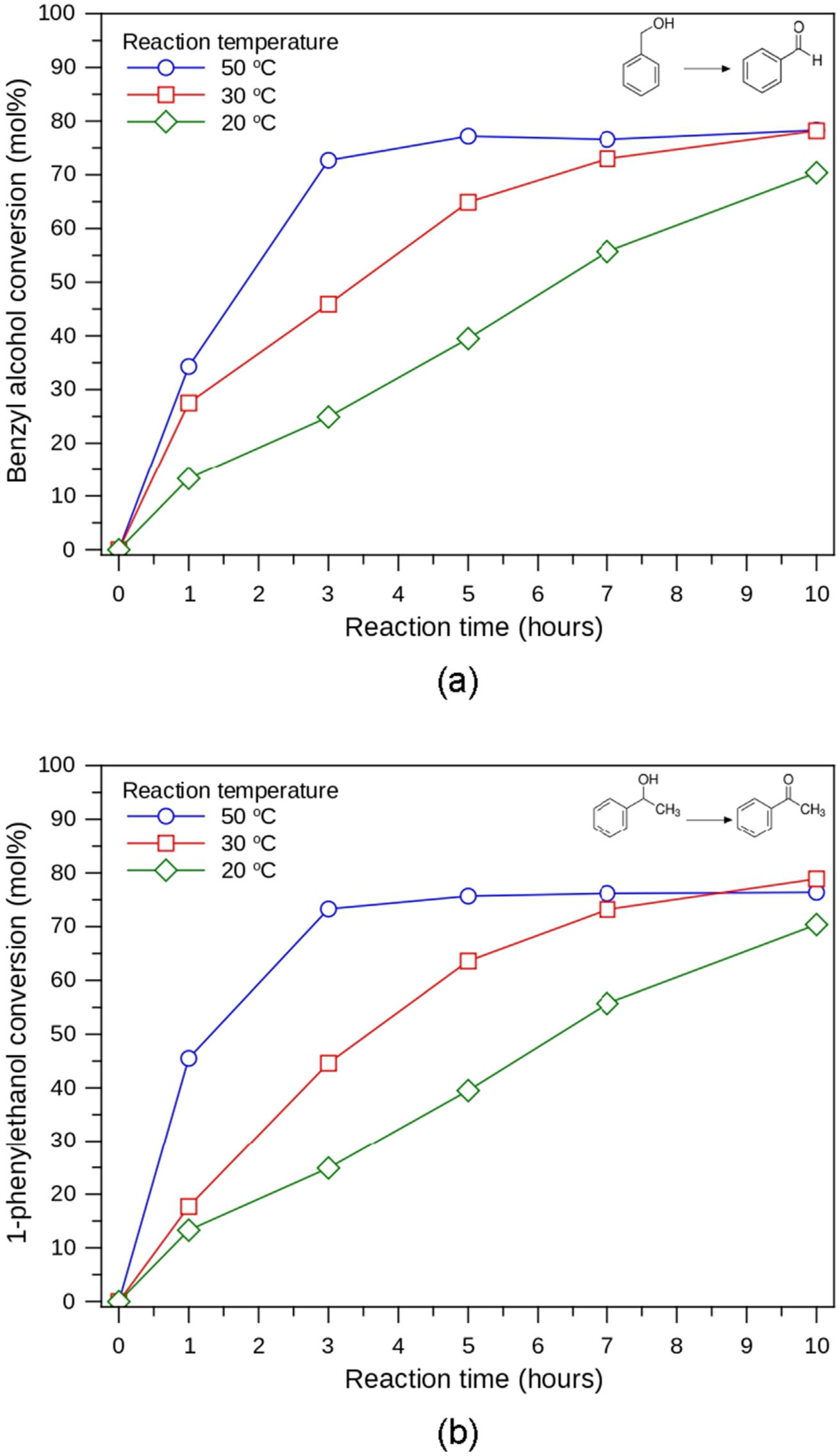


**Fig. 4 – Effect of temperature on benzyl alcohol (a) and 1-phenylethanol (b) glass-catalyzed oxidation by NaClO. Oxidant: 6.4 mmol, catalyst mass: 100 mg, catalyst mesh: 325–400, under stirring.**

synthesis using low-cost and greener reagents is highly desirable. The biphasic system enables a high selectivity for benzaldehyde under a wide range of experimental conditions (Table 4). The catalytic reaction proceeds in the organic phase, and the benzaldehyde is transferred to the organic phase avoiding further oxidation by sodium hypochlorite, a strong oxidant.

