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Self-combustion synthesis of Ni catalysts modified with La and Ce using Glycine–Nitrate Process (GNP)

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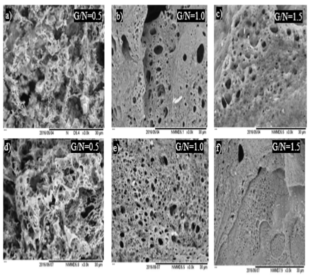
GRAPHICAL ABSTRACT



ABSTRACT

Combustion synthesis has become an attractive method for preparing oxides and metallic materials for various applications including catalysts. One common combustion route is glycine–nitrate process (GNP). GNP involves a self-sustained reaction between metal nitrates (oxidizer) and glycine (fuel). The process is known to be rapid and simple, and generates catalyst powders that are high purity, crystalline and homogenous. In this work, Ni catalysts modified with La and Ce were synthesized using GNP. A precursor solution containing a stoichiometric mixture of metal nitrates was initially mixed with glycine at various glycine-nitrate ratios (G/N=0.5, 1.0, 1.5). The glycine-nitrate solution was then heated to yield a gel-like liquid. The gel was further heated until it self-ignited and produced an ash powder. The catalyst ash was calcined at different temperatures (600–800°C) and then reduced at 700°C. Catalyst characterization was performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Once produced using GNP, the La element in Ni catalyst modified with La was presence in a form of LaNiO phase. After reduction, Ni catalyst modified with La contains only Ni and La_2O_3 phases. Meanwhile, Ce element in the Ni catalyst modified with Ce presence as CeO_2 phase after the GNP combustion. The CeO_2 phase remains after the reduction process and the reduced Ni catalyst modified with Ce composed of two separated phases; Ni and CeO_2. Glycine-nitrate (G/N) ratio shows a significant effect on the morphology of the catalysts. At G/N=0.5, where the fuel composition is less than the stoichiometric ratio, the 'cottonwool-like' and highly porous structure were observed for both Ni catalysts modified La and Ce. At the fuel composition higher than the stoichiometric ratio (G/N= 1.5), both catalysts become dense in structure and contain less pores.

Keywords: glycine-nitrate process (GNP), glycine-nitrate (G/N) ratio, calcination, reduction, Ni modified with La, Ni modified with Ce

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1. INTRODUCTION

Glycine–nitrate process (GNP) has been frequently employed for preparation of complex nanostructured metal oxides, aiming for fitted composition, phase, oxidation state and surface areas [1]. This method is preferred due to its simple process and effective in term of cost which permits high production rates [2, 3]. Moreover, GNP provides the desirable characteristics for most excellent catalyst such as fine crystalline powders, nanometer scale in particle size, highly chemical homogeneity, no impurities and narrow range of powder size distribution [4]. GNP involves a self-sustained combustion reaction between metal nitrates that act as oxidizers and fuel that acts as reducer. The fuel supplies energy required for the combustion and also acts as complexing agent.

Physical and chemical properties of the synthesized catalyst powders produced after the GNP are controlled mainly by the heat generated during the combustion that relied upon nature of the fuel and fuel-to-oxidant ratio. In GNP, volume of gas products generated during the rapid combustion dissipates heat and limits the temperature increase, thus decreases the chance for local sintering among catalyst particles and encouraging fine powder formation with high specific areas [5]. High crystallinity also can be achieved due to its short reaction time and moderate temperature [6]. Natures of the fuel and fuel to oxidizer ratio decide the maximum temperature reach during the process [7].

In present study, an attempt has been made to synthesize and characterize Ni catalysts modified with La and Ce using glycine–nitrate process (GNP). The effects of calcination, reduction and glycine-nitrate (G/N) ratio on the crystalline phase and morphology of Ni modified with La and Ni modified with Ce catalyst were examined. The combustion reactions between metal nitrate and glycine for synthesis of Ni modified with La and Ni modified with Ce catalysts using a GNP are given by Eq. 1 and Eq. 2, respectively. The lanthanum nickelate ($LaNiO_3$) produced in Eq. 1 can be further reduced into form its active form, Ni and La_2O_3 [8, 9].

$$Ni(NO_3)_2.6H_2O + La(NO_3)_3.6H_2O + mNH_2C_2O_2 + (2.25m - 6)\ O2 \rightarrow LaNiO_3 + (12 + 2.5m)\ H_2O + (2.5 + 0.5m)\ N_2 + 2mCO_2 \qquad \text{(Eq. 1)}$$

$$\mathrm{Ni(NO_3)_2.6H_2O} + 9\,\mathrm{Ce(NO_3)_3.6H_2O} + 14\mathrm{NH_2C_2O_2} + 21.5\,\mathrm{O_2} \rightarrow 9\,\mathrm{CeO_2} + \mathrm{NiO} + 95\,\mathrm{H_2O} + 5.5\,\mathrm{N_2} + 28\,\mathrm{CO_2} \qquad \text{(Eq. 2)}$$

