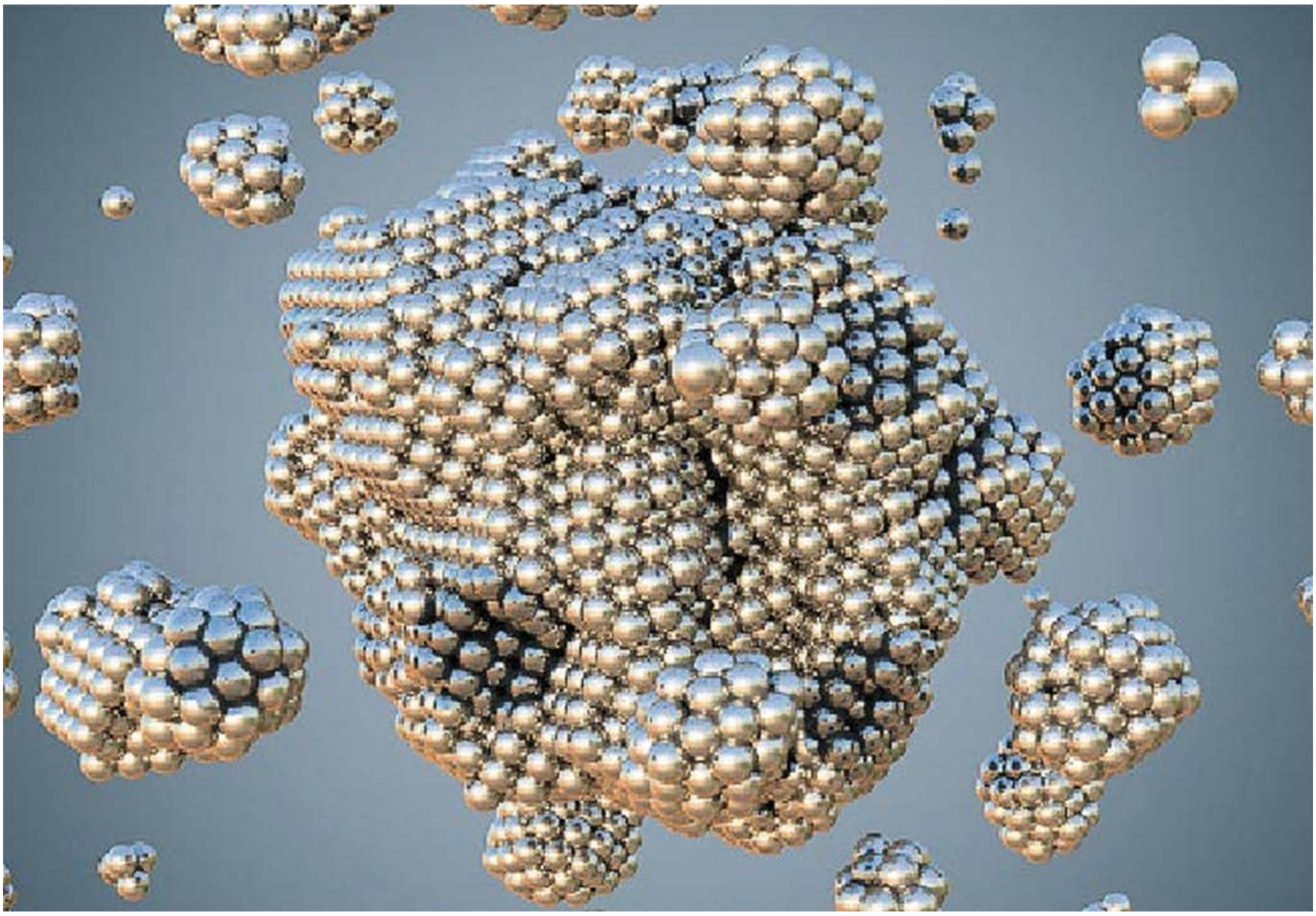

Figure 1: Illustration of nanosized clusters of transition metals.

The Private Life of Nanoclusters

A team of researchers finds a new table of elements for the catalytic activity of transition metals

September 4th, 2018 - The atomic-scale dynamics of metal nanoclusters determine their functional and chemical properties, such as catalytic activity. Indeed, many key industrial processes currently rely on nanocatalysts:the Fischer-Tropsch process on Fe, the water-gas shift reaction or methanol synthesis on Cu, and oxygen reduction in fuel cells on Pt/Co, just to name a few. With latest estimates indicating that catalytic chemical reactions contribute 30–40% of the global gross domestic product (GDP), revealing nanocluster's catalytic behaviours at the level of the single atomis an urgent task. However, the complex challenges are nanocatalyst's non-uniform structures coexisting within the same sample and their highly dynamic nature during catalysis. (And this made elucidation of the exact atomistic catalytic mechanisms virtually impossible until the German-British team, most of them are also author of the current Nature Communication paper) discovered that the electron beam in the atomic-resolution low-voltage transmission electron microscopy experiment acts simultaneously as the probe to image and the source of energy to drive the reaction; in fact they succeeded in filming reactions of molecules (1). (doi: 10.1021/acsnano.6b08228)

In their latest work the team applied their strategy on the comparison of atomic scale dynamics for the middle and late transition metal nanocatalysts, published in Nature Communications (2). (DOI: 10.1038/s41467-018-05831-z) Their analysis of the dynamical behaviour in atomically resolved time-series of TEM images revealed chemical transformations promoted by the different metal nanoclusters. The analysis enabled the researchers to rank 14 different metals both in order to their bonding with carbon (3) and their catalytic activity, showing significant variation across the Periodic Table of Elements. The complex atomic dynamics revealed directly by imaging in real time sheds light on atomistic workings of nanocatalysts, with key features mirroring heterogeneous catalysis, as shown by the Sabatier principle (4) – the cornerstone of heterogeneous catalysis that we can now demonstrate at the atomic-scale.

