

Surfactant-assisted Hydrothermal Synthesis of Ceria-Zirconia Nanostructured Materials for Catalytic Applications

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Abstract: CeO_2 - ZrO_2 oxides were prepared by the surfactant-templated method using cetyl trimethyl ammonium bromide (CTAB) as template and modified with chromium nitrate. These were characterized by XRD, FT-IR, TEM, SEM, BET and TPD- CO_2 . The XRD data showed that as prepared CeO_2 - ZrO_2 powder particles have single phase cubic fluorite structure. HRTEM shows mesoscopic ordering. Average particle size is 12-13 nm as calculated from particle histogram. The nitrogen adsorption/desorption isotherm were classified to be type IV isotherm, typical of mesoporous material. The presence of uni-modal mesopores are confirmed by the pore size distribution which shows pore distribution at around 60 Å. Catalytic activity was studied towards liquid-phase oxidation of benzene.

Keywords- Mixed rare earth oxide, Ceria-zirconia, BET, TEM, benzene oxidation.

I. Introduction

In recent years, ceria and ceria containing material have been thoroughly investigated for the three way catalyst (TWC) [1] application and oxidation catalysis (for example, diesel oxidation catalysts, DOC) because of their oxygen storage capacity (OSC) based on the unique redox behaviour between Ce^{3+} and Ce^{4+} . [2, 3] CeO_2 is included in materials used in fuel-cell processes [4], in oxygen permeation membrane systems [5], and as catalysts in numerous economically and technologically important industrial processes. The presence of CeO_2 promotes various catalytic reactions such as CO_2 activation, CO oxidation, CO/NO removal, low-temperature water-gas shift reaction, oxidation of different hydrocarbons, wet oxidation processes of organic compounds, the removal of total organic carbon from industrial wastewaters, methane reforming with CO_2 , SO_2 reduction with CO.

In the 1990s, many studies were committed to ZrO_2 - CeO_2 oxides, notably to their synthesis and their catalytic properties. [7-9] It is generally known that the incorporation of zirconium into the ceria lattice creates a higher concentration of defects thus improving the O^{2-} mobility; such mobility would explain the outstanding ability to store and release oxygen. [10] This property allows the oxidation of hydrocarbons and CO in rich atmospheres.

Phenol, a valuable intermediate for the synthesis of agrochemicals, petrochemicals and plastics has been mainly manufactured by the cumene process. But this multistep reaction generates phenol and acetone in equimolar amounts. Hence the synthesis of phenol by direct hydroxylation of benzene is attractive both economically and energetically. In the past, several catalysts have been examined using a number of oxidants. Benzene oxidation using hydrogen peroxide has been explored by various researchers. [11-13] Transition metal catalysts have also been demonstrated by researchers for the reaction in presence of comparatively costly oxygen as the oxidant, and a reducing agent. [14, 15] Furthermore, benzene is considered as a priority pollutant by the Environmental Protection Agency. Catalytic oxidation is considered as most promising method for its effective removal.

In the present work, we report the synthesis of ceria zirconia mixed oxides, modification with chromium, their structural characterization using different physico-chemical techniques. Activity of the catalysts towards liquid phase oxidation of benzene is also investigated.

II. Materials and Methods

2.1. Experimental process

$Ce(NO_3)_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$ were dissolved in a vessel with 500 mL deionized water to obtain a cerium/zirconium mixed solution with a Ce/Zr mole ratio of 1:2. And then it was slowly added to a 500 mL solution containing cetyl trimethyl ammonium bromide (surfactant/cerium nitrate=3.4 molar ratio) under agitation, followed by adding NH_4OH (28 wt %) into the mixture, the pH of the mixture was maintained at around 11. The gel was loaded into a stoppered Teflon bottle and heated hydrothermally at 100°C for 48 h. The resultant solid was recovered by filtration, washing and then it was dried in air at 80°C for 12 h. Finally, the sample was calcined at 600 °C for 4 h. It was then impregnated with an aqueous solution of chromium nitrate.

