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Structural Characterization of Nanosized Fe_2O_3-CeO_2 catalysts by XRD, EDX and TEM Techniques

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Structural characteristics of nanosized iron-ceria mixed oxide catalysts have been investigated using X-ray diffraction (XRD), IR spectra, thermogravimetry, EDX and transmission electron microscopy (TEM). The investigated oxides were obtained by hydrothermal method and were subjected to thermal treatments from 773 ^oK to 923 ^oK. The XRD results suggest that the sample primarily consists of nanocrystalline CeO_2 phase on Fe_2O_3. FT-IR gives the information of the chemical bonding and the morphology and particle size by TEM. Deposition of Fe_2O_3 on the surface of an appropriate oxide support of high specific surface area improves the catalytic activity. The TEM results reveal well-dispersed CeO_2 and Fe_2O_3 nanocrystals.

Keywords : Nanoparticles, mixed oxide, hydrothermal method

1. Introduction : Cerium oxide has been extensively used as catalyst and structural promoter to support metal or metal oxide catalysts because of its unusual chemical and physical properties in catalytic application [1]. Ceria (CeO_2) is an important rare earth oxide and has been widely investigated in the automotive exhaust purification, oxygen storage and release catalysis, and solid oxide fuel cell applications. Ceria (CeO_2) finds enormous applications in catalysts/catalyst supports [1, 2], oxygen ion conductors in solid oxide fuel cells [3 - 5], electrochemical oxygen pumps [6], UV absorbents [7], fluorescent materials [8] and amperometric oxygen ion monitors because of its high oxygen ion conductivity [9]. CeO_2 nanoparticles have been prepared by sol-gel processing [10, 11], sonochemical synthesis [12], a thermal decomposition process [13], hydrothermal synthesis [14], a polymeric precursor route [15] etc.

With catalytic nanoarchitectures, several advanced nanostructured bifunctional catalysts with a good catalytic performance have been synthesized. Novel designs and structural arrangement have been explored in the preparation of several heterogeneous catalysts with efficient molecular transport of gas or liquid phase reactants and products.

In the past decade, controlled synthesis of ceria-based nanomaterials with pure phase, desirable composition, uniform morphology, and tunable

surfaces has become one of the essential topics in materials science, since these materials exhibit unique properties when their sizes are reduced to nanometer scale.

In 1987, Matijevic *et al.* [16] obtained nano ceria powder, by aging at elevated temperatures, solutions of cerium nitrate salts in the presence of urea. Under the best experimental conditions ellipsoidal platelets of oxydicarbonate crystallized. Hirano *et al.* [17] also produced ceria using urea as precipitant. Synthesized particles were cubic or octahedral and ranged from10 to 25 nm. However using urea as precipitant, in both Ce(III) and Ce(IV) systems, resulted in production of non spherical particles with cubic or rod like morphology which does not generally have good sinterability. Zhou *et al.* [18] synthesized single-crystalline CeO_2 nanorods with well-defined crystal planes by a facile solution-based hydrothermal method, and suggested that these nanorods could show higher CO oxidation activity than CeO_2 nanoparticles.

In this work, supported nano ceria catalysts were prepared by hydrothermal method. The hydrothermal process has attracted a lot of attention since particles of the desired size and shape can be produced if parameters such as solution pH, reaction temperature, reaction time, solute concentration and the type of solvent are carefully controlled [19].

2. Materials and Methods :

2.1 Materials : All the reagents and solvents used were purified by standard methods and dried before the use. XRD was carried out on a Bruker D8-Advance X-ray diffractometer with CuKα radiation source (λ= 1.54178 A^0) scanning rate of 0.02 ^{0}/s was applied to record the pattern in the 2θ range of 20- 80^0. The FT-IR spectra obtained with a Nicolet iD1 spectrometer (4000 - 400 cm^{-1}) using KBr pellet technique. Scanning Electron Microscope image (SEM) and Energy Dispersive X-ray (EDX) technique (JEOL-JSM 6360A) were obtained at accelerating voltage 20 KeV. Sample were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. The morphology of the synthesized particles was observed by transmission electron microscopy (TEM, FEL TECNI G^2 20 ULTRA-TWIN).

