

Atomic-scale Imaging of Deactivation Mechanisms in Nickel-based Steam-reforming Catalysts

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Introduction

With recent developments, environmental transmission electron microscopy (ETEM) is now capable of imaging—with atomic resolution—transition metal catalysts during exposure to reactive gases at elevated temperatures (1-4). This capability provides detailed insight into the structure of complex supported metal nanocluster catalysts in their functioning state and allows in addition for direct monitoring of dynamic restructuring processes that may occur in response changes in the gas composition or in the course of a catalytic reaction. The dynamic insight opens up new ways for directly elucidating the atomic-scale processes involved in for instance catalyst deactivation phenomena and makes atomic-resolved ETEM an essential complement to the variety of *in situ* spectroscopic techniques that also provide important information about the temporal evolution of catalysts' structures. Specifically, the interplay of atomic-resolved ETEM with atomic-scale modeling of possible elementary processes at the exposed surfaces provides an important new approach for rationalizing complex deactivation phenomena occurring in catalysis.

The present contribution demonstrates the combined use of ETEM observations and density functional theory (DFT) calculations for atomic-scale studies of deactivation mechanisms in oxide-supported nickel nanocluster catalysts. This type of catalysts is often applied in the industrial production of hydrogen and synthesis gas by steam-reforming of hydrocarbons and may deactivate by different processes, including poisoning, sintering and fouling (carbon deposition) (5).

Results and Discussion

The contribution focuses mainly on carbon deposition in nickel-based steam reforming catalysts and in particularly on the formation of carbon nanofibers which eventually destroys the nickel catalyst (5).

In situ observations of carbon nanofiber growth are obtained by means of atomic-resolved ETEM (6-7). The nanofibers are formed by methane decomposition over supported nickel nanoclusters. In the experiments, the ETEM is applied in a dynamic mode in which the nanofiber formation is directly monitored by recording *in situ* time-lapsed image series. When the image series are replayed in the form of a movie, a direct visualization of the way in which graphitic nanofibers grow is obtained. Atomic-resolved ETEM movies show that the graphitic nanofibers develop through a reaction-induced reshaping of the nickel nanoparticles which assists the alignment of graphene layers into graphitic nanofibers. Specifically, the nucleation and growth of graphene layers are found to couple to a dynamic formation and restructuring of mono-atomic step edges at the nickel surface.

The observations are compared with results from density functional theory (DFT) calculations of the mechanisms and energetics in graphene growth on model nickel surfaces [6,8-9]. The finding that the step sites act as preferential growth centers is attributed by DFT to a stronger bonding of carbon atoms to step sites than to facet sites. Furthermore, the

calculations show that the dynamic behaviour of step edges on the nickel nanocrystals consistently can be explained by transport of carbon and nickel atoms confined to the surface region of the nickel nanocrystals, whereas bulk transport processes are limited of importance. The detailed interplay between the atomic-scale ETEM observations and DFT calculations allows a coherent growth mechanism to be established.

The results demonstrate that step sites play a key role as centers for graphene growth, and thus, the properties and dynamics of step sites are crucial for the stability of nickel nanocluster catalysts. Based on this knowledge, a more general understanding of the effect of many different promoters was developed: Potassium, sulfur, and gold promoter atoms have been found to bind preferentially to step edges of nickel, suggesting that these elements suppress graphite formation through a step blocking mechanism (5,9).

Significance

This presentation demonstrates how the interplay between atomic-resolved ETEM observations and DFT calculations can provide new insight into atomic-scale mechanisms involved in complex deactivation processes in catalysis.

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