



# Alcohol acetylation with acetic acid using borated zirconia as catalyst

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## ABSTRACT

The use of zirconium oxide doped with boron (borated zirconia) as catalyst in the acetylation of alcohols and phenol was studied. The catalysts were obtained by employing different preparation conditions, in order to observe the effect of the concentration of the precursor in the solution used to obtain the oxide, the concentration of the boron precursor, and the calcination temperature. All the solids showed amorphous characteristics and strong acidity. Boron addition increased the temperature range of the hydrated oxide stability, which depends on the boron concentration in the sample. Besides, the characterization by infrared spectroscopy showed an effect on the boron species present in the solid depending on the added concentration. The three preparation conditions under study affected the textural properties of the catalysts, as well as their acid strength. It was observed that in the acylation of alcohols using acetic acid as acylating agent and toluene as reaction solvent, at reflux temperature, the yield of acetylated product correlated with the acid strength of the catalysts, which depended on the preparation conditions. The best yield was achieved with a catalyst obtained using a high solution concentration of the oxide precursor (0.56 mmol Zr/cm<sup>3</sup>), an intermediate boron concentration (15 g B<sub>2</sub>O<sub>3</sub>/100 g support) and a relatively low calcination temperature (320 °C).

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## 1. Introduction

The research about processes for functional group protection is one of the most important fields in synthetic organic chemistry. The protection of functional groups is often necessary in several transformations along a synthetic sequence, particularly in the construction of polyfunctional molecules such as carbohydrates, steroids, nucleosides, and natural products [1].

The acylation of alcohols and phenols is one of the most frequently used transformations in organic synthesis as it provides an efficient and inexpensive means for protecting hydroxyl groups in a multistep synthetic process [2,3]. Among the various protecting groups used for the hydroxyl function, the acetyl group is the most convenient in view of its easy introduction, being stable to the acidic reaction conditions and also easily removable by mild alkaline hydrolysis [4].

The –OH group acetylation provides an efficient route for the synthesis of compounds with industrial value, for the production of medicines, flavors, fragrances, solvents, food preservatives, plasticizers, and cosmetics, among others [5]. The most common and inexpensive reagent used to perform the acetylation is the acetic anhydride, an activated derivative of the acetic acid, in the

homogeneous phase and in the presence of bases, such as tertiary amines [6,7], pyridine [1], 4-(dimethylamino)pyridine (DMAP) [8], 4-pyrrolidinopyridine (PPY) [9], tetramethylethylenediamine [10], and tributylphosphine [11].

Besides, protic or Lewis acids are known to catalyze this transformation, such as *p*-toluene sulphonic acid [12], ZnCl<sub>2</sub> [13], CoCl<sub>2</sub> [14], RuCl<sub>3</sub> [15], TaCl<sub>5</sub> [16], and metal triflates such as Sc(OTf)<sub>3</sub> [17], In(OTf)<sub>3</sub> [18], and Cu(OTf)<sub>2</sub> [19].

However, many of these methods have some drawbacks such as low yields, long reaction time, harsh reaction conditions, use of hazardous or expensive materials and not readily available reagents [15]. The use of homogeneous catalysts has several serious problems, such as difficulty in the separation and recovery of the catalyst, disposal of the spent catalyst, and corrosion problems [20]. The development of easily separable and reusable solid catalysts having high activity for the acetylation reaction is, therefore, of great practical importance. Recently, the use of acidic solid catalysts such as HY zeolite [21], montmorillonite K10 or KSF clay [22], and heteropolyacids [23], for the acetylation of alcohols or phenol by acetic anhydride, has been reported.

From the environmental point of view, a much convenient method for performing the acetylation reaction is the use of acetic acid as acylating agent, because only water is produced as by-product. Another advantage is the relatively cheaper route for industrial purposes when compared to the use of anhydrides or acid chlorides [24]. The catalysts employed in the acylation of alcohols or phenols with acetic acid include mineral acids [25], anhydrous

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**Scheme 1.** Alcohol acylation with acetic acid.

sulfate and catalytic amounts of sulfuric acid [26], titanium and tin salts [27], aluminum phosphate/molecular sieves [28], sulfated zirconia [29], ion exchange resins [30], Amberlyst-15 [29], and Lewis acids [31], among others.

