In-situ observation and analysis of Ni-based catalysts for dry reforming of methane

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Background incl. aims
Global warming is getting a tremendous issue because of the large release of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and so forth. Catalyst is one of promising solutions for global warming to reduce the greenhouse gases. Dry reforming of methane (DRM, $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$) is a powerful reaction utilizing the two greenhouse gases. Ni-based catalysts are useful owing to their high catalytic activities and lower cost compared with noble metals. However, they are easily deactivated via carbon formation during RDM reactions, which is referred to as coking by generation from side reactions. While improvements in catalytic activities have been reported so far [1-3], coking and catalytic deactivation have been not fully studied yet. In this work, structural and chemical changes of Ni nanoparticles during DRM process were investigated using in-situ scanning transmission electron microscopy (STEM) with electron energy-loss spectroscopy (EELS) analysis.

Methods
Ni nanoparticles supported Al_2O_3 catalyst (Ni/Al_2O_3) powders were prepared with different mass ratios of 5 and 10 wt% through the impregnation method. Al_2O_3 powders were dissolved with $Ni(NO_3)_2 \cdot 6H_2O$ into ethanol. After the remaining ethanol was evaporated at 80 °C, the powders were heated in H_2 gas at 600 °C for 6 h to reduce the oxidized Ni. The prepared Ni/Al_2O_3 catalysts were observed in the DRM mixture gas conditions (50% CO_2 and 50% CH_4) with pressure of 0.3 ~ 10 Pa and then, were gradually heated at 150 - 450 °C. In comparison, they were also observed in pure CH_4 gas.

For in-situ observations, our previously developed gas environment heating specimen holder system was used [4]. The Ni/Al_2O_3 powders were dispersed on a Si-based heater chip (E-chip, Protochips, USA), which was arranged in the specimen room at the tip of the specimen holder connecting to the heater controller outside of an electron microscope column. The chip was sandwiched between the two orifice plates to create a differential pumping effect leading to a higher environmental pressure in the specimen room. The powders were observed through a double aberration-corrected electron microscope (JEM-ARM200F, JEOL, Japan) operating at an accelerating voltage of 200 kV. In addition, ex-situ experiments were conducted compared with in-situ ones to examine electron irradiation damages.

Results
The TEM and STEM observations of the prepared Ni/Al_2O_3 powders show the Ni nanoparticles with the size of 5 to 50 nm were uniformly dispersed on the Al_2O_3 support powders. After the ex-situ experiment in the DRM gas (10 Pa) at 450°C for 6 h, the powders were covered with thick carbon films due to coking. During in-situ observation at 550°C after ~15 min of elevating temperature, the similar carbon films were also observed on the Ni nanoparticles. This comparison demonstrated that the in-situ observation had little electron irradiation effects on the structures and reaction phenomena. The carbon deposition was observed even at 350°C in the DRM gas, although the amount of carbon was much less than that in the pure CH_4 gas condition.

Next, the chemical bonding and valence state of the Ni nanoparticles on the Al_2O_3 supports were measured under the DRM conditions by in-situ EELS. Before the DRM gas flowing, the Ni nanoparticles were mainly metallic Ni. But after the gas flowing, most of the nanoparticles changed from Ni to oxidated Ni depending on temperature. Some Ni nanoparticles were oxidized at over 450°C and then reduced at over 550°C in the DRM gas. In addition, structural changes of the Ni nanoparticles were also observed with the oxidation and reduction reactions.

Conclusions

We observed the Ni nanoparticles on the Al_2O_3 supports through in-situ STEM and EELS to elucidate actual phenomena occurring on the Ni/Al_2O_3 catalysts under the DRM conditions. Carbon deposition on the Ni nanoparticles was observed even the in-situ observations. Furthermore, the change in the chemical bonding and valence state of the Ni nanoparticles were also measured on some Al_2O_3 supports depending on elevating temperature through in-situ EELS.

Keywords:

in-situ observation, catalytic materials, nanoparticles

Reference:

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