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To cite this article: M N A Shah et al 2016 IOP Conf. Ser.: Earth Environ. Sci. 36 012052

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Synergistic effect of Cu-doped into CesZrO₂ nanocatalysts

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Abstract. $Ce_{0.75}Zr_{0.25}O_2$ and $CuO/Ce_{0.75}O_{0.25}O_2$ nanocatalysts have been successfully prepared by combination of microemulsion and deposition precipitation methods. The synthesized nanocatalysts revealed as the cubic structure, homogeneous solid solution and the particles were in nanoscales. The copper particles were well deposited and dispersed on the entire of Ce_{0.75}Zr_{0.25}O₂ surface and pores which reflected by the lower the surface area of CuO/Ce_{0.75}Zr_{0.25}O₂ than Ce_{0.75}Zr_{0.25}O₂. The additional of copper catalysts able to active the catalysts to lower temperature up to < 250°C and stabilize the microstructure of catalysts.

1. Introduction

Nowadays, the total air pollution release to the atmosphere increase rapidly simultaneously with the increasing of the mass production of automobiles worldwide especially in the urban area. As we well known, air pollution contributes to the human health and environment damages. In order to avoid the huge effect of air pollution, many automobile manufactures has introduced the exhaust gas after treatment system or called as three-way catalysts (TWCs) in automobile engines to reduce the level of emission released to the tolerable limits. However, it is still insufficient to reach the desired emissions level, especially during cold-start portion of driving. As reported by Heck and Farrauto [1], the majority of carbon monoxide and unburned hydrocarbon emissions (60%-80% of the total emitted) are produced during the cold-start condition. Therefore, the emission from automobile still becomes the major contributor of air pollution in the atmosphere.

The catalytic components in three-way catalysts mainly consist of the noble metals such as Pt, Pd, and Rh as the active catalysts and cerium oxide (CeO₂) as oxygen storage/release component (OSC). As an OSC, CeO₂ plays the important role in increasing the effectiveness of TWCs during the cold start condition by maintaining the oxygen concentration in catalytic reaction. However, CeO₂ is easily to be sintered leading to the reduction of active surface area and the capabilities of oxygen to storage and release under fluctuating in exhaust system reduced during exposed to high temperature [2,3]. Consequently, it will reduce the effectiveness of TWCs in reducing emissions concentrations.

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The extensive research and development has been performed to overcome the drawback of CeO₂ at high temperatures, such as the incorporation of zirconium ions into the cerium structure. Li et al., [4] described that the insertion of Zr^{4+} ions into the cerium crystal creates a homogeneous solid solution, which can stabilize CeO₂ against sintering and enhance the thermal stability. In addition, this combination also enhanced the surface area and increased the dispersion of active catalysts, leading to the high catalytic performance of the TWCs [5]. The best ratio of cerium and zirconium for the ideal combination materials was the Ce_{0.75}Zr_{0.25}O₂ which promotes a good thermal stability and high surface area as reported by another author [5–7].

The introduction of copper as active catalyst into $CeZrO_2$ has been intensively explored Escribano et al., [8] reported the possibility of copper oxide as an active catalyst to oxidise the carbon monoxide and volatile organic compound. Radlik et al., [9] concluded that inclusion of CuO into $Ce_xZr_{(1-x)}O_2$ catalysts could promoted the oxygen mobility and water-gas shift reaction at lower temperatures in range 100 - 200°C. The replacement of copper oxide as active catalyst in TWCs offered a cheaper metal and a viable solution from both an economical and catalytically point of views.