On the other hand, the system formed by zirconium oxide doped with boron is a solid with acid characteristics that is employed in some organic reactions, such as the Beckmann rearrangement of cyclohexanone oxime [32], anisole benzylation [33], the transesterification of  $\beta$ -ketoesters [34], and the C-methylation of phenol with methanol [35].

In the present paper, the use of borated zirconia, obtained by varying preparation conditions (precursor concentration used for the oxide synthesis, boron precursor concentration, and calcination temperature), as catalyst in the alcohol acetylation reaction is studied. The yield obtained using acetic acid as acylating agent, toluene as reaction solvent, and reflux temperature (Scheme 1) is correlated with the properties of the materials used as catalyst.

## 2. Experimental

### 2.1. Materials

Commercial reagents and solvents were purchased from Aldrich and used without further purification.

### 2.2. Catalyst preparation

The supports were prepared from aqueous solutions of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  with a concentration of 0.06 and 0.56 mmoles  $\text{Zr}/\text{cm}^3$ , to which a 30%  $\text{NH}_4\text{OH}$  solution was added dropwise until a final pH of 10. The obtained products were aged for 72 h and filtered in vacuum. They were then washed with distilled water up to chloride elimination and dried at room temperature, giving the S2 and S4 materials, respectively. These solids were impregnated with aqueous solutions of  $\text{H}_3\text{BO}_3$  with 0.05, 0.3 or 0.7 mmoles  $\text{B}/\text{cm}^3$  concentration, in order to obtain boron concentrations in the solid of 2.5, 15 or 35, expressed as g  $\text{B}_2\text{O}_3/100$  g support. Then, the suspension was evaporated till dryness on a flat plate at low temperature. Afterward, the solids were calcined under  $\text{N}_2$  atmosphere at 320 °C for 5 h. The samples thus obtained will be named SXBY, where X is the number identifying the support and Y is the boron concentration. A portion of the S4B35 sample was also calcined at 500 and 750 °C.

### 2.3. Catalyst characterization

The specific surface area of the samples was estimated by the BET method from the nitrogen adsorption–desorption isotherms at  $-196$  °C, performed using Micromeritics equipment, model ASAP 2020, previously degassed at 100 °C for 1 h. The X-ray diffraction (XRD) patterns were obtained with Philips PW-1417 equipment, using  $\text{Cu K}\alpha$  radiation and Ni filter, 20 mA and 40 kV in the high tension source and a scanning rate of 1° per min. To obtain the infrared (FT-IR) spectra, Bruker IFS 66 equipment and pellets of the sample in KBr were used. The measurements were performed in the 400–4000  $\text{cm}^{-1}$  range. Differential thermal analysis (DTA) was carried out using Shimadzu DT 50 equipment, in argon atmosphere, with a sample weight of 25 mg, at a heating rate of 10 °C per min. For the potentiometric titration, 0.05 g of solid was suspended in

45  $\text{cm}^3$  of acetonitrile. The suspension was stirred for 3 h, and then titrated with a 0.05 N solution of n-butylamine in acetonitrile. The potential variation was measured with a Hanna 211 pHmeter, and a double-junction electrode.