The volume of the aqueous solution of metal used for impregnation depended on the amount of the

support. The modified ceria-zirconia catalyst was dried at 120°C for 2 hrs and then it was calcined at 400°C for 4 h. The ceria zirconia support was denoted as CeZr and chromium modified catalyst as 1CrCeZr and 2CrCeZr.

2.2. Characterization

Nitrogen adsorption measurements were performed at liquid nitrogen temperature with a Micromeritics Tristar 3000 surface area and porosity analyzer. XRD analysis was carried out using Rigaku D-Max Ni filtered Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) diffractometer equipped with diffracted beam monochromator at a scan rate of 50/min analyzer. ICP-AES were done on Thermo electron IRIS INTERPID II XSP DUO model. FT-IR spectra of the prepared samples were measured by the KBr pellet procedure over the range of 4000-500 cm^{-1} region using JASCO FTIR spectrometer. Transmission Electron Microscopy was carried out in ultra high resolution analytical electron microscope JEOL 3010. The sample was dispersed in ethanol through sonication and then drop casted on a carbon-coated copper grid. Scanning electron micrographs was taken using JEOL Model JSM-6390LV scanning electron microscope with a resolution of 1.38 eV. The powdered sample was dusted on a double sided carbon tape, placed on a metal stub and was coated with a layer of gold to minimize charge effects. Perkin Elmer TG analyzer instrument was used for carrying out thermo gravimetric studies. UV-VIS DR spectra were taken in the range 200-800nm on Labomed UV-VIS double beam UVD-500 spectrophotometer equipped with an integrating sphere assembly with a charged coupled device detector, using BaSO $_4$ as reflectance standard. Temperature-programmed desorption study of CO $_2$ was carried out in Micromeritics Pulse Chemisorb 2705.

2.3. Catalytic Activity

The liquid-phase oxidation of benzene was carried out in a 50 mL round bottom flask. In a typical reaction, the catalyst powder was suspended in a mixture of acetonitrile (10 ml) and benzene (2 mL) and kept in the oil-bath. The oxidant, hydrogen peroxide (H $_2$ O $_2$) was added to the system after attaining the reaction temperature. The reaction mixture was stirred using a magnetic stirrer. About 0.5mL of solution was withdrawn at regular intervals and analyzed on Chemito 8610 GC equipped with FID detector and an OV-17 packed column. The products obtained were identified by comparison with standard ones. The catalytic activity was expressed as the percentage conversion (wt%) of benzene and the selectivity for a product is expressed as the amount of the particular product divided by total amount of products multiplied by 100.

III. Results And Discussions

The nitrogen sorption isotherms of ceria zirconia mixed oxides (CeZr) are shown in Fig. 1. It can be classified as a type IV isotherm, typical of mesoporous material. The shape of the curve indicates the absence of a narrow pore size distribution as suggested by the lack of the typical step in the adsorption isotherm which is observed with ordered mesoporous structure. According to IUPAC classification, the hysteresis loop is of type H2 indicating complex mesoporous structure.

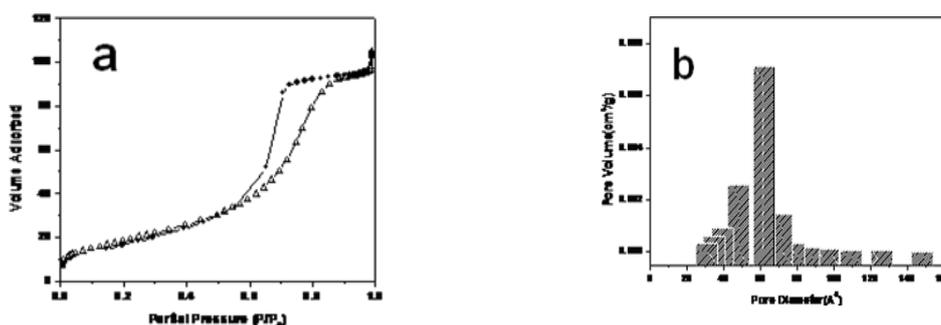


Fig. 1. Nitrogen adsorption–desorption isotherm (a) and Pore size distribution (b) of CeZr.

