

## Facile transesterification of $\beta$ -ketoesters under solvent-free condition using borate zirconia solid acid catalyst

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### Abstract

Transesterification of methyl/ethyl ketoesters with primary, secondary, allylic, cyclic and benzylic alcohols has been carried out in moderate to good yields under solvent-free condition using borate zirconia solid acid catalyst. The process has simpler work up procedure and the catalyst has been successfully recovered and recycled. The catalyst has been characterized by different techniques like X-ray diffraction, X-ray photoelectron spectroscopy, differential thermal analysis, temperature-programmed desorption of ammonia, scanning electron microscopy and surface area measurements. Transesterification using borate zirconia catalyst under solvent-free condition is an economical and environment friendly process.

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**Keywords:** Transesterification;  $B_2O_3/ZrO_2$ ; Solid acid catalyst; Heterogeneous catalysis

### 1. Introduction

Transesterification is an important organic transformation and provides essential synthons for number of complex natural products, pheromones and additives for paints [1]. Thus, number of procedures for transesterification have been reported, which are catalyzed by variety of protic or Lewis acids, organic bases, enzymes and antibodies. However, it is well known that traditional homogeneous acidic catalysts such as sulphuric acid and phosphoric acid can cause several environmental problems [2]. Therefore, several heterogeneous catalysts have been documented in the literature for transesterification. Sulphated tin oxide [3], zeolites [4], kaolinitic clay [5],  $Mo-ZrO_2$  [6],  $FeSO_4$  and  $CuSO_4$  [7] yettria-based strong Lewis acid [8], DMAP [9], Zinc [10], montmorillonite K-10 [11] and  $Mg-Al-O-t-Bu$  hydroxalcalcite [12] have been investigated to minimize the

problems associated with the homogeneous catalysts. However, the sulphated catalysts gets deactivated by leaching of sulphate ions during the course of reaction. Another disadvantage of all existing methods include the use of toluene as solvent to effect transesterification. And being high boiling solvent there is a possibility of losing product with low boiling point during separation. To avoid these problems, we have successfully carried out transesterification of ketoesters in solvent-free conditions for the first time using borate zirconia solid acid catalyst.

Arata and co-workers [13] have reported  $B_2O_3/ZrO_2$  catalyst containing 30 mol% of boron as a superacid catalyst (acidic strength  $H_0 = -13$ ) suitable for isomerization of butanes and pentanes. Xu et al. [14] have studied  $B_2O_3/ZrO_2$  catalyst for gas phase Beckman Rearrangement of cyclohexanone oxime. Recently we have studied the acidic properties of the catalyst for Friedel–Craft acylation and it showed comparable performance with conventional homogenous  $AlCl_3$  catalyst, as well as heterogeneous catalysts like zeolite H- $\beta$  and sulphated-zirconia [15]. It is also found to be an efficient catalyst for

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selective *ortho*-alkylation of phenol to corresponding *o*-cresol and 2,6-xyleneol [16]. This prompted us to initiate a systematic investigation on  $B_2O_3/ZrO_2$  catalyzed transesterification of  $\beta$ -ketoesters under solvent-free conditions and to our knowledge  $B_2O_3/ZrO_2$  catalyst has not been used for transesterification.

## 2. Experimental

### 2.1. Catalyst preparation

Borate zirconia (30 mol%) catalyst was prepared by impregnation method. Zirconyl oxychloride (22.54 g, AR grade, Loba) was dissolved in 100 ml distilled water, and aqueous ammonia (25%) was added dropwise with constant stirring (pH 10). The resultant precipitate of zirconium hydroxide was filtered and washed with distilled water till free from chloride ions. The residue was dried overnight at 85 °C in an oven. Boric acid (3.66 g, AR grade, S.D. Fine Chemicals) was dissolved in 50 ml distilled water. The zirconium hydroxide obtained above was added to the boric acid solution with stirring to obtain slurry. The obtained slurry was air dried at ambient temperature to get a solid, which was further heated in an oven at 110 °C for 5 h and calcined overnight at 650 °C. Pure zirconia and sulphated zirconia samples used for comparison were prepared as follows: zirconium hydroxide was calcined at 500 °C for 12 h to get pure zirconia and 5 g zirconium hydroxide was equilibrated with 25 ml of 2 N  $H_2SO_4$  for 2 h and then it was evaporated to dryness, calcined at 500 °C for 4 h to get the sulphated zirconia.

