Borated zirconia modified with ammonium metatungstate as catalyst in alcohol acetylation

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ABSTRACT

Samples of tungsten-modified borated zirconia were prepared to be used as catalyst in 2-phenoxyethanol acetylation. The borated zirconias were obtained by impregnation of two zirconias (S2 and S4) obtained by the micellar method using different zirconium precursor concentrations with boric acid solution containing 0.3 moles B/dm^3. These solids and the parent zirconias were impregnated with two concentration levels of ammonium metatungstate solutions (0.11 and 0.22 moles W/dm^3). The solids containing boron mainly have amorphous characteristics and strong acidity, while those that contain only tungsten showed stronger acidity and evidence of the presence of a crystalline phase. The specific surface area and the pore volume slightly decreased in the solids obtained by adding tungsten to borated zirconia, and more markedly in those that contain only tungsten, and the mean pore size increased with respect to the parent support. It was observed that in the 2-phenoxyethanol acetylation using acetic acid as acylating agent and tungsten-modified borated zirconia as catalyst, the yield to acetylated product was high and it is correlated with the acid strength of the catalysts. In turn, the solids that contain only tungsten have a correlation with the acidity, but lead to low yield values due to a poorer dispersion of the tungsten species. The best yield was obtained with the catalyst prepared with the borated S4 zirconia containing 15% g $B_2O_3/100$ g support and 12.5% g W/100 g support. Using this catalyst and the same reaction conditions, the acetylation of different alcohols and phenols was studied, the reactivity order being as follows: primary alcohols > secondary alcohols > phenols.

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1. Introduction

The search of new acid solids that can replace the classical acids for their use as catalysts in acid reactions in liquid phase is constant due to the need for developing clean processes, with environmental advantages.

An attractive material to be used as catalyst support is zirconia (zirconium oxide) due to its characteristics, such as high thermal stability. The addition of different oxoanions can change the acid properties of this material [1], e.g. the sulfated zirconia presents strong acid characteristics, but the loss of sulfate species during thermal treatments or catalyst regeneration is a disadvantage [2].
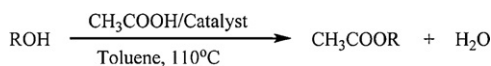
A material with strong acid characteristics can also be obtained by the addition of boron to zirconia, which has been used in diverse reactions, such as isomerization [3], transesterification [4], benzoylation [5], C-methylation [6], rearrangement [7], among others. In previous work [8], the properties of borated zirconia obtained by the micellar method, varying the preparation parameters with the purpose of finding the most suitable conditions for its use as acid catalyst, were studied. On the other hand, a widely studied catalyst is tungstated zirconia [9–11], as an environmentally friendly alternative to sulfated zirconia [12]. Tungsten-modified zirconia has been tested as catalyst in many reactions, such as *tert*-butylation [13], esterification [14], as well as in many major industrial applications [15]. So, it may be interesting to study the effect of the addition of a tungstate anion to borated zirconia.

The acetylation reaction is very important due to the wide spectrum of applications (see e.g. [16–18]), in particular for the protection of —OH groups [19], a reaction that is employed to obtain compounds of interest for the pharmaceutical, cosmetics or food industries, among others [20]. In previous work, alcohol acetylation using borated zirconia was carried out, with very good results [21].

In this context, borated zirconia modified with a tungstate anion was prepared in order to observe the effect of this addition on both the textural, physicochemical and acid characteristics of the materials and the behavior as catalyst in alcohol acetylation, with acetic acid instead of the classical acetic anhydride as acetylating agent. The acetic acid has advantages because it is cheaper and cleaner, and only gives water as by-product. Two levels of tungsten

$$ROH \xrightarrow[\text{Toluene, } 110°C]{CH_3COOH/Catalyst} CH_3COOR + H_2O$$

Scheme 1. Alcohol acetylation with acetic acid.

concentration, from ammonium metatungstate, were added to two borated zirconias, prepared by the micellar method using different preparation conditions. The unique boron concentration used was selected based on previous results [21]. For comparative purposes, only tungsten was added to the same bare zirconias. As generally the properties and the activity of a catalyst depend on the preparation method and conditions, the aim of this work is to study the influence of the characteristics of the obtained catalysts on the yield to acetylated products in alcohol acetylation with acetic acid (Scheme 1), carried out in liquid phase, as a contribution to the field of environmentally friendly catalyzed reactions.

2. Experimental

2.1. Sample preparation

The supports (named S2 and S4) were prepared from 18 g of $ZrOCl_2 \cdot 8H_2O$ dissolved in 800 and 400 cm^3 of water, respectively. An NH_4OH 30% solution was added dropwise till a final pH = 10. The obtained products were aged for 72 h and were filtered under vacuum. The precipitates were repeatedly washed with small quantities of distilled water to eliminate chlorides, up to negative reaction with $AgNO_3$.

