

Synthesis and Characterization of Ceria Based Catalysts

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Abstract: In this work five catalysts named CeO₂ (named Ceria), Fe/CeO₂ (called the Iron doped Ceria), Co/CeO₂ (named Cobalt doped Ceria), Ni/CeO₂ (Nickel doped Ceria), Cu/CeO₂ (Copper doped Ceria) were prepared. The catalysts prepared were subjected to several tests Like XRD, Microscopic Raman and Tunneling Electron Microscopy to determine their basic characteristic properties. The transition metals were introduced into the Ceria to form the Metal doped Ceria Catalysts using Sol-Gel method. Through this we compared the data obtained and concluded the catalyst which has best catalytic activity among these.

Keywords: Ceria, Nickel Doped Ceria, XRD, Raman, Copper Doped Ceria.

1. Introduction

This study aims at analyzing the performance of different catalyst prepared using Sol-Gel method. Sol gel method is one of the best method present for the preparation of Catalysts. Sol Gel may be described as "Formation of an oxide network through poly condensation reactions of a molecular precursor in a liquid." The basic idea behind the sol-gel method is that it helps in dissolving a compound in a liquid so that we can bring it back in solid form in a controlled manner. Sol Gel method also helps in mixing at an atomic level. Through sol gel method the metallic ions could be easily inserted into the ceria lattice, potentially bringing about a different synergistic effect such as higher oxygen mobility. Thus all in all Sol gel method is normally better than methods like impregnation method due to its atomic characteristic.

2. Experimental

2.1 Catalysts Preparation

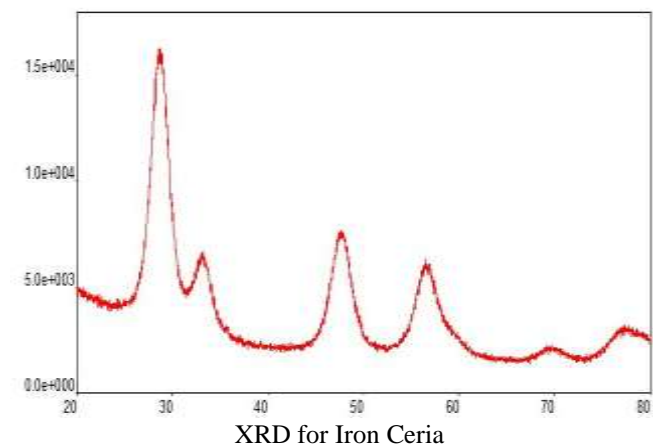
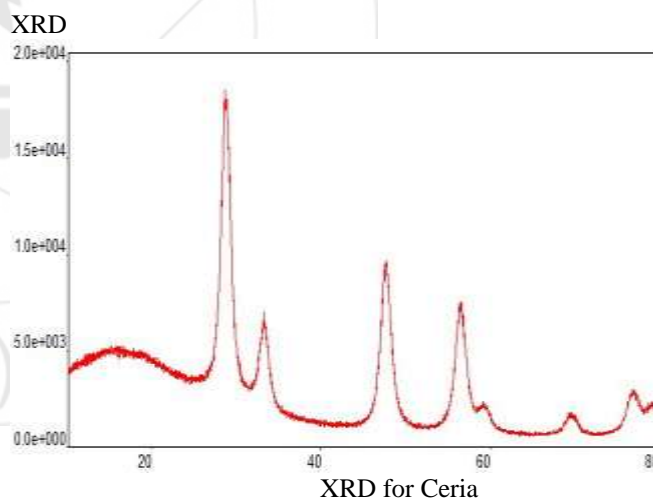
In the experiments performed, 5 catalysts were prepared using Sol Gel method namely -: Ceria (CeO₂), Iron doped with Ceria (Fe/ CeO₂), Nickel doped with Ceria (Ni/ CeO₂), Cobalt doped with Ceria (Co/ CeO₂), Copper doped with Ceria (Cu/ CeO₂).