### 2.2. Catalyst characterization

The powder X-ray diffraction analysis (XRD) of the catalyst was carried out using Rigaku X-ray diffractometer (Rigaku miniflex) equipped with a Ni filtered  $Cu K\alpha$  (1.542 Å) radiation and a graphite crystal monochromator. X-ray Photoemission spectra (XPS) were recorded on VG Microtech Multilab ESCA 3000 spectrometer using non-monochromatized  $Mg K\alpha$  X-ray source ( $h\nu = 1253.6$  eV). Temperature-programmed desorption (TPD-ammonia) profile of the catalyst was recorded on a Micromeritics Autochem 2910 apparatus. The surface morphology of the catalyst was observed using scanning electron microscopy (SEM, Philips XL-20). The thermal property of as synthesized  $B_2O_3/ZrO_2$  and  $ZrO_2$  was studied by TG/differential thermal analysis (DTA) (Mettler-Toledo, TGA/DTA 851) and determination of specific surface area surface area was carried out by BET (Brunner–Emmett–Teller)  $N_2$  adsorption using a NOVA 1200 Quanta chrome. The products were further identified by Mass and  $^1H$  NMR spectroscopy.

### 2.3. Typical procedure for transesterification

A mixture of ketoester (1 eq), alcohol (1 eq) and catalyst (10% by weight) were heated to 110 °C in a two-necked round-bottom flask provided with distillation condenser to remove methanol/ethanol. The reaction was monitored by thin layer chromatography. After completion of the reaction, the catalyst was filtered and the filtrate was washed with sodium thiosulfate. The organic layer was separated, dried over sodium sulfate, filtered and chromatographed over 35–40 g of silica gel (60–120 mesh) using 95:5 pet ether:ethyl acetate to afford the ester as a viscous colorless liquid in excellent yields. The catalyst was activated at 110 °C for 2 h before its use for transesterification and recycling experiments.

## 3. Results and discussion

Fig. 1 shows XRD pattern of  $ZrO_2$  and  $B_2O_3/ZrO_2$  calcined at 650 °C. It shows that pure  $ZrO_2$  is in the monoclinic phase, while  $B_2O_3/ZrO_2$  showed cubic structure showing stabilization of zirconia in to cubic phase. The surface area of the catalyst was found to be 114  $m^2/g$ . XPS study showed the binding energy of 191.9 eV for B 1s, which is in good agreement with standard value of 192 eV for  $B^{3+}$  state. DTA plot of  $Zr(OH)_4$  and  $Zr(OH)_4$  with  $B(OH)_3$  (Fig. 2) shows a sharp peak at 450 °C for pure  $Zr(OH)_4$  and one at 725 °C for  $Zr(OH)_4$  with  $B(OH)_3$ . The sharp peak at 450 °C corresponds to the change in phase from crystalline cubic phase to monoclinic phase for pure zirconia while the corresponding peak for borica supported zirconia is shifted to 725 °C. This suggests the enhanced thermal stability of cubic zirconia due to the addition of boron oxide. Fig. 3 shows TPD of  $B_2O_3/ZrO_2$  (a) compared with  $SO_4^{2-}/ZrO_2$  (b). Ammonia was desorbed below 400 °C in case

