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Article

Synthesis of Ni-CeO₂ catalyst for the partial oxidation of methane using RF thermal plasma

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ABSTRACT

Ni-CeO₂ catalysts with a nickel content of 50 mol% were prepared using RF thermal plasma, and their catalytic activities for methane partial oxidation were characterized. For the synthesis of Ni-CeO₂ catalysts, a precursor containing Ni (~5-μm diameter) and CeO₂ (~200-nm diameter) powders were heated simultaneously using an RF plasma at a power level of ~52 kVA and a powder feeding rate of ~120 g/h. From the X-ray diffraction data and transmission electron microscopy images, the precursor formed into high crystalline CeO₂ supports with nanosized Ni particles (< 50-nm diameter) on their surfaces. The catalytic performance was evaluated under atmospheric pressure at > 500 °C and a CH₄:O₂ molar ratio of 2:1 with Ar diluent. Although the Ni content was high (~50 mol%), the experimental results reveal a methane conversion rate of > 70%, selectivities of CO and H₂ greater than 90% and slight carbon coking during an on-stream test at 550 °C for 24 h. However, at 750 °C, the on-stream test revealed the formation of filament-like carbons with an increased methane conversion rate over 90%.

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1. Introduction

Thermal plasmas have attracted attention as a heat source for the preparation of nanosized powders [1–5]. As an ionized flow with temperatures of > 3000 °C [6,7], the massive enthalpies of thermal plasmas enable the micro-sized metal precursor to evaporate during its flight in the thermal plasma flame [1,5]. By quenching the resultant vapor species, nanosized metal particles are produced. However, refractory materials, such as Al₂O₃ and ZrO₂, show incomplete evaporation because of their high boiling points coupled with poor thermal conductivity [1,8]. If the mixture of precursors containing metal and refractory materials is injected into the thermal plasma flame, the preferential evaporation of metal powder can occur, and the metal vapors condense into nanosized metal catalysts dispersed on the refractory supports. Thermal plasma synthe-

ses of supported metal catalysts have been presented in the studies Zea et al. [9] and Vissokov [10], who reported the preparation processes of PdAg on carbon and Ni metal on Al₂O₃ catalysts, respectively, using a non-transferred DC arc plasma torch. They showed that nanosized metal particles were formed on the support materials. However, the surface area of the carbon support decreased because of the volatilization of oxygen groups caused by the strong arc plasma [9]. Moreover, the DC arc plasma treatment of Ni metal and Al₂O₃ oxides embedded Ni metal into Al₂O₃ droplets, which caused metal loss in the catalysts [10].

The DC arc torch produces a hot ionized jet with high velocities up to hundreds of m/s, and RF plasma torches provide a flame of a large size and mild velocities less than several tens of m/s [1,2,5]. In addition, the absence of electrodes allows solid precursors to be injected along the centerline of the RF torch.

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Because the trajectories along the centerline of the RF torch are heated continuously by the plasma flame, the RF plasma torch is stable and has a controllable heating route to inject the solid precursor along the centerline of the torches [1,11,12]. The evaporation process of the mixed solid precursors during the passage of the RF plasma torch can be controlled easily, depending on the physical properties of the mixture constituents, such as thermal conductivity and the melting and boiling points.

In this work, we explore the synthesis route of a nanosized Ni metal catalyst highly dispersed on a ceria support by the coinjection of Ni and ceria powders into an RF thermal plasma. As an oxide support of Ni catalysts for the catalytic partial oxidation of methane, ceria is widely used because of a high oxygen storage capacity and unique redox behavior, depending on the partial pressure of ambient oxygen [13–17]. The melting point of ceria is high at 2400 °C [18], which can help the ceria precursor travel the thermal plasma flame in the solid state. Therefore, the RF thermal plasma treatment of Ni and ceria mixtures allows the preferential evaporation of Ni metal. The Ni vapors can nucleate on CeO₂ surface by a quenching process. Because the preferential evaporation and nucleation processes of Ni powder occur during the in-flight treatment, the Ni-CeO₂ composite can form highly dispersed Ni on the CeO₂ support, which enhances their catalytic activity and resistance to carbon coking in the partial oxidation of methane [19].

