

# Benzoylation of anisole over borate zirconia solid acid catalyst

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Received 13 May 2002; received in revised form 15 July 2002; accepted 15 July 2002

## Abstract

$B_2O_3/ZrO_2$  solid catalyst containing 30 mol% boron oxide prepared by wet impregnation method and calcined at 500 °C showed efficient catalytic activity in liquid phase benzoylation of anisole with benzoyl chloride (BOC) in nitrobenzene solvent at 150 °C.  $B_2O_3/ZrO_2$  catalyst under study has shown comparable performance with conventional homogeneous  $AlCl_3$  catalyst as well as heterogeneous catalysts such as zeolite H-beta and sulphated zirconia with maximum conversion and selectivity to the corresponding 4-methoxy benzophenone (4-MBP). The effect of various experimental parameters such as temperature, nature of solvent, reaction time and the effect of various benzoylating agents has been discussed. The conversion of anisole to 4-MBP increases significantly with increasing reaction time and temperature. The maximum conversion of about 91% with yield of acylated product >96% and selectivity for 4-MBP >94% was observed after 22 h. 2-MBP was found to be <4%. The phenyl benzoate (3%) formed by the O-benzoylation of anisole was found to be a major side product. The catalyst was recycled three times without any appreciable decrease in the anisole conversion showing its stability. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:**  $B_2O_3/ZrO_2$ ; Solid acid catalyst; Anisole benzoylation; 4-Methoxybenzophenone

## 1. Introduction

The Friedel–Crafts acylation is one of the most important methods in organic chemistry for synthesizing aromatic ketones [1,2]. The reaction be-

tween anisole and benzoyl chloride to produce 4- and 2-methoxybenzophenone is of industrial importance as an intermediate for the production of fine chemicals. Friedel–Crafts acylation using conventional Lewis acids ( $AlCl_3$ ,  $FeCl_3$ ,  $BF_3$ ) or Brønsted acids (polyphosphoric acid, HF) has well-known drawbacks [3]. The major drawbacks are, need to use stoichiometric quantity of Lewis acids, difficulties in recycling of catalyst and associated environmental problems. Therefore, considerable interest is growing to develop cleaner

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technologies using heterogeneous catalysis. The acylation of anisole using heterogeneous catalysts such as zeolites, sulphated zirconia has been studied in depth for activity, selectivity and deactivation of the catalyst [4,5]. The deactivation of zeolites in the acylation of anisole has been recently studied and it is agreed that the deactivation is reversible and attributed to non-desorption of the product acetyl anisole from the catalyst [6]. The activity and selectivity of sulphated zirconia is greatly influenced by the method of preparation of the catalyst. However, high acidic strength is required for the surface to catalyze acylation. It is claimed that a superacid with acid strength stronger than that of 100% sulphuric acid is desired [7].

Benzylation of toluene with benzoic anhydride or benzoyl chloride was carried out in liquid phase over superacids of sulphated and supported metal oxides at 100 °C. Sulphated metal oxides and supported metal oxides of  $\text{WO}_3/\text{ZrO}_2$ ,  $\text{MoO}_3/\text{ZrO}_2$ ,  $\text{WO}_3/\text{TiO}_2$ ,  $\text{WO}_3/\text{SnO}_2$  showed activity for benzylation of toluene whereas  $\text{WO}_3/\text{Fe}_2\text{O}_3$  and  $\text{B}_2\text{O}_3/\text{ZrO}_2$  (5 wt% B) gave no yields [8].

$\text{B}_2\text{O}_3/\text{ZrO}_2$  with 30 mol% boron oxide is reported to be a superacidic ( $H_0 = -13.6$ ) catalyst [9] and to our knowledge, its activity for acylation reaction has not been studied in detail. We have studied benzylation of anisole using  $\text{B}_2\text{O}_3/\text{ZrO}_2$  catalyst and the present paper reports the results of this study (see Scheme 1).