The solids were then dried at room temperature and, subsequently, were impregnated with an aqueous solution containing 0.3 moles B/dm^3, prepared from H_3BO_3, for 12 h, under stirring, in order to obtain a boron concentration in the solid of 15% (w/w), expressed as g $B_2O_3/100$ g support. Afterwards, the solution was evaporated and the solids were dried in an oven and, finally, were calcined at 320 °C for 5 h under N_2 atmosphere (samples S2B15 and S4B15).

Each sample of borated zirconia previously obtained was divided into two portions, which were impregnated with an aqueous solution containing 0.11 or 0.22 moles W/dm^3, prepared from ammonium metatungstate (AMT), in order to obtain a tungsten concentration in the solid of 12.5% or 25% (w/w), expressed as g W/100 g support. The impregnation was carried out with stirring for 12 h. After evaporation of the excess solution, the solids were dried in an oven, and calcined at 320 °C for 5 h under N_2 atmosphere. The samples S2B15W12.5, S2B15W25, S4B15W12.5 and S4B15W25 were thus obtained.

At the same time, solids were prepared with the same tungsten contents in zirconia, without boron addition, under the same conditions as the previous samples, thus obtaining the materials S2W12.5, S2W25, S4W12.5 and S4W25.

2.2. Characterization

2.2.1. X-ray diffraction

The X-ray diffraction (XRD) patterns of the solids were obtained using Philips PW-1714 equipment with incorporated recorder. Cu Kα radiation, Ni filter, 20 mA and 40 kV in the high tension source, scanning angle between 5 and 60° 2θ, and a scanning rate of 2° per min were employed.

2.2.2. Textural properties

The specific surface area, the pore volume and the pore size of the solids were estimated from the N_2 adsorption–desorption isotherms at −196 °C, using Micromeritics, model ASAP 2020 equipment. Each sample was previously degassed at 100 °C for 1 h.

2.2.3. Differential thermal analysis

The differential thermal analysis (DTA) was carried out using Shimadzu DT 50 equipment under N_2 atmosphere, with a sample weight of 20 mg, a heating rate of 20 °C per min, Pt sample holders, and α-alumina as reference. A temperature range between 20 and 800 °C was studied.

2.2.4. Potentiometric titration

The obtained materials were potentiometrically titrated with the purpose of estimating their acidity. To this end, 0.05 g of solid was suspended in 45 cm^3 of acetonitrile, stirring for 3 h. The suspension was titrated with a 0.05 N solution of n-butylamine in acetonitrile. The potential variation was measured with Hanna 211 pH meter using a double junction electrode.

2.2.5. Acetylation reaction

A mixture of alcohol (1 mmol), acetic acid (5 mmol), toluene (5 cm^3) and catalyst (100 mg) was stirred at 110 °C for 14 h. The catalyst was separated by filtration and then washed twice with a small quantity of toluene (1 cm^3). The progress of the reaction was monitored by silica gel thin layer chromatography. The solution was concentrated under vacuum, and the residue was purified by column chromatography employing silica gel as the stationary phase and a mixture of hexane–ethyl acetate as the elution solvent. The reaction products were identified by chromatographic comparison with standard samples. The yield was calculated as mmol of purified product with respect to mmol of initial alcohol. For the experiments of reuse, the catalyst was treated after reaction by washing twice with hot toluene (3 cm^3), dried under vacuum at 20 °C for 5 h and then reused.

3. Results and discussion

The preparation of oxides can be performed by physical or chemical methods. The latter can lead to better chemical and morphological homogeneity. The liquid-phase chemical methods can be classified into sol–gel method, micellar method and mechanochemical synthesis [22]. Though the sol–gel method is now more widely used because it leads to a good size control to obtain nanoparticles, the micellar method is also utilized because ultrafine powders can be obtained. This oxide or oxide precursor preparation has the advantage of simplicity of reagent management, and consists in the reaction between solved cations and a precipitating agent. Though it may be carried out in the presence of another reagent, such as a surfactant, in the present study no other reagents have been added.

Different zirconium precursor concentrations were used in this study, thus obtaining the supports named S2 and S4 with mainly different textural and acidic properties [8]. The supports were impregnated with a unique boric acid solution concentration, chosen based on previous results obtained with similar solids as catalysts in acetylation reactions, in order to observe the effect of AMT addition [21].

