



Synthesis, Characterization, Magnetic Properties and Catalytic Performance of Iron Orthoborate

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The structural properties of iron orthoborate samples prepared by different synthetic approaches were comparatively investigated. The structural properties of the product were characterized by powder XRD, FT-IR, UV-Vis-NIR and SEM methods and the thermal stability was analyzed by the TGA/DTA technique. The room temperature magnetic properties of the product were investigated using the vibrating sample magnetometer technique. $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ was used as iron source and H_3BO_3 and B_2O_3 were used as boron sources. High temperature solid state synthesis method was used and the experiments were performed at Fe:B = 1:2, 1:3 and 1:4 mole ratios. High purity (99 %) iron orthoborate (Fe_3BO_6) was obtained from iron(III) sulfate and boric acid at 1:3 ratio. The product was observed to crystallize into orthorhombic crystal structure (Norbergite type) and cell parameters were determined as $a = 10.046(2) \text{ \AA}$, $b = 8.532(2) \text{ \AA}$ and $c = 4.467(1) \text{ \AA}$ values from ICDD data base. The use of Fe_3BO_6 in the catalytic reaction for the oxidation of benzyl alcohol under solvent-free conditions was tested without employing any oxidant. Benzaldehyde, dibenzyl ether and benzyl benzoate were observed to be the three main products.

Keywords: Iron borate, High temperature synthesis, Solid state reactions, Magnetic properties, Benzyl alcohol oxidation.

INTRODUCTION

Transition metal borates have some properties which are strongly dependent on their exact chemical composition and their microscopic physical structure. The materials, which are synthetic materials with potential uses due to electronic, magnetic and optical properties, are of continuing interest. Transition metal borates also display the important property of catalytic activity [1-3]. Borates are divided into two groups: orthoborate and metaborate. Both of the borate groups contain isolated trigonal BO_3^{3-} (Δ) and tetrahedral BO_4^{5-} (T). In the metaborates, simple units (Δ or T) join together to form a variety of polymeric chain and ring structures. The other form, orthoborates, have discrete Δ or T imbedded in a metal oxide framework. The orthoborates can be subdivided into three groups which correspond to the crystal modifications of CaCO_3 : aragonite-type structure (MnBO_3 and Fe_3BO_6), calcite-type structure (CrBO_3) and vaterite-type structure (YBO_3) [4-9].

In the traditional process, the iron borate compounds are usually prepared by solid-state reaction of anhydrous borate materials carried out by means of a high temperature reaction between finely-milled oxide powders and metal. The influence of various iron precursors (metallic Fe, Fe_2O_3) and boron sources (B_2O_3 , H_3BO_3) on iron orthoborate synthesis has been reported [10-13]. In this paper, we prepare Fe_3BO_6 using a different precursor. The correlations between the structural,

physical and magnetic properties and the catalytic performance of iron orthoborate are investigated.

EXPERIMENTAL

The initial materials employed for the solid-state syntheses included $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ (Sigma, 99 %), H_3BO_3 (Aldrich, 99.9 %) and B_2O_3 (Sigma, 99 %). Benzyl alcohol (Riedel, 99 %) was used for the catalytic performance of iron orthoborate. The experimental procedure involves; (i) Mixing and grinding of the different precursors, (ii) Heating the mixture to about 900 °C and (iii) Regrinding. Five experiments were prepared using different combinations for iron orthoborate.

Experiment 1: $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and H_3BO_3 were mixed in Fe:B = 1:2 ratio and manually ground in an agate mortar for 30 min. The mixture was heated in an ash-oven (900 °C, 9 h). The product (**A1**) was dried in a vacuum oven after washing with distilled water and ethanol.

Experiment 2: $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and H_3BO_3 were mixed in Fe:B = 1:3 ratio and manually ground in an agate mortar for 30 min. The mixture was heated in an ash-oven (900 °C, 9 h). The product (**A2**) was isolated as described in experiment 1.