## 2. Experimental

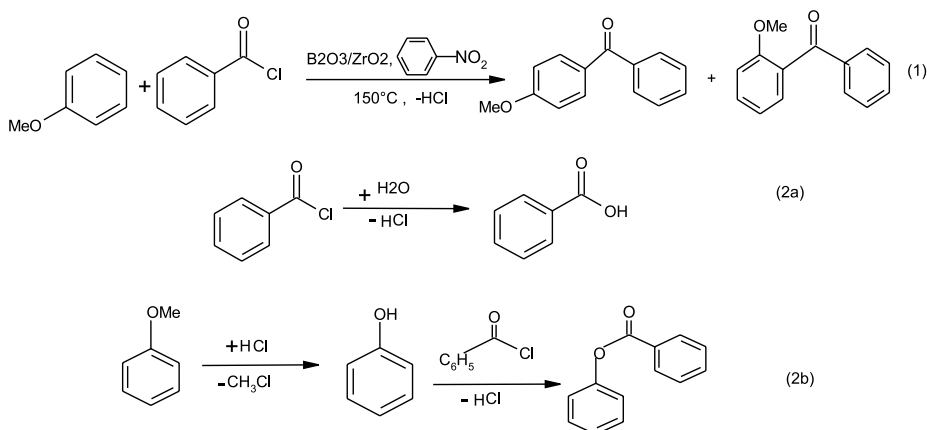
### 2.1. Chemicals

Anisole, benzoic anhydride, benzotrichloride, nitrobenzene (each 99% pure) (Merck),  $\text{AlCl}_3$ , boric acid, benzoyl chloride, chlorobenzene, nitromethane, ethylenedichloride, 1,1,2,2-tetrachloroethane (AR grade, S.D. Fine Chemicals) and zirconyl nitrate (AR grade, Loba) and zirconium butoxide (Fluka) were used for the preparation of the catalyst and for benzylation reactions.

### 2.2. Catalyst preparation

The 40.46 g of zirconyl nitrate [ $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ] was dissolved in 110 ml distilled water and aqueous ammonia (25%) was added to it drop wise with constant stirring till the solution became alkaline (pH = 10). The resultant solution was filtered and washed with distilled water till free from ammonium nitrate. The residue was dried overnight at 85 °C in an oven.

9.15 g boric acid [ $\text{H}_3\text{BO}_3$ ] was dissolved in 200 ml distilled water. The zirconium hydroxide obtained above was added to the boric acid solution with stirring to obtain slurry. It was air dried, heated in an oven at 110 °C for 5 h and calcined overnight at 550 °C. Sulphated zirconia was prepared using  $\text{Zr}(\text{OH})_4$  synthesized as mentioned above. Dried  $\text{Zr}(\text{OH})_4$  was added to 100 ml 1 N



Scheme 1.

H<sub>2</sub>SO<sub>4</sub>, stirred and filtered. The residue was dried at 110 °C and further calcined at 500 °C.

Commercially available zeolite H-beta (Si/Al = 30) in the powder form was procured from United Catalyst India. All the catalysts were freshly activated at 200 °C for 2 h and cooled before their use.

### 2.3. Catalyst characterization

The catalysts were characterized by X-Ray diffraction (Rigaku miniflex, CuK radiation), BET surface area (NOVA 1200 Quanta chrome), X-ray Photoelectron Spectroscopy (XPS) (VG Microtech Multilab ESCA 3000 spectrometer using non-monochromatized Mg-K $\alpha$  X-ray source ( $h\nu = 1253.6$  eV).

Temperature-programmed desorption (TPD) of ammonia was used to characterize the acid strength distribution of the B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> solid acid catalyst as well as of sulphated zirconia (prepared by aerogel technique) for comparison.