3.1. Catalyst characterization

The X-ray diffraction patterns of the S4B15W12.5 and S4B15W25 solids were similar to that of S4B15 borated zirconia (Fig. 1), and the same behavior was observed for the S2B15W12.5 and S2B15W25 samples, compared to S2B15. All the patterns presented a wide band centered at a 2θ value of 30°, indicative of solids with mainly amorphous characteristics. The peaks of maximum intensity of the tetragonal and monoclinic phases of zirconia could be present in this zone; however, lines attributed to these crystalline phases were not observed. Besides, though the patterns of boric acid or ammonium metatungstate calcined at 320 °C
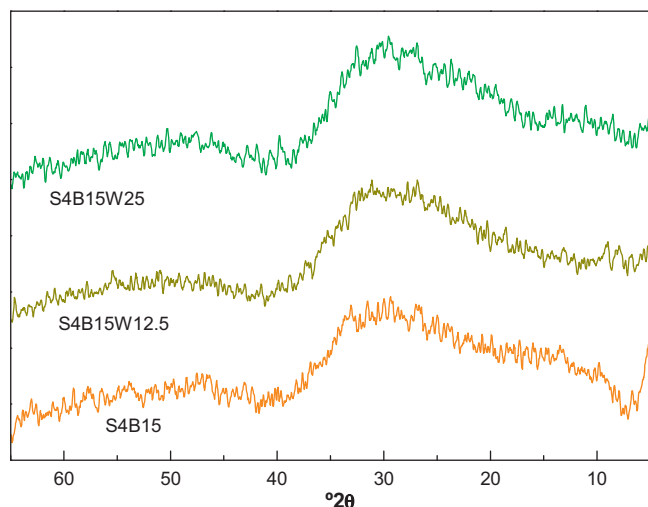
Fig. 1. XRD patterns of S4B15 borated zirconia, and S4B15W12.5 and S4B15W25 tungsten-modified samples.

Table 1
Textural properties of the prepared samples.

Sample	S_{BET}[a] (m^2/g)	Micropore area[b] (m^2/g)	V_p[c] (cm^3/g)	MPS[d] (nm)
S2	214	52	0.13	2.4
S2B15	245	25	0.14	2.3
S2B15W12.5	182	11	0.11	2.7
S2B15W25	144	13	0.10	2.7
S2W12.5	74	7	0.05	2.7
S2W25	94	9	0.06	2.6
S4	146	12	0.07	2.1
S4B15	185	60	0.10	2.1
S4B15W12.5	113	29	0.10	3.4
S2B15W25	149	33	0.10	3.4
S4W12.5	34	–	0.03	3.5
S4W25	27	–	0.02	3.5

[a] Estimated by the BET method.
[b] Estimated from t-plot analysis.
[c] Single point total pore volume at $p/p_0 = 0.98$.
[d] Mean pore size calculated by the BJH formula from the desorption branch.

presented lines attributable to boric oxide or to a tungsten oxide produced by a partial decomposition of metatungstate, respectively, such lines were not detected in the studied samples. This fact may be attributed to a good dispersion of the boron and tungsten species on the support or to crystallites small enough to give diffraction lines. However, in the S4W25 sample pattern, lines overlapped to such band in the 23–24° 2θ zone, where the WO$_3$ presents the lines of higher intensity, were visualized and a peak at a 2θ value of 9.5° appears, which coincides with the highest peak of ammonium metatungstate without thermal treatment (Fig. 2).

All the solids presented a pore size greater than 2 nm (Table 1), the lowest limit of mesoporous size according to IUPAC classification. The zirconias containing only boron, S2B15 and S4B15, have a specific surface area higher than that of the respective parent supports. This fact may be explained considering that boron is well dispersed on the surface of the hydrated zirconium oxide and inhibits particle growth, in a similar way to what was reported by Zhao et al. [23] for the Mo, W, Cu, Fe and Ni oxides supported on zirconia. Nevertheless, the specific surface area of the S2B15W12.5, S2B15W25, S4B15W12.5 and S4B15W25 samples, with tungsten addition to borated zirconia, decreased with respect to the value
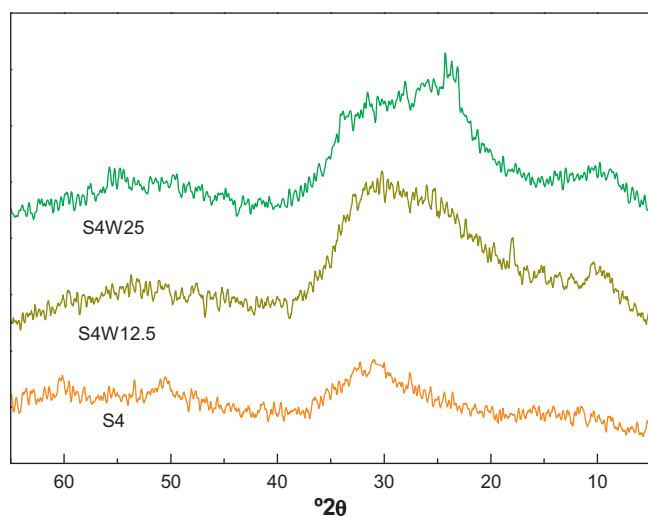
of the respective borated zirconia (Table 1); the decrease is in the range 20–40%. Besides, a low microporous component was observed for these samples, as the micropore area is 6–25% of the corresponding S_{BET} value. The pore volume remained almost constant in a relatively high value, and the mean pore size increased compared to the corresponding borated zirconia.