2.2 Methods : Cerium (III) nitrate hexahydrate [$Ce(NO_3)_3.H_2O$, Aldrich Chemical], hydrogen peroxide (30 % H_2O_2, Merck Chemical), Ammonia solution (28 % NH_4OH, Merck Chemical) and Ferric nitrate (Merck) were used as a starting materials.

Preparation of the nanocrystalline ceria and supported ceria by hydrothermal Method is described below -

1 M Cerium nitrate solution was mixed with 100 ml of 30 % H_2O_2 under vigorous stirring in an ice bath. After 10 min ammonia solution was added to this mixture and the color changes to dark brown. The solution was stirred at 3000 rpm for 4 h. The precipitates formed from the solution were aged for a day and turned yellow after aging. Then this solution was decanted and the wet precipitates were washed using ethanol several times until the pH was near neutral region. The wet precipitates were filled to 80 vol.% in a Teflon vessel held in an outer pressure vessel made of stainless steel. After the vessel was sealed, it was placed in a thermostatic oven and heated at 200 ^{0}C for 6 h. The final products were re-washed several times with ethanol and dried at 80 ^{0}C for 12 h. Finally, sample was calcined at 650 ^{0}C for 5 h.

For the synthesis of Fe supported on ceria catalyst the aqueous ferric nitrate (0.5 M) solution was added to the solution of cerium nitrate and then rest procedure is repeated same as above.

3. Results and Discussion :

3.1 XRD Analysis: X-ray diffraction (XRD) patterns of CeO_2 and Fe/CeO_2 given below in Figure (1). The XRD patterns obtained of the CeO_2 were compared with the standard data for CeO2 (JCPDS file No. 34-0394). The characteristic peaks corresponding to (111), (200), (220), (311), (222) and (400) planes located at 2θ = 28.83º, 33.2º, 47.9º, 56.7º, 59.4º, and 70.09º respectively are very close to the face centric cubic CeO_2, indicating that all samples can be identified to ceria with the cubic fluorite structure

[14]. The peaks are very sharp indicating well crystalline nature of the material. The measured diffraction angles were consistent with the standard XRD patterns of CeO_2, with extra peak of Fe_2O_3 indicating the incorporation of Fe on CeO_2. X-ray diffraction patterns of the synthesized pure ceria showed the presence of cubic fluorite structure and there was no other phase. The crystallite size of the CeO_2 and Fe/CeO_2 was calculated by using Scherrer equation; $t = 0.9 \lambda / B \cos\theta$, Where, t=Average crystallite size, λ= wavelength of X-rays, θ=the position of the reflection in XRD pattern in degrees, B=integral breadth of a reflection (in radians 2θ) located at 2θ and often calculated by using a solid reference standard. After addition of Fe, the crystallite size decreases. In CeO_2 sample the crystallite size was 17 nm and after addition of Fe the size decreases to 12 nm. The obtained XRD results indicate that the grain size of CeO_2 nanoparticles has been reduced after addition of Fe_2O_3 (JCPDS file No.86-0550).

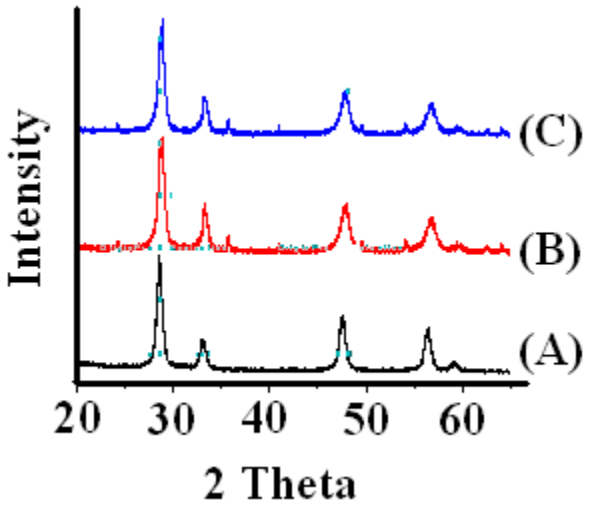


Figure (1) : XRD graph of A] Pure CeO_2, B] Fe/CeO_2 (0.5 : 1), C] Fe/CeO_2 (1: 0.5)

3.2. Scanning Electron Microscopy (SEM) : Scanning electron microscopy (SEM) images presented in Figure (2). SEM observations of the sample reveal that the particles are certain extent of aggregations of the particles.