In a nickel tube approximately 245 mg of the grained catalyst (0.4–0.5 diameter fraction) was pretreated under nitrogen (70 ml/min) upto 500 °C followed by cooling the sample to 120 °C and exposing it to a stream of nitrogen and ammonia. The physisorbed ammonia was removed over 1 h at 120 °C. After cooling down to 80 °C the TPD program (10 K/min, up to 600 °C) was started. Desorption of ammonia was detected by continuous running IR spectroscopy (FTIR system 2000, Perkin–Elmer). The band at 930 cm<sup>-1</sup> was used to obtain the ammonia desorption profile. Behind the IR-cell an absorption cell was situated, containing a known amount of sulphuric acid. The amount of desorbed ammonia was determined by a titration with sodium hydroxide to get the quantitative amount of acid sites at the catalyst surface.

### 2.4. Catalytic reactions

All catalytic reactions were carried out in liquid phase in a batch reactor, under atmospheric pressure. The typical reaction with benzoyl chloride as acylating agent was carried out as follows: Solution of 10 mmol anisole (1.08 g) in 15 g nitrobenzene, 12.5 mmol benzoyl chloride (1.75 g) and freshly

activated catalyst 20 wt% (0.216 g, based on anisole) were taken in the batch reactor and the mixture was continuously stirred. The temperature of the reaction was maintained by using oil bath. The samples were periodically withdrawn by syringe, extracted with diethyl ether and analyzed by Gas Chromatography (Hewlett–Packard 5890, equipped with capillary column SPB-1, 30 m, 0.53 mm ID and Flame Ionization Detector). Products were identified and quantified by using internal standard method and confirmed by GC/MS (SHIMADZU, DB-I column) as well as by GC/IR (Perkin–Elmer Spectrum 2001, DB-1, 25 m, 0.32 mm ID) spectra.

The catalyst was separated by filtration, washed with acetone, heated in an oven at 110 °C for 5 h and reused for recycle experiments.

The benzylation of anisole using AlCl<sub>3</sub> catalyst was also carried out for comparison in similar way by using 1.08 g of anisole (10 mmol) and 1.6 g of AlCl<sub>3</sub> (12 mmol). The product was analyzed by quenching it in a beaker containing ice and hydrochloric acid and extracting with diethyl ether.

## 3. Results and discussion

### 3.1. Structural characterization

The XRD pattern of B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> calcined at 500 °C showed the amorphous nature of the solid catalyst. The surface area of the catalyst was found to be 114 m<sup>2</sup>/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<sup>3+</sup> state).

TPD results on B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and sulphated zirconia are shown in Fig. 1. The ammonia was desorbed below 400 °C in case of B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> whereas in case of sulphated zirconia ( $H_0 = -14$ ) desorbed at much higher temperature at about 540 °C indicating the lower acidity of B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> compared to sulphated zirconia. The acid site density in case of B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> was found to 0.398 mmol/g which is considerable high for its use in acid catalyzed reactions.

### 3.2. Benzoylation reactions

The results obtained by liquid phase benzoylation of anisole with benzoyl chloride in presence of

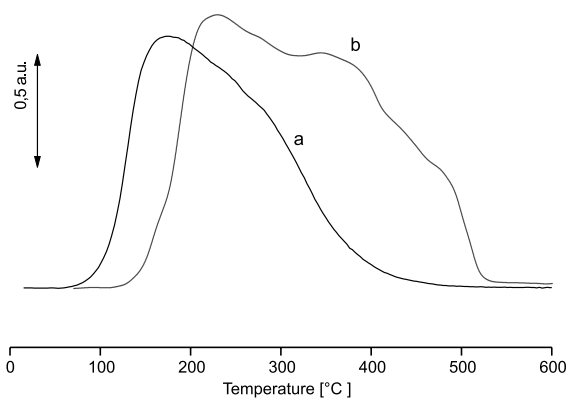


Fig. 1. TPD of ammonia on (a)  $B_2O_3/ZrO_2$ , (b) sulphated zirconia.

acid catalyst  $B_2O_3/ZrO_2$ ,  $SO_4^{2-}/ZrO_2$ , H-beta and  $AlCl_3$  after 22 h of the reaction under similar reaction conditions are given in Table 1.

