SYNTHESIS AND CHARACTERIZATION OF ORIGINAL AND VARIOUSLY METAL DOPED BARIUM TITANATES

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Abstract: In the present study, lead (Pb) and cobalt (Co) doped, Perovskite type BaTiO₃ were synthesized via reactive calcination method, for catalytic purpose. All the synthesized catalysts were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDX), X-ray Diffraction Studies (XRD) and Surface Area Analysis (SAA). The XRD analysis shows that ceramic materials formed have same crystalline patterns as BaTiO₃, with well defined cubic geometry. Results of SAA show that the surface area of the catalyst increases from 98 to 127 m²/g in the presence of single dopant i.e. lead or cobalt, and further increases to 269 m²/g, as a result of co-doping with lead and cobalt.

Key words: BaTiO₃, ceramics, perovskite, doping, XRD, materials.

Introduction

Perovskite type barium titanates (BaTiO₃) ceramics have enormous surface and electric properties, due to which they are widely used in high dielectric capacitors, positive temperature coefficient (PTC) resistors, transducers and ferroelectric memories (Lu, et al., 2003). Also, because of their high thermal stability and resistant to deactivation by coke deposition, these materials have been proved to be effective carriers for catalysts (Yang, et al., 2010; Li, et al., 2003).

There are several routes for the synthesis of barium titanates (BaTiO₃). Traditional synthesis involves physical mixing and grinding of Ba and Ti precursors, followed by sintering at high temperatures ranging from 1200 to 1300 ºC (Boulos, et al., 2005; Simmon, et al., 2005). However, this process involves high temperature and long time mixing; also the product is agglomerated and is of low purity (Wang, et al., 2007). Other methods used for synthesis of these materials are solution based, which include sol gel (Potdar, et al., 1999; Wang, et al., 2007; Li, et al., 2002), hydrothermal ((Boulos et al., 2005; Ciftci et al., 2001), co-precipitation (Potdar, et al., 1999; Simmon, et al., 2005; Parsadrao, et al., 1999), and polymeric precursor (Cho, et al., 1998) methods, etc. Despite of the advantages, these methods also have several shortcomings such as high cost, strict temperature control, long reaction procedure, requirement of inert atmosphere when use of alkoxide is involved and corrosion problems when using TiCl₂. Mechano chemical or reactive calcination is a very effective method for obtaining a highly dispersed perovskite type (BaTiO₃) ceramics.
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The process involves the mechanical action by milling process, during which heat is released, as a result of which new surfaces and different crystal lattice defects are formed and a solid-state reaction is initiated.

In the present study, the main focus was on the synthesis of Pb/BaTiO$_3$, Co/BaTiO$_3$ and Pb-Co/BaTiO$_3$ for catalytic purposes, through reactive calcinations. Lead and cobalt have been shown to be active species for catalytic cracking of petroleum and petroleum based oils in supported form (Rahimi, et al., 2011; Votler, et al., 1981). It was, therefore, intended to prepare Pb and Co doped BaTiO$_3$. The catalysts synthesized were characterized by SEM, EDX, XRD and surface area analysis.

**Experimental**

**Catalyst Preparation**

Various BaTiO$_3$ based catalysts were synthesized by reactive calcination method. In typical procedure, stoichiometric quantities of BaCO$_3$ (99 % Alfa Aesar) and TiO$_2$ (99 % Merck) were accurately weighed and transferred into tungsten carbide jar. Double de-ionized water was then added and wet mixing was performed for 4 h in planetary ball mill, using ZrO$_2$ balls of 2 mm diameter size. After milling, the slurry was dried in an oven at 90 °C for 6 h and then pressed into pellets. The pellets were then subjected to reactive calcination to get the required Perovskite phase in a furnace at 950 °C for 4 h with temperature increment of 5 °C/min and cooling rate of 10 °C/min. The calcined pellets were crushed into fine powder and sieved through 80 µm screen.