In turn, the textural characteristics of the zirconia samples containing tungsten, prepared by directly impregnating zirconia, were different to those obtained by modifying the borated zirconia. The first samples have a specific surface area (S_{BET}) markedly lower than that of the corresponding support. Thus, the S2W12.5 and S2W25 samples presented a specific surface area 60% lower than that of the S2 support, and S_{BET} notably decreased for the S4W12.5 and S4W25 solids, being around 80% lower than that of the parent S4 zirconia (Table 1). This behavior indicates that the preparation method used, involving an impregnation in excess of solution followed by evaporation of the excess solution, led to tungsten species that are not well dispersed on the support, as may be inferred from XRD results. So, the tungsten species do not help separate the particles and produce the inhibition of their later growth, as seems to be the process that occurs in the presence of boron. This effect is accompanied by a decrease of the pore volume (V_p) and an increase of the mean pore size (MPS), possibly due to a blocking of the smaller pores.

So, it was observed that the modification of zirconia with boron was more efficient than the modification with tungsten when referring to the preservation of the textural properties of the materials, a behavior that can be attributed to a better dispersion of boron species than tungsten species on the support.

By DTA analysis, the diagrams of all the samples presented an endothermic peak with a maximum at 40–50 °C, which can be assigned to a loss of physisorbed water. The borated zirconias with tungsten addition showed an exothermic peak placed at 720–730 °C in the DTA diagrams, which is assigned to the transformation of the amorphous hydrated oxide into a crystalline phase. The monoclinic phase of zirconia is stable up to 1200 °C, though a metastable tetragonal phase can appear up to 650 °C, due to the effect of impurities or to the crystallite size [24]. The exothermic peak appeared at a higher temperature than for the corresponding S2 and S4 parent supports, as is shown in Fig. 3 for the samples obtained from S4 zirconia, and at a slightly lower temperature than for the corresponding borated zirconia. The presence and the interaction of boron on the support preserves the microparticles of the hydrated oxide [8,30], thus increasing its thermal stability; however, the temperature at which the exothermic peak maxima appeared slightly decreased with tungsten addition. The increase of stability was attributed to the inhibiting effect on zirconia
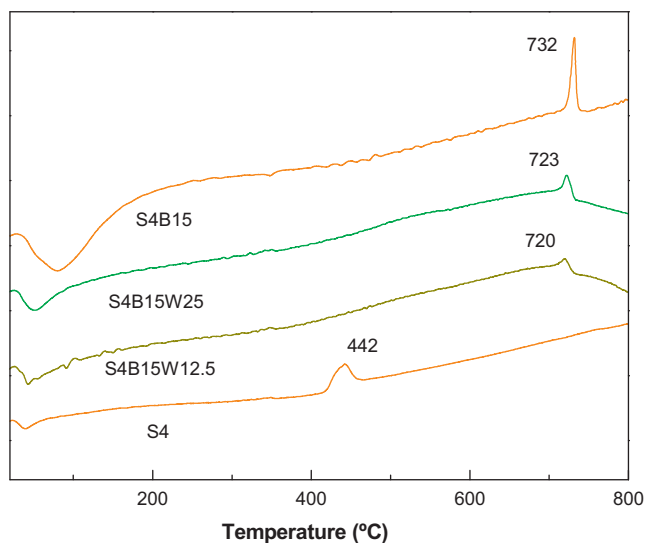

Fig. 2. XRD patterns of S4 zirconia, and S4W12.5 and S4W25 tungsten-modified zirconias.

Fig. 3. DTA diagrams of S4B15 borated zirconia, and S4B15W12.5 and S4B15W25 tungsten-modified samples.

crystallization that induces a good dispersion of the additives added to the oxide, as was reported for molybdenum or copper [23], sulfate or chromium [24], and nickel or aluminum [25] additions.

However, the behavior is different when zirconia is modified only with tungsten. While the parent support showed only one exothermic peak, the diagrams of the solids containing 12.5 or 25%W showed three wide exothermic peaks (Fig. 4). A comparison with the diagram obtained for ammonium metatungstate shows that the diagrams of the samples have similar features to those of AMT. This fact may be indicative of the presence of similar species, and the shifting of the maxima towards higher temperatures can be attributed to interaction with the support.

It can be remarked that the XRD pattern of AMT calcined at 320 °C was like the pattern of a tungsten and ammonium oxide (JCPDS 42-0452), which can be the product of a partial decomposition of ammonium metatungstate. When AMT was calcined at 450, 550 or 750 °C, WO_3 appeared, so the bands with maxima at 520 and 658 °C observed in DTA diagrams may be a consequence of structural changes of WO_3, which have not been elucidated yet.
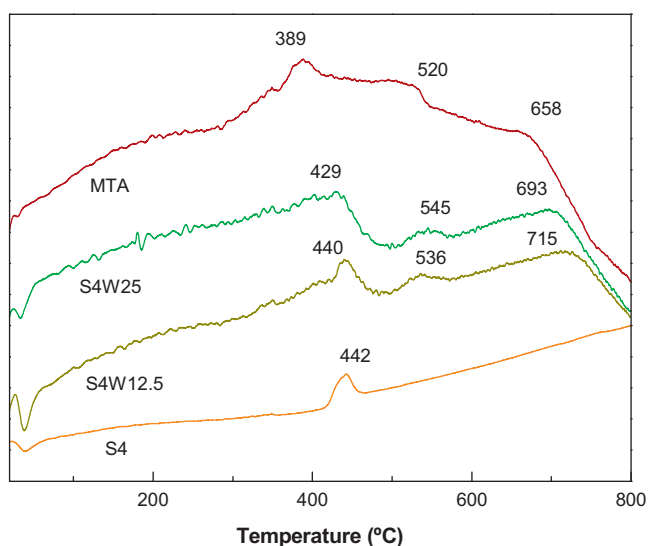