The reaction profiles of conversion of anisole with reaction time are illustrated in Fig. 2. The conventional catalyst  $AlCl_3$  was found to be more active than beta zeolite, catalyst  $B_2O_3/ZrO_2$ ,  $SO_4^{2-}/ZrO_2$ , after 1 h of the reaction time. After 22 h of reaction time, the conversion of anisole and selectivity for 4-methoxy benzophenone in case of  $B_2O_3/ZrO_2$  and other solid catalysts under study was found to be more than  $AlCl_3$  catalyst. The conversion of anisole was between 91 and 96%, with selectivities for 4-MBP and 2-MBP to be about 94% and 3%, respectively with yield of acylated products  $\sim 97\%$  and p/o-ratio  $\sim 32$ . The ester

phenyl benzoate was found to be the major side product  $\sim 3\%$ . It may be formed either by the O-benzoylation of anisole or demethylation of anisole to form phenol, which on O-benzoylation produces the phenyl benzoate. The conversion of anisole, ratio of 4-methoxybenzophenone to 2-methoxybenzophenone (p/o-ratio) in case  $B_2O_3/ZrO_2$  was found to be comparable with other solid catalysts under study indicating the suitability of  $B_2O_3/ZrO_2$  catalyst for benzoylation of anisole. In order to check the stability and catalytic activity of  $B_2O_3/ZrO_2$  catalyst in the benzoylation of anisole, three reaction cycles (fresh and two cycles) by using same catalyst were performed. No appreciable change in conversion and selectivity was observed.

However, it has also been shown that the catalytic activity of the boron-modified zirconia is significantly lower when the benzoylation reaction is performed at low temperature. Sulphated zirconia aerogels were found to be superior for benzoylation and gave high conversion at temperatures as low as 40 °C [4]. Comparing the overall acidity determined by ammonia-TPD there is no difference between SZ aerogels and boron-modified zirconia. Both catalysts exhibit surface acid site concentration between 0.35 and 0.4 mmol/g, which is significantly higher than found for pure zirconia which did not show any catalytic activity in this reaction. However, as can be seen from Fig. 1, sulphated zirconia has significantly stronger acid surface sites (desorption of ammonia occurs at quite higher temperatures).

Table 1  
Benzoylation of anisole using different catalysts<sup>a</sup>

Catalysts	Anisole conversion	Product selectivity (%)			Yield (%) <sup>d</sup>	P/O ratio	Activity <sup>e</sup> (mmol g <sup>-1</sup> h <sup>-1</sup> )
		4-MBP <sup>b</sup>	2-MBP	PB <sup>c</sup>			
$B_2O_3/ZrO_2$	91.0	93.6	2.9	3.4	87.8	32.3	14.8
$SO_4^{2-}/ZrO_2$	96.0	94.6	2.9	2.4	93.6	32.6	21.3
H-Beta	95.0	94.7	3.0	2.3	92.8	31.6	9.9
$AlCl_3$	83.0	93.0	4.0	3.0	80.5	23.2	33.3

<sup>a</sup> Reaction conditions: time = 22 h, Anisole/BOC molar ratio = 0.8, Catalyst = 20%, Solvent = nitrobenzene, Temp. = 150 °C.

<sup>b</sup> Methoxybenzophenone.

<sup>c</sup> Phenyl benzoate.

<sup>d</sup> Anisole conversion \* selectivity for MBP/100.

<sup>e</sup> Anisole converted at 1st h.

