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STUDY ON THE STRUCTURE, TEXTURE AND THERMAL STABILITY OF $CeZrYO_2$ NANOPARTICLES SYNTHESIZED VIA MICROEMULSION METHOD

(Kajian Terhadap Struktur, Tekstur dan Kestabilan Termal $CeZrYO_2$ Nanopartikel Disintesis Melalui Kaedah Microemulsi)

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Abstract

The $CeZrYO_2$ (CZY) was synthesized via microemulsion method. Phase structure, texture, and thermal stability of CZY nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2 adsorption-desorption and thermogravimetric Analysis (TGA). XRD analysis confirmed the cubic phase and homogeneous solid solution of CZY nanoparticles formed. TEM micrograph also revealed the CZY nanoparticles well-defined crystallite, spherical shaped and nanoscale size in range of 5 – 10 nm. The surface area of CZY nanoparticles was 219.50 m^2/g and isotherm profile was mesoporous type IV. It was also found that the synthesized CZY nanoparticles remain a good thermal stability, in the range of temperature more than 900^oC according to thermo gravimetric analysis.

Keywords: $CeZrYO_2$, Yttrium, nanoparticles, microemulsion

Abstrak

$CeZrYO_2$ (CZY) telah disintesis melalui kaedah mikroemulsi. Struktur fasa, tekstur, dan kestabilan termal nanopartikel CZY dicirikan oleh pembelauan sinar-X (XRD), mikroskop elektron transmisi (TEM), N_2 penjerapan - desorpsi dan analisis termogravimetri (TGA). Analisis XRD mengesahkan fasa kubik dan homogen nanopartikel larutan pepejal terbentuk. TEM mikrograf juga mendedahkan nanopartikel CZY kristal terbentuk dengan jelas, berbentuk bulat, dan bersaiz nano dalam lingkungan 5 – 10 nm. Luas permukaan nanopartikel CZY adalah 219.50 m^2/g dan isoterma profil adalah mesopori (Jenis IV). Ia juga mendapati bahawa nanopartikel CZY mempunyai kestabilan terma yang baik, dalam lingkungan suhu melebihi 900^oC mengikut termogravimetri analisis.

Kata kunci: $CeZrYO_2$, Yttrium, nanopartikel, microemulsi

Introduction

In recent years, the modification of ceria-zirconia that has bright potential in improvement of catalytic performance of three-way catalysts (TWCs) to eliminate the automotive emission has a great attention from researchers. It is due to the ceria-zirconia has limitation on the performance of oxygen storage and released during cold start emissions [1]. It is well known that the zirconia act as thermal stabilizer of ceria against the sintering phenomenon and it is not attributed to the oxygen mobility [2]. Therefore, the incorporation of ceria-zirconia has made the reduction of percentage composition of ceria as oxygen storage material in TWCs, resulting in the decrement of oxygen mobility rate under lower temperature.

Most researcher have suggested the modification of ceria-zirconia using rare earth metals such as the yttrium, Y to be a potential element to produce the efficient oxygen storage materials [3-5]. The addition of Y into ceria-zirconia provides two distinct properties: (i) high density of Ce^{4+} ions on the surface, and (ii) high reactive surface area, facilitating the dispersion active catalysts and oxygen mobility [5, 6]. Wang, et al. [7] reported that the introduction of Y lead to remarkable increased of surface area, increase the dispersion of Pd and strong interaction of between Pd-catalysts and support, which resulted the catalysts exhibit high catalytic activity.

However, the preparation techniques also have great influence on the structural and textural properties, especially on the homogeneous solid solution and surface area. It is well known that the homogeneous solid solution can create better properties and the high surface area which can be helpful or even essential in attaining a significant reaction rate [8]. The smaller size particle can provide the high surface area and it can minimize the sintering impact of modified ceria-zirconia and provide more Ce^{4+} ions to mobilize oxygen [9]. Therefore, water/oil microemulsion method have been proposed because it is able to produce the homogeneity of the mixed oxides formed, offering the nano-size range particles, high specific surface area and high metallic dispersion [10]. In this study, the $CeZrYO_2$ (CZY) nanoparticles were synthesized by water/oil microemulsion method. The effects of addition of yttrium into ceria-zirconia on the structure, texture and thermal stability were studied.