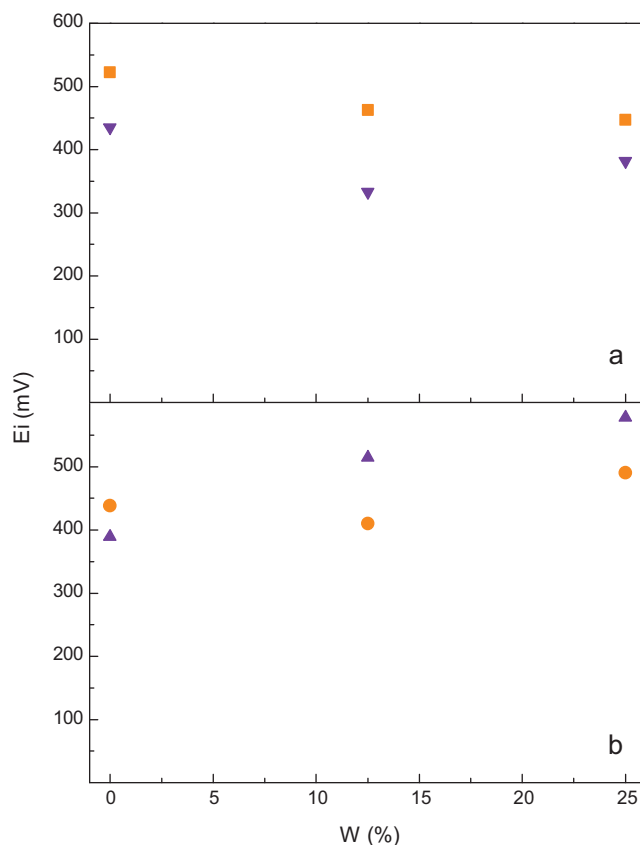**Fig. 4.** DTA diagrams of AMT, S4 zirconia, and S4W12.5 and S4W25 tungsten-modified samples.

Fig. 5. E_i values as a function of the tungsten content of samples containing (a) boron and tungsten and (b) tungsten, obtained from S2 zirconia (▼, ▲) and S4 zirconia (■, ●).

On the other hand, it is interesting to observe that the first band in the sample S4W12.5, with maximum at 440 °C, seems to be the result of the overlapping of the first band present in the AMT diagram with the main band of the S4 support. This fact may indicate that in this solid the thermal stability of the hydrated oxide did not increase, as was observed for the samples obtained from borated zirconia.

With regard to the acid characteristics of the solids, estimated by potentiometric titration with n-butylamine, it has been reported that the initial electrode potential (E_i) of the obtained curves 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) [26]. When the samples containing boron are considered, the addition of tungsten led to a decrease of the maximum acid strength compared with the parent borated zirconia (Fig. 5). The higher value of E_i observed for the samples prepared from the S4 support can be related to the higher initial potential value obtained for the parent support. E_i values were 389 and 438 mV for S2 and S4 supports, respectively. This behavior was attributed to a lower hydroxylation degree of the S4 solid that has a lower specific surface area than that of the S2 support as was already informed [21], taking into account the report by Hadjiivanov and Lavalley [27] about some sites that can be blocked in the more hydroxylated surfaces, thus leading to more acidic sites on the oxide surface when the dehydroxylation degree is higher. In turn, the acid strength increased when only tungsten was added to zirconia, significantly in the samples obtained from S2 zirconia.
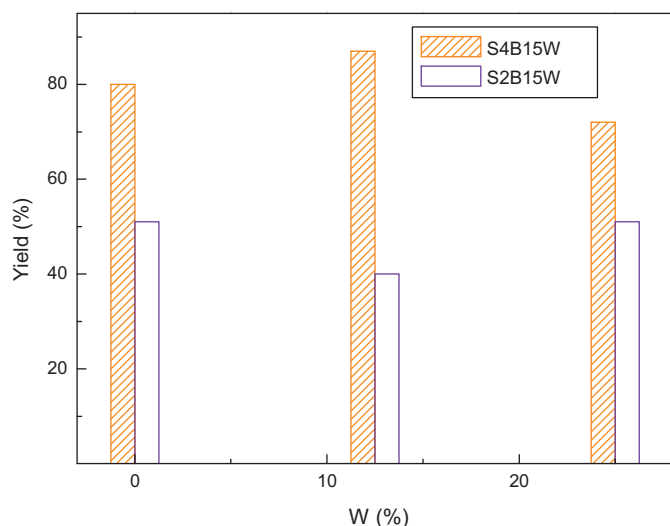
Fig. 6. Yield to acetylated product obtained with S2B15 and S4B15 borated zirconias, and S2B15W12.5, S2B15W25, S4B15W12.5 and S4B15W25 tungsten-modified samples.