2. Experimental

2.1. Catalyst preparation using RF thermal plasma

The RF thermal plasma system used for the preparation of Ni-CeO₂ catalysts is illustrated in Fig. 1. In this system, electromagnetic energy with oscillation frequencies of 2–4 MHz is

transferred to the RF thermal plasma using induction from an RF power supply (Trumpf, IG30/3000, Ditzingen, Germany), which has a maximum power level of 60 kVA. A water-cooled quartz tube with an inner diameter of 50 mm was used to confine the generated RF thermal plasma inside an RF plasma torch, which was mounted on a synthesis reactor. The synthesis reactor contains a cylindrical guide with an inner diameter of 300 mm and a length of 500 mm to expand the confined RF plasma flame as presented in Fig. 1. By expanding the plasma flame, the nucleation and condensation of the evaporated species can be enhanced as discussed in the simulation by Mendoza-Gonzalez et al. [20]. In this work, nanosized Ni-CeO₂ catalysts were synthesized by injecting a solid precursor containing Ni and CeO₂ powders into the RF thermal plasma. For this purpose, the feeding of the solid precursor was along the centerline of the RF plasma torch using a water-cooled injector, which is connected to the powder feeder as shown in Fig. 1. For the effective heating of the mixed solid precursor, Ni (99.9%; YeeYoung Cerachem, Seoul, Korea) and CeO₂ (99.9%; YeeYoung Cerachem) powders with diameters of 5 μm and 200 nm, respectively, were weighed at a molar ratio of 1:1, and mixed for 48 h using a ball mill. Fig. 2 presents the field emission scanning electron microscopy (FE-SEM) image of the mixed solid precursor, where the CeO₂ powders with diameters of 100–200 nm were distributed uniformly on the surface of microsized Ni metal. After RF thermal plasma treatment of the precursor, the nanocomposite powders were retrieved by filtration (Fig. 1). The operating conditions for this process are listed in Table 1.

2.2. Catalyst characterization

The morphologies and particle sizes of the powders were analyzed using FE-SEM (S4300, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM; JEM-4010, Jeol, Tokyo,

Fig. 1. A schematic diagram of an RF thermal plasma system used for preparation of Ni-CeO₂ catalysts.

Fig. 2. FE-SEM images of the solid precursor consisting of Ni (~5 μm) and CeO₂ (100–200 nm) powders.

Table 1

Operating parameter values for synthesis of Ni-CeO₂ catalysts by RF thermal plasma.

Operating parameter	Value
Plasma forming gas (Ar)	Flow rate (L/min)
Central gas	20
Sheath gas	90
Quenching gas	120
Operating pressure (torr)	~400
Plate power (kVA)	~52
Feeding rate of precursors (g/h)	~120

Japan). The crystalline structures of the powders were investigated by X-ray diffraction (XRD; X'pert PRO MPD, PANalytical B.V., Almelo, The Netherlands) with Cu K_α radiation source ($\lambda = 0.15406$ nm). In addition, the composition changes were evaluated by comparing the inductively coupled plasma-optical emission spectrometry (Optima 5300DV, PerkinElmer, Waltham, MA, USA) results between the precursors and powders. The local compositions of the particles were also examined using energy dispersive X-ray spectroscopy, (EDS; Link ISIS 6498, Oxford Instruments, Abingdon, UK) from the TEM images. The morphological properties of the powders, such as surface area, pore volume and pore size were calculated from N₂ adsorption-desorption isotherms using the Brunauer-Emmett-Teller method (ASAP 2020, Micromeritics, Norcross, GA, USA).

2.3. Catalytic performance test

For the Ni-CeO₂ nanocomposite, temperature-programmed reduction (H₂-TPR; AutoChem II 2920, Micromeritics) data were obtained to investigate the reducibility of Ni-based materials. The partial oxidation of methane was conducted over the Ni-CeO₂ nanocomposite at atmospheric pressure and a reaction mixture of molar ratio CH₄:O₂ = 2:1 with Ar diluent. The details of the test conditions are presented in Table 2. The methane conversion rate was calculated with the selectivity to H₂ and CO for the temperatures from 400 to 800 °C using to the following definitions:

$$(1) \text{CH}_4 \text{ conversion rate (\%)} = \left(\frac{\text{moles of CH}_4 \text{ consumed}}{\text{moles of CH}_4 \text{ introduced}} \right) \times 100$$

Table 2

Experimental conditions for catalytic performance of as-prepared composite.