Materials and Methods

Synthesis

The CZY nanoparticle was synthesized using water/oil microemulsion method. The similar procedure was adapted from Hadi and Yaacob [11]. CTAB/Butanol/Octane/Water system was used in this work. CTAB, butanol, n-octane were obtained from Merck Malaysia and the metals nitrate were obtained from Sigma Aldrich. The first microemulsion containing the 21% metals nitrate solution (Ce, Zr and Y) was prepared by mixing the 13% CTAB, 13% butanol and 53% octane under continuous stirring at room temperature until the clear solution was obtained. Similar procedure was also applied for second microemulsion containing the reducing agent (NaOH). Both microemulsions were then mixed under vigorous agitation for 3 hours and the colloidal precipitates were formed. The colloidal precipitates were left at room temperature for 24 hours. Then, it was washed with ethanol and deionized water for three times using centrifuge at 10,000 rpm for 10 minutes. Finally, the samples were dried at 110^{o}C for 24 hours.

Characterization

The X-ray diffraction (Model: Rigaku Ultima IV) patterns were recorded on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ= 0.15418 nm) operating at 40kV and 20mA at a scanning rate 1.2°/min in the range 2θ is 20° to 70°. The crystallite phases were identified according to the reference data from the International Center Diffraction Data (ICDD). Transmission electron microscopy (Tecnai G2 20) examined the microstructure studies of sample. The surface areas of synthesized samples were determined using Autosorb-1 Quanta Chrome Instrument TUSA, N_2 adsorption isotherms at -196°C. For the thermogravimetric analysis (TGA) was performed (METLER TOLEDO TGA SDTA851) in a temperature range of 50 to 1000˚C to observe the thermal stability and degradation of the synthesized CZY nanoparticles.

Results and Discussion

X-ray Diffraction Analysis

Diffractogram pattern of the CZY nanoparticles is presented in Figure 1. It can be seen that the pattern obtained are correspond to pure ceria (ICDD: 021306). Based on previous studies, Abu Shah, et al. [12] reported that the peaks of commercial CeO_2 has a cubic phase, in which at 2θ = 28.51, 33.04, 47.43, 56.1 and 59.05 are assigned to the (111), (200), (220), (311) and (222) planes, respectively. A symmetrical diffractogram pattern of the CZY nanoparticles and pure ceria was observed. These findings suggest that the synthesized CZY nanoparticles are symmetrically phase with pure ceria, in which the cubic phase was formed even though the insertion of yttrium. It is also observe that the diffractogram patterns of yttrium are undetected. It may be attributed to well-defined homogeneous solid solution formed [13]. In addition, the diffractogram of the CZY nanoparticles show the crystallites pattern, even though the CZY nanoparticles do not undergo the heating treatment. It can be concluded that the microemulsion method can produce the CZY nanoparticles with their cubic phase at room temperature and it does not require the further heating treatment.

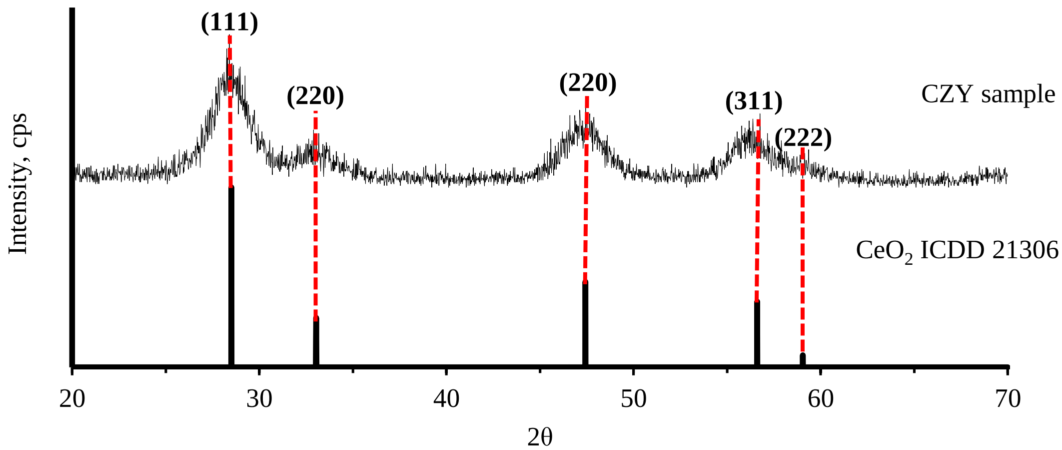

Figure 1. X-ray diffraction pattern of the CZY nanoparticles

Transmission Electron Microscopy Analysis

Figure 2 shows the transmission electron microscopy (TEM) of CZY nanoparticles. The micrograph of CZY nanoparticles reveals spherical shape of particles. This observation also reveals that the size particles of CZY in range of 5 – 10 nm. From other literature [14] also reported that the typical size of cerium-zirconia was obtained in range of 50 – 100nm, in which it is bigger than the CZY nanoparticles. It indicates that the CZY nanoparticle via microemulsion method able produced smaller size than the ceria-zirconia. The synthesized CZY also exhibits polycrystalline structure in which the existence of a bright diffraction rings in Figure 2 and clearly shows the lattice fringes with d spacing of 0.310 nm, which attribute to the plane (111). These findings may suggest that the well-defined crystalline of CZY nanoparticle was formed.