3.2. Acetylation reaction

The acetylation of 2-phenoxyethanol with acetic acid using borated zirconias modified with ammonium metatungstate led to high yield values, as can be observed in Fig. 6. The catalysts obtained from the parent S4 zirconia gave yields to acetylated product higher than the one corresponding to the S2 support, in accordance with their higher acid strength, as was already observed in a previous paper for borated zirconias with different boron content without the addition of tungsten [21]. The modification with tungsten only led to a higher yield for the S4B15W12.5 sample, showing that the expected effect is not efficiently achieved. On the other hand, the acetylation of 2-phenoxyethanol with acetic acid using tungsten-modified zirconia as catalyst did not lead to high yields to ethyl 2-phenoxyethanoate. The obtained values were 25%, 30%, 20% and 21% for the S2W12.5, S2W25, S4W12.5 and S4W25 samples, respectively. This was not expected because the acid strength determined for these samples is high (Fig. 5), but evidently the low surface area and poor tungsten dispersion, reflected in the lines observed by XRD, have an adverse effect.

Considering each group of samples containing tungsten, with and without boron (Fig. 7) individually, a direct relation to the acidity was found for the yield to acetylated product, which may be dependent on the preparation conditions of the materials. In this work it is clearly observed that the concentration of the zirconium oxide precursor used and the boron addition to zirconia previous to the modification with tungsten are important variables, tungsten addition and tungsten concentration being less important. The properties acquired by these materials, mainly regarding the surface area, acidity and dispersion, are important for their behavior as acetylation catalysts.

The reuse of the catalysts is significant for their utility. In order to investigate the reusable properties of the tungsten-modified borated zirconia, experiments were carried out for the reaction of 2-phenoxyethanol and acetic acid using the S4B15W12.5 catalyst. This process was repeated twice without important loss of catalyst activity. The corresponding acetate was obtained in yields of 89%, 87%, and 87% for successive reuses.

The Fischer esterification reaction is considered to be catalyzed by Brønsted acid sites [28] or by Lewis acid sites (metal ions in low coordination) [29]. Other authors have reported that both the Brønsted and Lewis acid sites are responsible for catalyzing the
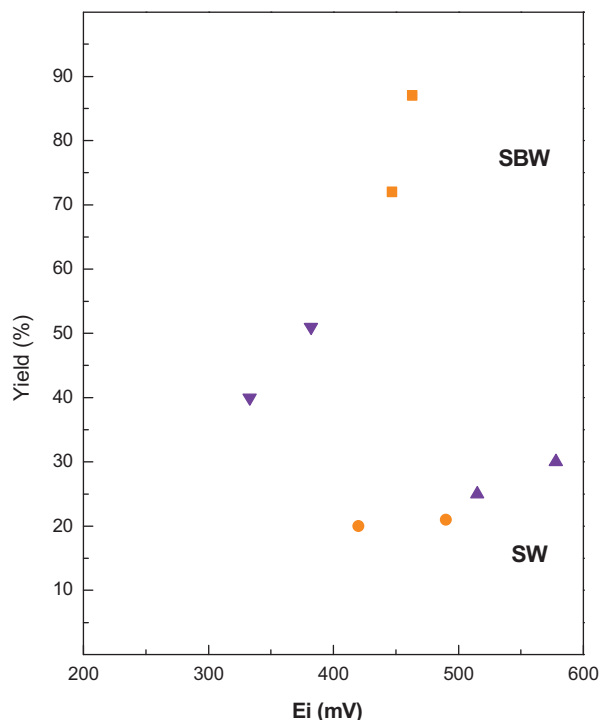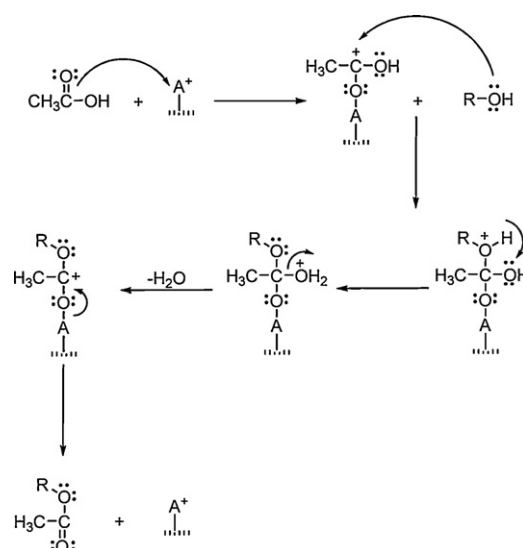

Fig. 7. Yield as a function of E_i for samples containing boron and tungsten (SBW) or only tungsten (SW), from S2 zirconia (▼, ▲) or S4 zirconia (■, ●).

acetylation reaction [30]. Due to the characteristics of the catalysts prepared here, they may present Brønsted and Lewis sites [4], so we assume that both types of sites synchronously affect the acetylation activity.