Grill and co-workers [5] used commercial bleach (≈5% aqueous sodium hypochlorite) and a nickel salt to convert benzyl alcohol directly to benzoic acid achieving 89% yield, with or without an organic solvent (dichloromethane). On the other hand, the oxidation of 1-phenylethanol reached only 33% after 4 h of reaction using dichloromethane as solvent. Mirafzal and Lozeva [53], using ethyl acetate as the solvent,

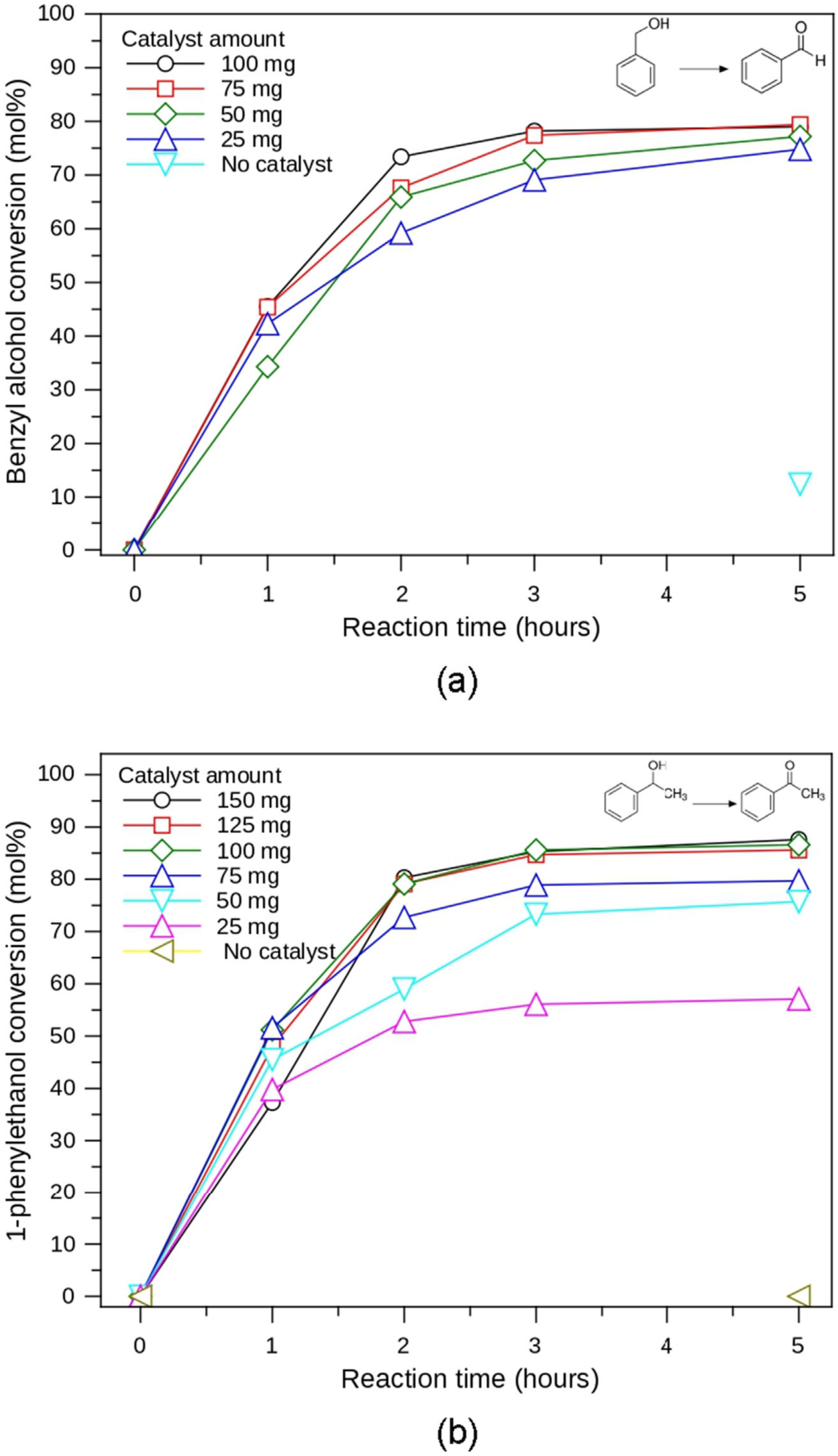


**Fig. 5 – Effect of catalyst mass on benzyl alcohol (a) and 1-phenylethanol (b) oxidation by NaClO. Reaction temperature: 50 °C, oxidant: 6.4 mmol, catalyst mesh: 325–400, under stirring.**

