Enhanced carbon tolerance of Ir alloyed Ni-Based metal for methane partial oxidation

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Abstract

Carbon plugging of active catalytic sites significantly degrades the performance of the hydrocarbon reformers. In this study, we show that small amount of Ir alloyed to Ni/ CeO2 nanoparticle exhibit promising improvements to the carbon tolerance properties. XRD analysis indicates that the synthesized nanoparticles are comprised of independent NiO and CeO2 particulates and that the added Ir atoms tend to stay on the surface consistent with the theoretical calculation results of the proposed Ir-Ni alloy. The Ir rich samples show higher methane cracking rate and better carbon removal characteristics. Also, the CO selectivity result shows that adding Ir can prolong the lifetime of the Ni active sites despite a slight drop in the initial partial oxidation reforming rate. Our findings highlight the enhancement effects of Ir on the Ni-based metal carbon tolerance properties and bring us one step closer to finding a solution for the carbon plugging problem.

Keywords: Physical chemistry, Materials chemistry, Materials science
1. Introduction

Catalytic methane partial oxidation (CPOM) using Ni-based catalysts is a one-step process in producing large amounts of hydrogen (H$_2$) which is used for various chemical synthesis process and fuel cell systems [1, 2, 3, 4, 5, 6]. Use of methane (CH$_4$) is advantageous since large quantities of CH$_4$ is already commercially available, and the high H$_2$ to C ratio makes it a highly efficient H$_2$ source. The chemical reaction of CPOM is as follows:

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2, \quad \Delta H = -36 \text{ kJ/mol},
\]

where $\Delta H$ is the enthalpy change during the chemical reaction. In spite of the benefits, whisker growth or encapsulated carbon coking on the Ni-based catalyst surface is problematic since it can lead to plugging of active catalytic sites and significantly degrade the reforming performance [7, 8]. Although the Ni active sites can be restored by purging of the carbon deposition by increasing the feed oxygen concentration, it lowers the energy density and the efficiency of the entire system [9]. Novel method such as chemical looping reforming using Ni-based catalyst by oxygen transfer have demonstrated less carbon deposition and high efficiency, and it may replace air oxidation process in the long run [6]. However, CPOM in air is still the dominate process in producing hydrogen, and many attempts are continuously being made to enhance the long-term performance of the catalytic metals.

Many previous studies have been attempted to redesign the catalyst using precious metals such as Ru, Rh, and Pt, or by introducing alloys such as Au/Ni, Co/Ni, and Sn/Ni [10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. A study by our group used dispersed Ir metals on CeO$_2$ and found permanent tolerance toward carbon deposition in anode catalysts [20]. Despite such success, using large amounts of precious metals significantly increase the cost of the catalysts and a complete overhaul of the conventional Ni-based catalyst is required. Therefore, our group recently proposed alloying Ni-based catalyst with small amounts of Ir which theoretical predict enhanced catalytic properties [21]. The ab-initio calculations showed that the Ir atoms, which tend to stay on the surface, increase the activation energy of the C=C bonds and suppress the formation of carbon agglomerates. The increased total surface energy resulting from the Ir inclusions reduces the stability of the carbon deposition and allow for easy removal.

Herein, we present experimental data showing enhanced carbon tolerance properties of proposed Ir alloyed Ni-based metal which is consistent with the recent theoretically predicted results [21]. We first perform transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis to verify that Ni and CeO$_2$ nanoparticles are formed independently during the synthesizing process. Then we use energy dispersive X-ray spectroscopy (EDX) to show that the Ir atoms prefer to stay on the surface of the alloy as predicted by the calculated surface phase diagram. Next, we
measure the methane cracking rate, carbon removal, and CO selectivity to reveal the enhanced carbon tolerance performance of the Ir-Ni-based catalyst.

2. Experimental

2.1. Catalyst powder synthesis and characterization

The CeO$_2$ support was prepared via glycine-nitrate process, a self-combustion method for synthesizing fine oxide particles, using Ce(NO$_3$)$_3$·6H$_2$O (made by Alfa Aesar) as the Ce precursor [22]. We used the CeO$_2$ precursor solution dissolved in glycine (made by Junsei) and water as the combustion fuel for the glycine-nitrate process (a nitrate-to-glycine molar ratio was 1.82). The calcination of the obtained CeO$_2$ powder was done at 600 °C for one hour. To improve the nanoparticle’s uniformity, the CeO$_2$ powder was pulverized using a ball milling for 12 hours to form particles with a surface area of approximately 45 m$^2$/g.