### 2.4. Acetylation reaction

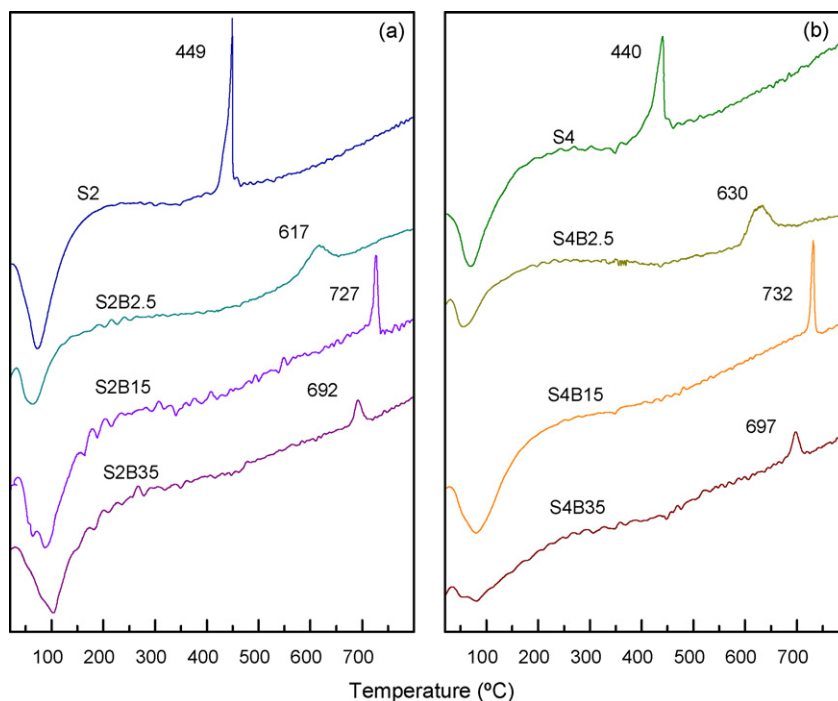
The reaction was carried out in a batch glass reactor equipped with a condenser. A mixture of alcohol (1 mmol), acetic acid (5 mmol), toluene (5  $\text{cm}^3$ ) and catalyst (100 mg) was magnetically stirred at 110 °C up to a final reaction time of 14 h. Then, the catalyst was separated by filtration and washed twice with a small quantity of toluene (1  $\text{cm}^3$ ). The progress of the reaction was monitored by silica gel thin layer chromatography. The organic solution was washed twice with 5%  $\text{NaHCO}_3$  solution (3  $\text{cm}^3$ ), with water (3  $\text{cm}^3$ ), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solution was then concentrated under vacuum, and the residue was purified by column chromatography using silica gel 230–400 mesh as the stationary phase and a mixture of n-hexane and ethyl acetate as the elution solvent. The isolated products were characterized by spectral studies ( $^1\text{H}$  and  $^{13}\text{C}$  NMR). The spectra were compared with those of standard esters. The yield was calculated as mmol of purified product with respect to mmol of initial alcohol.

## 3. Results and discussion

### 3.1. Catalyst characterization

The samples presented an endothermic peak with a maximum at 70–100 °C and an exothermic peak in the 690–730 °C range in the DTA diagrams. The first peak can be assigned to loss of physisorbed water, and the second peak corresponds to the transformation of the amorphous hydrated oxide into a crystalline phase. Zirconium oxide has three crystalline modifications – monoclinic, tetragonal and cubic –, the first one being stable up to 1200 °C. A metastable tetragonal phase can also exist up to 650 °C, whose occurrence has been interpreted as an effect of impurities or crystallite size [36]. The exothermic peak of all the samples appeared at a higher temperature than in the diagrams of the corresponding supports, as is shown in Fig. 1. The presence of boron preserved the hydrated oxide particles, increasing their thermal stability. A similar behavior was reported for samples of Mo or Cu oxides on zirconia [37], for zirconia doped with Ni or Al [38], or for zirconia with addition of sulfate or chromium ions [36], and the stability increase was attributed to the inhibiting effect on zirconia crystallization induced by the good dispersion of this type of additives.