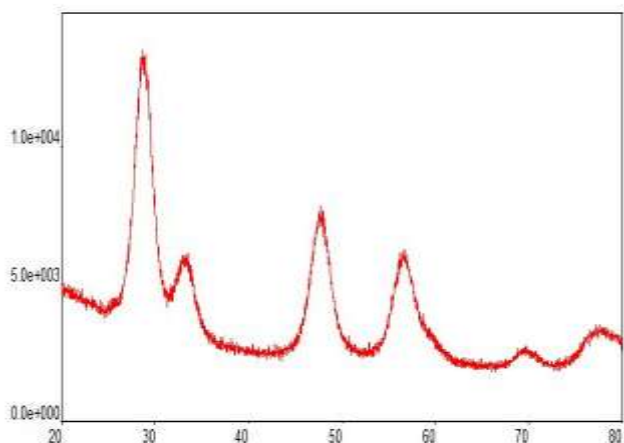
In the preparation technique Citric Acid was used as a complexing agent. CeO₂ and Citric Acid was taken in 1:1 molar ratio. 10 wt. % of Metallic salt was taken and all of them were poured into a beaker containing 30 ml of Ethanol. Now this solution was stirred on a stirrer at 60 degrees C until a gel was obtained. Now the obtained gel was kept in oven at 110 degree C for 3 hours. Then the powder obtained was crushed into fine particles and was further put in furnace at 400 degrees C for 4 hours for the calcination. The powder obtained was left inside the furnace to cool to room temperature. Thus the metal doped CeO₂ was obtained. For preparing the only Ceria Catalyst, the procedure was same except no metallic salt was used during the process.

2.2 Catalysts Characterisation

For the characterisation of the catalysts prepared three different tests were done on the samples. X-ray diffraction analysis was done and the x ray tube was performed at 40kV and 15mA. The x-ray powder diffract gram was recorded at 0.02 degree interval in the range of $10 \leq 2\theta \leq 80$. RAMAN test was performed at a laser wavelength of 514nm and a spectrum range of 100-2000. TEM pictures were performed on JEM-1400 electron microscope.

2.3 Results and Discussions

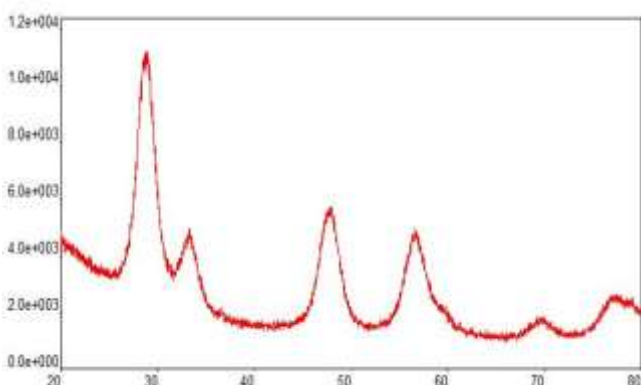




XRD for Cobalt Ceria

Average Particle Size-62.175 Ang. Or 6.2175 nm

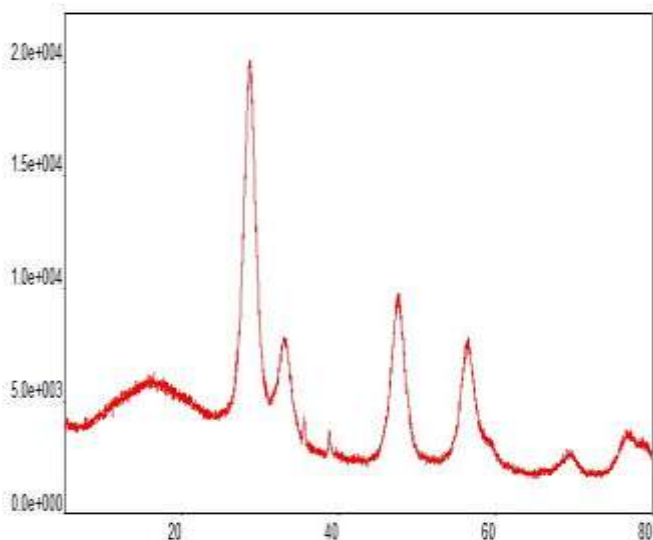
For Iron at 28.606 degree- 37.42 Ang.
 33.10 degree- 32.6 Ang.
 47.735 degree- 34.5 Ang.
 56.741 degree- 34.5 Ang.
 Average Particle Size-34.755 Ang. Or 3.4755 nm