achieved a 93% yield for the aldehyde when tetrabutylammonium bromide was applied as a phase transfer catalyst (PTC) to improve benzaldehyde selectivity. The authors concluded that in the absence of the quaternary ammonium salt, little or no reaction was evident. Okada et al. [54] have used $NaOCl \cdot 5H_2O$ crystals as the oxidant to convert benzyl alcohol to benzaldehyde with a 99% yield. However, the reaction was performed in dichloromethane using 1 mol% TEMPO and 5 mol% $Bu_4NHSO_4$. Similar results were also obtained by Abramovici et al. [55], and Lee et al. [56,57] using sodium hypochlorite as oxidant, a water-immiscible solvent, and a phase transfer catalyst (PTC); Vitaku and Christie [26]

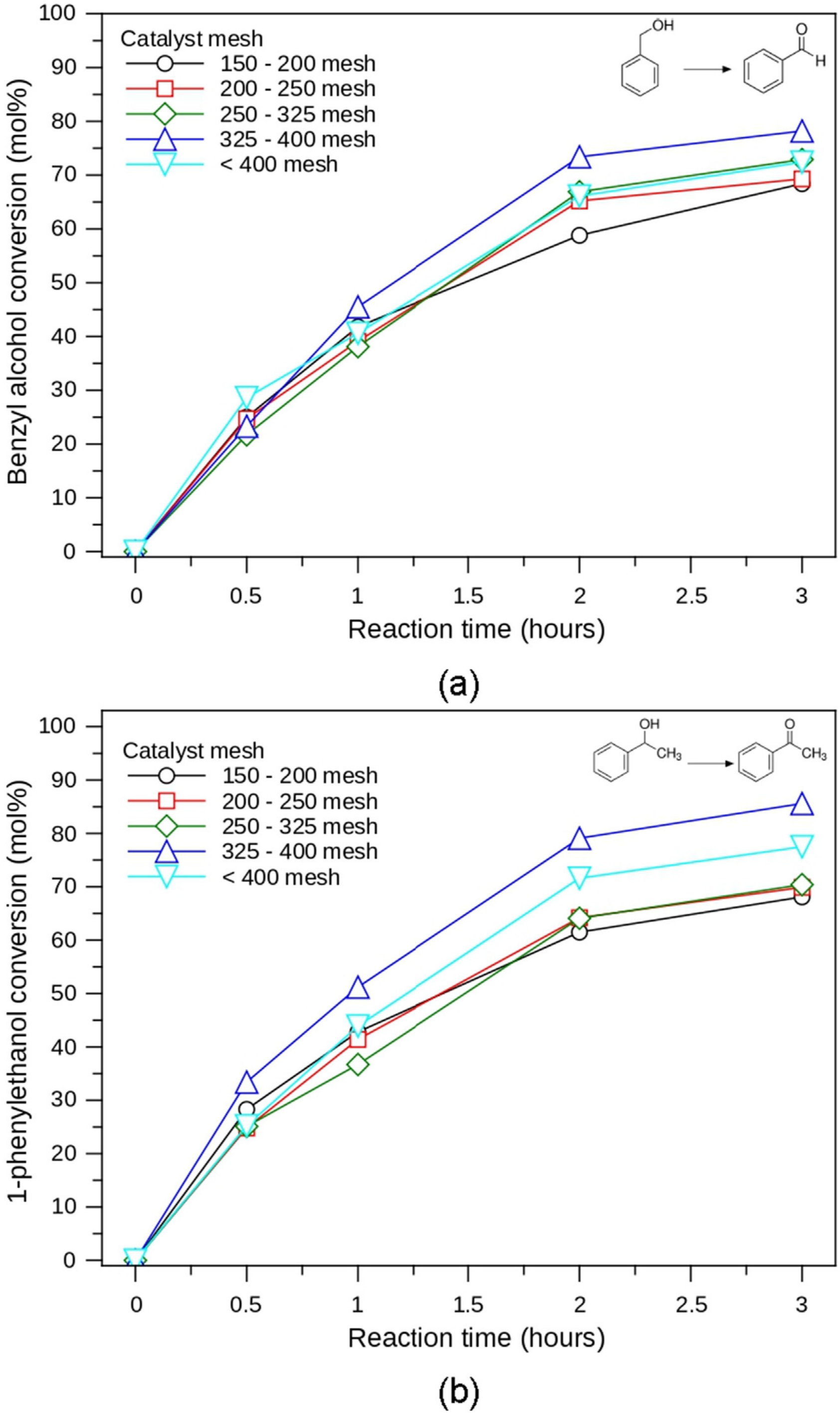


**Fig. 6 – Effect of catalyst particle size on benzyl alcohol (a) and 1-phenylethanol (b) oxidation by NaClO. Reaction temperature: 50 °C, catalyst mass: 75 mg for BnOH, 100 mg for BnEtOH, oxidant: 6.4 mmol, under stirring.**

used bleach as oxidant, ethyl acetate as the solvent, and $NaHSO_4$ as an acid source, and Fukuda et al. [45] using NaOCl with an imide compound-nitroxyl radical catalyst system.