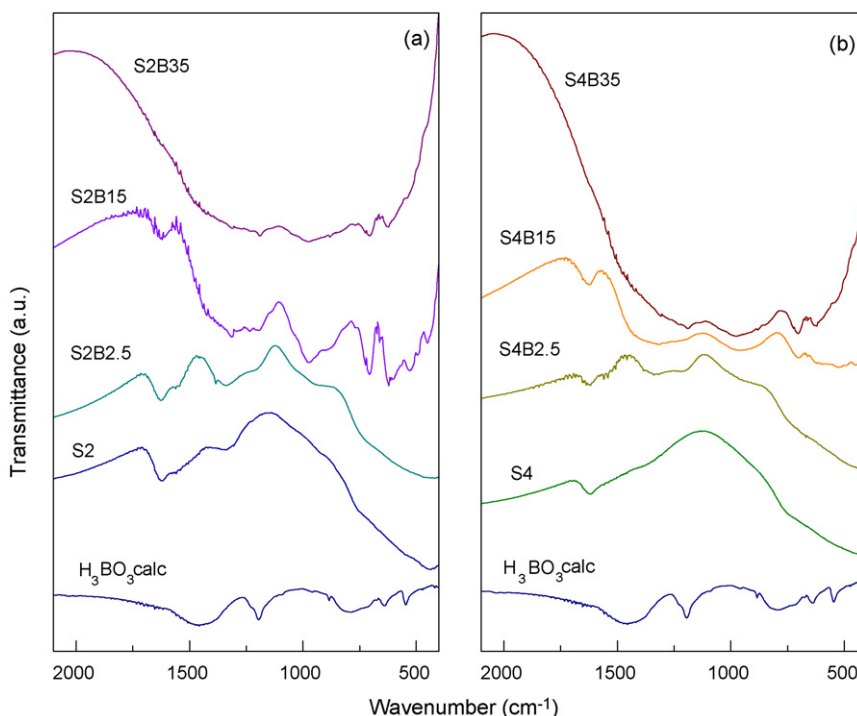
The temperature shift of the peak maximum increased for the samples with 15 g  $\text{B}_2\text{O}_3/100$  g support compared to that of the samples with 2.5 g  $\text{B}_2\text{O}_3/100$  g support, and then it slightly decreased for the samples with the higher boron contents. Boron interacting with the support induces the stability increase. Through adsorption isotherms of boric acid solutions on the support, the amount of boron interacting and not interacting with the support can be estimated. The amount of boron adsorbed on the support increases in the concentration range of boric acid solutions used to prepare the catalysts. Nevertheless, the adsorption of boric acid solutions on a support is a complex subject, especially in an extended range of solution concentration. Boric acid exists as monomer ( $\text{B}(\text{OH})_4^-$ ) in solution at low concentration, but at high concentration, poly-borate species ( $\text{B}_3\text{O}_3(\text{OH})_4^-$ , and also  $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$  or  $\text{B}_5\text{O}_6(\text{OH})_4^-$ ) are produced [39]. So, the number of adsorption sites covered may not be higher even if a higher interacting boron concentration is estimated, if a different poly-borate species is adsorbed. This fact may be the responsible of the slight decrease in the temperature of the peak position in the samples with higher boron contents.



**Fig. 1.** DTA diagrams of the borated zirconia catalysts obtained from S2 support (a) and S4 support (b).

The X-ray diffraction patterns of the catalysts calcined at 320 °C were equal to those of the respective supports. The materials have amorphous characteristics, showing a wide band centered at  $2\theta$  value of 30° in the patterns. No line indicating the presence of crystalline phases was observed. It is worth pointing out that the calcination of bulk boric acid up to 320 °C showed a boric oxide pattern by XRD; nevertheless, this oxide was not detected in the samples by this technique. This fact may be attributed to a good dispersion on the support as a noncrystalline phase or to the presence of crystallites small enough to

give diffraction lines. On the other hand, the S4B35 sample showed an amorphous nature when calcined at 500 °C, in agreement with the findings reported by Malshe et al. [35] for a sample with 30 mol%  $B_2O_3$ . However, when the solid was thermally treated at 750 °C, a temperature above that of the exothermal peak observed by DTA, the pattern presented lines mainly corresponding to the monoclinic phase of the zirconia, the most intense lines being placed at  $2\theta$  values of 28.2° and 31.5°, accompanied by a very small peak at  $2\theta$  value of 30.1° assigned to the tetragonal phase.