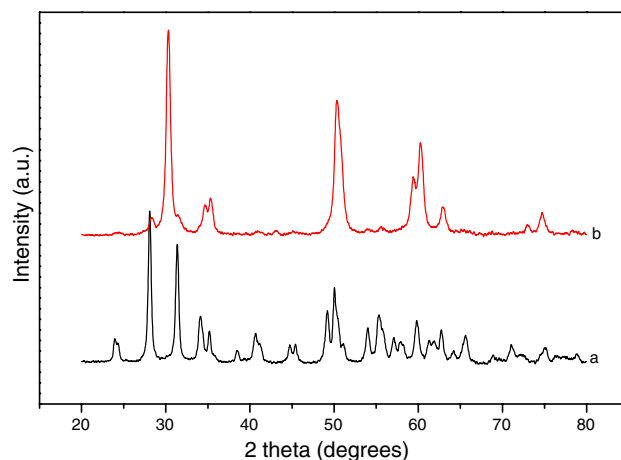


Fig. 1. X-ray diffraction pattern of: (a) pure  $ZrO_2$  and (b)  $B_2O_3/ZrO_2$ .

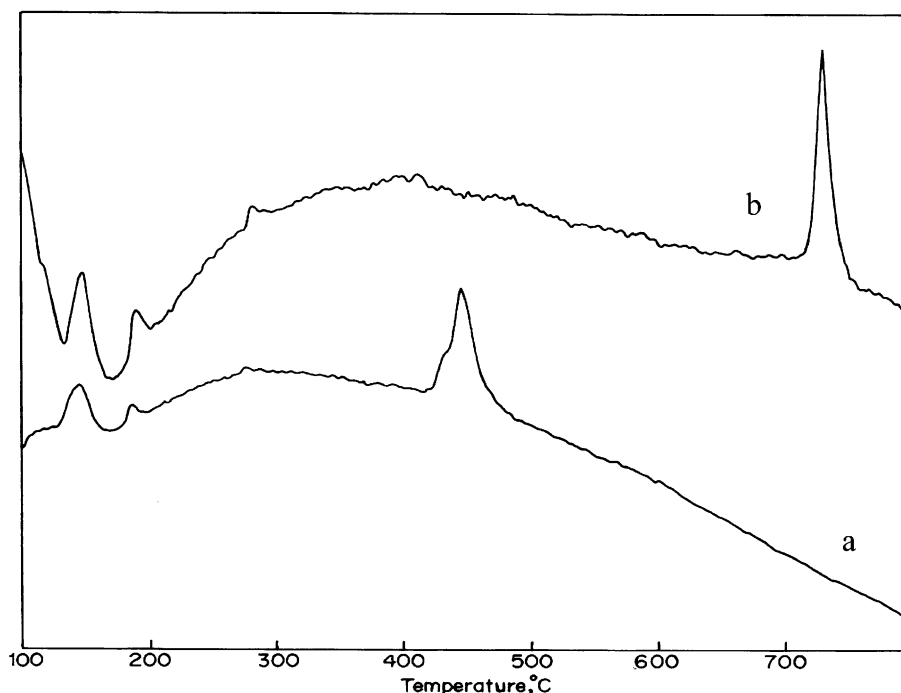


Fig. 2. DTA analysis of as synthesized: (a)  $\text{ZrO}_2$  and (b)  $\text{B}_2\text{O}_3/\text{ZrO}_2$ .

of  $\text{B}_2\text{O}_3/\text{ZrO}_2$  whereas in case of sulfated zirconia ( $H_0 = -14$ ) desorbed at much higher temperature at about  $540\text{ }^\circ\text{C}$ , indicating the lower acidity of  $\text{B}_2\text{O}_3/\text{ZrO}_2$  compared to sulfated zirconia. The acid site density in case of  $\text{B}_2\text{O}_3/\text{ZrO}_2$  was found to be  $0.398\text{ mmol/g}$ , which is quite high for its use as an acid-catalyzed reaction. Fig. 4 shows SEM of  $\text{B}_2\text{O}_3/\text{ZrO}_2$  sample calcined at  $650\text{ }^\circ\text{C}$ , which shows that the average particle size is in the range of  $2\text{--}3\text{ }\mu\text{m}$  that is in agglomerated form.