Experiment 3: $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and H_3BO_3 were mixed in Fe:B = 1:4 ratio and manually ground in an agate mortar for 30 min. The mixture was heated in an ash-oven (900 °C, 9 h). The product (**A3**) was isolated as described in experiment 1.

Experiment 4: $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and B_2O_3 were mixed in Fe:B = 1:2 ratio and manually ground in an agate mortar for 30 min. The mixture was heated in an ash-oven (900 °C, 9 h). The product (**A4**) was isolated as described in experiment 1.

Experiment 5: $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and B_2O_3 were mixed in Fe:B = 1:3 ratio and manually ground in an agate mortar for 30 min. The mixture was heated in an ash-oven (900 °C, 9 h). The product (**A5**) was isolated as described in experiment 1.

Characterization: Formation of Fe_3BO_6 was analyzed in terms of XRD pattern which was recorded on a Rigaku (model DMAX2200) diffractometer with filtered 1.5418 Å Cu lamp. The diffractograms were recorded in the range of 20–80° with a step size of 0.04 °/s. The purity of the products was determined by using the software CRYSFIRE [14] in correlation with ICDD card of Fe_3BO_6 (70-0880). The best result was obtained from iron sulfate and boric acid (**A2**, Fe:B = 1:3) where pure Fe_3BO_6 form was created ($\geq 99\%$). Iron and B contents were analyzed on an Oxford (model ED2000) XRF instrument. For **A2** (%): Fe 62.38 ± 0.05 , (B+O) 37.62 ± 0.02 ; calculated Fe 61.08, (B + O) 38.92.

Density of the product was measured by a Mettler Toledo density kit at room temperature and calculated according to the Archimedes' principle [15] with the following equation:

$$\rho_p = [W_{\text{air}} / (W_{\text{air}} - W_{n\text{-hexane}})] \cdot \rho_{n\text{-hexane}}$$

where ρ_p is the density of product, $\rho_{n\text{-hexane}}$ is density of *n*-hexane, W_{air} is the weight of the product in air and $W_{n\text{-hexane}}$ is the weight of the product in *n*-hexane.

The thermogravimetry (TG) and differential thermal analysis (DTA) was carried out on a Shimadzu DTG-60H instrument, typically heating a 10.00 mg sample from room temperature to 900 °C at a heating rate of 20 °C/min under nitrogen flow (15 mL/min). FT-IR transmittance spectra were measured at room temperature in KBr pellet with a powder sample by a using Perkin Elmer spectrum one model spectrophotometer in the frequency range 4000–450 cm^{-1} . The electronic spectra were recorded on Shimadzu UV-3600/UV-Vis-NIR spectrophotometer equipped with Praying Mantis attachment. The magnetic susceptibility measurement was carried out using Alfa Aesor magnetic susceptibility Balance. The structure and morphology of the product was investigated by scanning electron microscopy (SEM; Philips XL-30S FEG 12-24 kV).

M(T) (magnetization vs. applied field) measurement was performed by a vibrating sample magnetometer (VSM) with the quantum desing physical property measurement system (PPMS). M(T) measurement was done at room temperature with curves measured with steps of 100 Oe in the ± 5 kOe range and with steps of 1 kOe in higher field ranges.

The solid catalyst was then separated and the reaction products were analyzed by a Shimadzu GCMS-QP5050A instrument (optima column-5-1.0 μm , 50 m $\times$ 0.32 mm), temperature range: 8–250 °C (20 °C/min), carrier gas: helium (1 mL/min).

RESULTS AND DISCUSSION

The iron(III) borate phase can be prepared by a high temperature solid state reaction between various iron(III) and boron sources: Fe_3BO_6 with the orthorhombic crystal structure

(Fig. 1) [4]. The norbergite structure is distorted hexagonal close-packing of oxygen that can be written as “ $\text{Fe}_2\text{B}_{2/3}\text{O}_4$ ” from which it is clearly comparative to A_2BO_4 (olivine).