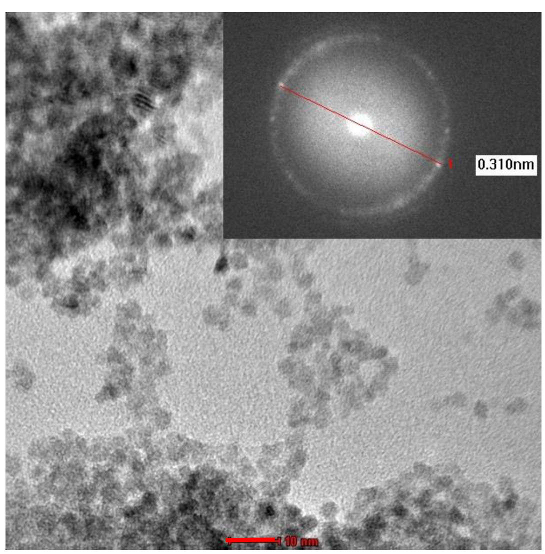

Figure 2.Transmission electron microscopy of CZY nanoparticles

N_2 Adsorption-Desorption Analysis

The specific surface area, total pore volume, and average pore size of CZY and commercial CeO_2 are listed in Table 1. The surface area of CZY nanoparticles is higher than the surface area of commercial CeO_2. This indicates that the microemulsion method able to produce high surface area particles. The isotherm profile of CeO_2-commercial clearly follows the type V, which have a weak adsorption and desorption. Instead, the CZY nanoparticles are follows the type IV which is mesoporous materials with a strong absorption and desorption as shown in Figure 3. It clearly proven that the narrow size of particles gives high surface area and strong substrate site. These results showed the potential characters of CZY nanoparticles are suitable to be applied in three-way catalyst.

Table 1.Textural property of commercial-CeO_2 and CZY nanoparticles

Identity	Specific Surface Area, m^2/g	Total Pore Volume, (10^{-3}) cm^3/g	Average Pore Size, nm
CeO_2-commercial	41.85	74.00	11.50
CZY	219.50	93.10	2.64

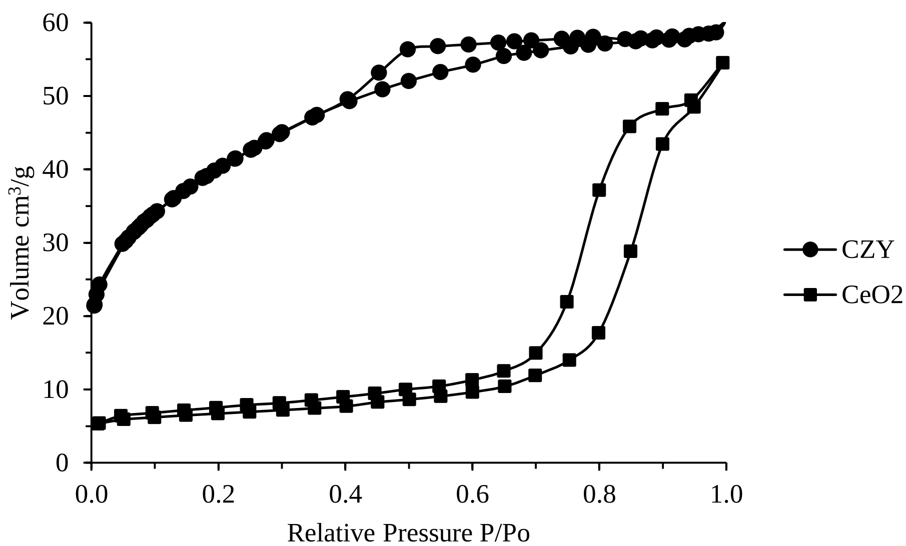

Figure 3. Isotherm profiles of CZY nanoparticles

Thermogravimetric Analysis (TGA)

