Periodic Table of Nanocatalysts

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August 23, 2018 – Researchers from Ulm and Nottingham have compared nanoclusters of 14 transition metals inside carbon nanotubes, used as nano test tubes, by C_S-corrected HRTEM at 80 kV. The electron beam both drove and imaged the reactions. The clusters became more dynamic as soon as they bonded to carbon, the metals could be ranked by their bonding with carbon and by their catalytic activity, and the two rankings formed the volcano plot known from heterogeneous catalysis, with the group 10 metals Ni, Pd and Pt as exceptions.

Catalysts made of tiny metal clusters drive a large share of the chemical industry, yet nobody can say exactly what their active centers look like while they work. A cluster of a few dozen atoms keeps changing its shape and size during a reaction, so its structure at the start says little about its activity. Researchers from the Electron Microscopy of Materials Science group at Ulm University and the University of Nottingham in the UK have now watched nanoclusters of 14 transition metals at work, each trapped inside a carbon nanotube that served as a miniature test tube. With an image-side C_S-corrected high-resolution transmission electron microscope (HRTEM) operated at 80 kV, they used the electron beam at the same time to trigger the reactions and to image them atom by atom. The comparison ranked the metals by how strongly they bond to carbon and by how actively they rebuild it, across a whole block of the periodic table.

Imaging metal–graphene interactions at atomic resolution has become a key aim of high-resolution TEM[1], and trapping metal atoms inside carbon nanotubes is a powerful way to study their structure and chemistry in detail[2]. In situ TEM can follow catalysts during reactions[3]–[5], but the influence of the electron beam itself has largely been neglected, although it can change the dynamics and performance of nanocatalysts dramatically.

Nano test tubes and an electron beam

The team filled carbon nanotubes with an inner diameter of about 1.4 nm with clusters of 20 to 60 atoms of each metal, from chromium to platinum (Fig. 1). The approach builds on ChemTEM, in which the electron beam triggers, controls and images chemical reactions at the same time[6]. The reaction rates are directly proportional to the dose rate of the beam, which is set by the microscope, so the results of single reactions can be captured as time series and combined into stop-frame movies. Each reaction starts when a fast electron transfers momentum directly to one atom and pushes it from its place, which may break a bond.

How much energy an electron can hand over depends on the mass of the atom. At 80 keV, a transition metal atom receives at most 1 to 4 eV. A carbon atom receives up to 15.8 eV, but in a perfect nanotube that is still below the roughly 17 eV needed to knock it out, so empty, defect-free tubes stay intact. Whatever happens to the tube walls is therefore caused by the metal. How these numbers compare with the bonding inside the metal clusters is explained in the box.

Beam energy versus metal bonding

The maximum energy $E_{T,max}$ that an 80 keV electron transfers to a metal atom falls slowly along a period, from 3.64 eV for Cr to 3.23 eV for Ni, but quickly down a group, from 3.23 eV for Ni to 1.78 eV for Pd and 0.97 eV for Pt. To move a metal atom out of its cluster for good, its metal–metal bonds must break, which is measured by the cohesive energy E_{coh} of the metal, between 2.9 eV for Mn and 8.9 eV for W.

The ratio $E_{T,max}/E_{coh}$ is therefore a rough guide to how strongly the beam stirs a cluster. Only for Mn does the transferred energy exceed the cohesive energy (118 %); Cr, Fe, Co and Ni follow with 72 to 89 %, while all other metals stay below 50 %, down to 12 % for W and Os. The experiments matched this simple picture with two exceptions, Fe and Ni, which moved less than expected. Electron-beam-driven quasi-melting was also compared with thermal melting of clusters in the Supplementary Information.

Fourteen metals under the beam

After 40 to 50 s of irradiation, corresponding to a dose of about 4 to 5 × 10^7 electrons per nm^2, the initially well-ordered clusters had changed to very different extents (Fig. 2a). Manganese was by far the most mobile. A compact Mn crystal became disordered after 15 s, broke into smaller clusters within 40 to 190 s and finally fell apart into single atoms after 210 to 230 s (Fig. 2b, Video 1). Cr and Co clusters also turned into an amorphous, liquid-like state but did not dissociate completely. All other metals kept changing their shapes, yet remained crystalline. The ratio of transferred energy to metal bonding explains most of this, but not all of it: Fe and Ni moved less than expected. The behavior of a cluster therefore depends not only on the metal itself but also on how it interacts with the surrounding nanotube.