The uptake at high pressure ($P/P_0 \sim 0.9-1.0$) is associated with the void spaces between the particles.[16] The presence of uni-modal mesopores are confirmed by the pore size distribution which shows pore distribution covering the range 30-80 Å with a maximum at around 60 Å for mesoporous CeZr as depicted in Figure 1. Surface area of the ceria zirconia sample was observed to be 70.1m 2 /g and on chromium modification surface area was decreased to 57.9 m 2 /g. A substantial decrease in BET surface area after impregnation is mainly due to the penetration of the dispersed chromia into the pores of the support.

X-ray diffraction pattern of prepared samples is shown in Fig. 2. Fig 2 shows the XRD patterns of ceria-zirconia. XRD of the prepared material consists of all the peaks corresponding to the cubic fluorite

structure. The peaks were observed at $2\theta \sim 29.66, 34.12, 49.1, 58.28$ in comparison with the pure ceria peaks at 2θ values of $28.78, 34.12, 47.68$ and 56.48 . [17, 18]. High 2θ values in the pattern reveal the presence of a minor zirconia rich phase. Shift of peaks towards higher 2θ values is due to the small ionic radius of Zr^{4+} (0.84\AA) in comparison with that of Ce^{4+} (0.97\AA). All the diffraction patterns exhibit broad peaks suggesting that as-prepared materials are nanocrystalline materials.

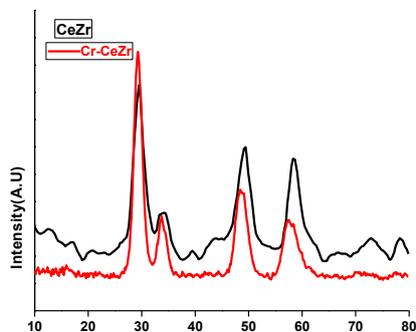


Fig. 2. XRD patterns of CeZr and 1CrCeZr.

FT-IR spectrum of representative catalysts is displayed in Figure 3. Broad absorption band located in the area from 3200 to 3600 cm^{-1} corresponds to O-H stretching vibration. The peaks at 1640 cm^{-1} corresponds to H_2O bending vibration and at around 1340 cm^{-1} is due to Ce-OH stretching vibration. Band in the area from 400 - 700 cm^{-1} is due to the CeO_2 stretching vibration. According to literature data [19] on the vibrational active modes in the fluorite structure, absorption at around 460 cm^{-1} the main maximum would be assigned to the transverse mode (TO) of the triply degenerated F_{1u} fundamental, and the shoulder to the longitudinal component (LO) of the same fundamental. The IR active mode in the 600 - 650 cm^{-1} range is caused by asymmetrically coupled asymmetric Zr-O-Zr stretching, and the mode arising from the symmetric Zr-O-Zr stretching is revealed in the 400 - 500 cm^{-1} region. [20]

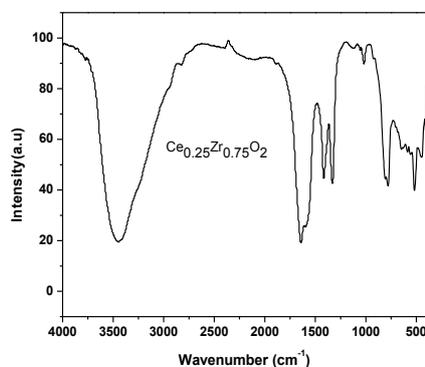


Fig. 3. FT-IR spectrum of CeZr.