2. EXPERIMENTAL

2.1 Catalyst Preparation

Catalyst precursors were prepared by dissolving nickel (II) nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, USA) with cerium (III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$ (Merck, USA) or lanthanum (III) nitrate hexahydrate, $La(NO_3)_3 \cdot 6H_2O$ (Merck, USA) at a desired stoichiometric amount. Glycine (NH_2CH_2COOH) (Merck, USA) was added into the metal nitrate solution at the various glycine-nitrate (G/N) ratio (G/N=0.5, 1.0, 1.5). The glycine-nitrate solution was then mixed and heated overnight on a hot plate stirrer (IKA, Germany) at 90°C to form clear, homogeneous and viscous gel-like solutions. The gel was then placed in a ceramic bowl and further heated to the temperatures of 180-250 °C until the gel was self-ignited, producing a catalyst ash. In order to remove the residual carbon and promote the crystallization, the catalyst ash was calcined at various sintering temperatures (600°C, 700°C and 800°C). Ni catalysts modified with La and Ce were then reduced under a flow of 10% H_2-N_2 mixture at 700°C for 2 hours.

2.2 Characterization

X-ray diffraction (XRD) analysis was performed using Miniflex II desktop powder diffractometer (Rigaku, Japan) to determine the crystalline structure of the catalyst prepared. Data sets were recorded in a step-scan mode in the 2θ ranged from 3° to 80° with intervals of 0.02 a counting time of 1 second per point. The morphology of Ni catalysts modified with La and Ce catalyst was characterized using TM3030 Plus tabletop scanning electron microscopy (SEM) (Hitachi, Japan).

3. RESULTS AND DISCUSSION

3.1 Phase analysis

Fig. 1 shows the XRD patterns for Ni catalysts with and without La, synthesized using GNP. Fig. 1a gives an XRD pattern for Ni catalyst without La after calcination at 600ºC. The patterns for Ni catalysts modified with La for as-prepared sample and when the catalysts were calcined at 600, 700 and 800°C are shown in Fig. 1b – 1e. These patterns are compared with one for a reduced Ni modified with La catalyst (Fig. 1f). The peaks belongs to NiO given by the planes (111), (200), (220), (311) and (222) at angles 37°, 43°, 63°, 76° and 79° were detected in Ni catalyst without La and Ni catalysts modified with La for as-prepared and calcined samples. These planes represent the cubic fluorite structure of NiO in the catalyst samples [10]. Ni catalyst without La is characterized by narrow and sharp peaks (Fig. 1a). This is corresponding to the formation of large crystallite. The peaks for Ni catalyst with La were slightly broadened with the addition of La, suggesting that the modification of Ni catalyst with La might has slightly altered the average size of Ni crystallites.

In overall, as the calcination temperature increases, the crystallinity increases, exhibits by the increase of the sharpness of the peaks at higher temperatures (Fig 1c –1e). After the calcination process, La element in Ni catalysts modified with La became visible in a form of $LaNiO_3$. The peak of $LaNiO_3$ given by (100) plane at 33° became more obvious as the calcination temperature was increased from 600 to 800°C (Fig. 1b – 1e). After the reduction process, the peak representing $LaNiO_3$ was entirely diminished while the peak belongs to La_2O_3 at (220) plane was detected at 77° (Fig. 1f). Previous research by Zhu et al. [11] also found the same phenomena when the $LaNiO_3$ was replaced by La_2O_3 in a Ni-containing La catalyst after reduction process.

Meanwhile, in the same reduced sample, all the (111), (200), (220), (311) and (222) planes for NiO disappeared and the (111) and (200) planes for metallic Ni become visible (Fig. 1f). This suggested that most of NiO phase in Ni catalysts modified with La have been reduced into metallic Ni after reduction process. Therefore, it can be concluded that the La element in Ni modified with La catalyst was initially presence in a form of $LaNiO_3$ phase before it was changed into La_2O_3 after reduction. A reduced Ni catalyst modified with La composed of separated phases of Ni and La_2O_3.