**Fig. 2.** FT-IR spectra of borated zirconia catalysts obtained from S2 support (a) and S4 support (b) and boric acid calcined at 320 °C.

The FT-IR spectra of the catalysts prepared from both supports presented similar behavior. They showed a wide band extended between 400 and 1700–2000  $\text{cm}^{-1}$  where, in turn, there are some wide bands and maxima. These complex spectra arise from the overlapping of bands corresponding to boron species and to the support. The spectra of the S2B2.5, S4B2.5, S2B15 and S4B15 samples presented bands with maxima at 1620 and 1320  $\text{cm}^{-1}$  (Fig. 2), assigned to bending vibrations of  $-(\text{H}-\text{O}-\text{H})-$  and  $-(\text{O}-\text{H}-\text{O})-$  bonds of the support.

The last band appears as a shoulder in the support spectrum, but in the catalysts it is a wide band extended between 1120 and 1550  $\text{cm}^{-1}$ , which could be attributed to tricoordinated boron bonded to the hydrated oxide structure, in a way similar to what has been reported for  $\text{TiO}_2$  doped with boron [40]. In addition, bands due to boron species were observed under 1100  $\text{cm}^{-1}$ , whose assignment is difficult because, though boron in tetrahedral coordination has strong absorption in such zone [41], the tricoordinated species also present bands in the same wavenumber range. In the S2B35 and S4B35 samples, it is not possible to visualize support bands, but two small peaks at 881 and 1190  $\text{cm}^{-1}$  were observed, a position that coincides with bands of boric acid calcined at 320 °C, whose spectrum is equal to that of a commercial  $\text{B}_2\text{O}_3$ . So, it can be assumed that small  $\text{B}_2\text{O}_3$  aggregates are present in the samples with high boron concentration, in addition to boron species interacting with the support.

The textural characteristics of the catalysts showed different behavior depending on the boron concentration. The specific surface area ( $S_{\text{BET}}$ ) and the pore volume ( $V_p$ ) decreased for the highest boron content (Table 1), while the mean pore size (MPS) did not vary. It can be assumed that boron dispersed on the surface of hydrated zirconium oxide separates the particles and inhibits their later growth, as has been reported by Zhao et al. [37] for Mo, W, Cu, Fe, and Ni oxides supported on zirconia. The S2B35 and S4B35 solids have a proportion of boron not interacting with the support, which inhibits particle growth to a lesser extent, and the boric oxide particles can block support pores, causing a detrimental effect both on  $S_{\text{BET}}$  and on  $V_p$ .

It has been reported that the initial electrode potential ( $E_i$ ) of the curves obtained by potentiometric titration with n-butylamine indicates the maximum strength of the acid sites that the titrated solid presents. Such strength can be classified according to the following scale:  $E_i > 100$  mV (very strong sites),  $0 < E_i < 100$  mV (strong sites),  $-100 < E_i < 0$  mV (weak sites), and  $E_i < -100$  mV (very weak sites) [42]. The behavior of the acid strength as a function of the boron concentration is similar for the samples obtained from both supports (Table 1). The samples with higher proportion of boron bonded to the structure of the hydrated oxide presented higher  $E_i$  (S2B15 and S4B15 samples), possibly due to a better dispersion. Boron on the surface of the support led to more acid solids than the parent support, since boron may increase the Lewis acidity of zirconium ions by an inductive effect, as proposed by Ravindra et al. [43] for boron on silica. In addition, Brønsted acid sites may be generated by the hydration of boron species. On the other hand, the higher  $E_i$  of the samples prepared from the S4 support can be

