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 $\text{BO}_3^{3-} (\Delta)$ and tetrahedral $\text{BO}_4^{5-} (T)$. In the metaborates, simple units ($\Delta$ or $T$) join together to form a variety of polymeric chain and ring structures. The other form, orthoborates, have discrete $\Delta$ or $T$ imbedded in a metal oxide framework. The orthoborates can be subdivided into three groups which correspond to the crystal modifications of $\text{CaCO}_3$: aragonite-type structure (Mn$\text{BO}_3$), calcite-type structure (Cr$\text{BO}_4$) and vaterite-type structure (Y$\text{BO}_3$) [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$\text{O}_3$) and boron sources ($\text{B}_2\text{O}_3$, $\text{H}_2\text{BO}_3$) on iron orthoborate synthesis has been reported [10-13]. In this paper, we prepare Fe$_3\text{BO}_6$ 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 Fe$_2$(SO$_4$)$_3$·H$_2$O (Sigma, 99%), H$_3$BO$_3$ (Aldrich, 99.9%) and B$_2$O$_3$ (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:** Fe$_2$(SO$_4$)$_3$·H$_2$O and H$_3$BO$_3$ were mixed in Fe:B = 1:2 ratio and manually ground in an agate mortar for 30 min. The mixture was heated in a vacuum oven (900 °C, 9 h). The product (A1) was observed to crystallize into orthorhombic crystal structure (Norbergite type) and cell parameters were determined as $a = 10.046(2)$ Å, $b = 8.532(2)$ Å and $c = 4.467(1)$ Å values from ICDD data base. The use of Fe$_3$BO$_6$ 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.

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

- **Experiment 3:** Fe$_2$(SO$_4$)$_3$·H$_2$O and H$_3$BO$_3$ were mixed in Fe:B = 1:4 ratio and manually ground in an agate mortar for 30 min. The mixture was heated in a vacuum oven (900 °C, 9 h). The product (A3) was isolated as described in experiment 1.
Experiment 4: Fe$_2$(SO$_4$)$_3$·H$_2$O and B$_2$O$_3$ 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: Fe$_2$(SO$_4$)$_3$·H$_2$O and B$_2$O$_3$ 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$_3$BO$_6$ 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 ICCD card of Fe$_3$BO$_6$ (70-0880). The best result was obtained from iron sulfate and boric acid (A2, Fe:B = 1:3) where pure Fe$_3$BO$_6$ form was created (≥ 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:

$$\rho_p = \frac{W_{air} - W_{n-hexane}}{\rho_{n-hexane}}$$

where $\rho_p$ is the density of product, $\rho_{n-hexane}$ is density of n-hexane, $W_{air}$ is the weight of the product in air and $W_{n-hexane}$ 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 × 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$_3$BO$_6$ with the orthorhombic crystal structure (Fig. 1) [4]. The norbergite structure is distorted hexagonal close-packing of oxygen that can be written as “Fe$_3$B$_{2/3}$O$_4$” from which it is clearly comparative to A$_3$BO$_4$ (olivine).

Structure: The powder XRD pattern of Fe$_3$BO$_6$(99 %) is shown in Fig. 2. Impurity phase has been observed as an FeO$_x$ phase [15]. Three sharp peaks were observed at 20 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$_3$BO$_6$ [ICDD 70-0880]. XRD analyses revealed that the sample prepared has norbergite structure.

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$_3$BO$_6$ is consistent with four formula units per distorted hexagonal structure [4,15].
TABLE-1
CRYSTALLOGRAPHIC DATA FOR Fe₃BO₆

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>Fe₃BO₆</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>274</td>
</tr>
<tr>
<td>Sample form</td>
<td>Soft gray, powder</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Norbergite</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>Unit cell dimensions (Å)</td>
<td>a = 10.048 (2); b = 8.531 (2);</td>
</tr>
<tr>
<td></td>
<td>c = 4.466 (1)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>382.82</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density (g/cm³)</td>
<td>4.756</td>
</tr>
<tr>
<td>Experimental density (g/cm³)</td>
<td>4.813 (± 0.01)</td>
</tr>
</tbody>
</table>

Table 1: Crystallographic data for Fe₃BO₆.

Spectroscopic and magnetic studies: The lowest energy term for the free ion is ⁴S, which splits in a weak octahedral field to give ⁶A₁g as the ground state for d⁵. In the ⁶A₁g octahedral complex, all transitions are not only Laporte forbidden but also spin forbidden [16]. No electronic transition is observed on UV-spectrum which d⁵ electron configuration indicates is similar to high spin sequence. Experimental magnetic susceptibility result (µₑf = 5.38 µ₆B) is compatible with the electronic spectrum.

The IR spectrum of Fe₃BO₆ is shown in Fig. 4 where the isolated metal orthoborates allow us to easily establish the presence of the BO₃ and BO₄ 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.

The morphology of Fe₃BO₆ 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.

**Table 2: Infrared band wavenumbers (cm⁻¹) of Fe₃BO₆**

<table>
<thead>
<tr>
<th>Wave type</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Wave type</th>
<th>Wavenumber (cm⁻¹)</th>
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<tr>
<td>ν(BO₃)</td>
<td>1460</td>
<td>ν₁(BO₄)</td>
<td>884</td>
</tr>
<tr>
<td>ν₂(BO₃)</td>
<td>805</td>
<td>ν₂(BO₄)</td>
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<td>ν₃(BO₃)</td>
<td>1194</td>
<td>ν₁(Fe-O)</td>
<td>479</td>
</tr>
<tr>
<td>ν₄(BO₃)</td>
<td>570</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The temperature and magnetic field dependencies of the magnetization of iron orthoborate sample were measured. Fig. 5 shows σ(H) curves of Fe₃BO₆ at 300 K. The σ values obtained at 300 Oe is 0.98 emu/g. The sample shows weakly ferromagnetic behaviour at room temperature, the σ(H) curve (370 Oe) indicates some magnetic impurity contribution [20].

Catalytic studies: Fe₃BO₆ 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 BzOH/Fe₃BO₆ ratio at 165 °C. The system was heated at a prescribed temperature
(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).

The catalytic reactions were run at different temperatures by employing 0.5 g Fe$_3$BO$_6$ 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).

**Conclusion**

In summary, Fe$_3$BO$_6$ was prepared in 99 % pure form by a solid state reaction between Fe$_2$(SO$_4$)$_3$·H$_2$O and H$_3$BO$_3$ after a series of experiments to investigate the effect of reaction conditions on the formation of Fe$_3$BO$_6$. 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$_3$BO$_6$. Magnetization measurements revealed that Fe$_3$BO$_6$ 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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**REFERENCES**