The morphology analysis was carried out and is shown in figure 4, 5 and 6. It can be seen from Fig.4 that majority of the ceria crystals consists of aggregated small crystallites of a few nanometres and very homogeneous in size. Sample shows mesoscopic ordering as observed from HRTEM. The lattice fringes of nanocrystalline zirconia can also be well detected by the high resolution TEM image. The selected area electron diffraction (Fig 4d) pattern of the sample exhibited continuous concentric rings, implying that the samples consisted of many very small crystallites with well-defined lattice planes. Average particle size is 12 - 13 nm as calculated from particle histogram (Fig 4e). Figure 5 shows the HRTEM and SAED pattern of chromia modified sample. Figure 6 contain scanning electron microscopic pictures of some representative catalysts. After calcination, the particles become irregular shaped and larger sized due to the collapse in structure after heat treatment.

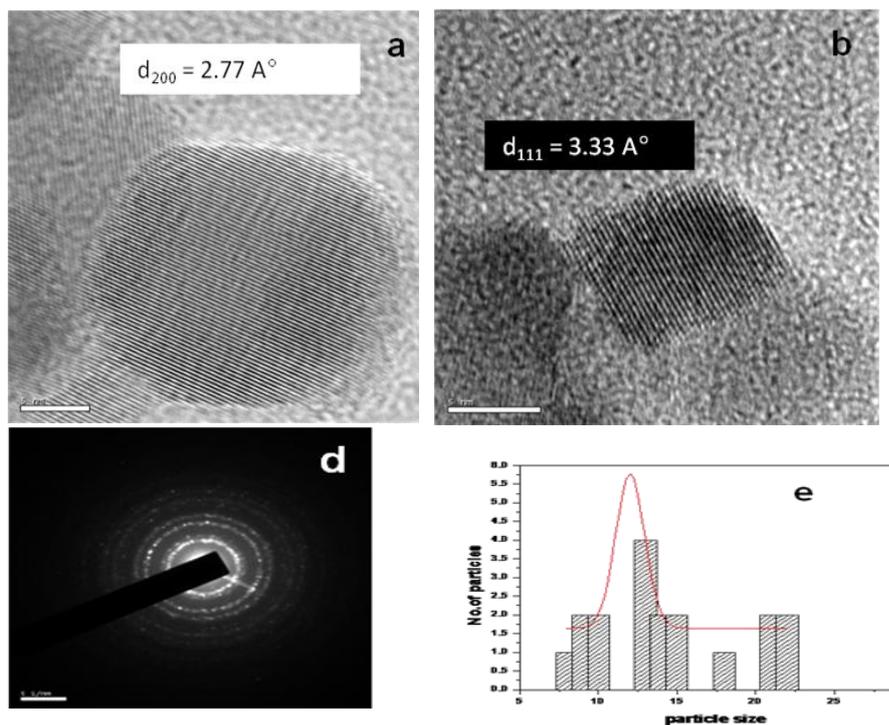


Fig. 4. HR-TEM, SAED pattern (d) and particle size histogram (e) of CeZr.

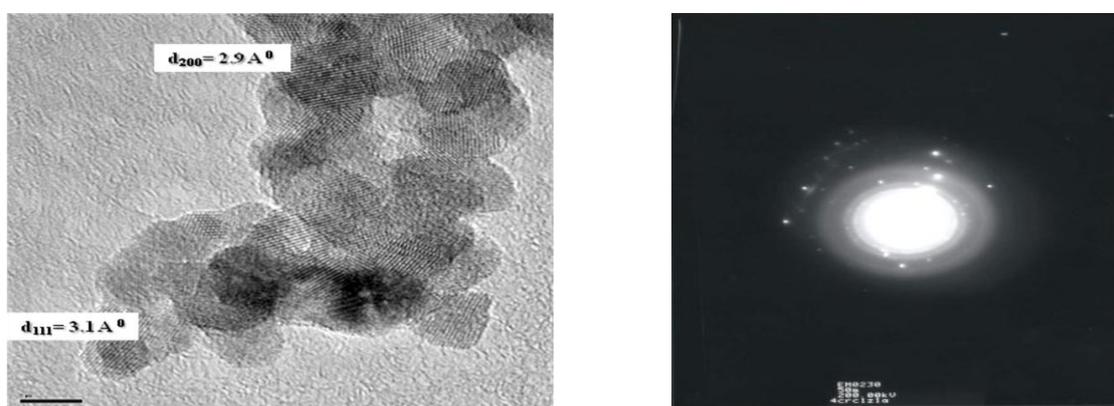


Fig. 5. HR-TEM, SAED pattern of 2CrCeZr.