Fig. 7 shows the proposed process for benzyl alcohol and 1-phenylethanol oxidation by NaOCl using the borophosphate glass as the catalyst. Based on the compound distribution in the organic and aqueous phases (Table 3), the pathway for the catalytic process is composed of six steps. First, benzyl alcohol or 1-phenylethanol dissolves in acetonitrile (1). After the oxidant (NaClO) addition and the formation of the biphasic system, a small amount of alcohol is transferred to the aqueous phase (2). During the reaction, the glass catalyst is dispersed in the aqueous phase where BnOH (3) and BnEtOH (5) oxidation occurs. The products are transferred back to the organic phase (6). As a consequence of a small solubility of benzaldehyde in the aqueous phase,

**Table 3 – Concentrations of the BnOH, BnCHO, BnCOOH, BnEtOH and BnCOCH mmols, at the end of reaction, in the organic (O) and aqueous (A) phases, determined by HPLC. Values between () represent the percentage of compounds in the aqueous phase related to the organic phase after centrifugation (3400 rpm, 6 min).**

| Test* | *phases* | BnOH | BnCHO | BnCOOH | BnEtOH | BnCOCH |
|---|---|---|---|---|---|---|
| | | mmols (x $10^{-3}$) | | | | |
| I | O | 186.3 | 531.1 | N.D.[a] | 181.5 | 448·9 |
| | A | 2.3 | 2.1 | 33.9 | 0.8 | 1.0 |
| | O/A | (1.3%) | (0.4%) | – | (0.4%) | (0.2%) |
| II | O | 180.8 | 612.1 | N.D.[a] | 105.7 | 597·3 |
| | A | 2.2 | 2.8 | 29.7 | 0.5 | 1.6 |
| | O/A | (1.2%) | (0.5%) | – | (0.5%) | (0.3%) |
| III | O | 173.3 | 615.6 | N.D.[a] | 103.6 | 575.5 |
| | A | 2.0 | 2.5 | 27.6 | 0.5 | 1.4 |
| | O/A | (1.1%) | (0.4%) | – | (0.5%) | (0.2%) |

* I: Temperature test, 50 °C (Fig. 4).
* II: Mass catalyst test, 75–100 mg (Fig. 5).
* III: Catalyst mesh, 325–400 mesh (Fig. 6).
[a] N.D. = no determined (below HPLC quantification limit).

benzoic acid is formed only as a by-product of benzaldehyde oxidation by NaOCl (4).

To test the proposed mechanism, considering that benzaldehyde is more reactive (it undergoes autoxidation under exposure to air at room temperature) [9] and susceptible to oxidation than benzyl alcohol [1] (that is considered an intermediary on benzyl alcohol oxidation by NaOCl to benzoic acid) [5], the BnCHO susceptibility to oxidation was evaluated applying the standard reaction conditions described in Fig. 8. Initially, benzaldehyde is dissolved in acetonitrile (1). After the addition of NaOCl and the formation of the biphasic system, a small amount of BnCHO is transferred to the aqueous phase (2). where its oxidation to benzoic acid took place (3). Even being more reactive than BnOH, BnCHO conversion achieved only 24.4 mol%. At the end of the reaction, the medium was centrifuged, and compound distribution was determined in both phases (values % described in Fig. 8). Benzaldehyde is present mainly in the organic phase, whereas 0.5% ($3.27 \times 10^{-3}$ mmol) is present in the aqueous phase. The concentration of benzoic acid in the organic phase is 17.4% ($2.68 \times 10^{-2}$ mmol), whereas 82.6% ($1.28 \times 10^{-1}$ mmol) of benzoic acid is present in the aqueous phase.

