

Dynamic Structural Changes due to Metal-Support Interaction under Reactive Conditions

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For our understanding of processes that are induced by the interaction of a material with its surrounding, observation of isolated systems in vacuum, such as in conventional transmission electron microscopy (TEM), is not sufficient. However, direct insights in catalytic function can only be obtained when the system is studied in a functioning state. Indeed, the ability of a catalyst to convert educts to their respective products is fundamentally linked to ad- and desorption of molecular species, which will have an impact on the state of the catalyst itself. E.g. adsorption induced shape changes of nanometer size of noble metal particles is a well known example [1].

With the availability of microelectromechanical (MEMS) based nanoreactors for *in situ* TEM experiments in gaseous environments [2], reaction induced modifications of catalyst structure can now be studied in real time, at atomic resolution and at pressures of one bar and above. Specifically, this enables to bridge the pressure gap between the low pressure, quasi-static [3] and the high pressure, non-equilibrium state [4].

In order to investigate the relevance of the strong metal-support interaction (SMSI, [5]) induced encapsulation of platinum particles we recently performed a series of operando TEM experiments. Encapsulation by a thin layer of partially reduced support material has previously been used as a rationale to explain specific catalytic behavior, e.g. suppressed or enhanced catalytic selectivity [6] or resistivity against sintering effects [7]. Indeed, coverage of metal particles alters their adsorption behavior, accessibility of active sites and can act as a protective layer against sublimation.

The SMSI state that is induced during high-temperature reductive activation (**Fig. 1 A**) can be reverted by a sequence of high temperature oxidative treatment and low temperature reduction. Although this treatment does in fact reliably restore the unencapsulated state of platinum, little is known about the mechanism responsible for overlayer retraction. Our experiments revealed that the encapsulated state of platinum particles is maintained when the catalyst is exposed to oxygen at high temperature, in this case by an oxidized form of the SMSI layer (**Figure 1 C**). Thus, there exist stable overlayer configurations under hydrogen as well as under oxygen at high temperature. However, questions remained regarding the stability of an encapsulated state under reactive redox conditions, i.e. to the simultaneous presence of hydrogen and oxygen. As will be shown, the system adapts a dynamic behavior and thus reveals yet another manifestation of metal support interactions. They can be linked to catalytic activity and determine particle dynamics and migration behavior (**Figure 1 B**) and can only be observed if the chemical potential of the constituent gas species, and thus the gas pressures and temperature, are sufficiently high to overcome the static, quasi-equilibrium state. The study shows that the state of the

catalyst under reactive conditions differs significantly from the well-studied, classical SMSI state, highlighting the need for operando TEM studies for our understanding of the behavior of an active catalyst and thus, the structure activity correlation relevant for catalytic function [8].

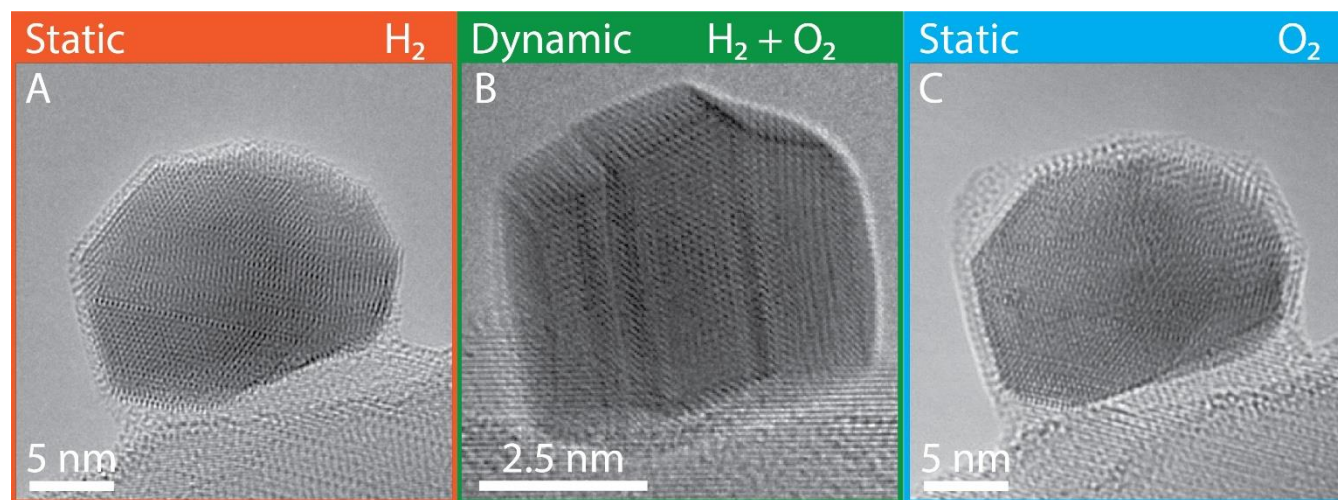


Figure 1 *in situ* TEM micrographs of the platinum titania system at elevated temperature. **A** under hydrogen atmosphere, **B** under hydrogen oxygen mixed feed, **C** under oxygen atmosphere.

References:

- [1] Y Kuwauchi et al., *Angew. Chemie Int. Ed.* **51**(31), p. 7729. doi: 10.1002/anie.201201283
- [2] R Spruit, Delft University of Technology (2017).
- [3] PL Hansen et al., *Science* **295**(5562) (2002), p. 2053. doi: 10.1126/science.1069325
- [4] S Zhang et al., *Nano Lett.* **16**(7) (2016), p. 4528. doi: 10.1021/acs.nanolett.6b01769
- [5] SJ Tauster, SC Fung and RL Garten, *J. Am. Chem. Soc.* **100**(1) (1978), p. 170. doi: 10.1021/ja00469a029
- [6] JC Matsubu et al., *Nat. Chem.* **9**(2) (2017), p. 120. doi: 10.1038/nchem.2607.
- [7] H Tang et al., *Angew. Chemie - Int. Ed.* **55**(36) (2016), p. 10606. doi: 10.1002/anie.201601823.
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