Test material	Ni-CeO ₂ 100 mg
Gas components	CH ₄ :O ₂ :Ar = 4:2:94, Total flow rate of 100 cm ³ /min
Gas chromatography (Yong Lin, YL6100)	Detector: TCD, FID Column: Carboxen-1000 packing column Carrier gas: N ₂
Furnace condition	Temperatures: room temperature to 800 °C Holding time at measured temperature: 30 min
Reactor	Quartz Tube with inner diameter of 6 mm

$$(2) \text{CO}_2 \text{ conversion rate (\%)} = \left(\frac{\text{moles of CO}_2 \text{ consumed}}{\text{moles of CO}_2 \text{ introduced}} \right) \times 100$$

$$(3) \text{CO selectivity} = \frac{\text{moles of CO produced}}{(\text{moles of CH}_4 \text{ consumed} + \text{moles of CO}_2 \text{ consumed})}$$

$$(4) \text{H}_2 \text{ selectivity} = \frac{\text{moles of H}_2 \text{ produced}}{(2 \times \text{moles of CH}_4 \text{ consumed})}$$

From the H₂-TPR data and the partial oxidation of methane, the catalytic performance of the Ni-CeO₂ nanocomposite was estimated. The degree of carbon deposition was examined from the variation in catalytic activities during 24-h tests for the partial oxidation of methane at 550 and 750 °C. Moreover, FE-SEM, TEM and thermogravimetric analysis, (SDT Q600, TA Instruments, New Castle, DE, USA) after the 24-h test were performed to show the resistance to carbon deposition of the catalysts and the amount of carbon deposition.

3. Results and discussion

Fig. 3 and Fig. 4 show the FE-SEM and TEM images of the composites, respectively. The inset in Fig. 4 presents the EDS data corresponding to the numbered areas in the image. From the comparison between FE-SEM images in Fig. 2 and Fig. 3, micro-sized solid precursors are formed into small particles with sizes under 100 nm. In addition, the TEM image and the EDS data in Fig. 4 show that the particles mainly consist of CeO₂ particles with sizes of several tens of nm, which are covered with very small particles of high Ni content. The solid precursor was Ni powder of almost 5-μm diameter covered with CeO₂

Fig. 3. FE-SEM image of the as-prepared Ni-CeO₂ composite.

Fig. 4. TEM image of the as-prepared Ni-CeO₂ composite. The inset shows the EDS analysis data corresponding to the numbered area in the TEM image.

particles (~200-nm diameter) as shown in Fig. 2, the electron microscope observations of the composites indicate that the micro-sized Ni powders in the solid precursors instantaneously evaporated during their passage in the RF thermal plasma flame. The produced vapors condensed into very small particles on the surfaces of the ceria. However, the ceria particles in the solid precursors reduced in size by RF thermal plasma attrition and did not fully evaporate because of their high boiling point and poor thermal conductivity. Therefore, ceria particles with reduced sizes became the seeds for the nucleation of Ni vapor during the quenching process at the central guide cylinder shown in Fig. 1, which creates nanosized CeO₂ supports (< 100-nm diameter) with highly dispersed Ni-rich particles on their surfaces as shown in Fig. 4.

Table 3 shows the inductively coupled plasma-optical emission spectrometry results of the composite. The Ni content was reduced to 4.2 at.% compared with the original value. In our experiment, the particles were retrieved at the filtration part shown in Fig. 1, and the composition changes in Table 3 may occur because of the complicated interactions between the trajectories of the in-flight treatment precursors during their travel from the RF torch to filtration. If the loss of Ni results from this transportation process, the composition change will occur systematically in our equipment, and the difference can be reduced by adjusting the starting Ni concentration to consider the loss of Ni in the system. In addition, the morphological properties of the catalyst were measured by the Brunauer-Emmett-Teller method. The surface area, pore volume and pore size are 56.64 m²/g, 0.29 cm³/g and 21.04 nm, respectively. The as-prepared Ni-CeO₂ composite has a high surface area, indicating that the micro-sized precursor was successfully formed into a nanosized composite by RF thermal plasma.