The 5.0 wt % Ni/CeO$_2$, (4.9 wt % Ni – 0.1 wt % Ir)/CeO$_2$, (4.5 wt % Ni – 0.5 wt % Ir)/CeO$_2$, and (4.0 wt % Ni – 1.0 wt % Ir)/CeO$_2$ catalyst powders were prepared via impregnation of cubic CeO$_2$ supports with nickel and/or iridium precursor solution, Ni(C$_5$H$_7$O$_2$)$_2$ (made by Aldrich) and IrCl$_3$·xH$_2$O (made by Alfa Aesar), of appropriate concentrations. We will omit wt % from the nomenclature indicating the catalyst powder from here on. The metal precursors were dissolved in an aqueous solution (distilled water: ethanol = 50:50). The atomic structure of the catalyst powders was characterized using a TEM (Titan 80-300, FEI) equipped with an EDX (PV9761, EDAX). The crystalline phases of the prepared powders were analyzed by XRD (D/Max 2500, Rigaku) using Cu Kα radiation.

2.2. Measurement of catalyst performance

The methane cracking rate of the alloy metals was measured by loading each sample with equal mass in a flow-through type reactor. Then CH$_4$/He (25/100 sccm) mixture gas was fed for 15 minutes while maintaining a temperature of 600 °C. The amount of carbon deposition after the methane cracking reaction was quantitatively measured by a CHNS-O elemental analyzer (EA1108, Fisons). After the measurement, the samples were reloaded in the reactor until the amount of carbon deposited in each sample became equal in preparation for the carbon stability test. Note that the sample with least amount of carbon deposited after 15 minutes was reloaded in the reactor for the longest time. Next, the carbon removal was measured by weighing each deposited coke using the thermogravimetric method in flowing dry air using a thermal gravimetric analyzer (Q600, TA Instruments).

Methane partial oxidation for Ni with various concentrations of Ir added by using a fixed-bed tubular quartz reactor operated at ambient pressure condition. The mixture
of catalyst (100 mg) and quartz (500 mg) powders (a surface area \( \sim 1 \text{ m}^2/\text{g} \)) was placed on a porous quartz bed inside the reactor. The reduction of the catalyst powders was done under a hydrogen atmosphere at 600 °C for two hours and then purged with He for 30 minutes. A flow rate of 280 sccm gas mixture with a volumetric ratio of \( \text{CH}_4:\text{O}_2:\text{He} = 2:1:10 \) was feed in, and the exhaust gas mixture was monitored using gas chromatography (6890N, Agilent) equipped with a thermal conductivity detector. A bonded polystyrene-divinylbenzene based capillary column (HP-PLOT Q, Agilent) and molecular sieve were used to separate CO, CO\(_2\), N\(_2\), CH\(_4\), and H\(_2\). Based on the measurement, CH\(_4\) conversion (\( X_{\text{CH}_4} \)) and CO yield (\( Y_{\text{CO}} \)) given by

\[
X_{\text{CH}_4}(\%) = \frac{F_{\text{CH}_4,\text{out}} - F_{\text{CH}_4,\text{in}}}{F_{\text{CH}_4,\text{in}}} \times 100,
\]

\[
Y_{\text{CO}}(\%) = \frac{F_{\text{CO, out}}}{F_{\text{CH}_4,\text{in}}} \times 100,
\]

where \( F_i \) is the molar flow rate of species \( i \), were found at various temperatures for the metal samples. Also, we found the long-term CO selectivity (\( S_{\text{CO}} \)) which is given as

\[
S_{\text{CO}}(\%) = \frac{F_{\text{CO, out}}}{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}} \times 100.
\]

by maintaining the reaction for 25 hrs at 600 °C.

3. Results and discussion

3.1. Elemental analysis of the Ir-Ni/CeO\(_2\) nanoparticle

The TEM image of the synthesized (Ir – Ni)/CeO\(_2\) nanoparticles, with diameters approximately 13.9 nm, is shown in Fig. 1(a). The photo illustrates that the clusters of Ir-Ni particles coexist with diamond-shaped CeO\(_2\) supports indicating a successful formation of the nanoparticles. To show that the Ir, Ni, and Ce did not exist as a compound, XRD analysis was carried out to investigate the crystallinity. The XRD patterns are obtained from the sample after calcination at 600 °C for one hour in the air, and the result is shown in Fig. 1(b). The figure shows that the NiO and CeO\(_2\) peaks are distinguished indicating that the two compounds exist independently. However, the Ir peaks are not visible since the amount of Ir added falls below the detection limit of the XRD analysis.