XRD for Nickel Ceria

For Cobalt at 28.699 degree- 38.06 Ang.
 33.19 degree- 32.6 Ang.
 47.767 degree- 35.7 Ang.
 56.67 degree- 33.3 Ang.
 Average Particle Size- 34.915 Ang. Or 3.4915 nm

For Nickel at 28.700 degree- 39.2 Ang.
 33.26 degree- 34.9 Ang.
 47.72 degree- 41.8 Ang.
 56.76 degree- 36.2 Ang.
 Average Particle Size- 38.025 Ang. Or 3.8025 nm



XRD for Copper Ceria

For Copper at 28.617 degree- 44.7 Ang.
 33.22 degree- 41.7 Ang.
 47.60 degree- 43.2 Ang.
 56.453 degree- 45.0 Ang.
 Average Particle Size-43.65 Ang. Or 4.365 nm

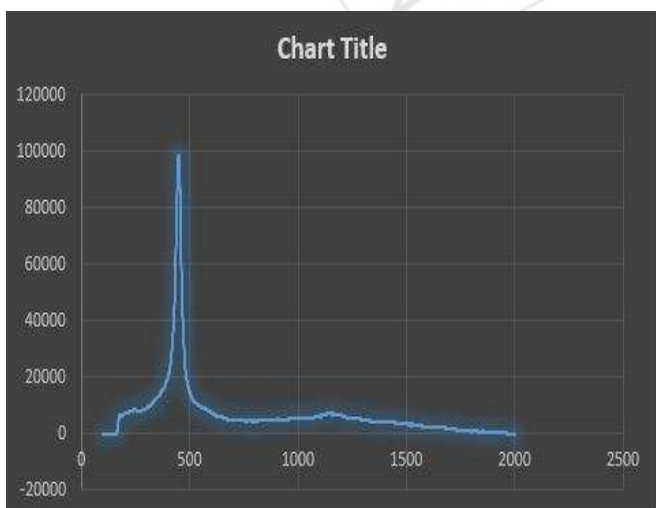
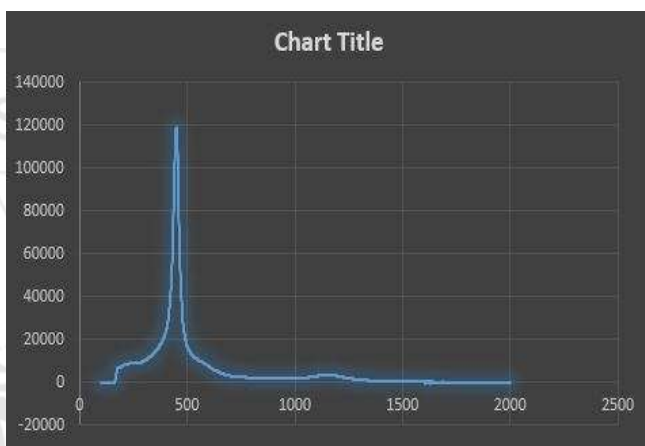
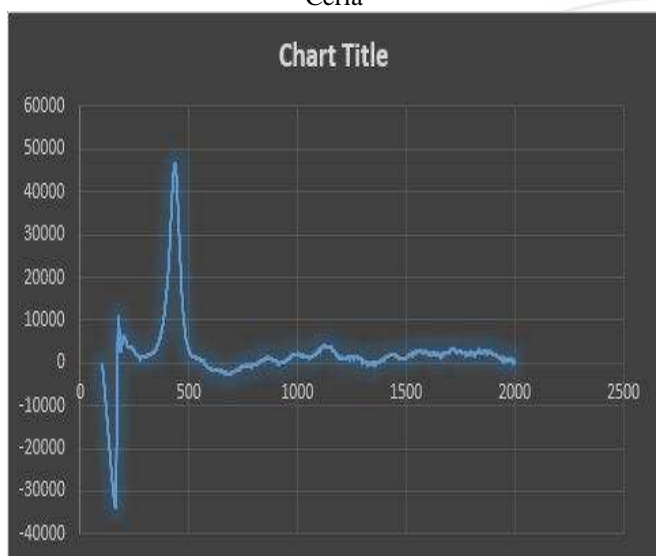
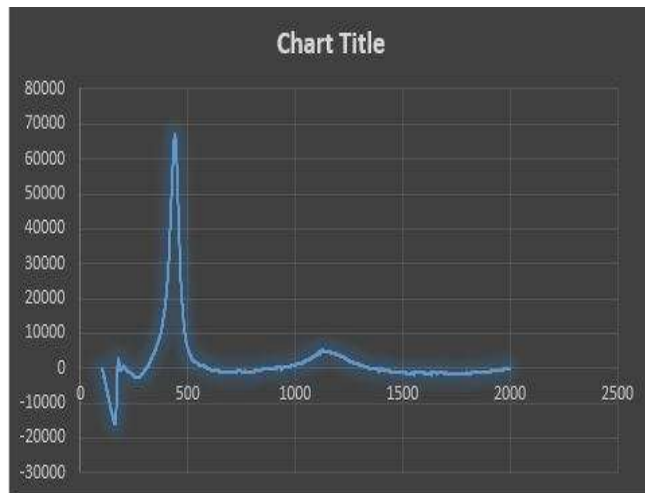
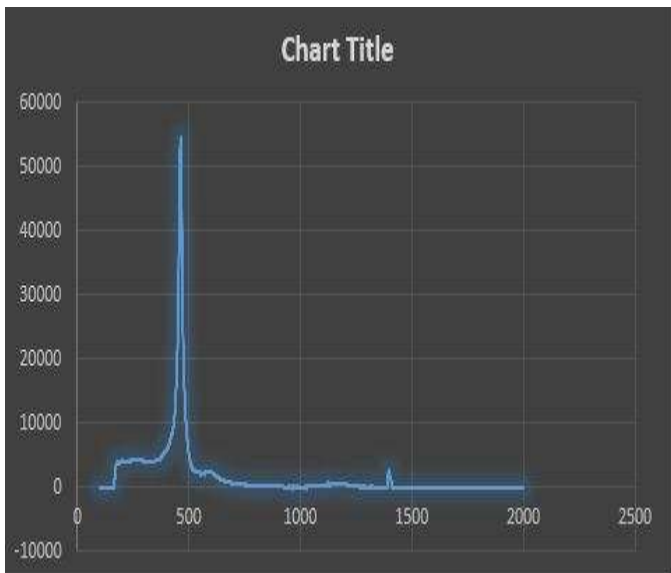
No peaks of Iron oxide are detected. The decrease in cell parameter after the iron modification is due to incorporation of Fe³⁺ in the CeO₂ structure. In the same way no peaks of CoO are observed in Cobalt modified crystals. In the case of Nickel also, we cannot see the trace of any Nickel compound but in the case of Copper two peaks are visible corresponding to crystalline CuO at 2θ approximately equal to 35 and 39 degrees.