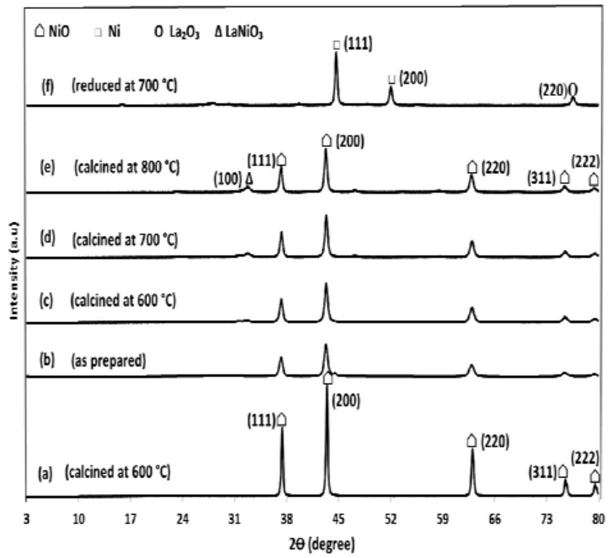

Fig. 1 XRD patterns of a) Ni without La (calcined at 600°C); b) Ni modified with La (as-prepared); (c) Ni modified with La (calcined at 600°C); d) Ni modified with La (calcined 700°C); e) Ni modified La (calcined at 800°C); f) Ni modified with La (reduced at 700°C).

Fig. 2 gives the XRD patterns for Ni catalysts with and without Ce. Fig. 1a shows an XRD pattern for Ni catalyst without Ce after calcination at 600ºC. Meanwhile, Fig. 2b – 2e show the patterns of Ni modified with Ce catalysts for as-prepared sample and after calcination at different temperatures. These patterns are compared with a reduced sample of Ni modified with Ce catalyst (Fig. 2f). All patterns for as-prepared and calcined catalysts (including Ni catalyst without Ce) show the presence of (111), (200), (220), (311) and (222) planes for NiO at 37°, 43°, 63°, 76° and 79°, respectively. Similar to the patterns from Fig. 1, the planes represent the cubic fluorite structure of NiO in the catalyst samples [10]. Like Ni catalysts modified with La, the peaks were slightly widened when the catalysts were added with Ce, suggesting that the modification of Ni catalyst with Ce has slightly reduced the average size of Ni crystallites.

In Fig. 2b, the pattern for as-prepared Ni modified with Ce catalyst shows the presence of metallic Ni, demonstrated by the (111), (200) and (220) planes at 45°, 52° and 77°, respectively. The presence of metallic Ni in this as-prepared sample may be due to the localized reducing environment during the combustion process [12]. The calcination of the catalyst has resulted in the disappearance of these metallic Ni planes (Fig. 2c– 2e). However, the peaks for metallic Ni ((111) plane at 45°) and ((200) at 52°) were reappeared and become obvious when the sample was reduced under a flow of H_2-N_2 mixture at 700°C (Fig. 2f). During the reduction process, oxides available in NiO phase were removed from the catalyst. This is proven by the disappearance of the peaks belongs to NiO ((111), (200), (220), (311) and (222) NiO planes at 37°, 43°, 63°, 76° and 79° angles) in the reduced Ni modified with Ce catalyst (Fig. 2f). The peaks belongs to metallic Ni in Fig. 2f become noticeable, suggesting that the NiO phase were reduced, resulting in most metallic Ni phase in the Ni modified with Ce catalyst.

The (111), (200), (220) and (311) of CeO_2 planes at 28°, 33°, 47° and 53°, respectively in the as-prepared and calcined Ni catalyst modified with Ce are belongs to the cubic fluorite structure of CeO_2 [13]. These planes were remained after reduction process. In addition, a new peak belongs to CeO_2 (220) at 77° was appeared after the reduction process (Fig. 2f). The presence of CeO□ peaks after reduction process was also reported by Bhavsar and Veser [14].This reveals that the CeO_2 phase in Ni modified catalyst was produced directly from the GNP. The CeO_2 remains after the reduction process and presence together with Ni in two separated phases (Ni and CeO_2) in the Ni modified Ce catalyst.

In order to evaluate the catalytic activity of the catalyst, the Ni crystallite sizes must be determined [15]. The crystallite sizes were calculated from the diffractograms according to the Scherrer equation [16]. The crystallite size for Ni catalyst without La or Ce when calcined at 600°C was35.2 nm. The Ni catalysts modified with La and Ce when calcined at the same temperature (600°C) provides the crystallite size of 18.9 and 31.2 nm, respectively. Hence, the crystallite sizes in Ni catalysts modified with La and Ce were smaller compared to the one for Ni without La and Ce. This may be happened due to the contraction of Ni lattice once the La^{3+} or Ce^{3+} ions were incorporated into the lattice of nickel during the synthesis process [17]. However, after the catalysts were reduced under a flow of H_2 for 2 hr, there was a slight increase in the Ni crystallite size when the crystallite size are 27.3 and 39.6 nm for Ni modified with La and Ce catalysts, respectively. One possible explanation of this phenomena is that the Ni particles might have formed clusters during catalyst reduction [18].