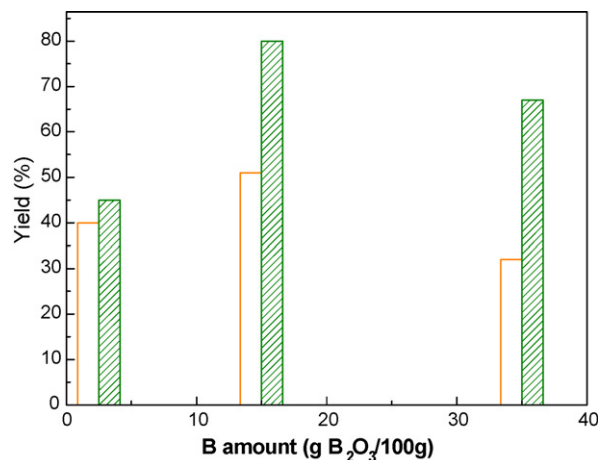


Fig. 3. Influence of the boron content of catalysts obtained using the S2 and S4 supports on the acetylation of 2-phenoxyethanol with acetic acid (solvent: toluene, reaction temperature and time: 110 °C, 14 h; catalyst mass: 100 mg).

related to the highest acid strength of the support, which in turn may be due to a lower hydroxylation degree of this material that has the lowest specific surface area. A higher amount of zirconium ions may be exposed on the surface, as was pointed out by Hadjiivanov and Lavalley [44], who have reported that some zirconium ion sites are blocked on the hydroxylated surface, and that the most acidic Lewis sites on oxide surfaces should be created at a higher dehydroxylation degree.

### 3.2. Catalytic activity in acetylation

The effect of the catalyst amount utilized in the acetylation reaction of 2-phenoxyethanol with acetic acid was studied by employing the S4B35 catalyst. The yields obtained when using 25, 50 and 100 mg of catalyst were 21, 39 and 67%, respectively. So, there was an increase in the catalytic activity when the catalyst amount increased. Although a constant yield of acetylated product was not achieved, it was decided not to increase the catalyst amount and to use 100 mg in the following runs, because this value is rather high for the samples with a higher boron content, i.e., 0.06 mmol B/mmol initial alcohol.

The experiments to observe the effect of boron concentration were firstly carried out with the borated zirconia samples prepared from the S4 support. The yield obtained in the acetylation of 2-phenoxyethanol with acetic acid is shown in Fig. 3. The values achieved were 45, 80 and 67% for the S4B2.5, S4B15 and S4B35 catalysts, respectively. So, the increase in the boron amount added to the support leads to an increase in the yield of acetylated product up to 15 g  $\text{B}_2\text{O}_3$ /100 g support, and then it decreases. The observed behavior is similar to that obtained for the acid strength of the samples, measured by potentiometric titration. It is worth pointing out that the yield obtained with commercial  $\text{B}_2\text{O}_3$  was low (5%), possibly due to the low surface area of the bulk compound ( $S_{\text{BET}} = 5 \text{ m}^2/\text{g}$ ).

Table 1  
Textural and acid properties of the catalysts.

Sample	ZrOCl <sub>2</sub> concentration (mmoles Zr/cm <sup>3</sup> )	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_p^a$ (cm <sup>3</sup> /g)	MPS <sup>b</sup> (nm)	$E_i$ (mV)
S2B2.5	0.06	200.1	0.10	2.3	184
S2B15	0.06	244.5	0.14	2.3	435
S2B35	0.06	92.1	0.05	2.2	415
S4B2.5	0.56	125.1	0.05	2.2	289
S4B15	0.56	185.1	0.10	2.1	522
S4B35	0.56	34.0	0.02	2.5	480

<sup>a</sup> Single point total pore volume at  $p/p_0 = 0.98$ .

<sup>b</sup> Mean pore size calculated by the BJH formula from the desorption branch.

The results obtained in similar tests carried out with catalysts prepared from the S2 support are also shown in Fig. 3. Similarly to the above-mentioned catalysts, an increase of boron from 2.5 up to 15 g B<sub>2</sub>O<sub>3</sub>/100 g support raised the acetylated product yield from 40 to 51%, which then decreased to 32% when the catalyst containing 35 g B<sub>2</sub>O<sub>3</sub>/100 g support was used.