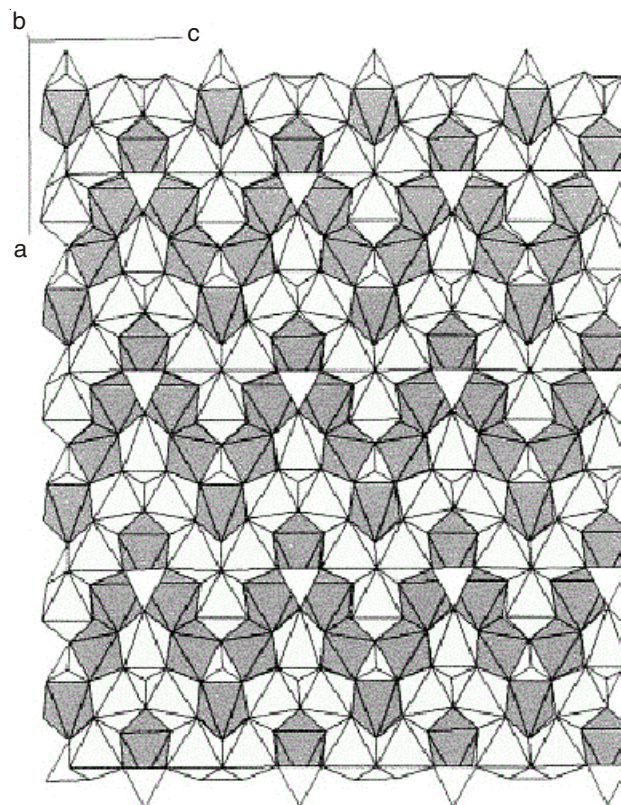


Fig. 1. Norbergite structure

Structure: The powder XRD pattern of Fe_3BO_6 (99 %) is shown in Fig. 2. Impurity phase has been observed as an FeO_x phase [15]. Three sharp peaks were observed at 2θ values of 31° (2 2 1), 35° (2 3 0) and 53° (6 0 0); and smaller peaks at 48° (3 1 2), 61° (6 2 1) and 63° (3 5 1), in the order of decreasing intensity. The results matched properly with the reported data for Fe_3BO_6 [ICDD 70-0880]. XRD analyses revealed that the sample prepared has norbergite structure.

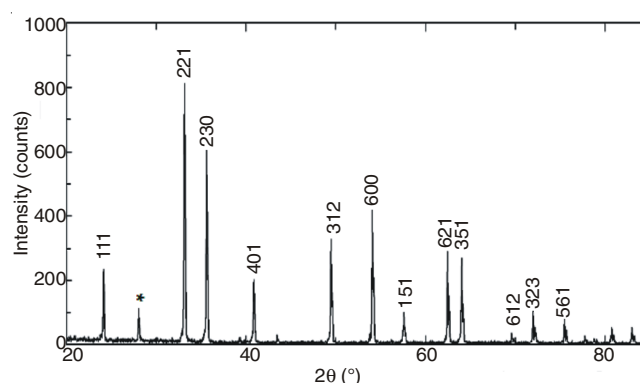


Fig. 2. XRD patterns of Fe_3BO_6 (*Impurity oxide phase: FeO_x)

Table-1 gives the lattice parameters $a = 10.048(2)$ Å, $b = 8.531(2)$ Å and $c = 4.466(1)$ Å, calculated from refined parameters indexed with the Pnma system. The measured density of Fe_3BO_6 is consistent with four formula units per distorted hexagonal structure [4,15].

TABLE-1
CRYSTALLOGRAPHIC DATA FOR Fe_3BO_6

Empirical formula	Fe_3BO_6
Molecular weight (g/mol)	274
Sample form	Soft gray, powder
Crystal system	Norbergite
Space group	Pnma
Unit cell dimensions ($\text{\AA}$)	a = 10.048 (2); b = 8.531 (2); c = 4.466 (1)
Volume ($\text{\AA}^3$)	382.82
Z	4
Calculated density (g/cm^3)	4.756
Experimental density (g/cm^3)	4.813 (± 0.01)
Refinement method	CRYSFIRE
Data range	20-80°

The morphology of Fe_3BO_6 was also analyzed by scanning electron microscopy. The low magnification image in Fig. 3a shows the panoramic morphology. An enlarged image (Fig. 3b) shows clear norbergite/distorted hexagonal shapes.