The mechanism of the reaction can be described as proceeding through the adsorption of acetic acid on Brønsted and Lewis sites, forming a protonated acetic acid intermediate, as shown in Scheme 2. The alcohol would react with this protonated intermediate to form the corresponding ester and water.

To explore the potential of this catalytic system and extend the scope of this acetylation method, the acetylation of various alcohols (primary, secondary, tertiary and benzylic), and phenols with electron-donating and electron-withdrawing groups was studied.

Scheme 2. Reaction mechanism for the acetylation of alcohols with acetic acid (A^+: Brønsted or Lewis acid site).

Table 2
Acetylation of different alcohols and phenol using S4B15W12.5 catalyst.[a]

Entry	Substrate	Product	Product yield (%)
1			83
2			75
3			71
4			62
5			Traces
6		–	–
7			15
8			15
9			10
10			Traces

[a] Reaction conditions: alcohol 1 mmol; acetic acid 5 mmol; toluene, 5 cm^3; mass of S4B15W12.5 catalyst: 100 mg; reaction temperature and time: 110 °C, 14 h.

The reactivity of the selected compounds was tested using the same reaction conditions and S4B15W12.5 as catalyst, which is the solid that gave the highest conversion in 2-phenoxyethanol acetylation. Results of the obtained yields are listed in Table 2. It must be pointed out that the reactions were clean and the products were isolated by liquid column chromatography in pure form without further purification. The reaction is very selective and no competitive side reactions take place, as the gas-chromatography/mass

spectrometry analysis showed. However, an important effect of the alcohol structure on the yield to the reaction products was found.

The observed reactivity trend for alcohols and phenols can be conceptualized using the catalysis model for esterification (Scheme 2). Initially, two components contribute to the alcohol or phenol reactivity: an inductive effect and a steric effect. The inductive effect is dependent on nucleophilicity of the alcohol. The steric component affecting alcohol reactivity is also a decisive

factor for Fischer acid-catalyzed esterification [21]. Steric hindrance increases with molecular size, inducing electronic repulsion between nonbonded atoms of reacting molecules. This repulsive hindrance decreases the electronic density in the intermolecular region and disturbs the bonding interaction [31].

The reactivity of 2-phenylethanol and 3-phenylpropanol primary alcohols, and 4-methylbenzyl alcohol, a benzylic alcohol (Table 2, entries 1–3), was higher than that of 1-phenylethanol, a secondary alcohol (Table 2, entry 4).

The yield difference between primary and secondary alcohols can be attributed to steric effects that considerably affect the acetylation rate. The presence of bulky groups, not far from the reaction center, either in the alcohol or in the acid, slows down the esterification rate, in our case, where the most sterically hindered alcohols give a lower yield. Similarly, very bulky menthol (a secondary alcohol) and triphenylmethanol (a tertiary alcohol) give only traces or no reaction is detected under similar reaction condition (Table 2, entries 5 and 6).

On the other hand, the yield in phenol acetylation is still lower than that of the primary and secondary alcohols, reaching only yields of 10–15% for different phenols (Table 2, entries 7–9). This behavior can be attributed to its low nucleophilicity, due to the electronic delocalization by resonance in the benzene ring. 4-Nitrophenol, a phenol with a strong electron-withdrawing group, fails to give the expected acetylation product (Table 2, entry 10). In sum, the reactivity order toward acetylation with acetic acid with the studied catalysts was as follows: primary alcohols > secondary alcohols > phenols.

4. Conclusions

Tungsten-modified borated zirconias have characteristics that depend on the preparation method used, the concentration of zirconium precursor employed in obtaining the parent zirconias, as they confer different textural and acidic characteristics to the two supports that were then impregnated and, to a lesser extent, on tungsten concentration. The solids were predominantly amorphous and mesoporous, presenting very strong acidity.

The addition of boron increased the range of stability temperature of the hydrated oxide, as a result of good dispersion. This fact also led to good tungsten dispersion, when the behavior is compared to that of samples in which only tungsten is added to zirconia.

The acetylation of 2-phenoxyethanol with acetic acid employing borated zirconias modified with tungsten led to good yields to acetylated product, unlike tungstated zirconias that gave low yields. The better yields were reached with the catalysts obtained using borated zirconia prepared with a high concentration of zirconium precursor as support.

The alcohol and phenol structure is key in the yield to the acetylation product. The strong electron-withdrawing group has an adverse effect. The reactivity order toward acetylation with acetic acid using tungsten-modified borated zirconias was as follows: primary alcohols > secondary alcohols > phenols, and depended on two factors, an electronic and a steric effect.