**Table 4 – Benzyl alcohol (BnOH) conversion and benzaldehyde (BnCHO) selectivity according to the test, determined by HPLC. Benzaldehyde selectivity was calculated after centrifugation and phase separation. Only traces (below HPLC quantification limit) of benzoic acid (BnCOOH) were present in the organic phase.**

| Experimental | | Conversion | Selectivity |
|---|---|---|---|
| | | BnOH (mol%) | BnCHO (%) |
| Temperature (°C) | 20 | 58.6 | 98.9 |
| | 30 | 78.2 | 97.5 |
| | 50 | 78.3 | 94.0 |
| Catalyst amount (mg) | 25 | 74.8 | 95.0 |
| | 75 | 79.4 | 95.3 |
| | 100 | 79.0 | 95.7 |
| Granulometry (mesh) | <400 | 72.4 | 97.3 |
| | 325–250 | 72.9 | 96.8 |
| | 250–200 | 69.3 | 97.3 |
| | 200–150 | 68.4 | 97.1 |

In this sense, whilst the solubility of BnOH in water is 40 g $L^{-1}$ (25 °C) [7], the solubility of BnCHO is 4 g $L^{-1}$ (20 °C). Thus, the BnOH is transferred to the aqueous phase to react with $^{-}$OCl, and the BnCHO, once formed, is transferred to the organic phase (ACN), avoiding further oxidation by $^{-}$OCl, which results in high selectivity. Following the same pattern, the water solubility of 1-phenylethanol and acetophenone at 25 °C is 1.95 g $L^{-1}$ and 6.1 g $L^{-1}$, respectively [58]. Therefore, we can infer that even with ketone being more water-soluble than the secondary alcohol, the reaction occurred with satisfactory yields, and acetophenone is transferred to ACN once formed, Table 3.

The application of sodium hypochlorite as the oxidant for aldehydes/alcohols/amines conversion using phase transfer catalysis (PTC) is performed with a water-insoluble solvent (usually a chlorinated solvent) [53,55,56,59] and a quaternary ammonium salt, whose function is transporting $^{-}$OCl to the organic phase [56]. In these cases, the oxidation mostly occurs in the organic phase, whereas in the mechanism of Fig. 7 the reaction takes place in the aqueous phase without quaternary ammonium salt for phase transference. In our reaction condition, no trace of $^{-}$OCl was determined by iodometric titration (Supplementary Information Section 2) in the corresponding organic phase, supporting this statement.

The effectiveness of $^{-}$OCl in the reaction is pH-dependent, being less effective and slower whereas the pH increases from 8 to 13 [3,46,55,59]. At the same time, pH lower than 7 has the opposite trend due to the fast decomposition of the hypochlorite solution [55]. Borophosphate glass reduces the pH of the solution from ≈13 (the original pH of NaOCl) to ≈ 9. The pH decreasing enables the formation of HOCl and, consequently, the oxidation [3,45]. Catalytic reactions were evaluated without the glass catalyst adjusting the pH of NaOCl solution to 9.00 ± 0.05 with HCl and NaOH. Fig. 9 shows the conversions obtained by glass-catalyzed reactions and uncatalyzed reactions (without and with pH adjustment). The pH decrease of NaOCl solution from 13 to 9 increases the conversion from 0.6 mol% to 12.4 mol% to 50.5 mol% and 44.7 mol

% for BnEtOH and BnOH, respectively, whereas the glass-catalyzed reactions reach conversions of 87.0 mol% for BnEtOH and 78.5 mol% for BnOH.

The pH reduction of NaOCl solution in the glass-catalyst reactions occurred due to the controlled release of the catalyst during the reaction. The ICP-OES analysis (Supplementary Information, Table S2) demonstrated the presence of P in the aqueous phase, with values varying between 6 and 15 wt% depending on the test. The *in situ* release of phosphate groups reduces the pH and activates the oxidant, i.e. NaOCl. The $Al^{3+}$ ion released to the aqueous phase was negligible (maximum value 0.14 wt%). Furthermore, the role of phosphate-based glasses for catalytic purposes [32,35] is demonstrated by the ineffectiveness of four commercial silica-based glasses evaluated (Supplementary Materials Table S3 entry 1–4).

### 3.2.2. *Glass-catalyst recycling and additional tests*

To evaluate the efficacy of glass-catalyst recycling, the catalyst was recovered by centrifugation, cleaned, dried, and applied again as a catalyst for benzyl alcohol and 1-phenylethanol oxidation by NaOCl. Fig. 10 shows the glass-based catalyst performance after three cycles for both reactions.

The reuse of the glass-based catalyst can be accomplished without a significant decrease in the conversions, mainly between the first and the second cycle of reaction. The conversions reduce just 14.5% and 25.8% for BnOH and BnEtOH, respectively, in the third cycle. In this sense, even with a partial glass release during the process, the catalysis remains with high selectivity.