RAMAN-
 Raman Spectroscopy is very sensitive to the presence of Oxide microcrystals. Raman Spectroscopy is also used for detecting oxygen vacancies in the materials.

The Raman Spectrum contains a known peak within the range 440-465 cm⁻¹, which is clearly visible among all these graphs. This peak is related to the Raman Active F_{2g} mode and corresponds to the oxygen symmetric breathing vibration around Ce⁴⁺.

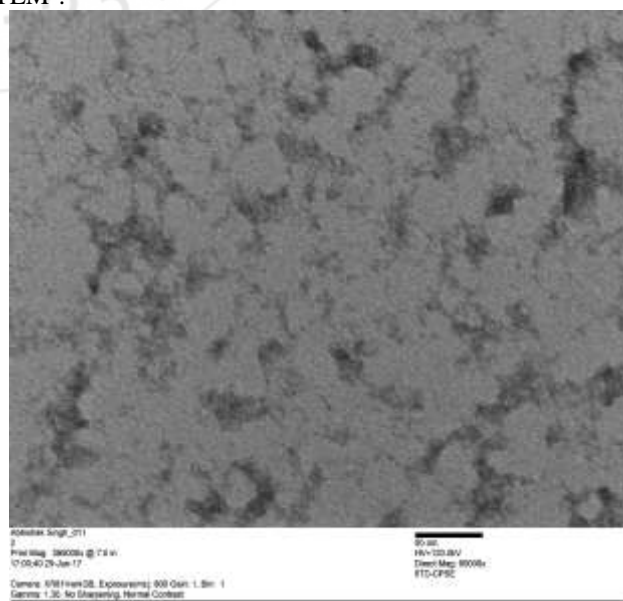
The particle size of the ceria based materials are calculated based on the four main peaks corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1).