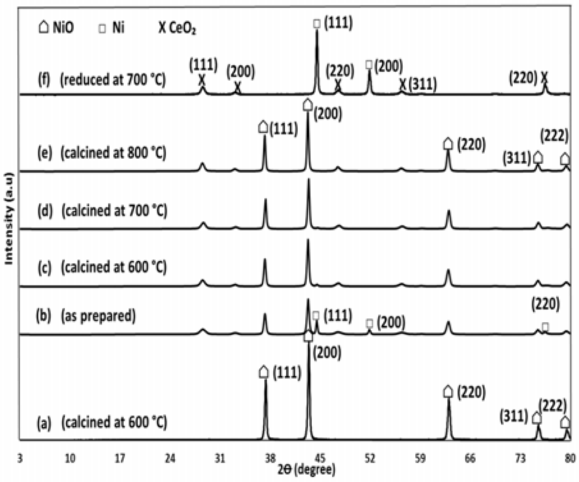

Fig. 2 XRD patterns of a) Ni without Ce (calcined at 600°C); b) Ni modified with Ce (as-prepared); (c) Ni with modified Ce (calcined at 600°C); d) Ni modified with Ce (calcined 700°C); e) Ni modified with Ce (calcined at 800°C); f) Ni modified with Ce (reduced at 700°C)

3.3 Morphology analysis

SEM micrographs of Ni catalysts modified with La and Ce at various glycine-nitrate (G/N) ratios are shown in Fig. 3. At G/N ratio of 0.5, Ni catalyst modified with La (Fig. 3a) and Ni catalyst modified with Ce (Fig. 3d) have 'cottonwool-like' structures. As the G/N ratio increased from 0.5 to 1.0, the catalysts formed a 'spongy-like' structure with random-size pores (Fig. 3b and 3e). At G/N= 1.5, both catalysts become denser with much lesser pores on their surfaces (Fig. 3c and 3f). Porous structure developed on catalysts produced from GNP is a result of large volume of gases generated from the combustion. Meanwhile, the pores size is directly related to the flame temperature and the nature of combustion [15]. The stoichiometric ratio of G/N for NiO, Ni modified with La and Ni-modified with Ce are G/N= 1.11, 1.33 and 1.44, respectively. Thus, the G/N= 0.5 is considered as fuel-lean, while G/N = 1.5 is a fuel-rich. The 'cottonwool-like' and highly porous structure observed for the catalysts at G/N=0.5 is due to the low flame temperature, which is associated with fuel-lean composition [15]. As the G/N ratio increases to G/N= 1.0, close to the stoichiometric ratio, the structure changed from 'cottonwool-like' to 'spongy-like' structure as the agglomeration increases due to higher flame temperature [15]. At G/N ratio above the stoichiometric ratio (G/N=1.5), the flame temperature decreases again with the increasing of fuel due to the incomplete combustion. This also led to the sintering of catalyst particles [19, 8]. Therefore, it can be observed that at fuel-rich composition (G/N=1.5), the catalyst becomedense and the porosity was the least.

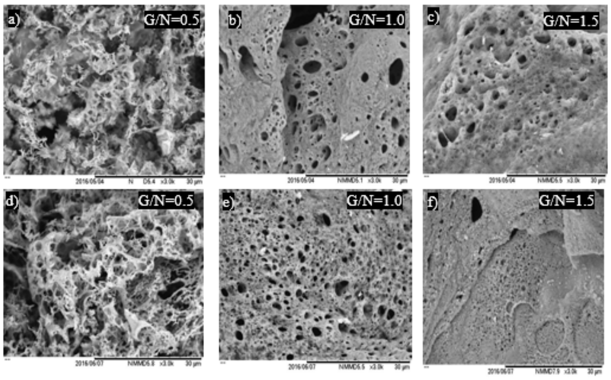

Fig. 3 SEM images of Ni catalysts modified with La (a – c) and Ce (d – f) at glycine-nitrate ratio (G/N) = 0.5, 1.0 and 1.5.

4. CONCLUSION

Ni modified with La and Ni modified with Ce catalysts have been successfully synthesized using glycine-nitrate combustion process (GNP). XRD analysis shows that La element in Ni catalyst modified with La was initially existed as $LaNiO_3$ phase. After reduction under a flow of H_2, the $LaNiO_3$ was changed into La_2O_3 and the reduced Ni modified with La catalyst composed of separated phases of Ni and La_2O_3. Meanwhile, CeO_2 phase in Ni modified with Ce catalyst was produced directly from the glycine-nitrate combustion process. The CeO_2 remains after the reduction process. The reduced Ni modified with Ce catalyst composed of active Ni and CeO_2. The effect of glycine-nitrate (G/N) ratio on the morphology of the catalysts has been analyzed using SEM. When the G/N ratio employed is less than the stoichiometric ratio, the 'cottonwool-like' and highly porous structure were observed for both Ni catalysts modified La and Ce. At the fuel composition higher than the stoichiometric ratio, both Ni catalysts modified La and Ce catalysts become dense in structure and contain less pores.

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