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Synthesis, Characterization and Thermal Decomposition Kinetics of Cerium Oxalate Rods

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Abstract: Cerium oxalate rods are prepared from cerium nitrate hexa hydrate using oxalic acid as the precipitating agent. From the rod like cerium oxalate, CeO_2 rods are prepared by thermal decomposition method. Synthesized ceria was characterized using FT-IR, XRD and SEM analysis. Kinetics of thermal decomposition of cerium oxalate to cerium oxide in static air was studied using TG-DTA technique. Cerium oxalate undergoes multistep kinetic behavior. First stage of decomposition corresponds to dehydration of 10 mole of water (α = 0.05-0.35) and second stage (α = 0.48-0.9) corresponds to decomposition to ceria. Integral form of modified Coats - Redfern method was used for establishing reaction mechanisms for the decomposition reaction. The activation energy needed for the removal of water molecules and to the formation of ceria was determined using isoconversional method such as KAS and FWO method. Ea needed for the removal of water molecule was found to be 43.667 KJ/mol (KAS) and 42.995 KJ/mol (FWO). Activation energy required for the formation of ceria was found to be 128.27(KAS) and 127.8(FWO) method.

Introduction

Rare earth oxide, ceria, has unique properties such as catalytic, redox, oxygen storage and release. Different morphologies of ceria such as nanorod (Zhang *et al*., 2006**)**, mesoporous ceria with nano crystalline pore walls (Laha and Ryoo, 2003) and hierarchically layered mesoporous ceria (Zhang *et al.,* 2006) have been reported. CeO_2 have wide application such as the solid oxide fuel cells, insulators, high refractive index materials, UV-blockers, polishing materials, gas sensors, high temperature oxidation resistance, free-radical scavengers, etc. Since the O-H group present on the surface of ceria even below at 700^{o}C, it is more reactive as an adsorbent for the removal of pollutants from the water (Pavel *et al*., 2014). Due to the higher oxygen ion conductivity, ceria is the major component in the low temperature solid oxide fuel cell. Doping of ceria with rare earth elements (Gd, Nd, La and Th) enhances the oxygen ion conductivity and mechanical properties (Kenji *et al.* 1999). Further oxygen storage capacity of ceria was increased on doping with metallic cations (e.g., $Ca^{2+,}$ Ba^{2+}, Pb^{2+}, etc.).

In the present work, cerium oxalate was prepared from cerium nitrate hexa hydrate. Kinetics of thermal decomposition of cerium oxalate to ceria was studied by using TG-DTA technique. Ea of the formation of ceria was determined using isoconversional methods such as Kissinger-Akahira-Sunose and Flyn-Wall-Ozawa methods.

Experimental

All the reagents used were of analytical grade and used without any further purification. Cerium nitrate hexa hydrate (Himedia) and Oxalic acid (Merck) were used for the preparation of cerium oxalate. Cerium nitrate hexahydrate was dissolved in 50mL of water. The required amount of oxalic acid was dissolved in distilled water and added drop

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wise in to the above solution under magnetic stirring. The mixed solution was stirred for 6h at room temperature. Then the precipitate was collected, washed with ethanol and water. Further, it is dried at 80°C and calcined at 600°C for 6h. FT-IR, XRD, and SEM were used for the characterization purpose.

Results and Discussions

Fourier Transform – Infra Red (FT-IR) Spectroscopy

Fig.1 shows the FT-IR spectrum of cerium oxide prepared by the thermal decomposition of cerium oxalate. The band at 1460-1472 cm^{-1} is attributed to stretch due to δ(C-O)+δ(O-C=O). The band observed at 423.45 cm^{-1} represents Ce-O stretching frequency of formed CeO_2.

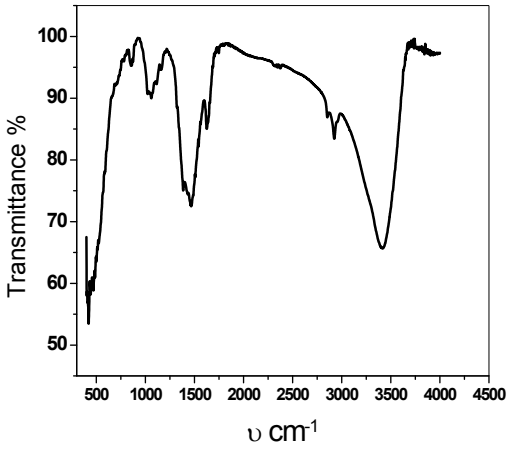

Fig.1. FT-IR spectrum of CeO_2

X- ray Diffraction (XRD)

Fig. 2 shows the XRD pattern of CeO_2 samples. XRD pattern shows the diffraction peaks corresponding to the crystalline plane (111), (200), (220) and (311). It confirms the cubic fluorite structure of ceria. The average crystallite size of ceria calculated using Scherrer equation from XRD pattern is 9.026nm. Cubic fluorite structure of ceria gives isolated peaks which confirm the polycrystalline nature of ceria.

