

In-situ TEM observation of Ni/Al₂O₃ catalysts for dry reforming of methane

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Ni-based catalysts are useful for dry reforming of methane (DRM, $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$) owing to their high catalytic activities and lower cost compared with noble metals. However, these catalysts have some disadvantages, such as a high activity temperature and high possibility of deactivation. During a DRM reaction, Ni-based catalysts are easily deactivated via carbon formation, a process that is referred to as coking, generated from side reactions. Therefore, retaining their activities without using water and steam for inhibiting carbon formation would be challenging in actual applications. Although several researchers have reported improvements in catalytic activities and stabilities [1], coking and catalyst deactivation have not been completely understood and overcome yet. In this work, structural and chemical changes of Ni nanoparticles during the DRM process were elucidated using in-situ transmission electron microscopy (TEM) with electron energy-loss spectroscopy (EELS) analysis.

Two Ni/Al₂O₃ catalyst powders with different mass ratios (5 wt% and 10 wt%) were prepared through the impregnation method, as shown in Fig. 1(a). Firstly, Ni(NO₃)₂·6H₂O and Al₂O₃ were dissolved into ethanol. After 8 h of stirring, the remaining ethanol was evaporated at 80 °C. Then, the powders were heated in 5% H₂ + 95% Ar at 600 °C for 6 h to refine the particle size and reduce oxidized Ni. In this study, 5 wt% and 10 wt% Ni/Al₂O₃ were imaged in gas conditions at approximately 0.3 and 13 Pa pressure, respectively. To avoid carbon contamination, each TEM observation started at a temperature of 150 °C before introducing the gases, and the electron dose through the specimen was kept lower than 10 pA/cm². The specimens were then gradually heated to 350 °C and 450 °C to react with CH₄ or DRM (a mixture gas containing 50% CO₂ and 50% CH₄) gases.

For in-situ observations, our previously developed specific gas heating specimen holder was used [2]. A Si-based heater chip (E-chip, Protochips, USA) with Ni/Al₂O₃ powder was arranged in a specimen room at the tip of the specimen holder and connected to a heater controller outside of the TEM column (JEM-ARM200F, JEOL, Japan). The chip was then sandwiched between two orifice plates to create a differential pumping effect, which enabled a higher environmental pressure in the specimen room without breaking the column vacuum. The pressure in the specimen room was monitored in the form of a voltage value measured via a multimeter using a tiny vacuum gauge near the Ni/Al₂O₃ powder.

Under CH₄ conditions, the Ni nanoparticles exhibited significant changes in their positions and shapes during in-situ observations. Furthermore, some graphitic structures were observed above 450 °C on the surface of the Ni particles under the both pressure conditions (0.3 and 13 Pa), as shown in Fig.1(b). This indicates that carbon can form on the Ni nanoparticles by decomposing the introduced CH₄ gas. In addition, a few small Ni particles were formed from the larger 10 wt% Ni/Al₂O₃ particles. Pure Al was also detected near a NiO particle, which is formed via decomposition of the Al₂O₃ support.

On the other hand, under DRM conditions, the graphitic structure could not be observed, but several Ni₃C-like structures were observed. The coking phenomena were not obvious, thus demonstrating that the presence of CO₂ in the DRM gas inhibits coking. Some types of Ni-Al compounds were also found, presumably due to the interaction of the Ni nanoparticles with the Al₂O₃ support.

The Ni valence changes during TEM observations were evaluated through the white line ratio (WLR) from the in-situ EELS analysis. The valence states increased overall, showing that Ni nanoparticles under CH₄ gas conditions were oxidized because of oxygen from the Al₂O₃ support, whereas they were oxidized mainly because

of the CO₂ gas under the DRM condition. However, some Ni nanoparticles still remained, which might be attributed to the reduction of the formed NiO particles and the interaction with the support. Thus, under both conditions, oxidation and reaction of the Ni nanoparticles simultaneously occurred during the reaction processes.

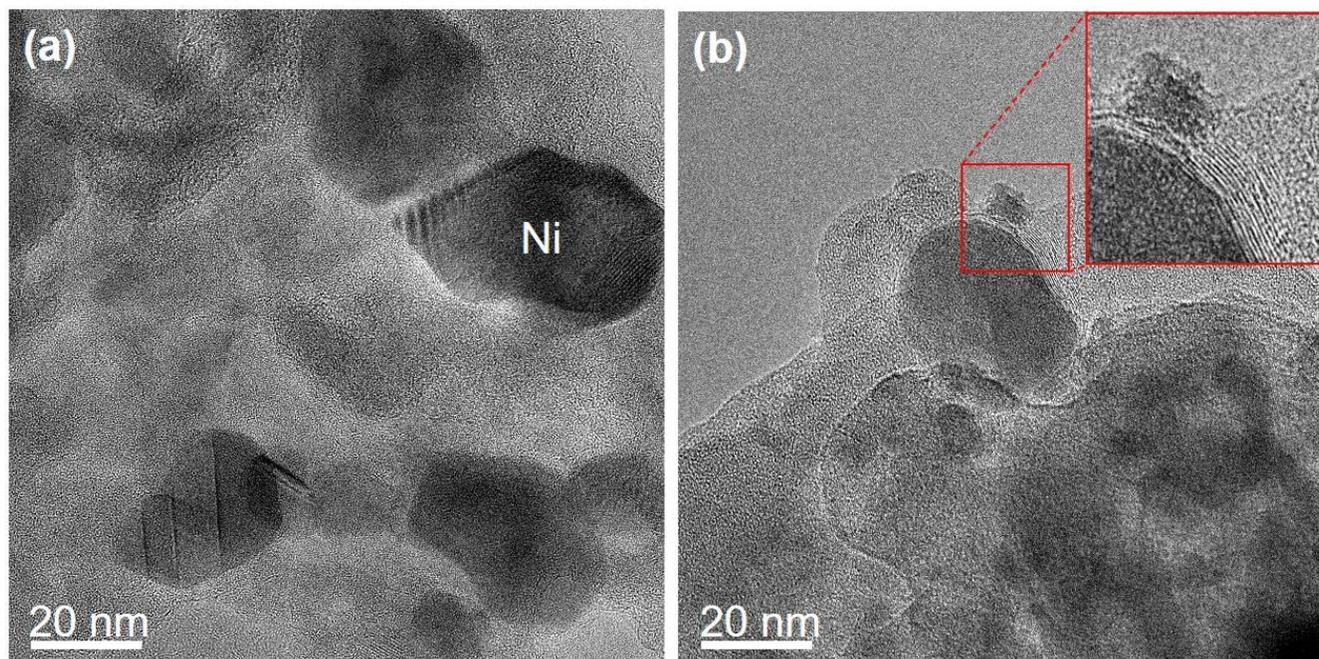


Figure 1. TEM images of 10 wt% Ni/Al₂O₃ catalysts (a) before gas introduction at 150 °C, and (b) in pure CH₄ gas at 450 °C.

References

- [1] A. Guerrero-Ruiz et al, *Applied Catalysis A General* 170 (1998) 177.
- [2] A. Hashimoto et al, *AMTC Letters* 6 (2019) 108.