Numerous combination preparation techniques have been applied to develop the metals loaded $Ce_{0.75}Zr_{0.25}O_2$ catalysts, such as co-precipitation and impregnation [10,11], sol gel and incipient wetness impregnation [12], solid state chemical reaction and incipient wetness impregnation and etc. However, the combination of microemulsion and deposition precipitation methods to synthesis the ceria-zirconia mixed oxides and loaded catalysts still have limited exploration. Even thought, the microemulsion was able to enhance the homogeneous mixing of catalysts components and narrow size distribution with tunable size [13,14]. Besides, the deposition precipitation method aiming to prepare well dispersed active catalyst particles on support, with a narrow particle size distribution [15,16] Therefore, the combination of microemulsion and deposition precipitation method was proposed to enhance the thermal stability and microstructure properties of the TWCs.

In our work, the microemulsion method was employed to synthesize the $Ce_{0.75}Zr_{0.25}O_2$ nanomaterial as support catalysts and the copper catalysts were loaded via deposition precipitation method. The synergistic effects of copper doped into ceria-zirconia structure were explored through x-ray diffraction, N₂-adsorption desorption, field emission scanning electron microscopy, transmission electron microscopy and temperature programmed reduction. We aspired that our work may help to understand the synergistic effects copper doped into ceria-zirconia in term of catalytic properties especially the activation catalysts at lower temperature.

2. Materials and Experimental Procedure

2.1 Catalyst preparation

In this research, the catalysts were synthesized in two steps of preparation procedure. In the first step, $Ce_{0.75}Zr_{0.25}O_2$ catalyst support was produced using water/oil microemulsion synthesis. The method was adopted from Laguna et al., [17]. The microemulsion system consisted of cetyltrimethylammonium bromide (CTAB, Merck Malaysia, 99%) as the surfactant, 1-butanol (Sigma Aldrich Malaysia) as the co-surfactant, n-octane (Merck Malaysia) as the continuous oil phases and cerium nitrate ($Ce(NO_3)_2$), Merck Malaysia, 99.9%) and zirconium nitrate (ZrO(NO₃)₂, Merck Malaysia, 99.9%) aqueous solutions as the dispersed phase. Typically, two microemulsions with different aqueous phases were prepared. In microemulsion 1, the CTAB, 1-butanol and n-octane were mixed and stirred. The mixture of $Ce(NO_3)_2$ and $ZrO(NO_3)_2$ in a percent weight ratio of 0.75:0.25 as an aqueous phases. Then the aqueous phases of containing Ce^{3+} and Zr^{4+} ions was added under vigorous stirring until the transparent liquid. The same procedures were applied for aqueous phase of NaOH for microemulsion 2. These two microemulsions were mixed under constant stirring, allowing the reacting species to come in contact with each other due to the dynamic nature of the dispersed droplets. This leaded to precipitation of particles within the aqueous micro droplets and the reaction to take place between the hydroxide, OH^{-1} ions and metals ions (Ce^{3+} and Zr^{4+}). The surfactant layer around each droplet acted as a barrier restricting the growth of the particle beyond the water domains. The mixture of microemulsion 1 and 2 was stirred for 3 hours to ensure the colloidal precipitates (oxidation state zero) formed and then be aged for 24 hours. The colloidal precipitates were washed with ethanol (3 times) and di-ionized water (3 times) by centrifuge at 10,000 rpm for 10 minutes. The precipitates were dried at temperature of 110°C for 24 hours and was calcined at 500°C for 6 hours in heating rate at 5°C/min.

In the second step, CuO/Ce_{0.75}Zr_{0.25}O₂ nanocatalysts were synthesized by deposition-precipitation method. The preparation procedure was adopted from Hadi & Yaacob [13] with a slightly modification. The synthesized Ce_{0.75}Zr_{0.25}O₂ was suspended in a solution of copper nitrate, Cu(NO₃)₂ at 4wt% of copper loading. The mixture was stirred for 3 hours. Cu²⁺ ions were expected to be deposited onto the surface and pores of Ce_{0.75}Zr_{0.25}O₂ and it was exclusively precipitated by adding an aqueous solution of 0.5M Na₂CO₃ to keep the pH at constant of 10 and the temperature raised-up to 70 °C. The suspension further stirred for 2 hours. The resulting solid was washed with de-ionized water in a centrifuge for 3 times and dried at 100 °C for 24 hours. Finally, the sample was calcined at 500 °C for 5 hours.