In addition to the glass-catalyst recycling, we have tested acetonitrile recovery by applying two daily common and simple laboratory procedures of solvent recovery—fractioned distillation and vacuum distillation. The recovered acetonitrile was applied as the solvent in a new cycle of BnOH and BnEtOH oxidation, Supplementary Information Table S5. The reaction where ACN recovered by fractioned distillation was used as solvent achieved good conversions after 3 h of reaction (57.6 mol% for BnOH and 58.8 mol% for BnEtOH). In addition, the acetonitrile recovered by fractioned distillation presented only traces (below the HPLC quantification limit) of both alcohols and the reaction products (Supplementary Information Table S4). These results demonstrated that not only the solvent can be easily recovered by a simple method and recycled in a new reaction cycle, but also the reaction products can be easily isolated from the solvent.

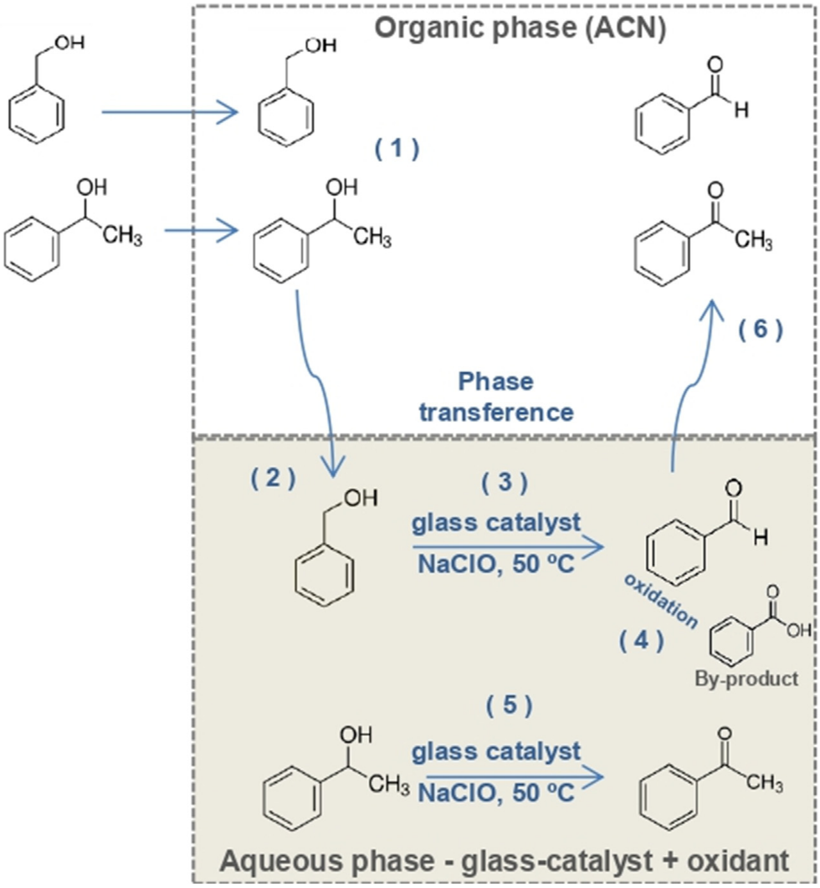


**Fig. 7 – Proposed mechanism of benzyl alcohol and 1-phenylethanol oxidation in a biphasic ACN–NaOCl system under standard conditions (10 mL ACN, 6.4 mmol NaClO, 0.75 mmol alcohols, glass-catalyst, 50 °C, under agitation). Initially, BnOH or BnEtOH are dissolved in acetonitrile (ACN) (1). With the addition of the oxidant and the formation of a biphasic system, fractions of BnOH are transferred to the aqueous phase (2). where it is oxidized to BnCHO (3). Only traces of BnCOOH are formed as a by-product (4). The same process occurs with BnEtOH (1, 2), which is oxidized to acetophenone (5). The lower water solubility of the formed BnCHO and BnCOCH may induce the diffusion of these species to the organic phase (6).**