The Ir content variation within the nanoparticle is observed by measuring the Ir to Ni signal ratio using EDX analysis. The data was collected by moving from the surface region (point A) to the bulk region (point B), as indicated by the red arrow in Fig. 2(a) and the result is shown in Fig. 2(b). The figure shows that a high concentration of Ir is found near the surface region, but as one moves deeper into the bulk (from point A to B), the Ir content rapidly diminishes. In other words, in the stable Ir-Ni nanoparticle,
more Ir atoms exist on the surface rather than in the bulk region. This result is consistent with the calculated surface phase diagram using DFT (Density Functional Theory) calculations in which the surface free energy is at its minimum when the Ir atoms are placed near the surface [21]. Both experimental and theoretical results indicate that when Ir is added to the Ni-based catalyst, most of the Ir atoms will be near the surface creating exposed Ir sites during the reforming process.

Fig. 1. (a) A TEM image of as-synthesized (1.0Ir – 4.0Ni)/CeO₂ nano-particles. The hexagonal CeO₂ and the Ir-Ni metal is visible in the inset. (b) XRD patterns of the synthesized samples after calcination. The black circles show the reference CeO₂ peaks while the two small peaks marked with dashed lines are characteristics of NiO.
3.2. Enhanced carbon cracking rate

The carbon weight change ($\Delta W/W_0 = \text{weight change/initial weight}$) of the catalyst samples after a fixed period of reforming process can be an estimation of the catalytic performance. Here, we assume that any weight gain after the process is due to the deposited carbon during methane cracking and we do this to simulate an extreme condition where a significant amount of carbon is deposited onto the catalyst samples. The result of the carbon weight gain measured is shown in Fig. 3(a). The figure shows that as the Ir ratio ($W_{Ir}/W_{Ni} = \text{weight of Ir/weight of Ni}$) is increased, the carbon weight is also increased. Since the only source of weight gain is from carbon, we can conclude that more methane has been cracked. Note that as the Ir to Ni ratio approaches 1.0/4.0, the carbon weight gain ratio saturates to approximately 23%. Such trend indicates that rapid enhancement of the reforming rate is expected when small amounts of Ir is added; however, when Ir content is over 1% (or 20% with no CeO$_2$), no more enhancement is expected due to saturation effects. Subsequently, we measure the carbon weight change (weight change/initial weight = $\Delta W/W_0$) using the

Fig. 2. (a) Scanning TEM image of Ir-Ni alloy CeO$_2$ nano-particle which shows both clustered Ir-Ni nanoparticles and cubic CeO$_2$ support. (b) The elemental EDX analysis of the Ir-Ni nanoparticle. (c) Normalized Ir/Ni ratio measured using EDX analysis as a function of the distance from point A along the line connecting A (surface region) and B (bulk region).

Fig. 3. (a) The elemental carbon weight change (weight change/original weight = $\Delta W/W_0$) as a function of increasing Ir content in the Ir-Ni alloy CeO$_2$ nano-particle after being subjected to CH$_4$/He gas at 600 °C for 15 minutes. (b) The elemental carbon weight change (weight change/original weight = $\Delta W/W_0$) as a function of increasing Ir content in the Ir-Ni alloy starting from equal carbon amounts. (c) The thermo-gravimetric analysis which measures the carbon weight (final weight/initial weight = $W/W_0$) as a function of temperature for various Ir content in Ir-Ni alloy nano-particle.

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identical samples after setting the initial carbon deposition weight to the same value. Fig. 3(b) shows the carbon weight change of the samples which were exposed to dry air at 600 °C after a fixed amount of time. Again, it is quite likely that any change in the weight is due to carbon removal. The carbon weight loss measurement indicates how easily carbon can be removed from the catalyst surface and is an indication of the adsorbed carbon agglomerate stability. The figure shows that as the Ir ratio is increased, the carbon weight loss is also increased which is similar to the carbon weight gain in Fig. 3(a). Note that the carbon loss is more than the carbon gain since the amount of carbon deposited in each sample was set to an identical value after the carbon gain experiment. Also, we measure the carbon weight loss as a function of temperature using the identical samples used to predict the methane cracking rate. Fig. 3(c) shows the sample weight (final weight/initial weight = $W/W_0$) as a function of temperature for various Ir content in the Ni-based nanoparticle. The figure indicates that a sharp reduction of the carbon content is observed starting from approximately 300 °C to approximately 500 °C regardless of the amount of Ir content. Although the carbon weight for the catalyst samples having none or low Ir content {$(5.0\text{Ni})/\text{CeO}_2$ and $(4.9\text{Ni} - 0.1\text{Ir})/\text{CeO}_2$} is maintained at approximately 87 and 82%, respectively, the carbon weight for the samples having high Ir content {$(4.5\text{Ni} - 0.5\text{Ir})/\text{CeO}_2$ and $(4.0\text{Ni} - 1.0\text{Ir})/\text{CeO}_2$} is reduced to approximately 72 and 71%, respectively. Indeed, the increased carbon removal rate is not a direct indication of carbon agglomerate stability but an indication of its type, under the identical experimental conditions used here, the carbon types are expected to be identical, and we can conclude that the carbon deposited, in any form, on the alloy catalyst can be easily removed compared to that on pure Ni-based catalyst. Therefore, more active catalytic sites are expected to be maintained during the methane cracking process. Note that the possible change of the deposited carbon is not a scope of this study but should be further investigated in subsequent studies.