2.2 Characterizations

The phase and crystal structure were characterized by X-ray Diffraction (XRD) of Rigaku Ultima IV using Cu K α radiation ($\lambda = 0.15418$ nm). The scans of 2 θ were taken in range 20° to 70° at scanning rate of 1.2°/min. The crystallize size were calculated by Scherrer's equation, referring the most prominent peak (111). The crystalline phases were identified according to the reference data from the International Center Diffraction Data (ICDD). The surface area of the samples was determined using the Autosorb-1 Quanta Chrome Instrument TUSA. For morphology studies, the micrographs of samples were obtained by a field emission scanning electron microscopy, DSM 982 Gemini Supra 40 VP and transmission electron microscopy Tecnai G2 20. The catalytic properties of samples were examined by temperature programmed reduction (Chemisorb 2750, micromeritics brand). In this evaluation, a 50 mg sample was pre-treated under N₂ (20 ml/min) at 200°C for 1 hour, followed by cooling to 50°C. The sample was exposed in hydrogen 5% (v/v) H₂/Ar (flow rate: 20 ml/min) from 50 to 700°C at a heating rate of 10°C/min [9]. The consumption of hydrogen was detected by thermal conductivity detector.

3. Result and Discussion

3.1 X-ray Diffraction Analysis

Figure 1 shows the XRD patterns of the samples. All of the peak profiles show the typical main reflections of CeO₂ cubic phase with fluorite structure and it matches with XRD patterns of pure CeO₂ (ICDD No: 21306). The characteristics peaks are located at $2\theta = 28.59$, 33.03, 47.30, 56.03, and 59.18 which corresponding to (111), (200), (220), (311) and (222) planes, respectively. No segregation peaks are observed, only the symmetrical XRD patterns of synthesized Ce_{0.75}Zr_{0.25}O₂ to pure CeO₂ are observed, which suggest that the prepared sample is homogeneous. This finding may be explained through the recent studies by Dobrosz-Gómez et al., [5], which reported that the molar ratio of Ce⁴⁺ and Zr⁴⁺ ions have great significant effect to the phase structure. They found that the insertion of zirconia into ceria at molar ratio from $0 \le x \le 0.25$ will produce cubic phase solid solution, while at the molar ratio of $0.5 \le x \le 0.75$, the tetragonal phase was formed. They also claimed that the ions of Zr⁴⁺ incorporated into the CeO₂ lattice to form a solid solution. Therefore, in this study we might indicate that the insertion of zirconium (Zr⁴⁺) ions have dissolved into the lattice of CeO₂ to form a CeZrO₂ solid solution. A similar result also reported by Li et al., [4,18,19].

The diffractogram pattern of the CuO/Ce_{0.75}Zr_{0.25}O₂ catalyst as shown in figure 1(c) also presents the symmetrical patterns to the cerium oxide which the phase structure is maintained as the cubic fluorite structure and no CuO phase is detected. It may cause of the low concentration of copper components deposited in the catalyst (< 4 wt%), which under X-ray diffraction limit. Besides, the Radlik et al., [9] have suggested that the insertion of copper catalysts are well dispersed on the entire catalysts surfaces although the CuO phase not detected via XRD analysis. It is may be due to highly dispersion of CuO on the Ce_{0.75}Zr_{0.25}O₂. The low intensities of the peaks for all samples indicate that the crystallite sizes of the samples are in very small particles. Jani et al., [7] reported that, the width of the peaks and intense signifies the hugeness and smallness of crystallite size. As can see in table 1, the crystallite size increases during the additional of copper catalysts up to 8.1 nm and the broadening peak (111) for all samples shows the parallel finding which the broad peak correspond to small crystallite size. Conversely, the crystallite size of cerium oxide has bigger size up to 9.1 nm than cerium zirconium oxides which is 6.6nm. It is due to the insertion of small ionic radius of Zr^{4+} (0.084 nm) into ceria (Ce⁴⁺ = 0.097 nm and Ce³⁺ = 0.114) structure, make the degrees of crystal lattice shrinking and the crystallite size decreases [4,5].