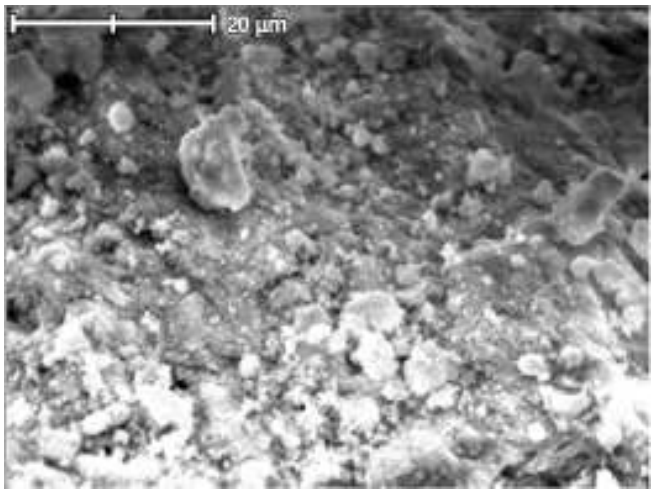


Figure (2) : SEM images of Fe/CeO_2 (0.5:1) hydrothermal treated at 650 °C for 5 h.

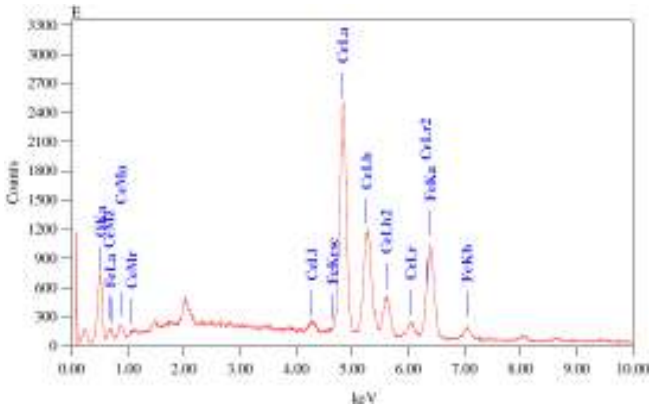


Figure (3) : EDX graph of Fe/CeO_2

The chemical analysis (EDX) of the Fe:Ce nanocomposite allows the detection of the Fe, Ce present in the nanocomposite sample (Figure 3).

3.3. FTIR Studies : The FT-IR spectra of the catalysts are shown in Figure (4). FTIR spectra of nano ceria and Fe/CeO_2 prepared by hydrothermal treatment. The FTIR measurements were done by using the KBr pellet technique [20]. The peak which observed at 3360 cm^{-1} is related to the -OH stretching vibration due to H_2O in the sample. The absorption peak at around 1620 cm^{-1} may be attributed to the O-H vibration of water. The one peak located in the area from 400 to 750 cm^{-1} to the CeO_2 stretching. The rest of the peaks were also similar with each other which indicate the formation of pure phase of CeO_2. Water from the environment gets absorbed on the ceria particle surface creating two small peaks at 920 and 1020

cm^{-1}, as we increase the amount of Fe in the catalyst the intensity of these peaks gets reduced. This might be because of physical nature of iron.

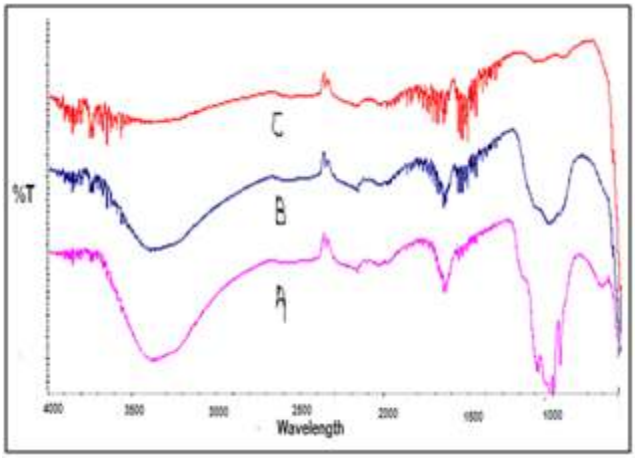
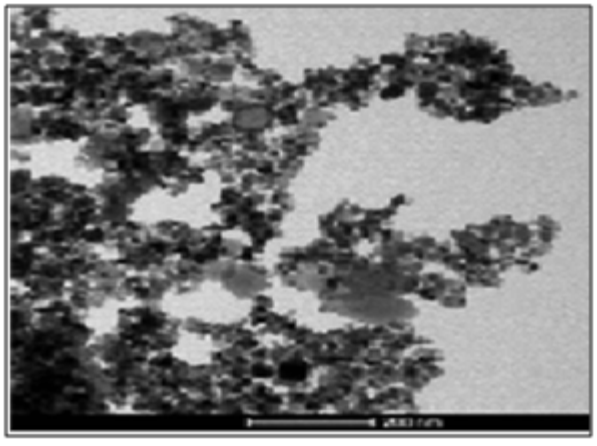