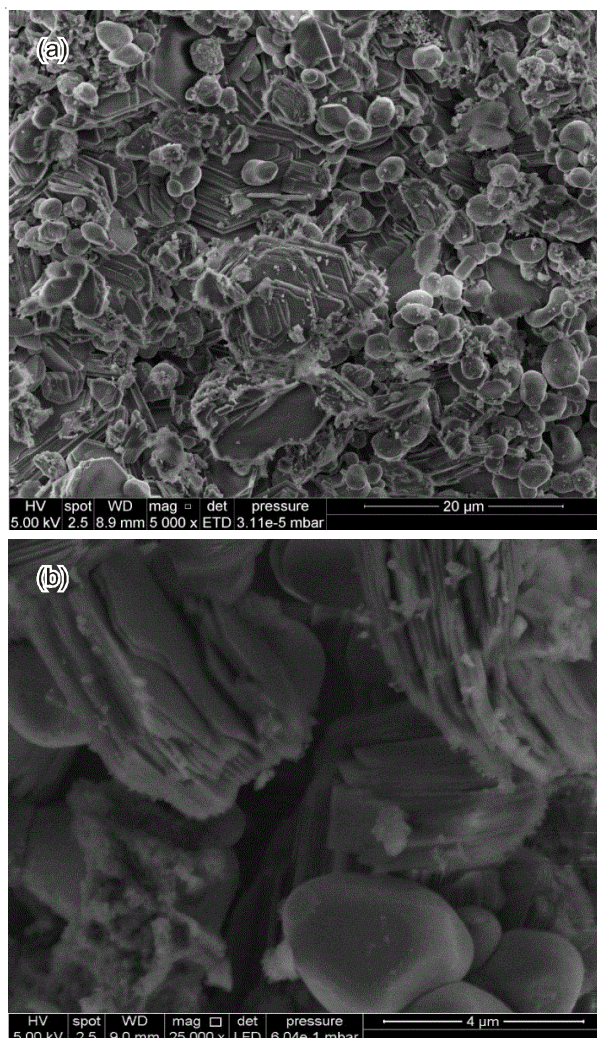


Fig. 3. (a) Low magnification (b) Enlarged SEM images of Fe_3BO_6

Significant mass loss was not observed in the TGA and DTA curves throughout the long temperature range up to 900 °C. DTA curve indicated that no structural phase transitions (neither endothermic nor exothermic) take place. This behaviour verifies the thermal stability of the product.

Spectroscopic and magnetic studies: The lowest energy term for the free ion is ^6S , which splits in a weak octahedral field to give $^6\text{A}_{1g}$ as the ground state for d^5 . In the d^5 ground state ($^6\text{A}_{1g}$) octahedral complex, all transitions are not only Laporte forbidden but also spin forbidden [16]. No electronic transition is observed on UV-spectrum which d^5 electron configuration indicates is similar to high spin sequence. Experimental magnetic susceptibility result ($\mu_{\text{eff}} = 5.38 \mu_B$) is compatible with the electronic spectrum.

The IR spectrum of Fe_3BO_6 is shown in Fig. 4 where the isolated metal orthoborates allow us to easily establish the presence of the BO_3 and BO_4 groups in the structure [17-19]. All the experimental results are collected in Table-2. The OH vibration peak observed at 3300 cm^{-1} belongs to moisture on the face similar to during cooling.

