31

Electron Microscopy Advances in Catalysis

Stig Helveg

Haldor Topsoe A/S, Haldor Topsøes Allé 1, DK-2800 Kgs. Lyngby, Denmark.

Electron microscopy has become indispensable for studying heterogeneous catalysts. In particular, the ability to acquire atomic-resolution and -sensitive images is beneficial for uncovering catalyst surfaces. However, surfaces of most materials tend to restructure in reactive environments and such changes feedback on the catalyst performance. It has therefore remained an important milestone to extend the high-vacuum conditions residing in electron microscopes with reactive environments confined to the specimen region to enable *in situ/operando* studies in which the catalyst surface structure and properties are simultaneously evaluated.

Our contributions to the advancement of gas cells have enabled atomic-resolution electron microscopy of catalysts under the exposure to reactive gasses at pressures of up to atmospheric levels and temperatures of up to several hundred centigrade [1-2] as well as made concurrent measurements of catalytic functionality an emerging competence [3]. These "live" observations offer unprecedented new insight into the surface dynamics and reactivity and establish a foundation for studies of dynamic properties and functions in catalysis at the atomic level [3-6]). However, the observations made 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. Hence, in the quest to enable chemical meaningful observations, it is therefore mandatory to suppress beam-induced alteration by exercising control over the electron dose, dose-rate and energy. In this respect, low-dose-rate in-line electron holography has been demonstrated as a viable concept for atomic-resolution observations of catalysts in the genuine state [7-9].

In this presentation, I will outline our efforts on advancing electron microscopy for "live" observations of catalysts at atomic-resolution and illustrate their application with studies within e.g. hydrotreating, methanol synthesis and emission control catalysis (e.g. fig. 1). Moreover, it will be discussed how the atomic-scale observations can beneficially be combined with reactivity data, calculated or measured, from simpler model systems to extend our understanding of dynamic properties and functionality in catalysis.

References:

- [1] PL Hansen et al, Science **295** (2002), p. 2053.
- [2] JF Creemer *et al*, Ultramicroscopy **108** (2008), p. 993.
- [3] SB Vendelbo *et al*, Nature Mater **13** (2014), p. 884.
- [4] M Ek *et al*, Nature Commun **8** (2017), p. 305.
- [5] C Dahl-Petersen et al, ACS Nano 12 (2018), p. 5351.
- [6] S Helveg, J Catal. **328** (2015), p. 102.
- [7] JR Jinschek and S Helveg, Micron **43** (2012), p. 1156.
- [8] S Helveg *et al*, Micron **68** (2014), p. 176.
- [9] M Ek et al, Adv Struct Chem Imag 2 (2016), p. 4.

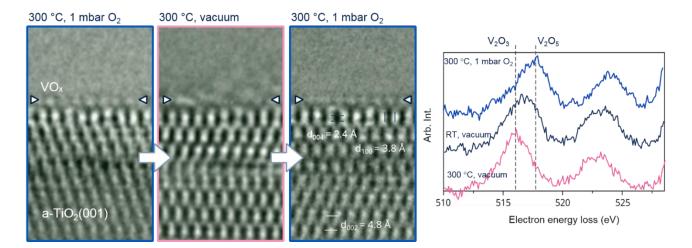


Figure 1. Atomic-resolution electron microscopy of a VO_x/TiO_2 catalyst under oxidizing and reducing conditions. Adapted from [4].