Figure 4: FTIR Spectra of (A) Pure CeO_2, (B) Fe/Ceo_2 (0.5 : 1), (C) Fe/CeO_2 (1: 0.5)

3.4 TEM analysis : TEM investigation on Fe/CeO_2 nanoparticles calcined for 5h at 650 ^{0}C are shown in Figure (5). Ceria and Fe/CeO_2 samples calcined at 650 ^{0}C showed the nano structure which is evident from the TEM. In the sample of mixed oxides, a homogeneous distribution and spherical sized particles of ~10 nm are observed. The diffraction pattern also shows more crystallinity for higher ceria sample. The crystalline phases are in agreement with the XRD pattern. The ceria-iron mixed oxides are potential nanocatalysts for acid catalyzed reaction.



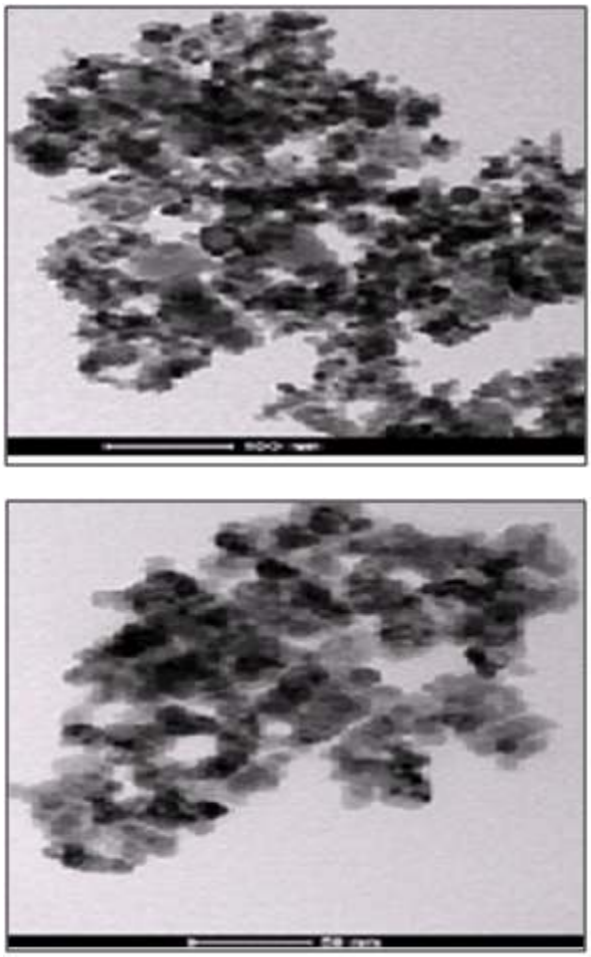


Figure (5) : TEM images of Fe supported on ceria.

4. Conclusions : Well-crystallized and good dispersed nano-ceria and nano iron-ceria catalysts were obtained by hydrothermal synthesis using an oxidizer H_2O_2. The crystallite size of samples from XRD and TEM indicates formation of nanocrystalline CeO_2 and Fe/CeO_2 catalysts. As per the standard data of XRD Fe/CeO_2 and CeO_2 indicating the cubic fluorite structure. The peaks are very sharp indicating well crystalline nature of the material. In this sample of mixed oxides, a homogeneous distribution and spherical sized particles of ~ 10 nm are observed. The crystalline phases of TEM are in agreement with the XRD pattern.

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