Observing catalyst structures and dynamics at atomic resolution

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Over the past decade, electron microscopy has become indispensable for studying heterogeneous catalysts at the atomic-scale [1]. The ability to acquire atomic-resolution images with single-atom sensitivity has opened up for unprecedented insight into catalyst structures and dynamics. However, the progress has also shown that observations at the atomic-level require an intense electron illumination that generally alters the catalyst during observation. The electron-induced alterations are particular pronounced at the catalyst surface as they expose a variety of sites of reduced atomic coordination. In the quest to suppress electron-induced alterations and to enable chemical meaningful observations, it therefore becomes mandatory to exercise control over the electron dose, dose-rate and energy. Here, we demonstrate low dose-rate in-line electron holography as a viable concept for atomic-resolution observations of catalysts in the genuine state [2-4]. The imaging scheme employs bright field transmission electron microscopy (TEM) as the most efficient way to detect single atoms using the fewest elastically scattered electrons. The image acquisition is done with low electron dose-rates of down to 1-100 $e^{-}Å^{-2}s^{-1}$ to inflict the weakest object excitation and to offer time for reversible object restoration between successively delivered electrons. As a result, the individual atomic-resolution images are dominated by noise, and recovery of image signal can be accomplished by averaging over a series of consecutively acquired images of the object. For this purpose, in-line holography based on focal image series is particular attractive as residual aberrations are corrected and the exit wave (EW) function recovered with enhanced signal that is quantitatively interpretable. Applications of the concept of low dose-rate in-line electron holography in catalysis research will outlined. The EW phase images of carbon-supported single-layer MoS_2 nanocrystals with edge-attached Co promoter atoms will be shown [6]. This catalyst is relevant for hydrodesulfurization processes in oil refineries. A systematically examination of the MoS_2 structures at different dose-rates reveal that lower dose-rates sharpen up the atomic column contrast and reduce smearing of the edge contrast. This suppression of beam-induced atom dynamics enables a quantitative analysis of the exit wave for retrieving the stoichiometric arrangement in the Co-Mo-S nanocrystals in three dimensions.

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