The thermal stability of CZY nanoparticles are examined via TGA. In Figure 4, TGA and DTG profile show four (4) major peaks during the thermal course. Firstly, the initial point of the weight loss is shown at T < 100 ˚C. It indicates the removal of water molecule and excess of volatile compound during synthesis route. The second point of the weight loss is observed at range 200°C > T > 350˚C with a weight loss of 0.24 mg/min. It may be attributed to the transformation of degree crystallinity of CZY nanoparticles. According to the Toshiyuki Masui, et al. [15], the amorphous phase of the sample may change to a better crystallinity at temperature of 250^{o}C. The third peak is observed at range 450°C > T > 700 °C with a weight loss of 0.12 mg/min. It indicates the reducibility transformation of $Ce^{4+} \rightarrow Ce^{3+}$ ions, which the removal of oxygen atom from ceria and makes the reduction of weight of sample. Some literatures report that the reducibility of the modification ceria activate at temperature ~ 400-700 ^{o}C [2, 6, 16, 17]. The last peak is observed at range 900°C > T > 1100 °C with a very small weight loss (0.05mg/min). It may due to the decomposition of ceria, which the changing of oxidation number ceria (+3 → 0) and indicating the chemical deactivation of CZY nanoparticles. The results also revealed that the peak 4 shows the lowest weight losses which of < 0.04 mg/min, indicating the CZY nanoparticles have a good thermal stability in the range of temperature more than 900^{o}C.

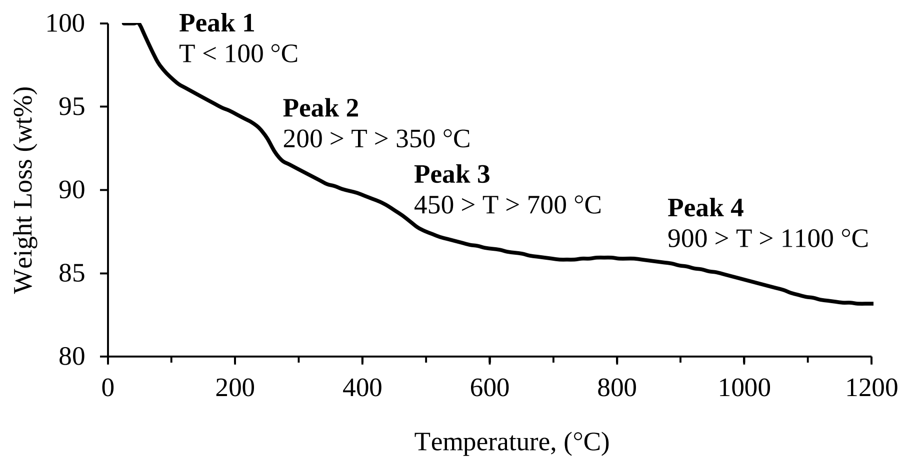

Figure 4(a). Thermogravimetric analysis (TGA) profile of CZY nanoparticles

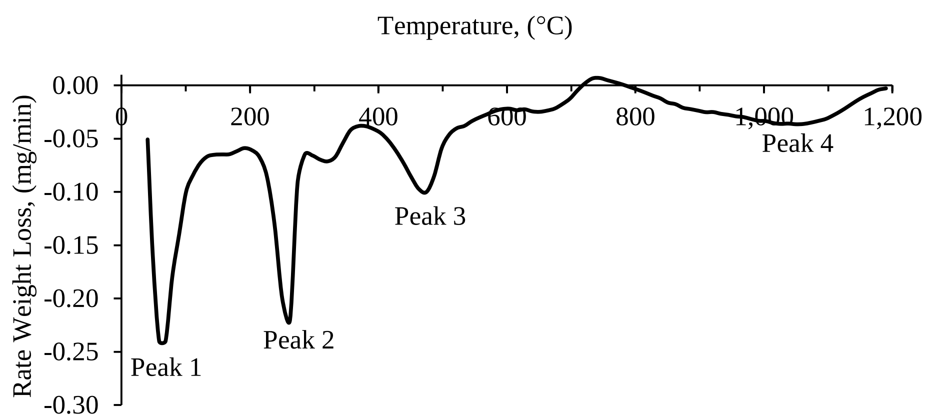

Figure 4(b). Derivative thermogravimetric analysis of CZY nanoparticles

Conclusion

The CZY nanoparticle was successfully synthesized via microemulsion method under room temperature. These findings may suggests that the synthesized CZY nanoparticles via microemulsion method was produced a homogeneous solid solution and well-defined crystalline formed. The insertion of yttrium into ceria-zirconia structure formed the (fcc) cubic phase. The particle size of synthesized CZY was nanoscale in the range of 5 – 10 nm. The smaller size CZY nanoparticles provided the high surface area of CZY nanoparticles was 219.50 m^2/g. The presence of yttrium in ceria-zirconia structure improved thermal stability of ceria-zirconia nanoparticles in the range of temperature more than 900^{o}C.

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