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Preparation and Characterization of Nanosized $\text{PrFe}_{(1-x)}\text{Co}_{(x)}\text{O}_3$ Perovskite

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Abstract: $\text{PrFe}_{(1-x)}\text{Co}_{(x)}\text{O}_3$ ($x = 0.2, 0.4, 0.6, 0.8$) perovskites prepared by citrate method. The overall process involves sol-gel auto combustion at elevated temperature with important steps as formation of homogenous gel, drying of gel and self-combustion of dried gel in air. Auto combustion of dried gel results in nanosized catalyst particles. The formation of the perovskite structure has been shown by X-ray Diffraction (XRD) of samples and Surface area values were determined by using Brunauer-Emmett-Teller (BET) method of surface area analysis. SEM (Scanning Electron Microscopy) have been performed on sample to study the morphology and particle size of perovskite. These analysis were further used to check the activity and selectivity of $\text{PrFe}_{(1-x)}\text{Co}_{(x)}\text{O}_3$ based catalyst for the treatment of organic effluents in waste water.

Keywords : Perovskite, Nano particle, Sol-gel, SEM, Auto combustion.

Introduction:

Perovskite oxides of general formula ABO_3 form an interesting category of materials, where 12-coordinated A-site may be occupied by rare earth, alkaline earth, alkali or other large ions and the 6-coordinated B-sites are usually filled with transition metal cations. Due to greater stability of perovskite framework a large number of metallic trivalent cations can occupy the A- and B- sites provided that the tolerance factor $t = (r_A + r_B)/\sqrt{2}(r_B + r_O)$ is in the range of 0.8-1.0.⁽¹⁾

These materials have been studied widely in aspect of their stability, framework stability, complete oxidation and low costs. These properties and other unique characteristics of perovskite type compounds make them one of the most widely investigated area of research aspect in field of material science.

The perovskite composition can be changed by replacement of part of A and/or B cations with other cations with different oxidation states, which on other hand lead to formation of structural defects such as anionic or cationic vacancies and/or change in oxidation state of transition metal cation arise in order to maintain the electroneutrality of the compound. The presence of these defects or physical change affects the catalytic activity of the catalyst.

Substitution effects of various impurity ions into A and B sites of perovskite oxides have received much attention due to their potential as substituent materials for various application in solid oxide fuel cells⁽²⁻⁴⁾, catalyst⁽⁵⁾, chemical sensors⁽⁶⁻⁹⁾ and magnetic materials⁽¹⁰⁾ etc.

The preparation of LaFeO_3 , PrFeO_3 and other related compounds have been achieved by many processes, including solid-solid reaction, Molten NaOH reflux, co-precipitation, sol gel and citrate methods. ⁽¹¹⁻¹⁵⁾

The conventional solid state chemistry method is still being frequently used for preparation of perovskite compounds. The high reaction temperature (greater than 1000°C), long reaction times, aggregation of resulting particles, irregularity in shape and wide size distribution are the major drawbacks of solid state route. On the other hand sol- gel process provides high purity, good chemical homogeneity, lower calcination temperature which makes it as an attractive and effective alternative to synthesize materials with better control of particle size and morphology.

In this work $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ with $0.2 \leq x \leq 0.8$ are prepared by sol gel process. The stability of perovskite structure upon Co substitution and structural vacancies due to replacement of Fe(III) with a lower charge cation were studied.

Experimental:

Materials:

Praseodymium oxide (Pr_6O_{11}), Iron (III) nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], Cobalt (II) nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] were obtained from Lobachemie. Concentrated Nitric acid (HNO_3), and citric acid anhydrous were obtained from Merck. All reagents were used as received.

Method:

All synthesis were performed under ambient atmosphere and same reaction parameters. Stoichiometry ratio was used to convert the praseodymium nitrate using concentrated HNO_3 .

A solution of praseodymium nitrate, cobalt nitrate and ferric nitrate was obtained by dissolving calculated equivalent quantity as per catalyst stoichiometry of $\text{Pr}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Citric acid was added to above solution in proportion of 1:1 w.r.t. metal nitrate solution. The mixture was dried to convert it to gel at $100-110^\circ\text{C}$. , formed gel further goes into auto combustion to give semi powder similar to xerogels which is ground to powder. Calcination of powder between 600°C and 800°C for 8 hours resulted in the desired perovskite oxide of nanosized. All gels of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ were dried and calcined at same condition.

Characterization:

Various technique such as XRD and SEM were employed to characterise these powders. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the range of $10-85^\circ$ for a period of 2s in the step scan mode. SEM picture was recorded with JEOL model 1200EX instrument at accelerating voltage of 12kV. The specific surface area was determined by the BET method from N_2 adsorption data obtained at -196°C (77K).

Results and Discussion:

Powder XRD analysis of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ for various composition showed the presence of pure crystalline perovskite phase with no contaminants of praseodymium or cobalt oxides. The pattern of the $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ showed sharp and intense peaks corresponding only to crystalline perovskite-like structure.