The comparison between the results obtained with both series of catalysts allows us to observe the influence of the zirconium precursor concentration employed to prepare the supports. A higher yield was obtained with the catalysts obtained using the S4 support, in accordance with their higher acid strength. As mentioned above, this is related to the characteristics of the starting support, particularly a lower hydroxylation degree.

The acetylation reaction is considered to be catalyzed by Brønsted acid sites [45] or by Lewis acid sites (metal ions in low coordination) [46]. Other authors have reported that both the Brønsted and Lewis acid sites are responsible for catalyzing the acetylation reaction [47]. Due to the characteristics of the catalysts prepared here, they may present Brønsted and Lewis sites [34], so we assume that both types of sites synchronously affect the acetylation activity.

The reaction mechanism for the acetylation of alcohols with acetic acid could be described as a general Fischer esterification and has several steps:

- Adsorption of acetic acid on Brønsted and Lewis sites on the catalyst surface, forming a protonated acetic acid intermediate, increases the electrophilicity of carbonyl carbon.
- Carbonyl carbon is attacked by the nucleophilic oxygen atom of the alcohol leading to the formation of an oxonium ion.
- Proton transfer in the oxonium ion gives a new oxonium ion.
- Loss of water from the latter oxonium ion, and subsequent deprotonation leads to the ester, being regenerated the acid site on the catalyst surface.

The reuse of the catalyst is an important aspect of any industrial process. With this point in mind, the reusability of the S2B15 and

**Table 2**

Reuse of S2B15 and S4B15 catalysts in the acetylation of 2-phenoxyethanol with acetic acid<sup>a</sup>.

Catalyst	Catalytic cycle	Acetylated product yield (%)
S2B15	1st	51
S2B15	2nd	49
S2B15	3rd	49
S4B15	1st	80
S4B15	2nd	78
S4B15	3rd	78

<sup>a</sup> Solvent: toluene, reaction temperature and time: 110 °C, 14 h; catalyst mass: 100 mg.

**Table 3**

Influence of calcination temperature of the S4B35 catalyst on the acetylation of 2-phenoxyethanol with acetic acid<sup>a</sup>.

Entry	Calcination temperature (°C)	Acetylated product yield (%)
1	320	67
2	500	19
3	750	–

<sup>a</sup> Solvent: toluene, reaction temperature and time: 110 °C, 14 h; catalyst mass: 100 mg.

S4B15 catalysts was tested by carrying out repeated runs of the reaction, keeping the reactant molar ratio and temperature constant. After performing the reaction with the fresh catalyst and its separation by filtration, the catalyst was dried in a vacuum system at room temperature, and used in a next reaction cycle performed under the same previous conditions. It is evident that, after three cycles, both catalysts keep their activity, so they can be recycled and reused (Table 2).

When the 2-phenoxyethanol acetylation yields using the S4B35 catalyst and the same catalyst calcined at 500 °C are compared, a decrease in the catalytic activity was observed for the highest calcination temperature (Table 3). This fact may be possibly due to an increase in the size of the small B<sub>2</sub>O<sub>3</sub> aggregates present in this sample when the calcination temperature was increased. When

**Table 4**

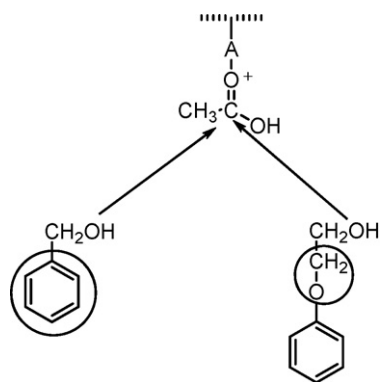
Acetylation of different alcohols and phenol using borated zirconia as catalyst<sup>a</sup>.

Entry	Alcohol	Product	Acetylated product yield (%)
1			67
2			69
3			25
4			35
5			10

S4B35 catalyst mass: 100 mg.

<sup>a</sup> Solvent: toluene, reaction temperature and time: 110 °C, 14 h.