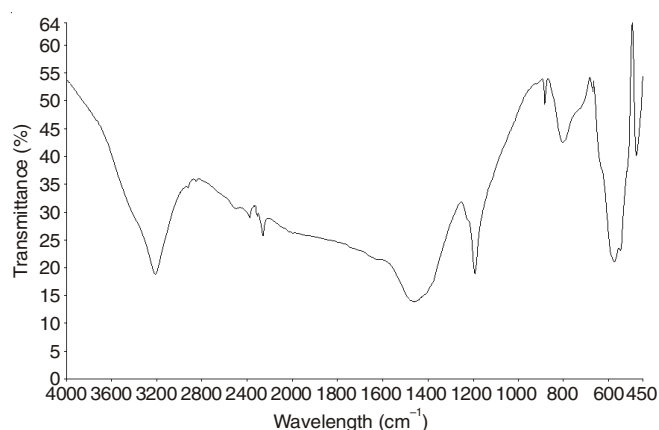


Fig. 4. FT-IR spectrum of Fe_3BO_6

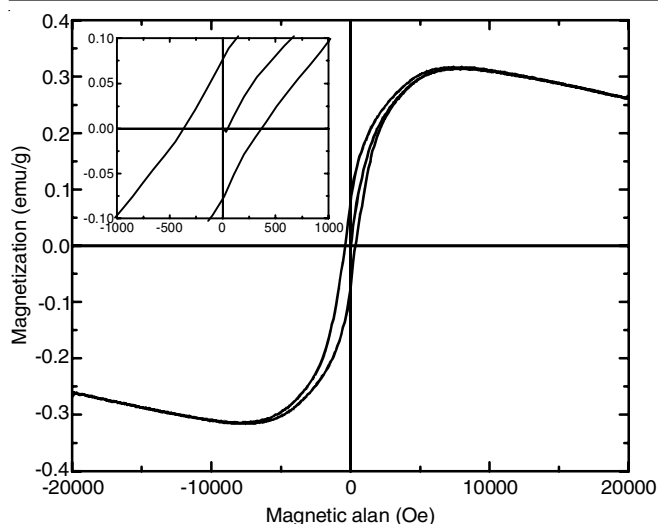
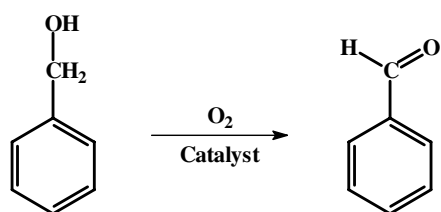
TABLE-2
INFRARED BAND WAVENUMBERS (cm^{-1}) OF Fe_3BO_6

Wave type	Wavenumber (cm^{-1})	Wave type	Wavenumber (cm^{-1})
$\nu(\text{BO}_3)$	1460	$\nu_1(\text{BO}_4)$	884
$\nu_2(\text{BO}_3)$	805	$\nu_4(\text{BO}_4)$	576
$\nu_3(\text{BO}_3)$	1194	$\nu(\text{Fe-O})$	479
$\nu_4(\text{BO}_3)$	570	—	—

The temperature and magnetic field dependencies of the magnetization of iron orthoborate sample were measured. Fig. 5 shows $\sigma(H)$ curves of Fe_3BO_6 at 300 K. The σ value obtained at 300 Oe is 0.98 emu/g. The sample shows weakly ferromagnetic behaviour at room temperature, the $\sigma(H)$ curve (370 Oe) indicates some magnetic impurity contribution [20].

Catalytic studies: Fe_3BO_6 was tested for the first time as a heterogeneous catalyst and benzyl alcohol oxidation reaction was chosen as the test reaction (**Scheme-I**). The experiments were performed in solvent-free conditions without employing any oxidizing agent other than the air present in the reflux atmosphere.

The oxidation reaction was performed in a magnetically-stirred three-neck flask equipped with thermometer and reflux condenser. The reaction in the flask was charged with benzyl alcohol (10 mL) and a prescribed amount of catalyst (0.5 g) was added so that the conversion of benzyl alcohol increased regularly with the amount of the catalyst until $\text{BzOH}/\text{Fe}_3\text{BO}_6$ ratio at 165 °C. The system was heated at a prescribed temperature

Fig. 5. Magnetization (M) vs. applied field (H) loops of Fe_3BO_6 Scheme-I: Oxidation of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

(25–150 °C) for a period of 10 h. At higher loadings no further increase in the conversion was noticed. While conversion remained almost constant, the decrease in the selectivity for benzaldehyde was correlated with the increase in the selectivities of second generation products (dibenzyl ether and benzaldehyde) from benzaldehyde. Best performance was achieved for a reaction period of 4–5 h. Benzyl alcohol conversion increased while selectivity for benzaldehyde decreased during the longer reaction time (Fig. 6).