Fig. 5 presents the XRD data of the solid precursors and the

composites. From the comparison between these two XRD graphs, the crystalline peaks for CeO₂ were enhanced in the composites. Because the partially evaporated CeO₂ particles condense into very small particles during the quenching process, their contribution to the crystalline peak enhancement is negligible. Therefore, these enhanced peaks originated from CeO₂ particles with reduced sizes, which crystallized during the RF thermal plasma heat treatment. However, Ni and NiO crystalline peaks were decreased and increased, respectively, in the composites, compared with those in the precursor. Because the inert gas of Ar is used in this work as listed in Table 1, these changes in Ni and NiO crystalline peaks indicate that reactions may occur between Ni metal and the lattice oxygen of CeO₂. For example, NiO particles can form from Ni vapors and free oxygen escaping from the lattices of CeO₂ during the RF thermal plasma heating process. The NiO can condense on the surfaces of CeO₂ or into free NiO particles. With this in-flight formation of NiO particles, most Ni vapors can be directly nucleated into Ni metal particles on the surface of CeO₂. In addition, we expect that NiO layers between the Ni metal and CeO₂ supports can form by incorporating Ni ions into the lattice of CeO₂ because the heated CeO₂ surface is hot enough to cause a high temperature reaction between the nucleated Ni metal and CeO₂ lattices. Thus, highly dispersed Ni/NiO particles on nanosized CeO₂ supports were synthesized by the RF thermal plasma treatment of Ni metal and CeO₂ powders with sizes of almost 5 μm and 200 nm, respectively, as shown in Fig. 3 and Fig. 4.

To investigate the reduction properties of these highly dispersed Ni/NiO particles on CeO₂ supports, a H₂-TPR test was conducted, and the results are shown in Fig. 6. For comparison, Fig. 6 also presents the results of the H₂-TPR test for a commercial NiO powder (637130; Sigma-Aldrich, St Louis, MO, USA) with diameters of ~50 nm and the CeO₂ powder used as a support material in this work. For the nanocomposite shown in Fig. 6, high reduction peaks were observed at the temperatures of 225, 350 and 750 °C. Among these, the reduction peak at 350 °C is extremely intense. Compared with the test results of the commercial NiO and CeO₂ powders, the consumption of H₂ at 225 and 750 °C represents the reduction of free NiO and CeO₂, respectively. As reported in previous studies [14,21,22], the

Fig. 5. Comparison of XRD graphs between mixture precursor (1) and the as-prepared Ni-CeO₂ composite (2).

Table 3

Atomic ratio of Ni to Ce for the as-prepared Ni-CeO₂ composite obtained from ICP-OES analysis result.

Item	Constituent (at.%)	
	Ni	Ce
Weighed (1)	50.0	50.0
As-prepared (2)	45.8	54.2
Difference between (1) and (2)	−4.2	+4.2

Fig. 6. Comparison of H₂-TPR graphs between commercial NiO powders (~50 nm), CeO₂ powders (~200 nm) and the as-prepared Ni-CeO₂ composite.

reduction peaks in the temperature range of 300–400 °C are the reduction of NiO solid solution particles on a CeO₂ surface, and have a significant effect on catalytic performance at low temperatures.

To examine the catalytic performance, we partially oxidized methane using the nanocomposite under the test conditions listed in Table 2. Fig. 7 shows the methane conversion rate from 400 to 800 °C. The composite shows a high methane conversion rate of ~76% at a low temperature of 550 °C. For the temperatures higher than 550 °C, the conversion rates were elevated to the values higher than 90%. In addition, the H₂ and CO selectivities were ~90% at 550 °C as observed in Fig. 8, which shows the selectivities to H₂ and CO for the temperatures between 400 and 800 °C. As expected from the H₂-TPR results shown in Fig. 6, the high catalytic activities at a low temperature (~550 °C) are because of the numerous active metal sites, which are highly dispersed NiO solid solution. The high Ni content of 50 mol% in the mixture precursor provides an abundance of active metal sites.

Fig. 9 presents the methane conversion rates for 24-h test at 550 and 750 °C, showing the catalytic stability of the catalyst.

Fig. 7. Methane conversion rate of the as-prepared Ni-CeO₂ composite for the temperature ranges from 400 to 800 °C.

Fig. 8. Selectivity for H₂ and CO at the temperatures from 400 to 800 °C. The test conditions are listed in Table 2.

The figure shows that the conversion rates were maintained with slight variation during the test despite the high Ni content of 50 mol%. Because the degradation of catalytic performance is accompanied by carbon deposition on the active metal sites, the catalyst was analyzed by TEM after the 24-h tests at 550 and 750 °C. Fig. 10 shows images for the test temperatures of 550 and 750 °C, respectively. These figures show a low amount of carbon deposition on the catalyst used in the 24-h test at 550 °C despite the high Ni content of 50 mol%. However, solid carbon was coated on the Ni metal for the catalyst after the 24-h test at 750 °C.