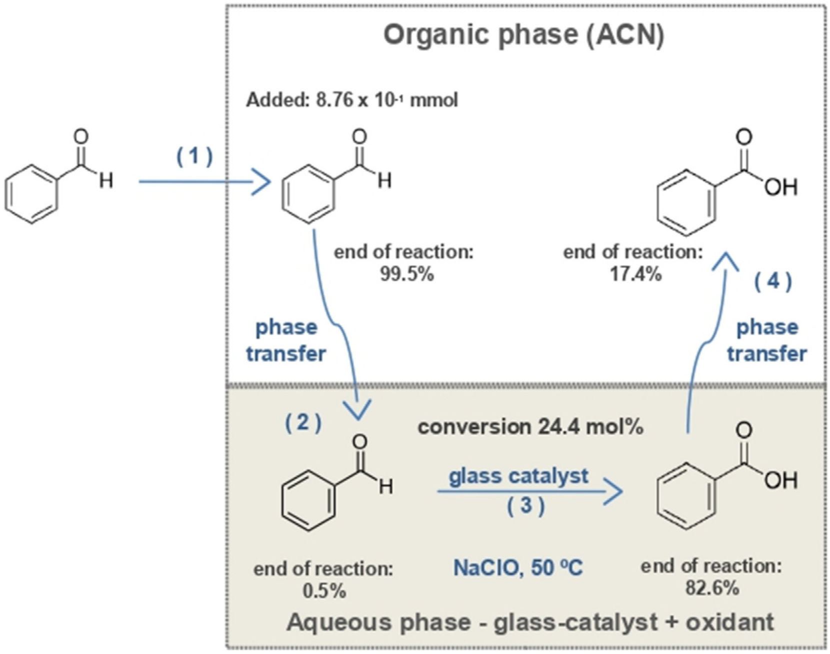


**Fig. 8 – Benzaldehyde oxidation applying standard conditions (10 mL ACN, 6.4 mmol NaClO, 0.75 mmol BnCHO, 75 mg glass-catalyst with 325–400 mesh range, 50 °C, 3 h under agitation). Following the proposed process, benzaldehyde is dissolved in ACN (1). After the addition of the oxidant and the formation of a biphasic system, fractions of BnCHO are transferred to the aqueous phase (2). where it is oxidized to BnCOOH (3). The low water solubility of BnCHO induces only 24.4 mol% of conversion. On the other hand, benzoic acid remains rather in the aqueous phase than in the organic phase (4).**

Besides the high benzaldehyde selectivity, relatively mild reaction conditions, and the possibility of catalyst and solvent recovery, our proposed reaction also allowed the simultaneous oxidation of benzyl alcohol and 1-phenylethanol, as can be seen in Supplementary Information Fig. S1. The oxidation of both alcohols was concomitant and allowed good conversions (BnEtOH 79.6 mol% and BnOH 71.2 mol%), in addition to exempting the need for isolated reactions if a mixture of aldehyde and ketone is required as the product.

Some common organic solvents were combined with NaOCl 11 wt% to investigate the salting-out formation: acetone, dimethyl sulfoxide (DMSO), and isopropyl alcohol do not form the biphasic system; on the other hand, it was formed with ethyl acetate and dimethyl carbonate (DMC).

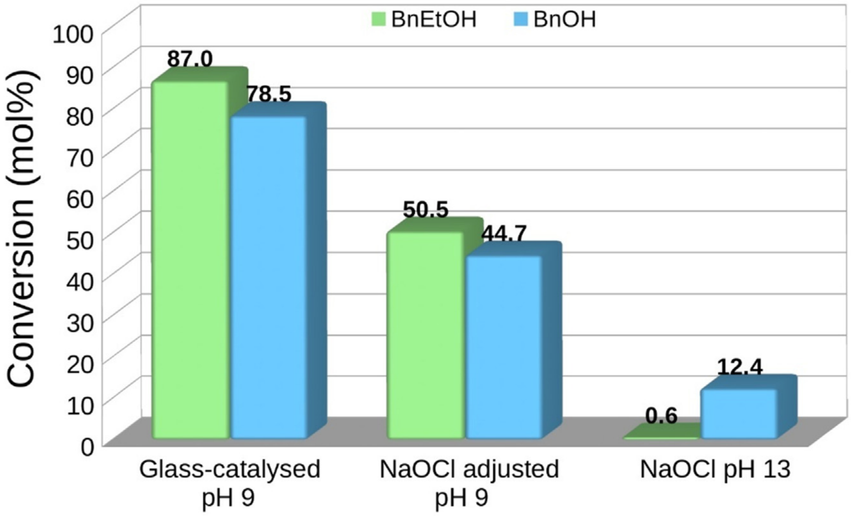


**Fig. 9 – Alcohol conversions obtained by glass-catalyzed reaction (resulting in NaOCl pH 9) and uncatalyzed reactions—NaOCl with unchanged pH 13 and adjusted pH 9. Reaction conditions: 10 mL ACN, 6.4 mmol NaClO, 0.75 mmol BnCHO, 100 mg of 325–400 mesh glass-catalyst (in glass-catalyzed reaction), 50 °C, 3 h under agitation.**

Based on this, ethyl acetate was tested as a solvent (see Supplementary Information Table S3 entries 5–6) instead of acetonitrile, but lower conversions were achieved for both alcohols—BnOH 28.8 mol% and BnEtOH 17.3 mol%—compared to reactions that have used ACN as solvent. The same trend was observed for DMC, resulting in similar conversions—BnOH 28.7 mol% and BnEtOH 13.8 mol% (see Supplementary Information Table S3 entry 7).