The powdered material was milled again in a ball mill for 8 h in the presence of double distilled water. The samples was dried in an oven and then stored in glass vials.

Pb/BaTiO$_3$, Co-BaTiO$_3$ and Pb-Co/BaTiO$_3$ were prepared following the same procedure, using stoichiometric quantities of PbO (99 % Fluka) and Co(NO$_3$)$_2$. 6 H$_2$O as Pb and Co precursors.

**Characterization**

The catalysts so synthesized in the laboratory were characterized by X-ray diffraction, Scanning Electron Microscopy SEM and Surface Area Analysis. The phase analysis of the the original and variously doped catalysts was carried out by X-ray diffraction (XRD; model JDX-9C, JOEL, Japan) analysis at room temperature, with CuK$\alpha$ radiation and a nickel filter. The diffraction spectra were obtained using Cu (K-\(\alpha\)) radiation having 1.54178A$^0$ wave length.

The surface morphology of each catalyst was examined by Scanning Electron Microscope Model JEOL-Jsm-5910; Japan, under high vacuum microprobe. The instrument was equipped with Schottky field emission source that produces an electron probe with a diameter of about 3 to 8 nm at the sample. The accelerating voltage and emission current used for SEM imaging were 15 kV and 6 nA. The samples mounted on stubs were kept at a working distance of 19.8 to 22.4 mm, and were tilted at an angle of 30° from the primary electron beam to face the electron energy analyzer.

The surface area of each of the catalysts was determined by Quantachrome Nova Station A surface area analyzer, using nitrogen sorption-desorption method. The sample degassing temperature and time was 200 ºC and 4 h, respectively. Surface area of each catalyst was
calculated from the nitrogen adsorption isotherm data, using Brunauer, Emmett and Teller (BET) equation.

The pore sizes and pore volumes of the catalysts were calculated from N₂ physisorption isotherm data with the help of Barrett, Joyner, Halenda (BJH) model.

**Table 1. EDX analysis of un-doped and variously doped BaTiO₃**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ba</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>58.45</td>
</tr>
<tr>
<td>Pb/BaTiO₃</td>
<td>54.69</td>
</tr>
<tr>
<td>Co/BaTiO₃</td>
<td>58.75</td>
</tr>
<tr>
<td>Pb-Co/BaTiO₃</td>
<td>55.45</td>
</tr>
</tbody>
</table>

**Table 2. Surface properties of un-doped and variously doped BaTiO₃**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BJH Surface area (m² g⁻¹)</th>
<th>Pore Volume (cc g⁻¹)</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO₃</td>
<td>98.53</td>
<td>0.24</td>
<td>127.03</td>
</tr>
<tr>
<td>Pb/BaTiO₃</td>
<td>198.88</td>
<td>0.62</td>
<td>127.01</td>
</tr>
<tr>
<td>Co/BaTiO₃</td>
<td>131.52</td>
<td>0.38</td>
<td>129.5</td>
</tr>
<tr>
<td>Pb-Co/BaTiO₃</td>
<td>269.59</td>
<td>0.87</td>
<td>130.36</td>
</tr>
</tbody>
</table>

The pore sizes and pore volumes of the catalysts were calculated from N₂ physisorption isotherm data with the help of Barrett, Joyner, Halenda (BJH) model.

**Results and Discussion**

Barium titanate (BaTiO₃) powder was synthesized using reactive calcination method. The process involved milling of the metals precursors, i.e. BaCO₃ and TiO₂ in the presence of water in a ball mill, followed by calcination at temperature of 950 °C. Initially, the molar ratio of Ba and Ti was 1, during the process; BaTiO₃ synthesized via reaction given below:

\[ \text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2 \]

