

Deactivation Mechanism of Ni Nanoparticles in Dry Reforming of Methane Revealed by Operando TEM

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Many studies have shown that catalysts are metastable and dynamic systems, where the nature of the active state depends on the applied chemical potential, associated “chemical dynamics” and the formation of transient active sites.^{1,2} Therefore, active surfaces could be unstable at non-active conditions, leading to misinterpretation of inactive structures as active states in *ex situ* studies.¹ Recent progress in the development of *in situ* and *operando* techniques allows access to live information at high temporal and spatial resolution for the first time.³⁻⁵ Operando transmission electron microscopy (TEM) allows to directly probe the active-state/-sites of catalysts under relevant reaction conditions and at high resolution. The structure-function relationship remains unsolved in many catalytic reactions, including in the important industrial reaction - dry reforming of methane (DRM). This lack of fundamental understanding of DRM is hindering the choice and design of efficient catalyst material since an empirical approach to discovering new catalysts still prevails. Using *operando* TEM techniques presents a unique opportunity to gain fundamental insights into the DRM reaction to reveal what constitutes the active structure.

In this work, we used *operando* TEM to study DRM using nickel (Ni) catalyst nanoparticles (NPs). First, Ni NPs were deposited on the microelectromechanical systems (MEMS) chip using the magnetron sputtering method. The *operando* TEM instrumentation included: an aberration-corrected FEI Titan TEM operated at 300 kV, a home-built gas-feeding setup and a gas-cell DENSsolutions “Climate” TEM holder which was directly connected to a HIDEN HAL/3F QMS mass spectrometer to analyse the outgoing gas.⁶ This setup allowed to directly correlate structural and morphological changes of the catalysts to the different stages of their activity.² In addition, it allowed for a fast gas exchange to study transient states of the active catalyst.

TEM imaging of the as-deposited Ni NPs showed the formation of a thin nickel-oxide (NiO) film (**Fig. 1a**) due to the exposure to air during the assembly of the gas-cell TEM holder. Thus, to obtain metallic Ni NPs (which is required for DRM), *in situ* reduction inside the column of TEM was performed (**Fig. 1**). The reduction process was monitored during the temperature ramp from room temperature (RT) to 700 °C by selected area electron diffraction (SAED). Radial profiles of SAED patterns confirmed that the phase transition from NiO to metallic Ni occurred already at 280 °C (**Fig. 1d,f**). TEM imaging showed that the Ni NPs after reduction had a broad size distribution and irregular shapes (**Fig. 1c,e**). Next, the gas feed of methane (CH₄) and carbon dioxide (CO₂) was introduced at 700 °C to study structural and morphological changes of Ni NPs in DRM (**Fig. 2**). Twelve minutes after the introduction of gas feed, a significant decrease in the catalyst activity was observed due to the growth of graphitic layers over Ni NPs (**Fig. 2f**). Graphitization of Ni NPs was confirmed by real-time SAED, which showed that structural changes of Ni NPs occurred in the first few minutes of DRM reaction (**Fig. 2a,b**). In addition, changes in the intensity of the diffraction reflections, including broadening and shifts could

be assigned to the formation of different Ni carbide phases-Ni_xC_y (**Fig 2c**). Ni carbides which formed at reaction conditions were most likely responsible for the overgrowth of Ni NPs and the subsequent catalyst deactivation. This suggests that Ni carbide is the active phase for growth of graphitic layers over Ni NPs, which is an agreement with previously reported *ex situ* studies on DRM over Ni-based catalysts.⁷ Furthermore, high-resolution TEM imaging confirmed the formation of multi-layer graphitic growth on the surface of Ni NPs. Larger Ni NPs were found to be significantly more active for the growth of graphitic layers compared to smaller ones, thus leading to faster catalyst deactivation (**Fig. 2e**). Smaller NPs were found to suffer much less frequently from graphitic layers encapsulation and therefore suffered less deactivation. It was also observed that non-supported Ni NPs deactivated rapidly during the DRM reaction. Furthermore, using this operando TEM approach, we were also able to directly correlate the information on real-time structural changes of Ni NPs in DRM to the catalyst activity. Conversion of methane and carbon dioxide to hydrogen and carbon monoxide was detected and monitored throughout the *in situ* experiment.

Using an *in situ* TEM approach we were able to gain crucial insights into the important industrial reaction of DRM. This leads us closer to a more mechanistic understanding of the reaction and ultimately our aim of rational design of better catalysts.