Ute Kaiser, Professor in Experimental Physics and Leader of the Group of Electron Microscopy for Materials Science at Ulm University, who conducted the studies in the frame of the SALVE project (www.salve-project.de) says "Aberration-corrected transmission electron microscopy in combination with carbon nanotubes as test reactors now allowed us for the first time to study systematically the changes in the atomic structure of metal nanoclusters caused by their catalytic activity and their defect formation rate. Our extensive systematic study enabled fundamental conclusions for the understanding of catalysis at the level of the single atoms. We found that also the metal catalysts are changing during their reaction with carbon and proposed a new classification of the transition metals with respect to their catalytic activity." Professor Kaiser has recently been appointed a Honorary Professor at the University

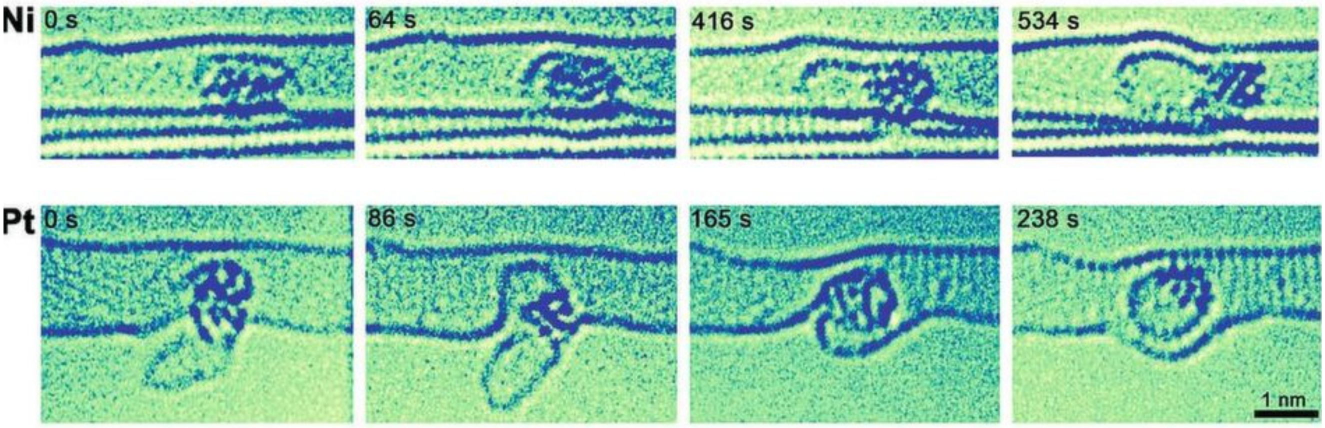

Figure 2: Time-series images of nanocrystals during continuous irradiation. First line: A Ni nanocluster abstracts carbon atoms from a point of contact with the host NT and promotes the formation of a new carbon structure. Second line: A Pt nanocluster abstracts carbon atoms from the host NT, restructures them into a carbon shell, incorporates them into the host NT and forms a new carbon shell inside the NT.

of Nottingham in recognition of her rich contribution to the collaboration between Ulm and Nottingham, spanning over nearly a decade, that delivered over 20 high-calibre joint publications on the topic of electron microscopy for molecules and nanomaterials.

Most of the TEM data was analyzed, compiled and interpreted by Kecheng Cao, PhD student at Ulm University. Kecheng Cao says: „In the last year I have combined data of 14 transition metals to analyze the catalytic behavior in the carbonic lattice of the nanotubes. I have isolated several processes that occurred differently depending on the presence of the transition metal. The compilation of all data resulted in clear correlations, which were never observed with other technologies before. This shows that the aberration corrected TEM is a top tool to study the dynamics of transition metals in nanocontainers."

Andrei Khlobystov, Professor of Nanomaterials and Director of the Nanoscale & Microscale Research Centre (nmRC) at the University of Nottingham says: "From the point of view of fundamental chemistry, a global comparison of chemistry of transition metals across the Periodic Table has always been extremely challenging because most metal nanoclusters and their organometallic compounds are highly sensitive to air, leading to substantial uncertainties in any laboratory experiment attempting systematic measurements and comparison of metal-carbon bonding. In our study, instead of laboratory flasks or test tubes, we employ the World's tiniest test tubes – single walled carbon nanotubes – atomically thin cylinders of carbon with internal diameters of 1-2 nm that have held a Guinness World Record since 2005. The combination of the nano test tube and TEM allows us to watch not only the dynamics of metal nanoclusters but also their bonding with carbon that shows a clear link with the metal's position in the Periodic Table. Therefore, our study provides a first qualitative glimpse of a global perspective of metal-carbon bonding."

Elena Besley, Professor of Theoretical and Computational Chemistry at Nottingham says "Reaching inside the tiniest building blocks of metals, this study demonstrated that metal nanoclusters entrapped in carbon nano test tubes provide a universal platform for studying organometallic chemistry and enable a direct comparison of the bonding and reactivity of different transition metals as well as elucidation of the structure-performance relationship for nanocatalysts – vital for the discovery of new reaction mechanisms and more efficient catalysts of the future."

Unravel the intimate lives of the tiniest building blocks of metals, this study demonstrated that metal nanoclusters entrapped in carbon nano test tubes provide a universal platform for studying organometallic chemistry and enable direct comparison of the bonding and reactivity of different transition metals as well as elucidation of the structure-performance relationship for nanocatalysts – vital for the discovery of new reaction mechanisms and more efficient catalysts of the future.

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