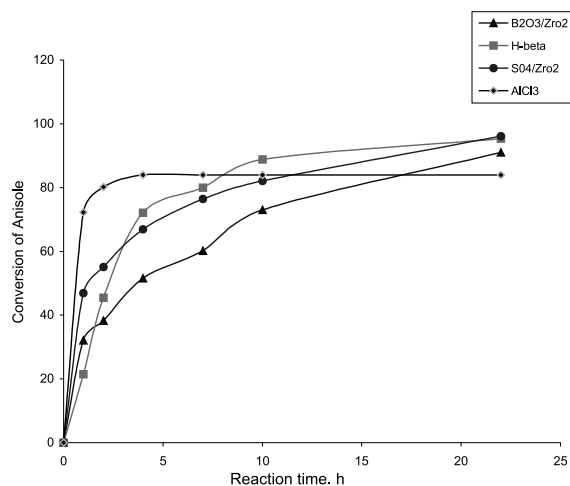


Fig. 2. Conversion of anisole (%) versus reaction time (h).

### 3.3. Influence of solvents

The various commonly used solvents like ethylene dichloride (EDC), 1,1,2,2-tetrachloroethane (TCE), nitromethane (NM), chlorobenzene (CB) and nitrobenzene (NB) were tested for benzylation of anisole at their reflux temperature (except for nitrobenzene BP 211 °C, reaction at 150 °C) under similar other conditions. Fig. 3 shows the conversion of anisole after 5 h of reaction time. In the reaction without any solvent very low conversion 20% is observed. Only the high boiling solvents like TCE (BP 147 °C) and nitrobenzene (BP 211 °C) showed better conversion for anisole

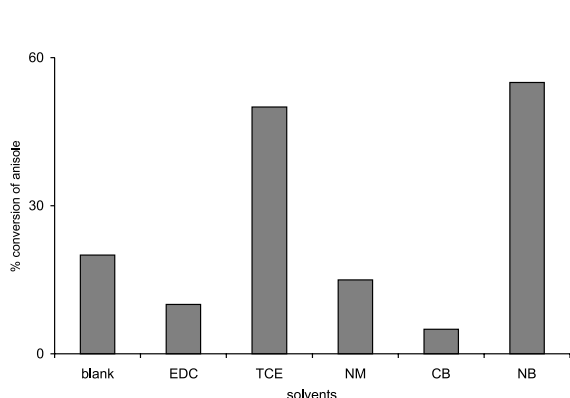


Fig. 3. Influence of solvents on the conversion of anisole. Reaction conditions: time = 5 h, anisole/BOC mole ratio = 0.8, Catalyst amount = 20 wt% of anisole, Temp. = at the reflux.

(>50%). Therefore, further reactions were carried out by using nitrobenzene as a solvent.

### 3.4. Influence of temperature

The influence of temperature on the rate of benzylation was studied over  $B_2O_3/ZrO_2$  in the range 100–150 °C as shown in the Fig. 4 under identical conditions. Low Conversion of anisole 21% and 31% obtained at 100 and 125 °C, respectively, while significant change in anisole conversion 91% was observed at 150 °C indicating the influence of temperature. However, product distribution was not significantly influenced by temperature.

### 3.5. Influence of benzoylating agents

Benzylation of anisole was examined by using different benzoylating agents like benzoyl chloride (BOC), benzoic anhydride (BOA) and benzotrichloride (BOT) over  $B_2O_3/ZrO_2$  under identical conditions. Among these acylating agents benzoic anhydride showed less conversion of anisole (5%) under these conditions. Like benzoyl chloride, benzotrichloride, one of strongest known benzoylating agent, showed equivalent conversion for anisole (91%) but less selectivity for the corresponding 4-MBP (62%) and better selectivity for 2-MBP (12%) and PB (16%) as shown in Fig. 5. Thus

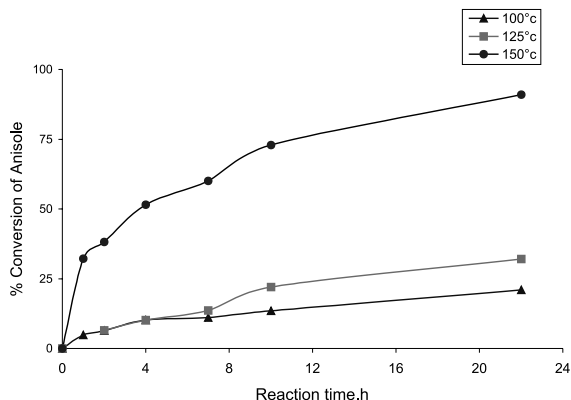


Fig. 4. Influence of temperature on the conversion of anisole. Reaction conditions: time = 5 h, solvent = nitrobenzene, anisole/BOC mole ratio = 0.8, Catalyst amount = 20 wt%.