References

[1] M.A. Cortés-Jácome, C. Angeles-Chavez, E. López-Salinas, J. Navarrete, P. Toribio, J.A. Toledo, Appl. Catal. A: Gen. 318 (2007) 178–189.
[2] J.D. Hansen, A.L. Kustov, S.B. Rasmussen, R. Fehrmann, C.H. Christesen, Appl. Catal. B: Environ. 66 (2006) 161–167.
[3] M. Scheithauer, T.-K. Cheung, R.E. Jentoft, R.K. Grasselli, B.C. Gates, H. Knözinger, J. Catal. 180 (1998) 1–13.
[4] B. Madje, P. Patil, S. Shindalkar, S. Benjamin, M. Shingare, M. Dongare, Catal. Commun. 5 (2004) 353–357.
[5] P. Patil, K. Malshe, P. Kumar, M. Dongare, E. Kemnitz, Catal. Commun. 3 (2002) 411–416.
[6] K. Malshe, P. Patil, S. Umbarkar, M. Dongare, J. Mol. Catal. A: Chem. 212 (2004) 337–344.
[7] B. Xu, S. Cheng, S. Jiang, Q. Zhu, Appl. Catal. A: Gen. 188 (1999) 361–368.
[8] M. Blanco, L. Osiglio, Proceedings 6° Congreso de Metalurgia y Materiales Binacional CONAMET/SAM, Santiago de Chile, Chile, 2006, p. 214.
[9] P. Wongmaneenil, B. Jongsomjit, P. Praserthdam, Catal. Commun. 10 (2009) 1079–1084.
[10] K. Ngaosuwan, X. Mo, J.G. Goodwin Jr., P. Praserthdam, Appl. Catal. A: Gen. 380 (2010) 81–86.
[11] C.D. Baertsch, K.T. Komala, Y.-H. Chua, E. Iglesia, J. Catal. 205 (2002) 44–57.
[12] R.A. Boyse, E. Ko, J. Catal. 171 (1997) 191–207.
[13] B.M. Reddy, M.K. Patil, G.K. Reddy, B.T. Reddy, K.N. Rao, Appl. Catal. A: Gen. 332 (2007) 183–191.
[14] S. Ramu, N. Lingaiah, B.L.A. Prabhavathi, R.B.N. Prasad, I. Suryanarayana, P.S. Sai Prasad, Appl. Catal. A: Gen. 276 (2004) 163–168.
[15] E.I. Ross-Medgaarden, W.V. Knowles, T. Kim, M.S. Wong, W. Zhou, C.J. Kiely, I.E. Wachs, J. Catal. 256 (2008) 108–125.
[16] K. Arata, H. Nakamura, M. Shouji, Appl. Catal. A: Gen. 197 (2000) 213–219.
[17] R. Sakthivel, H. Prescott, E. Kemnitz, J. Mol. Catal. A: Chem. 223 (2004) 137–142.
[18] A. Bordoloi, N.T. Mathew, B.M. Devassy, S.P. Mirajkar, S.B. Halligudi, J. Mol. Catal. A: Chem. 247 (2006) 58–64.
[19] T. Green, P. Wutz, Protective Groups in Organic Synthesis, Wiley, New York, 1991.
[20] M. Alizadeh, T. Kermani, R. Tayebee, Monatsh fur Chemie 138 (2007) 165–170.
[21] L. Osiglio, G. Romanelli, M. Blanco, J. Mol. Catal. A: Chem. 316 (2010) 52–58.
[22] M. Fernández-García, A. Martínez-Arias, J.C. Hanson, J.A. Rodríguez, Chem. Rev. 104 (2004) 4063–4104.
[23] B.-Y. Zhao, X.-P. Xu, H.-R. Ma, D.-H. Sun, J.-M. Gao, Catal. Lett. 45 (1997) 237–244.
[24] T. Yamaguchi, Catal. Today 20 (1994) 199–217.
[25] J.C. Duchet, M.J. Tilliette, D. Cornet, Catal. Today 10 (1991) 507–520.
[26] L.R. Pizzio, M.N. Blanco, Micropor. Mesopor. Mater. 103 (2007) 40–47.
[27] K. Hadjiivanov, J.-C. Lavalley, Catal. Commun. 2 (2001) 129–133.
[28] A. Khder, E. El-Sharkawy, S. El-Hakam, A. Ahmed, Catal. Commun. 9 (2008) 769–777.
[29] S. Barbosa, M. Dabdoub, G. Hurtado, S. Klein, A. Baroni, C. Cunha, Appl. Catal. A: Gen. 313 (2006) 146–150.
[30] Y. Wang, W. Li, React. Kinet. Catal. Lett. 83 (2004) 195–203.
[31] Y. Liu, E. Lotero, J.G. Goodwin Jr., J. Catal. 243 (2006) 221–228.