For Ceria at 28.395 degree- 64.9 Ang.
 33.14 degree- 65.4 Ang.
 47.589 degree- 59.8 Ang.
 56.35 degree- 58.6 Ang.

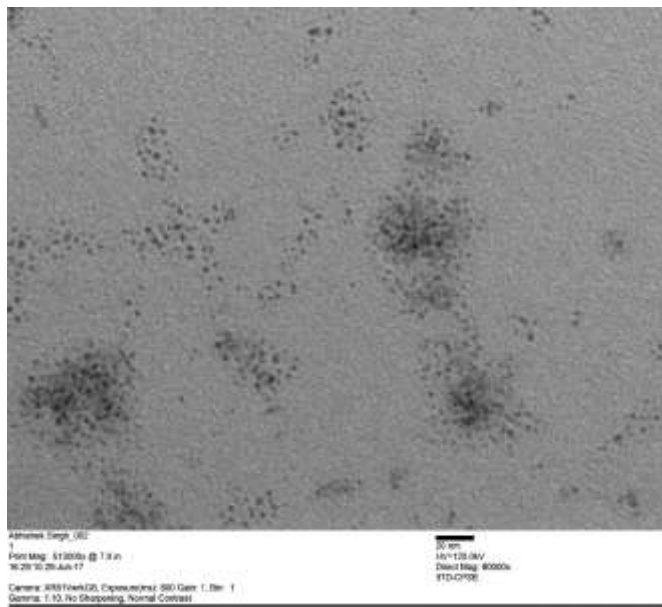


From the graphs we can see that the peaks near 1140 cm^{-1} is unavailable in the case Ceria but when Ceria is doped with the elements, we can see that peaks near 1140 cm^{-1} are visible. These peaks at near 1140 cm^{-1} is assigned to the presence of oxygen vacancies in the compound which is indicative of the presence of Ce^{3+} ions.

TEM:-



Ceria



Nickel-Ceria

The TEM pictures of Ceria and Nickel doped with Ceria is shown in the above pictures. The size of Nickel doped Ceria particles at different position are 4.286 nm; 3.7143 nm; 4.85 nm; 2.85nm. Average of the particle size being-: 3.925 nm. Similarly the particle size of the catalysts like Ceria came out to be 6.7120 nm, for Iron doped Ceria- 3.2322nm, for Cobalt doped Ceria- 3.5233nm and for Copper Doped Ceria- 4.570nm.

3. Conclusion

The catalysts in this experiment are prepared using Sol-Gel Method. The color of different catalysts are as follows-: Ceria -: White; Iron Doped Ceria -: Light Red; Cobalt Doped Ceria -: Black (ash like) Colour; Nickel Doped Ceria -: Black (ash like) color; Copper Doped Ceria -: Light Green Color. From the XRD test we can see that the size of the particles keeps on increasing from Iron to Copper with Iron being the smallest and Copper being the largest. The size of Ceria particles is the largest so we can say that by doping Ceria with various metals the size decreases and thus the activity of the catalyst increases as the activity of the catalyst increases with decreasing the size of the particles.

Through the various graphs of the Raman Spectroscopy we can conclude that the Oxygen vacancy in the materials keeps on decreasing from Iron to Copper as the intensity of the peak keeps on decreasing from Iron to Copper. The peak is not present in the case of Ceria. So, by doping with different catalysts we can Increase the oxygen vacancy in the material. Through the TEM test we can see that the size of the Nickel doped ceria and the other catalyst is coming out to be approximately same as the size from the XRD results. So, by the results obtained it can be stated that the catalytic activity of the Iron doped Ceria is more as compared to the other prepared Catalysts.

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