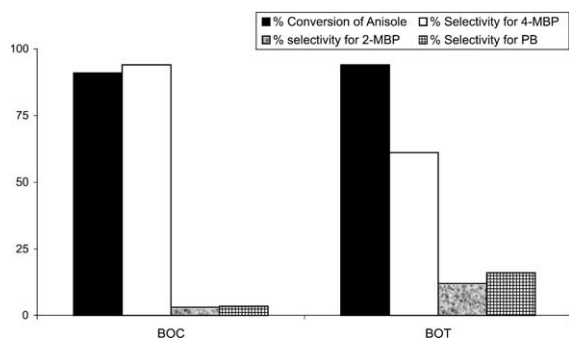


Fig. 5. Influence of benzoylating agents. Reaction conditions: time = 22 h, solvent-nitrobenzene, anisole/acylating agent, mole ratio = 0.8, Catalyst amount = 20%, Temp. = 150 °.

benzoyl chloride is the active and selective acylating agent for this reaction.

$B_2O_3/ZrO_2$  catalyst under investigation possesses both Lewis and Brønsted acid sites. Former sites are considered to be responsible for benzoylation. Electron cloud on the oxygen of  $ZrO_2$  is pulled by the three coordinated boron, which has an empty p-orbital. The negative charge of boron is diffused into  $B_2O_3$  bulk by the resonance between the lone pair of oxygen and the empty p-orbital of boron enhancing the Lewis acidity of the catalyst and was reported as a superacid catalyst [9]. Because the TPD results as well as its catalytic activity for benzoylation of anisole indicates that  $B_2O_3/ZrO_2$  with 30%  $B_2O_3$  has lower acidity than sulphated zirconia we doubt the superacidity of this system based on our results. However, it is a suitable catalyst for isomerization reactions of butanes and pentanes [10].

#### 4. Conclusion

$B_2O_3/ZrO_2$  solid acid catalyst containing 30 mol% boron oxide prepared by wet impregnation method and calcined at 500 °C is found to be an efficient catalyst for the benzoylation of anisole with benzoyl chloride as benzoylating agent using nitrobenzene as a solvent at 150 °C temperature. The maximum conversion of anisole ~91% with selectivity for 4-MBP more than 93% and for 2-

MBP 3% with satisfactory yield ~97% with p/o-ratio ~32 was observed after 22 h. Phenyl benzoate formed by O-benzoylation is found to be major side product. This catalyst shows comparable performance with the conventional heterogeneous catalysts like H-beta, sulphated zirconia and  $AlCl_3$  homogeneous catalyst under these reaction conditions. The activity of the catalysts was almost constant during three recycle experiments showing the suitability of this catalyst for benzoylation of anisole. Comparing the acid strength and catalytic activity of  $B_2O_3/ZrO_2$  with sulphated zirconia aerogels leads us to the conclusion that the stronger surface sites are mainly responsible for the catalytic reaction. Therefore, the superacidity of this catalyst system stated by Hinto et al. [9] seems to be doubtful. However even the weaker sites (of boron modified zirconia) are suitable catalytic sites; but, it needs higher reaction temperatures to obtain comparable conversions compared to SZ.

Since it is known that SZ-aerogels deactivate faster due to coke formation, the advantage of the boron modified zirconia may be that it is a suitable catalyst because of weaker surface sites leading to longer catalyst life.

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