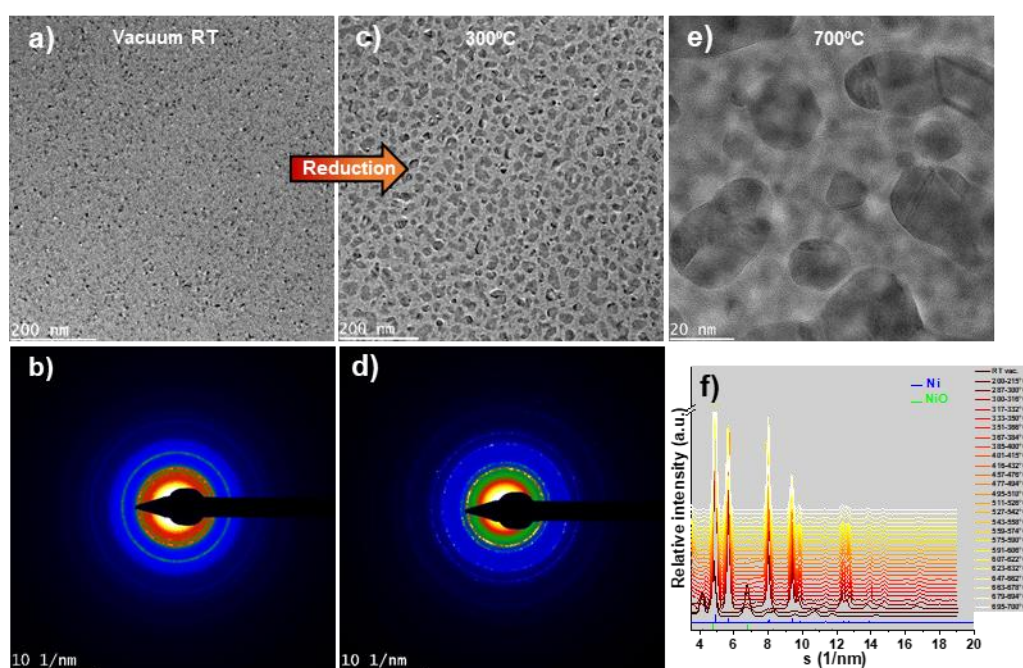


Figure 1. *In situ* reduction of as-prepared Ni NPs visualized by TEM. (a) TEM image of as-deposited Ni NPs imaged in vacuum depicts uniformly formed NiO thin film, which is also (b) confirmed by SAED analysis. (c) TEM image of reduced Ni NPs at 300 °C, (d) with corresponding SAED pattern that confirms the presence of only metallic phase. (e) HRTEM of Ni NPs after reduction at 700 °C, and (f) evolution of averaged radial profiles extracted from SAED patterns acquired during temperature ramp from RT to 700 °C. Reduction conditions: 20% H₂ in He, temperature ramp 5°C/min from RT to 700 °C.

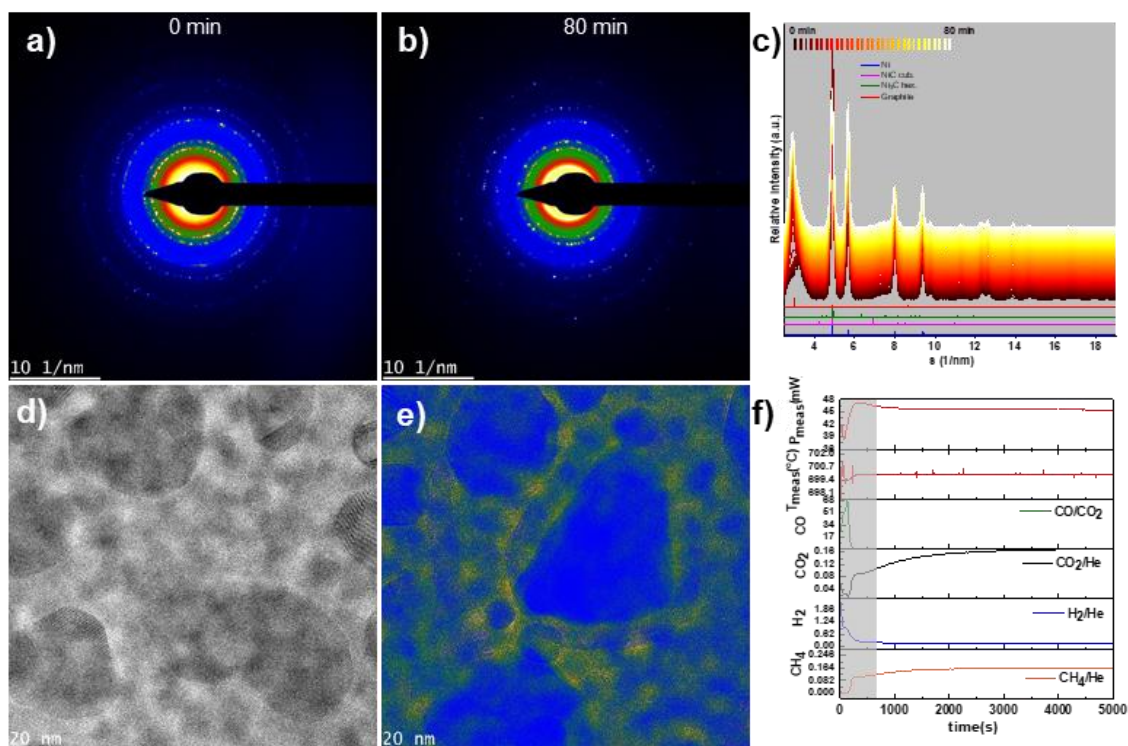


Figure 2. Operando TEM observation of structural changes on Ni NPs during the introduction of gas feed for DRM. Continuously acquired SAED patterns are shown here for (a) 0 minutes (b) 80 minutes, together with (c) corresponding averaged diffraction radial profiles. HRTEM images of Ni NPs show; (d) clean metallic surface (active) at the beginning of the gas-feed introduction, and (e) fully covered surface (non-active) with multi-graphitic layers after 80 min, (f) MS data for DRM over Ni NPs at 700 °C. Gas feed: CH₄:CO₂=4:3. Grey square in (f) depicts catalyst deactivation.

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