The results of carbon deposition depending on temperature are supported by the thermogravimetric analysis of the catalysts after 24-h tests at 550 and 750 °C as shown in Fig. 11. In this figure, the decrease of mass in the range of 200–300 °C was caused by the hydrogenation reaction between water and amorphous carbon. The burning of graphitic carbon causes a mass decrease in the temperature range of 470–650 °C [17,19,23]. The amounts of carbon deposition were estimated as 0.58 and 2.39 wt.% for the catalysts tested at 550 and 750 °C, respectively. Therefore, these catalysts show good re-

Fig. 9. Methane conversion rate of the as-prepared Ni-CeO₂ composite for 24-h test of CH₄ partial oxidation at 550 (1) and 750 °C (2).

Fig. 10. FE-SEM (a, c) and TEM (b, d) images for the as-prepared Ni-CeO₂ after 24-h test of CH₄ partial oxidation at 550 (a, b) and 750 °C (c, d).

Fig. 11. TGA data of the as-prepared Ni-CeO₂ after 24-h test of CH₄ partial oxidation at 550 (1) and 750 °C (2). TGA data were obtained at the conditions of 10 °C/min and atmospheric pressure.

sistance to carbon deposition when reacted at a low temperature of ~550 °C. As reported in other studies [13–15,19], highly dispersed active metal sites on ceria support show a high resistance to carbon deposition. In addition, RF thermal plasma is favorable for a mass evaporation of Ni metal and dispersing the nucleated Ni particles on a ceria support as shown in the TEM image in Fig. 4. The results shown in Figs. 9, 10 and 11 reveal that the in-flight treatment of precursor with high Ni content using RF thermal plasma is a useful route to prepare high performance Ni-CeO₂ catalysts with a high resistance to carbon deposition when used as a catalyst at a low temperature of ~550 °C.

4. Conclusions

We prepared a highly dispersed nanosized Ni/NiO catalyst on a ceria support by the coinjection of Ni and ceria powders into an RF thermal plasma. The RF thermal plasma treatment of the Ni and ceria mixture showed the preferential evaporation of Ni metal and an in-flight reaction between Ni metal and the

CeO₂ support, which formed highly dispersed active metal sites on the CeO₂ surface despite the high Ni content of 50 mol%. H₂-TPR and XRD results of the catalysts reveal that many active metal sites are NiO solid solution on the CeO₂ surface, and this layer improves the resistance of the catalyst to carbon deposition. The results indicate high catalytic activities at the temperatures of ≥550 °C during the partial oxidation of methane. No carbon deposition is occurred for the catalyst used in the 24-h test at 550 °C despite the high Ni content of 50 mol%. From these advantages of the catalyst, the in-flight treatment of Ni metal and CeO₂ support by the RF thermal plasma can be used for the synthesis of Ni-CeO₂ catalysts with highly dispersed active metal sites at a high Ni content of 50 mol%.

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Graphical Abstract

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Synthesis of Ni-CeO₂ catalyst for the partial oxidation of methane using RF thermal plasma

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Epoxides were Ni-CeO₂ nano catalyst was prepared by in-flight treatment of Ni and CeO₂ powders in RF thermal plasma. The as-prepared catalyst showed high catalytic activities during the partial oxidation of methane.

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采用射频热等离子体合成Ni-CeO₂催化剂用于甲烷部分氧化

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摘要: 采用射频热等离子体制备了Ni含量为50 mol%的Ni-CeO₂催化剂, 考察了其在甲烷部分氧化反应中的催化活性. 在催化剂制备过程中, 采用功率为52 kVA的射频等离子体火炬将Ni(直径约5 μm)和CeO₂粉末(直径约200 nm)混合物同时加热, 粉末添加速率约为120 g/h. X射线衍射和透射电镜表征结果表明, 所用前驱体形成了高结晶的CeO₂载体, 其表面Ni颗粒的粒径较小(< 50 nm). 在常压、500 °C以上、反应物中CH₄:O₂ = 2:1(摩尔比), 并用Ar稀释的条件下考察了所制样品的甲烷部分氧化反应性能. 结果表明, 尽管所制样品中Ni含量较高(~50 mol%), 但在550 °C反应24 h后, 甲烷转化率为70%以上, CO和H₂选择性大于90%, 有少量积碳. 然而, 在750 °C反应24 h时, 催化剂表面形成了丝状碳, 甲烷转化率升至90%以上.

关键词: 射频热等离子体; 甲烷; 部分氧化; 镍催化剂; 氧化铈; 积碳

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