The results of the transesterification reaction between  $\beta$ -ketoesters with alcohols at  $110\text{ }^\circ\text{C}$  under solvent-free conditions using borate zirconia solid acid catalyst are

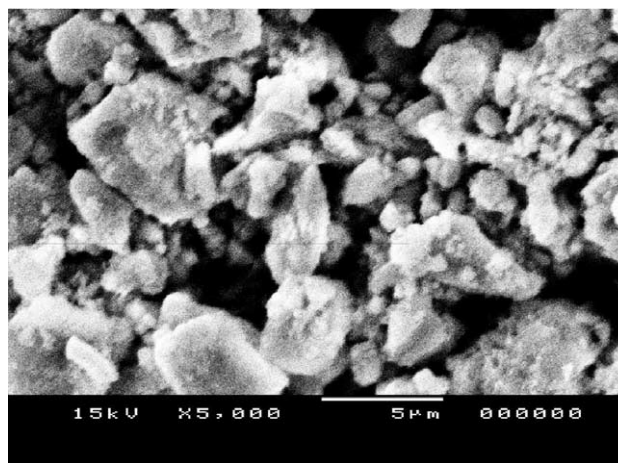


Fig. 4. SEM image of borate zirconia.

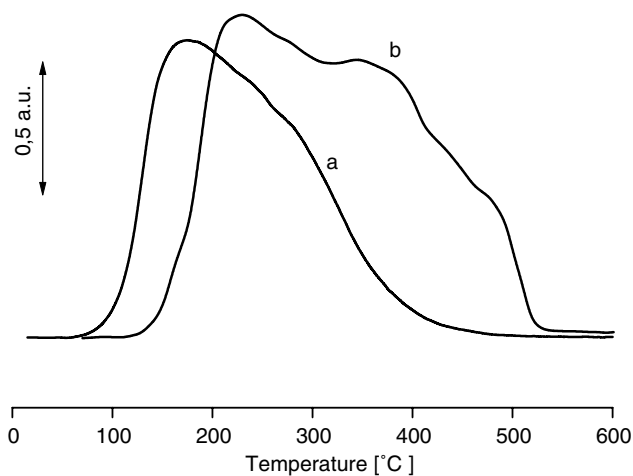
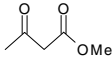

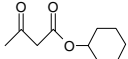
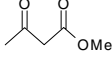

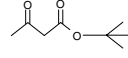
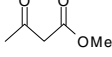

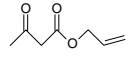
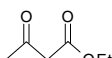

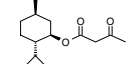
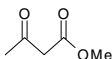

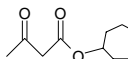
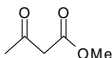

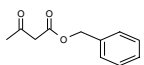
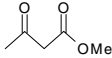
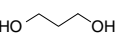
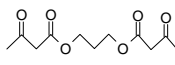
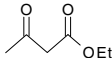
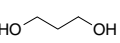
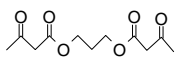
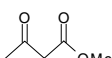

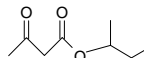
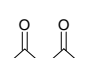

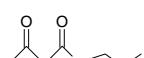
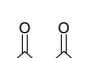
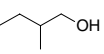
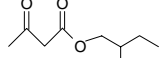
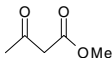
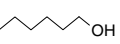
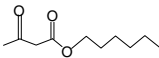


Fig. 3. Temperature-programmed desorption of ammonia: (a)  $\text{B}_2\text{O}_3/\text{ZrO}_2$  and (b)  $\text{SO}_4^{2-}/\text{ZrO}_2$ .