Scheme 2. Steric effect in different alcohols.

calcined at 750 °C, no reaction was detected, which may be related to the structural change toward a crystalline phase of the zirconia inhibits boron interaction, and also a decrease in  $S_{\text{BET}}$  took place ( $11 \text{ m}^2/\text{g}$ ).

The same reaction conditions were used to observe the behavior of a sample of borated zirconia, calcined at 320 °C, as catalyst in the acetylation of other alcohols and phenol with acetic acid (Table 4). The reactivity of the primary alcohols 2-phenoxyethanol and 2-phenylethanol (entries 1 and 2) was higher compared to that of the benzylic alcohol and 4-methyl-benzylic alcohol (entries 3 and 4). They achieved a yield of acetylated product (67–69%), which was nearly twice that of the benzylic alcohols (25–35%).

The yield difference between primary and benzylic alcohols can be attributed to steric effects that considerably affect the acetylation rate considering a Fisher esterification mechanism [48]. The presence of bulky groups, not far from the reaction center, either in the alcohol or in the acid, slows down the esterification rate, as is indicated in Scheme 2 for two of the studied alcohols. The aim is to show that the most sterically hindered alcohols can lead to a lower yield.

The acetylation of a sterically hindered tertiary alcohol (triphenylmethanol) was also performed, in the same conditions as 2-phenoxyethanol reaction, and only traces of acetylated product were detected.

Similar differences in the behavior of primary and benzylic alcohols in the acetylation with acetic acid were reported by Mirkhani et al. [49], using a cerium polyoxometallate as catalyst.

On the other hand, the yield in the phenol acetylation (Table 4, entry 5) was still lower than that of benzylic alcohols, reaching a yield of 10%. This behavior can be attributed to its low nucleophilicity, due to the electronic delocalization by resonance in the benzene ring. An additional experiment with 4-nitrophenol, which is less nucleophilic due to the electron-withdrawing group  $\text{NO}_2$ , in identical conditions to phenol acetylation, only gave traces of the acetylated product.

In sum, the reactivity order toward acetylation with acetic acid with the studied catalysts was as follows: primary alcohols > benzylic alcohols > phenol.

It should be noted that in all the tests performed, the selectivity was high because after the isolation and purification by column, all the unreacted starting alcohol or phenol was practically recovered.

It is worth mentioning that in the acetylation of benzylic alcohol with acetic acid in ionic liquids with metallic triflates as catalyst, yields between 21 and 64% at 12 h of reaction have been reported [50]. Unlike the materials employed in the present work, the solvents and catalysts are expensive, and though in this case the reaction was carried out at low temperature, an activity decrease with the reuse using triflates as catalyst was observed. In addition, borated zirconia could be appropriate to the selective acetylation

in multifunctional organic compounds. Besides, alcohols could be acetylated in the presence of phenol, and even the acetylation of phenol with electron donor substituents could be selective in presence of phenols with electron-withdrawing groups.

#### 4. Conclusions

The behavior of borated zirconia, obtained using different preparation conditions, as catalyst in the acetylation reaction of alcohols and phenol with acetic acid was studied in the present work. The characteristics of the catalysts depend on the preparation conditions used, which were finally shown in the acid strength of the materials.

A good agreement between the results obtained in the acetylation of 2-phenoxyethanol and the catalyst acidity was observed. The most appropriate catalyst was borated zirconia calcined at 320 °C containing 15 g  $\text{B}_2\text{O}_3/100 \text{ g}$  of a support obtained using a high concentration of  $\text{ZrOCl}_2$  precursor in the starting solution, achieving a yield of 80% in acetylated product in 14 h under reaction. Besides, the catalysts kept their activity after three catalytic cycles. Though the yield was lower for benzylic alcohols and phenol, the methodology employed is a clean alternative for the acetylation reaction, tending toward eco-efficiency due to the use of relatively cheap catalysts, which can easily be prepared in the laboratory and stored for an extended period of time. In addition, water is obtained as by-product of the reaction when acetic acid is employed as acylating agent in replacement of the classical agents.

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