((a); $\overline{CeO_2}$, (b); $Ce_{0.75}Zr_{0.25}O_2$ and (c); $CuO/Ce_{0.75}Zr_{0.25}O_2$)

3.2 Specific Surface Area

The surface area of $Ce_{0.75}Zr_{0.25}O_2$ and $CuO/Ce_{0.75}Zr_{0.25}O_2$ nanocatalysts are listed in Table 1. The surface areas of samples decrease after the deposition of CuO onto $Ce_{0.75}Zr_{0.25}O_2$. This indicates the well dispersion of CuO inside of the pores and on the surface of $Ce_{0.75}Zr_{0.25}O_2$. During deposition process, the Cu^{2+} ions are filled well onto the available pores on the $Ce_{0.75}Zr_{0.25}O_2$ and this phenomenon leads to the formation of homogeneous solid solution $CuO/Ce_{0.75}Zr_{0.25}O_2$. According to the BET surface area, the diameter of particles can be estimated using the following equation (1) with assumption the mixed oxides are spherical.

$$d_{BET} = \frac{6}{S\rho}$$
(1)

Where, the S is specific surface area, m^2/g and ρ is density of the particles g/m^3 . By assuming, the density of CuO/Ce_{0.75}Zr_{0.25}O₂ is not obviously changing due to very small amount of CuO exist, density of Ce_{0.75}Zr_{0.25}O₂ and CuO/Ce_{0.75}Zr_{0.25}O₂ is 6.940 g/cm³. It can be seen also the size of CuO/Ce_{0.75}Zr_{0.25}O₂ is 69.2 nm which is bigger than the size of Ce_{0.75}Zr_{0.25}O₂, indicating the influence of CuO crystal in Ce_{0.75}Zr_{0.25}O₂ structure. This findings support the XRD result; the increment of crystallite size by the addition of CuO.

3.3 Field Emission Scanning Electron Microscopy, FESEM

To observe the surface morphology and roughness, FESEM analysis was performed on the $Ce_{0.75}Zr_{0.25}O_2$ and $CuO/Ce_{0.75}Zr_{0.25}O_2$. FESEM micrographs of samples are shown in Figure 2. The

results show that the roughness and morphology for both samples are quite similar, even though the deposited of copper oxide. It supports the XRD and BET results. The high portions of small pores are observed on the surface of samples. However, the presence of CuO reduces the number of available pores, indicating the CuO well deposited on the pores of $Ce_{0.75}Zr_{0.25}O_2$, as shown in Fig, 2(b). Meanwhile, both samples show a uniform particles shape which is spherical and CuO particles are homogenously dispersed on the surface and pores of $Ce_{0.75}Zr_{0.25}O_2$. Based on the results, it is safe to say that the microemulsion method able to produce the uniform shape distribution with high available pores and it leads to the homogeneity of CuO dispersion on $Ce_{0.75}Zr_{0.25}O_2$.



Figure 2. FESEM micrographs of synthesized samples ((a) $Ce_{0.75}Zr_{0.25}O_2$, (b) $CuO/Ce_{0.75}Zr_{0.25}O_2$)