Fig.1 is the X-ray diffraction (XRD) spectra of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ (with $x=0.2,0.4,0.6,0.8$) powders obtained from $\text{Pr Fe}_{(1-x)}\text{Co}_x\text{O}_3$ dried gel directly heated at 800°C for 8 hours.

XRD patterns reveals that diffraction lines of the $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ in samples with ($0.2 \leq x \leq 0.8$) show a shift to higher 2θ values with increase in concentration of cobalt ions. This shift of diffraction lines is due to transformation of perovskite structure resulting from the alignment distortion of octahedral coordination by gradual substitution of Fe ions by cobalt. This observation of study is in agreement with the study of Hongto Cui et. al. for the synthesis of Co-substituted LaFeO_3 and LaNiO_3 ⁽¹⁶⁾.

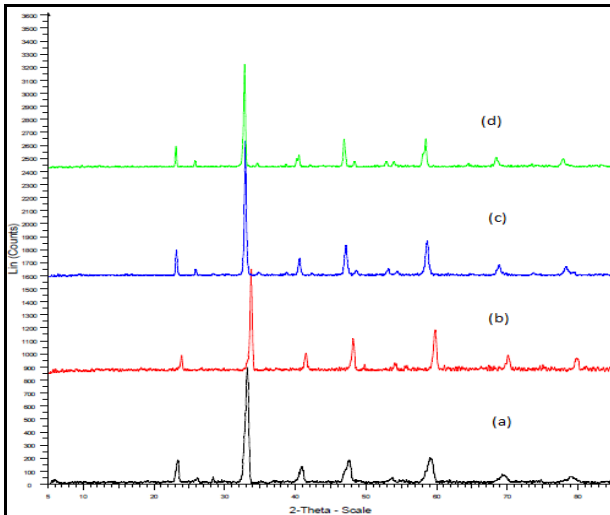


Fig.1 XRD patterns of (a) $\text{PrFe}_{0.2}\text{Co}_{0.8}\text{O}_3$ (b) $\text{PrFe}_{0.4}\text{Co}_{0.6}\text{O}_3$ (c) $\text{PrFe}_{0.6}\text{Co}_{0.4}\text{O}_3$ (d) $\text{PrFe}_{0.8}\text{Co}_{0.2}\text{O}_3$ materials

SEM (scanning electron microscopy) has been also used as tool for particle size and morphology of obtained powders. Micrographs of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ (with $x=0.2,0.4,0.6,0.8$) clearly showed that each of the particle is low density porous materials which is favourable to a catalytic application. Images of SEM shows particle size in range of 80-250nm.

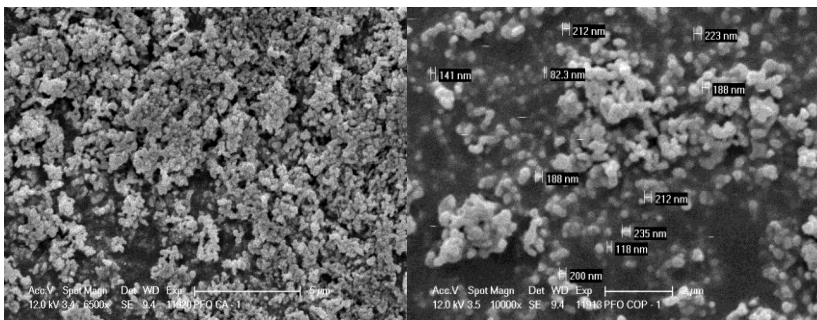


Fig. 2. Scanning electron micrographs of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ (with $x=0.2,0.4,0.6,0.8$)

The BET surface area of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ (with $x=0.8,0.6,0.4,0.2$) with respective value of 'x' nanocrystals calculated from N_2 isotherms at -196°C are 6.7, 5.4, 4.3 and $2.2 \text{ m}^2/\text{g}$ respectively. It can be seen that Perovskite structure $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ shows a increase in surface area with increase in concentration of cobalt ion.

Conclusion:

A simple sol gel process is used for the preparation of nanosized powders of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ (with $x=0.2,0.4,0.6,0.8$). The overall process of synthesising pure nanosized $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ involves three steps; formation of sols, formation of dried gel and combustion of dried gel at elevated temperature to obtain pure $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ perovskite powder. Auto combustion is process of heat induced exothermic oxidation-reduction reaction between nitrate ions and carboxyl group. Nano sized powders of 80-250nm particle sizes were prepared by this technique using simple nitrate precursors. The average particle size and morphology of these powders was investigated by SEM.

The doping of Cobalt (Co) at B site of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ leads to distortion in catalyst structure, thus providing enhanced catalytic activities. Increased surface area of catalyst is also linked with its higher catalytic activity with more reaction sites. These properties will be used for further study of $\text{PrFe}_{(1-x)}\text{Co}_x\text{O}_3$ catalyst in treatment of organic effluents in waste water.

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