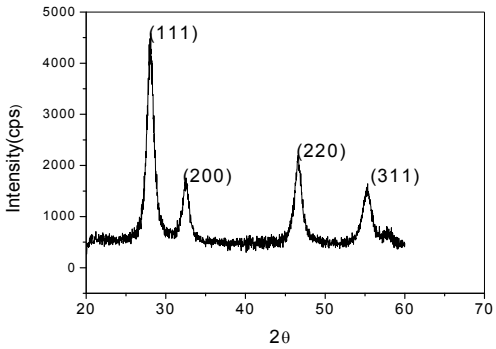

Fig.2. XRD pattern of CeO_2 samples

Scanning Electron Microscopy (SEM)

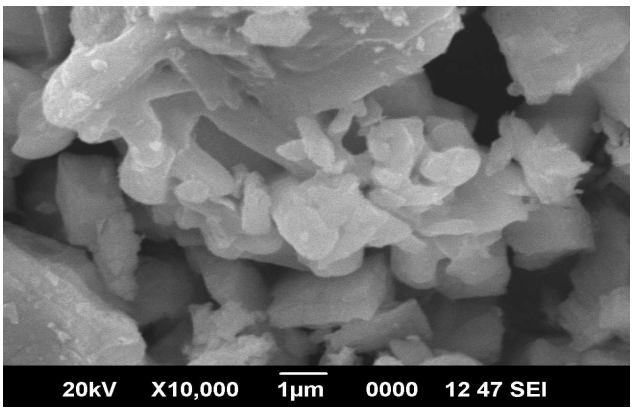

Fig.3 SEM image of rod like ceria

Fig.3 shows the SEM image of rod like ceria. It depicted that polycrystalline CeO_2 nanoparticles are aggregated to form micro structural rods of ceria. Secondary particles are formed along with aggregated particles. Average grain size of primary and secondary particles of aggregated CeO_2 is 662.42nm and 305.94nm respectively.

Kinetic Analysis

Kinetics of the thermal decomposition of cerium oxalate to ceria was done using TG data. Two steps of thermal decomposition is required for the formation of ceria. First stage of decomposition corresponds to dehydration (α = 0.05-0.35) and second stage corresponds to decomposition (α =0.48-0.9). Integral form of modified Coats-Redfern method(Eq.1) was

used for establishing reaction mechanisms for the decomposition reaction.

$$\ln\left[g(\alpha)/T^2\right] = \ln AR/\beta E - E/RT + \ln\left(1-2RT/E\right) \cong \ln AR/\beta E - E/RT \quad (1)$$

where, $g(a)$ is the integral form of conversion function. For the correct $g(a)$ function, the plot of ln $[g(a)/T^2]$ against $1/T$ should give a straight line. The best reaction mechanism identified for the thermal decomposition of cerium oxalate rods are F_1 [g(α)= -ln(1-α)], A_2 [g(α)= -ln(1-α)$^{1/2}$], A_3 [g(α)= -ln(1-α)$^{1/3}$], and A_4 [g(α)= -ln(1-α)$^{1/4}$].

Determination of Ea

Ea for the decomposition reaction can be calculated by isoconversional methods such as KAS (Kissinger, 1957) (Kissinger-Akahira-Sunose) and FWO (Ozawa, 1965) (Flynn–Wall–Ozawa) methods. Ea needed for the removal of water molecule is found to be 43.667 KJ/mol (KAS) and 42.995 KJ/mol (FWO). Activation energy required for the formation of ceria was found to be 128.27(KAS) and 127.8 (FWO) method.

Conclusion

CeO_2 rods are prepared by thermal decomposition of rod like cerium oxalate. Kinetics of the thermal decomposition of cerium oxalate to cerium oxide in static air was studied using TG-DTA technique. Cerium oxalate undergoes multistep kinetic behavior. The best reaction mechanism identified for the thermal decomposition of cerium oxalate rods are F_1, A_4, A_3 and A_2. Ea needed for the removal of water molecule is found to be 43.667 KJ/mol (KAS) and 42.995 KJ/mol (FWO). For the formation of ceria, cerium oxalate requires an activation energy of 128.27 KJ/mol (KAS) and 127.8 KJ/mol(FWO) method.

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