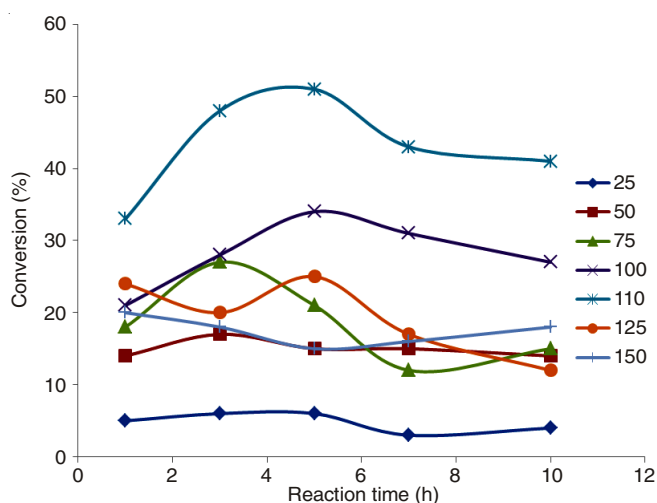


Fig. 6. Effect of reaction time on conversion of benzyl alcohol

The catalytic reactions were run at different temperatures by employing 0.5 g Fe_3BO_6 for 10 mL of benzyl alcohol. Significant conversion was not noted at low temperatures (< 80 °C).

Raising the temperature to 100 °C led to a consistent enhancement in conversion. Optimum reaction temperature for highest benzaldehyde selectivity was 110 °C. Substantial amounts of dibenzyl ether and benzaldehyde are produced at higher temperatures (Fig. 7).

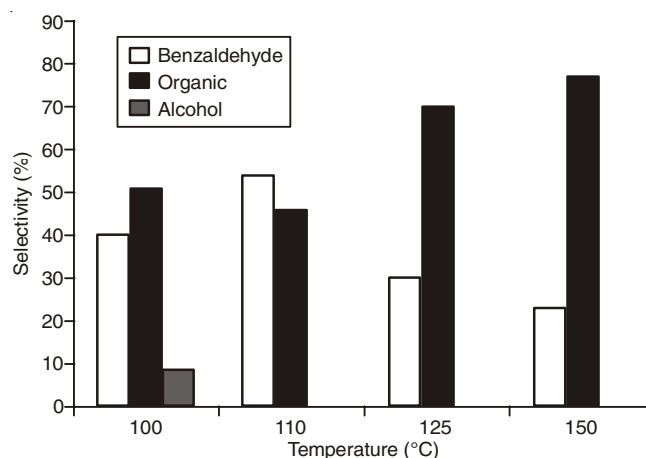


Fig. 7. Effect of reaction temperature on the product selectivities

Conclusion

In summary, Fe_3BO_6 was prepared in 99 % pure form by a solid state reaction between $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and H_3BO_3 after a series of experiments to investigate the effect of reaction conditions on the formation of Fe_3BO_6 . Rietveld refinement of powder XRD data shows the structure has a norbergite (distorted hexagonal) system with four formula units in the unit cell for the pycnometric density of Fe_3BO_6 . Magnetization measurements revealed that Fe_3BO_6 is weakly ferromagnetic at room temperature. Further studies are needed to investigate the complex magnetism of iron orthoborate at low temperature. The use of iron orthoborate in catalytic reactions was investigated for the first time. The solvent-free partial oxidation of benzyl alcohol to benzaldehyde proceeded with moderate conversion. The acidic nature of the catalyst promotes the sequential reactions of the reactants and products and the selectivity. Further research is needed to achieve better performance for other organic solvents and other catalytic reaction types.

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