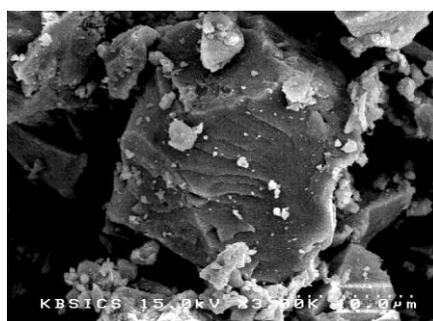


Fig. 6. SEM image of CeZr.

Thermogram corresponding to Ce-Zr mixed oxide shows weight loss at 206 °C which is attributed to the removal of structural hydroxyl group(Fig 7). A small weight loss at 311°C may be due to the removal of surfactant. Weight loss at around 440 °C can be due to the transition from amorphous into crystalline form.

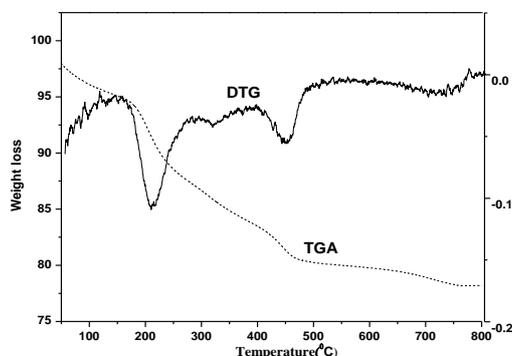


Fig.7. TG-DTA analysis of CeZr.

The spectra, in general, are broad and exhibited a myriad of poorly resolved peaks. Broad absorption bands are observed in the range of 200–350 nm (Fig 8). These bands are attributed to localized O–Ce charge transfer transitions involving a number of surface Ce 4+ ions with different coordination numbers 21. Interband and O₂--Zr⁴⁺ transitions of substituted fluorite lattice 22 occur prominently around 340nm.

TPD spectrum of CO₂ obtained after CO₂ adsorption is shown in Fig.9. Two desorption peaks appear at 199°C and 369°C. It is clear that there are two kinds of CO₂ adsorption sites on CeO₂-ZrO₂ surface indicating two kinds of basic sites on the surface of the catalyst. The peak at lower temperature may be assigned to a monodentate carbonate interacting with CeO₂-ZrO₂. The desorption peak at a higher temperature may be assigned to a bidentate carbonate. The latter species being bonded to the oxide surface by two lattice oxygen ions should exhibit a higher thermal stability than the former ones. [23, 24]

Fig. 8. DR UV-vis spectra of CeZr.

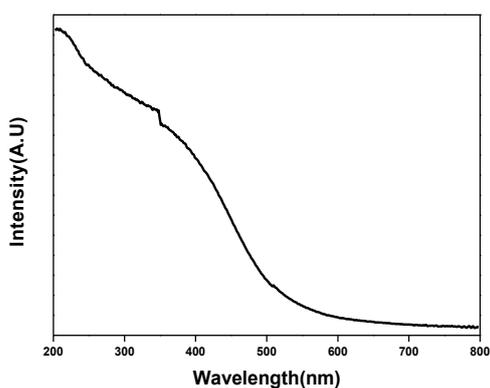
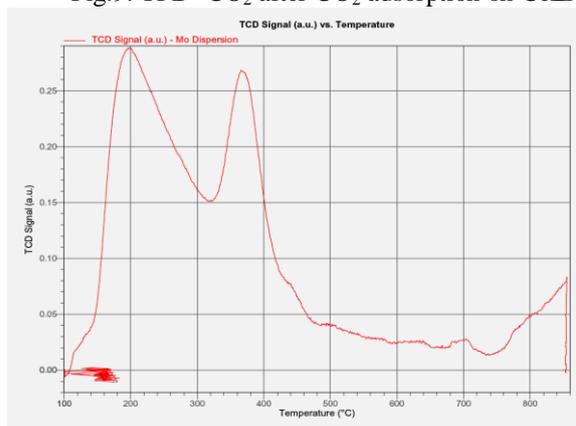


Fig.9. TPD -CO₂ after CO₂ adsorption on CeZr



IV. Catalytic activity: Oxidation of benzene

The catalysts prepared were used in a one-step liquid-phase oxidation of benzene with H₂O₂ as the oxidant and acetonitrile as the solvent.

