Comparison of Atomic Scale Dynamics for 14 Kinds of Transition Metal Nanocatalysts

Cao, K.[1], Zoberbie, T.[1], Biskupek, J.[1], Botos, A.[2], McSweeney, R.L.[3], Kurtoglu, A.[2], Stoppiello, C.[2], Markevich, A.V.[2], Besley, E.[2], Chamberlain, T.W.[3], Khlobystov, A.N.[3] and Ute, K.[1]

[1] Ulm University, Electron Microscopy of Materials Science, Germany, [2] University of Nottingham, School of Chemistry, United Kingdom, [3] University of Nottingham, School of Chemistry, United Kingdom

Catalysis of chemical reactions by nano-sized clusters of transition metal catalysts holds the key to the long-term provision of sustainable energy and the continued expansion of our technological horizons. However the atomistic pathways of chemical transformations facilitated by nanocatalysts still remain largely unknown due to uncertainties associated with the highly labile structures of the metal nanoclusters, changing during the reaction significantly, affecting the reaction pathways. [1]

The introduction of hardware aberration correctors into the TEM technology together with the use of carbon-nano-test-tubes offer a radically new way to study and compare chemical processes at the atomic level.[2] Our use of a precisely shaped electron beam to supply the energy to drive chemical reactions and capture their progress in real time coupled with a detailed understanding of the mechanisms by which the electron beam interacts with atoms of the sample, enables the determination of fundamental thermodynamic parameters and reveals mechanisms of chemical reactions at the single-molecule level.[3-5]

In this study we reveal and explore reactions of nm-sized clusters of 14 technologically important metals in transparent carbon-nano-test-tubes using time-series imaging by a FEI Titan 80-300 kV at 80 kV employing the electron beam simultaneously as an imaging tool and stimulus of the reactions.[6,7] We discovered the metal-carbon bonding and their dynamics at the scale of the single atoms and arranging, for the first time, the transition metals in the order of their binding with carbon and their catalytic activity, which differ significantly from the order in the Periodic Table of Elements. It reveals that the metal nanoclusters become more dynamic once they are engaged in reactions with carbon - one of the most unexpected outcomes of this analysis, having significant implications for understanding the atomistic workings of catalytic cycles at the nanoscale. Equally important are our findings that the tiny metal clusters obey the Sabatier principle as heterogeneous catalysts (with three important exceptions), despite the absence of a well-defined surface, and that different metals exhibit drastically different tendencies towards defect formation in the graphenic lattice of the nanotube. This knowledge provides a new guide for the development of better catalysts for important processes involving C-C bond dissociation and formation, such as cracking and reforming that can now be rationally designed and tested on the basis of our atomic-scale experiments.

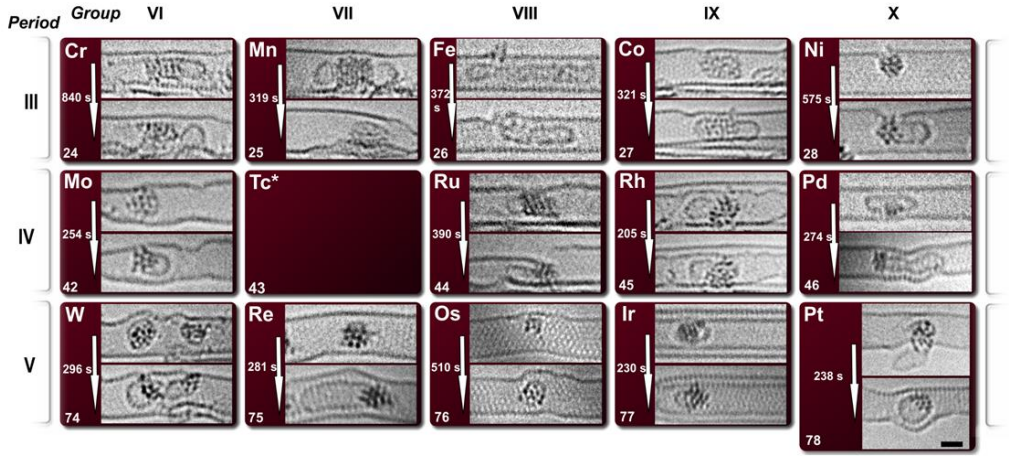

Figure 1: Typical examples of 80 keV TEM images of the 14 transition metal nanoclusters highlighting the different catalytic behaviours. Scale bar, 1 nm.

References

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