3.4 Transmission Electron Microscopy, TEM

In meantime, the structural evolution and physical size distribution as well as the shape of the synthesized catalysts are also studied by transmission electron microscope (TEM). The micrographs of $Ce_{0.75}Zr_{0.25}O_2$ and $CuO/Ce_{0.75}Zr_{0.25}O_2$ are presented in Figure 3. Nano sizes of particles are observed in both samples. The particles are distributed in a narrow size distribution with an average particles size of is around 8 nm for $Ce_{0.75}Zr_{0.25}O_2$ and around 10 nm for $CuO/Ce_{0.75}Zr_{0.25}O_2$. A slightly agglomerate of particles is also observed in both samples. It is due to strong interaction between ultrafine particles $Ce_{0.75}Zr_{0.25}O_2$ and $CuO/Ce_{0.75}Zr_{0.25}O_2$. Besides, almost all of particles are in spherical shape, as found in FESEM analysis. No explicit CuO particles can be visually identified on TEM micrographs of $CuO/Ce_{0.75}Zr_{0.25}O_2$ due to the highly dispersion of CuO, a good agreement to XRD results.

Samples	Density, S kg/m ³ Ar	Surface Area (m ² /g)	Crystallite/Particle Size, d (nm)		
			d _{XRD}	D_{BET}	d _{TEM}
CeO ₂	7215	24.5	9.1	33.9	-
$Ce_{0.75}Zr_{0.25}O_2$	6940	45.9	6.6	18.8	8
CuO/ Ce _{0.75} Zr _{0.25} O ₂	6940	12.5	8.1	69.2	10

Table 1. Textural properties of samples



Figure 3. TEM micrographs of synthesized samples ((a) $Ce_{0.75}Zr_{0.25}O_2$, (b) $CuO/Ce_{0.75}Zr_{0.25}O_2$)

3.5 Oxygen mobility

In order to investigate the catalytic properties, CuO/Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Zr_{0.25}O₂ samples are examined by H_2 -temperature programmed reduction. The H_2 -TPR profiles, which indicate the reducibility of Ce compounds to release oxygen, are presented in Figure 4. The reduction peak of Ce_{0.75}Zr_{0.25}O₂ identify at temperature 466°C, while the reduction peak of CuO/Ce_{0.75}Zr_{0.25}O₂ towards to lower temperature up to 250°C are assigned to the reduction of Cerium (4+) to (3+) and the removal of lattice oxygen [4]. It indicates the existence of CuO; the reduction peak progressively shifted towards lower temperature which contributes the enhancement of the catalytic properties to active at lower temperature. A similar finding was reported by Deng et al., [21] & Jung et al., [22]. Therefore the additional of CuO into the Ce_{0.75}Zr_{0.25}O₂ structure able to enhance the activity of the catalysts at lower temperature and it also maintain the microstructure stability.



Figure 4. H₂-TPR profile of samples

4. Conclusion

The findings of study could be summarized as follows:- the uniform spherical nanoscales CuO/Ce_{0.75}O_{0.25}O₂ and Ce_{0.75}Zr_{0.25}O₂ have been successfully synthesized by the combination of microemulsion and deposition precipitation methods. The synthesized $CuO/Ce_{0.75}Zr_{0.25}O_2$ nanocatalysts reveals the highly dispersion of CuO, maintain as a cubic phases and mix as a solid solution. The additional of zirconium into cerium oxide structure able to increase the surface area up to

45.9 m²/g. The copper catalysts may well deposit on the entire of $Ce_{0.75}Zr_{0.25}O_2$ surface and pores, which is reflected by the decreasing of surface area. According to morphology observation, the roughness of $Ce_{0.75}Zr_{0.25}O_2$ reduces with the presence of CuO. It is also found that the CuO/Ce_{0.75}Zr_{0.25}O₂ exists in a homogeneous solid solution and well dispersion of CuO. The particles size of CuO/Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Zr_{0.25}O₂ is 8 nm and 10 nm, respectively. The addition of copper catalysts able to activate the catalysts at lower temperature as examined by the oxygen mobility in temperature programmed reduction.

5. References

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Acknowledgement

The authors would like to acknowledge FRGS No project 600-RMI/FRGS 5/3 (26/2013). We would also thank to Universiti Teknologi MARA (UiTM) for supporting the research.