In case of Co/ BaTiO₃, the molar ratio of Ba/Ti was 1/0.99 whereas the molar concentration of Co was 0.01. As dopant, cobalt replaces the Ti atom in the crystal lattice, therefore, the composition of the product is [Ba (Ti₀.₉₉ Co₀.₀₁)O₃]. In case of Pb/ BaTiO₃, the molar ratio of Ba and Ti was 0.95/1, and the molar concentration of Pb remains 0.045, whereas Pb replaces Ba atoms in the crystal lattice, therefore, the composition of the product is as [Ba₀.₉₅₅ Pb₀.₀₄₅ (TiO₃)]. Similarly, in case of Pb- Co/ BaTiO₃, the molar ratio of Ba and Ti was 0.955/0.99, whereas the molar concentration of Pb and Co was 0.045 and 0.99, respectively, hence the composition of the product is as [Ba₀.₉₅₅ Pb₀.₀₄₅ (Ti₀.₉₉ Co₀.₀₁)O₃].

All the catalysts synthesized in the laboratory were characterized by surface area, XRD, EDX and SEM analysis. The EDX analysis of the BaTiO₃ indicated in Table 1, shows that the % wt of Ba, Ti and O was 58.45, 20.53 and 20.58 %, respectively. In case of Co/BaTiO₃, and Pb/BaTiO₃, the % wt of Co and Pb was found to be 4.00 and 0.252 %, respectively, whereas the wt % of Co and Pb, in case of Pb-Co/BaTiO₃ was 3.94 and 0.25 %, respectively. These results indicated that % wt composition of the catalysts is very close to theoretical stiochiometric values.
Fig. 1 Electron micrographs of original and variously doped BaTiO$_3$ catalysts (a) original BaTiO$_3$ (b) Pb/BaTiO$_3$ (c) Co/BaTiO$_3$ (d) Pb–Co/BaTiO$_3$

Fig. 2. XRD Patterns of original and variously doped BaTiO$_3$ catalysts (a) original BaTiO$_3$ (b) Pb/BaTiO$_3$ (c) Co/BaTiO$_3$ (d) Pb–Co/BaTiO$_3$
Results of surface area and pore dimension analysis of the catalysts is given in Table 2, which shows that the surface area, pore volume and pore diameter of the catalysts increase after doping with Pb and Co. In case of Pb-Co/BaTiO₃, almost three fold increase in the surface area as well as the pore dimension has been observed. This increase may be attributed to spacing of the parent titanate galleries by the metal species, which is more enhanced when both metals are present together.

Micrographs of the original and variously doped BaTiO₃ catalysts are provided in Fig. 1. The micrograph of undoped BaTiO₃ indicates granular particles of about 200 to 400 nm size. The particles size is, however, not uniform, and agglomerated particles in the form of stacks can be seen. The micrograph of the Pb/BaTiO₃ shows similar granules, but particles agglomeration is more pronounced. Also, the granule size is larger than original BaTiO₃. Similarly, the micrograph of Co/BaTiO₃ shows highly agglomerated particles. The micrograph of Pb-Co/BaTiO₃ shows larger irregular shaped pellets, which show that due to incorporation of Pb and Co ions, the size of BaTiO₃ granules has enormously increased.

The XRD analysis of original and variously doped BaTiO₃ is provided in Fig. 2. The results indicate the characteristic pattern of Perovskite phase (Lu, et al., 2003). However, the peaks are broadened which established the absence of tetragonality of the phase, which might be attributed to the formation of cubic phase as a result of high temperature during the reactive calcinations (Gracia, et al., 2000). It is also pertinent to note that there are no major changes in the XRD patterns of the original and variously doped titinates, which suggests that the dopants might have occupied the crystal lattices by replacing Ba with Pb and Ti with Co, respectively.

**Conclusion**

Reactive calcination is a method which can be successfully used for the synthesis of Pb and Co doped BaTiO₃. The process is simple and consists of ball milling of the metal precursors in the presence of water followed by sintering at about 950 °C. XRD analysis indicates that BaTiO₃ based materials with cubic crystalline geometry can be effectively synthesized by this process. The surface area of BaTiO₃ found to increase with the addition of the dopants and enormous increase in surface area was observed in case of Pb/ BaTiO₃, and Pb-Co/BaTiO₃.

**References**