given in Table 1. All the reactions are carried out with standard substrates like methyl acetoacetate and ethyl acetoacetate with various alcohols like primary, secondary, allylic, cyclic and benzylic under identical conditions (Scheme 1). It is evident from Table 1 that the conversion of methyl/ethyl ketoesters to higher homologues appears to be efficient and practical through this procedure. Transesterification with tertiary alcohols is often problematic in acid catalyzed reaction and indeed fail to undergo transesterification with  $\text{Ti}(\text{OEt})_4$ [17]. However, with the present catalyst even the less reactive *tert*-butyl alcohol smoothly underwent transesterification affording the corresponding  $\beta$ -ketoesters in

Table 1  
Transesterification of  $\beta$ -ketoesters using borate zirconia solid acid catalyst

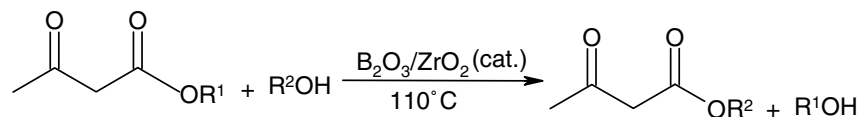
Entry	$\beta$ -Keto ester	Alcohol	Time (h)	Product	% Yield <sup>a</sup>
1.			3		85 (78)
2.			5		58
3.			4		70
4.			3		95
5.			3.5		89
6.			4		84 (82 <sup>c</sup> )
7.			3.5		87 <sup>b</sup>
8.			4		92 <sup>b</sup>
9.			3		81
10.			2.5		88
11.			3		78
12.			3		86

<sup>a</sup> Isolated yields.

<sup>b</sup> Yield with sulphated zirconia.

<sup>c</sup> Yield after third cycle.

<sup>d</sup> Two equivalence of ester used.



Scheme 1.

moderate yield (entry 2). It should be pointed out that transesterification of  $\beta$ -ketoesters with unsaturated alcohols is rather difficult as it is offset by facile decarboxylation rearrangement, i.e., Coroll rearrangement [18]. However,  $\beta$ -ketoesters underwent smooth transesterification using this method even with unsaturated alcohol like allyl alcohol (entry 3). It is important to mention that the reaction appears to be specific only for the transesterification of  $\beta$ -ketoesters, other esters like  $\alpha$ -ketoesters,  $\gamma$ -ketoesters and normal esters failed to un-

dergo the reaction. The difference in the reactivity of the  $\beta$ -ketoesters from the other esters in transesterification may be probably due to the formation of acyl keten intermediate in the former as proposed by Campbell and Lawrie [19]. The catalyst was recovered and recycled at least three times and did not show any appreciable loss of activity (entry 6). Transesterification of methyl acetoacetate with cyclohexanol has also been carried out using sulphated zirconia under the similar conditions used for borate zirconia (entry 1), which showed lower

yield (78%), and lower activity may be due to the leaching of sulphate ions during the course of reaction.

B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> possess both Lewis and Bronsted acid sites. The enhanced activity of this catalyst is because of the three-coordinated boron, which has an empty orbital and pulls electron cloud on the oxygen of ZrO<sub>2</sub>. The negative charge of boron is diffused into B<sub>2</sub>O<sub>3</sub> bulk by the resonance between the lone pair of oxygen and the empty orbital of boron enhancing the Lewis acidity of the catalyst responsible for better catalytic activity in solvent-free condition.

#### 4. Conclusion

In conclusion we have demonstrated that B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> serve as an efficient, selective, inexpensive and general catalyst to effect transesterification of  $\beta$ -ketoesters with various alcohols for the first time under solvent-free condition. The obvious advantage of heterogeneous catalysis in terms of simple operation coupled with the simpler work up and recyclability of catalyst. We believe this will present a better and more economical alternative to the existing methodologies and will find wide-spread application in industries as well as in organic synthesis.

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