3.3. Enhanced reforming rate

Fig. 4(a) and (b) shows the CH$_4$ conversion ($X_{\text{CH}_4}$) and CO yield ($Y_{\text{CO}}$) at different temperatures after methane partial oxidation using Ni metal samples with varying amount of Ir content. The figure shows that although there is a slight drop in the CH$_4$ conversion and CO yield for the samples with more Ir (most likely due to a small decrease in the number of catalytic sites), the initial partial oxidation performance is near identical. Although the above data is for initial reaction (for the first 2 hours), we expect such trend to continue through the long-term performance test.

Finally, the long-term performance of the proposed Ir-Ni-based catalyst is investigated by monitoring the CO selectivity during partial oxidation of methane. The time variation of the CO selectivity of four different samples each having $W_{\text{Ir}}/W_{\text{Ni}}$
The figure shows that the CO selectivity of Ni/CeO$_2$ constantly degrades indicating continuous plugging of active Ni sites by carbon agglomerates. However, for the samples having high Ir content, the CO selectivity of the sample is maintained even after 25 hours of continuous operation, suggesting better long-term performance. The results also show that initially, the CO selectivity of the Ir-rich samples are consistently lower compared to that of low or no Ir content samples. This is expected since the Ir inclusions slightly reduce the Ni active sites for the catalytic conversion to occur. However, as time passes, the tables are turned since more and more Ni active sites of the low or no Ir content samples are plugged due to carbon deposition while the Ni active sites are maintained for the Ir-rich samples. Note the figure shows that even small amounts of Ir, i.e., 0.1%, can be effective in ensuring good performance.

**Fig. 4.** CH$_4$ conversion and CO yield for samples each having $W_{Ir}/W_{Ni}$ ratio of 0.0/5.0, 0.1/4.9, 0.5/4.5, and 1.0/4.0 at various reaction temperatures. Methane partial oxidation was done under gas mixture (CH$_4$:O$_2$:He = 2:1:10) flow rate of 280 sccm.
catalytic performance and Ir concentrations over 1% is not necessary due to saturation effects. For all Ni catalyst (no CeO2), this may mean adding only 2% of Ir can effectively improve the carbon tolerance performance.

4. Conclusions

We have experimentally verified that adding a small amount of Ir to the Ni-based catalyst show high CH4 conversion and high carbon tolerance properties. EDX analysis of the nanoparticle indicates that the Ir atoms prefer to stay near the surface just as predicted by the previously presented \textit{ab-initio} calculations by our group. The experiment under extreme conditions (i.e., a mixture of CH4 and He) suggest that the Ir rich samples result in higher methane cracking rate. Also, higher carbon weight loss for the Ir rich samples during the purging process indicate that the Ir inclusions improve the carbon removal characteristics of the Ni-based catalyst. Methane partial oxidation experiment under a mixture of CH4, O2, and He shows that all the samples result in an equal initial CH4 conversion and CO yield. The long-term CO selectivity measurements show that the Ir rich Ni-based catalysts are expected to maintain their performance for a longer period compared to that of no or Ir poor Ni-based catalysts despite the slight initial drop. Therefore, this study indicates that the proposed Ir-Ni-based catalyst is a promising solution for the carbon plugging problem in the hydrocarbon reforming process.

\textbf{Fig. 5.} The time variation of the CO selectivity of four different Ir-Ni alloy nanoparticle samples each having $W_{\text{Ir}}/W_{\text{Ni}}$ ratio of 0.0/5.0, 0.1/4.9, 0.5/4.5, and 1.0/4.0. The measurement was taken after partial oxidation of Methane under a gas mixture (CH4:O2:He = 2:1:10) of flow rate 280 sccm and a temperature of 600 °C for 25 hrs.
Declarations

Author contribution statement

Kiyong Ahn: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Jong-Ho Lee: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Hyoungchul Kim: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Jedo Kim: Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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