## 4. Conclusions

The depolymerization of phosphate chains with the addition of 10 mol% $Al_2O_3$ in borophosphate glass ($NaH_2PO_4$/$H_3BO_3$ ratio = 2) is associated with the formation of phosphate-aluminum structures that cross-link to each other, enhancing the glass-network strength, increasing the chemical resistance, and making this glass moisture resistant, which makes this material attractive for applications in various fields. In this sense, borophosphate glass effectively catalyzed benzyl alcohol and 1-phenylethanol oxidation by aqueous 11 wt% sodium hypochlorite using acetonitrile as a solvent, under mild conditions. The reaction conditions oxidant amount, temperature, mass, and particle size of the catalyst were screened to achieve high alcohol conversions (87.0 mol% for 1-phenylethanol and 79.4 mol% for benzyl alcohol) and benzaldehyde selectivity above 95%. The addition of NaOCl to the reaction results in a biphasic organic-aqueous system. HPLC analysis allowed us to infer that a small amount of the alcohol is transferred to the aqueous phase, where it is oxidized. Once formed, benzaldehyde and acetophenone are transferred back to the organic phase. The formation of the biphasic system prevents benzaldehyde oxidation, even employing a strong oxidant, and can be an interesting option for processes that look for intermediary compounds. Furthermore, the proposed biphasic system exempted the use of PTC. The ICP-OES analysis allowed us to infer that the catalytic activity of borophosphate glass occurs due to partial liberation of phosphate-based groups to the aqueous oxidant, reducing the pH of NaOCl from 13 to 9, which enables the formation of HOCl and, consequently, the oxidation. Based on this, the use of phosphate-based glasses as the catalyst is something unexplored and promising: it is easily and quickly produced with low-cost raw material, and its chemical properties can be modified according to the application required, i.e. control the dissolution during the reaction, it can be used as a host for several metal ions, and as an active material for supported nanoparticles applied in catalysis.

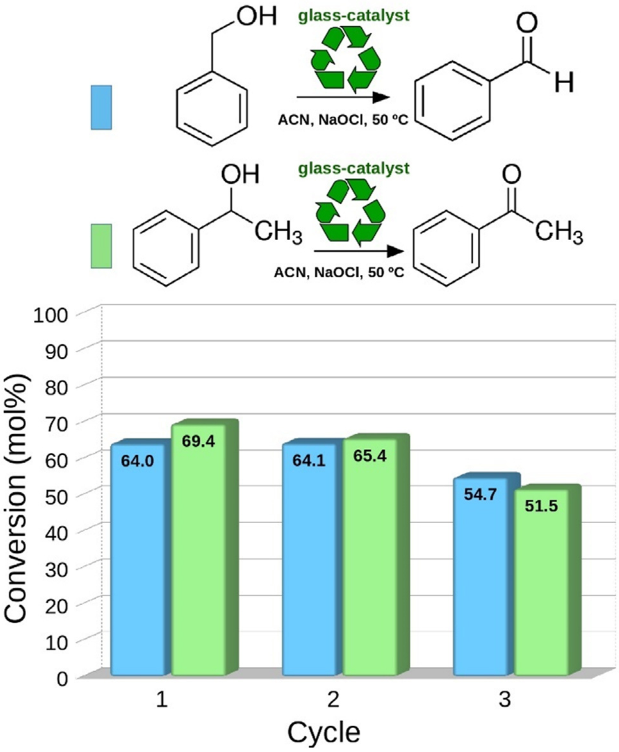


**Fig. 10 – Glass-catalyst recycling on benzyl alcohol and 1-phenylethanol oxidation by NaClO. Reaction conditions: 10 mL ACN, 0.75 mmols alcohol, 6.4 mmols NaOCl, 100 mg of 325–400 mesh catalyst for BnEtOH and 75 mg of 325–400 mesh for BnOH, 50 °C, 3 h under stirring.**

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmrt.2022.05.105.

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