The effect of temperature on the oxidation of benzene was studied by performing the reaction at three different temperatures over chromia modified ceria zirconia with other parameters kept constant and the results are shown in Fig.10. The best results were obtained at 60 °C. When the reaction temperature rose up to 343 K, a sharp increase in the oxidation activity (51%) and phenol selectivity (85%) was observed. Further increase of temperature decreased the activity as well as phenol yield. This may arise due to the phenol being further oxidized to hydroquinone and 1,4-benzoquinone at the higher temperature. Vaporization of benzene can also occur at this temperature which can result in the decreased activity. [25]

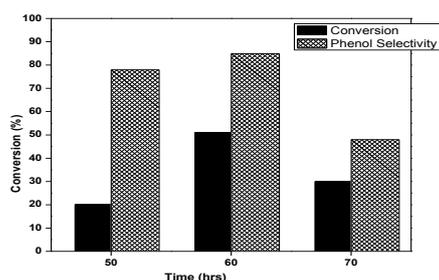


Fig. 10. The effect of temperature on benzene oxidation with Cr-CeZr as the catalyst (Catalyst mass = 100 mg, Benzene: H₂O₂ = 1:2 ratio (vol); acetonitrile = 10ml and reaction time=5h).

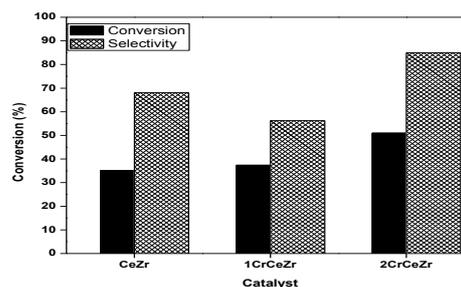


Fig. 11. The oxidation of benzene over catalyst with different metal loading.

Benzene was oxidized using catalyst with different metal loadings under the optimum reaction conditions at 60 °C (Fig 11). When the amount of chromium increased, the benzene conversion is increased. So the oxidation rate directly depends on the metal content.

For the oxidation of aromatics with hydrogen peroxide over modified metal oxides, it has been proposed that the hydroxylation of the aromatic ring occurs via the heterolytic mechanism, involving the formation of a metalloperoxide species [26–30]. We have not carried out any mechanistic studies in the present work, it is tentatively suggested that a heterolytic cleavage of hydrogen peroxide proceeds via the formation of metallo peroxide. Similar observations have been noticed in literature over metal oxide dispersed analogues [31, 32].

V. Conclusions

Nanocrystalline powders of ceria zirconia mixed oxides were successfully synthesized using CTAB as surfactant via hydrothermal method. The technique used here is simple and cost effective. The X-ray diffraction (XRD) analysis suggests that as-prepared materials are nanocrystalline materials. The nitrogen adsorption/desorption isotherm can be classified as a type IV isotherm and hysteresis loop is of type H2 indicating complex mesoporous structure. Pore size distribution which shows pore distribution covering the range 30-80 Å with a maximum at around 60 Å. HRTEM investigation reveals the existence of several nano crystallites with well defined lattice planes. Average particle size is 12-13 nm as calculated from particle histogram. A single step oxidation of benzene to phenol under mild reaction conditions was carried out successfully over supported ceria zirconia mixed oxide as catalysts with H₂O₂. Incorporation of chromia exhibited a promoting effect towards the oxidation reaction. The obtained results suggest the scope of tailoring reaction engineering design for better utilization of this system.

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