How the metals attack the tube

The metal clusters touch the carbon atoms of the tube wall and make defects there, at rates that differ widely from metal to metal (Fig. 3a). From more than 120,000 HRTEM images recorded in time series, the researchers identified five stages of a common sequence (Fig. 3b). In stage 1, one to four carbon atoms are lost and the cluster bonds to the defect, still separated from the opposite wall by a van der Waals gap of 0.3 nm. In stage 2, the cluster bonds across the whole channel and the gap closes. In stage 3, the tube contracts sharply around the cluster and metal atoms poke through the wall. In stage 4, almost all carbon around the cluster is gone, and the cluster is held only by the two severed tube ends, until in stage 5 the test tube breaks apart completely. Fe and Ni reached stage 5 and ruptured the nanotubes during

imaging. The behavior was reproducible from tube to tube as long as the clusters had about the same size. Comparing which stage each metal reached, and how fast, gave the first ranking (series 1):

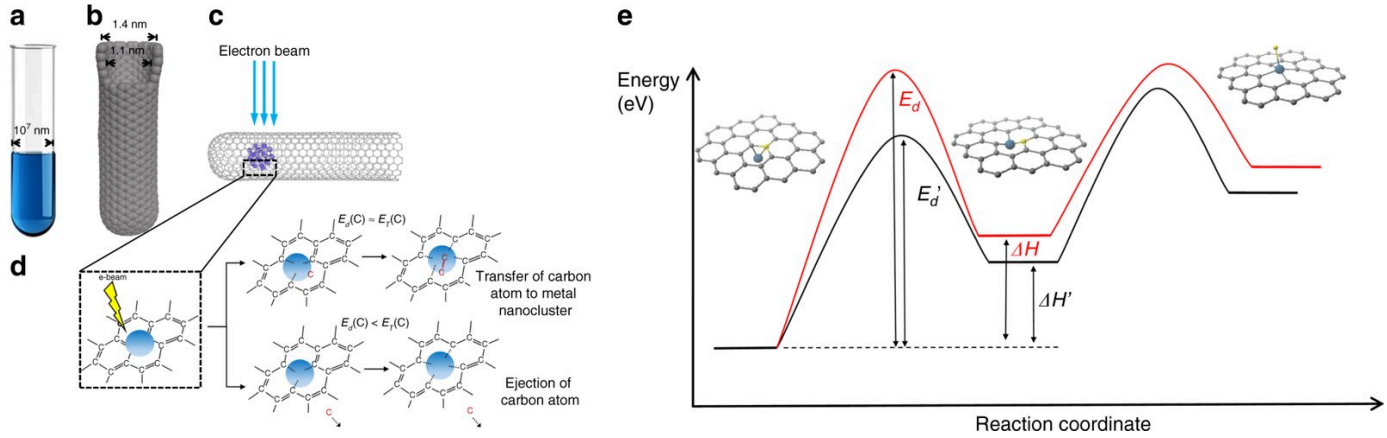

Fig. 1: Nano test tubes and the electron beam.

Ni > Pt > Os > Fe ⩾ Re > Mn ⩾ Co > Ru ⩾ Mo > W > Cr > Ir ⩾ Rh > Pd

For a defect to appear, a C–C bond must break first, and the metal then bonds to the dangling carbon bonds (Fig. 1d). The metal plays a double role: it lowers the energy needed to displace a carbon atom, and it stabilizes the vacancy through metal–carbon (M–C) bonds (Fig. 1e). Both roles are linked by the Bell–Evans–Polanyi principle, which relates the activation energy of similar reactions to their enthalpy, so the ease of defect formation is ultimately set by the bonding between cluster and carbon. Strong bonding of metal atoms to single vacancies[7],[8] and double vacancies[9],[10] in graphitic lattices had been shown before for isolated cases[11]–[13]. Earlier ChemTEM studies of single metals, nickel[14],[15] and rhenium[16], and of the metal triads W–Re–Os[17],[18] and Fe–Ru–Os[18] had hinted at a link with the position of the metal in the periodic table[17],[18]. A calculation for a single ruthenium atom shows how much the metal helps (box below, Fig. 4).

Theory: a metal atom helps break the tube

Calculations for a single ruthenium atom on a graphitic lattice show both roles of the metal (Fig. 4). Without the metal, knocking out a carbon atom requires 22.3 eV; next to the Ru atom only 19 eV. The metal also stabilizes the resulting single vacancy: its formation energy drops from 7.85 eV to 1.39 eV. A second carbon atom can then be ejected, and the double vacancy is stabilized in the same way, with 2.33 eV instead of 7.88 eV.

How strongly a given metal bonds to carbon thus decides how stable the defect is, how quickly further carbon atoms are knocked out next to it, and into which new carbon structures the tube evolves, such as protrusions, carbon shells or internal nanotubes.

Organometallic chemistry suggests only trends within a group, for example that heavier transition metals form stronger M–C bonds[19]. The global view of the new study showed no simple correlation between a metal's position in the periodic table and its efficiency in attacking carbon. This points to a complex interplay of valence electron configuration, electronegativity and atomic size, as discussed in comparative theoretical studies of transition metals on carbon[7]–[10].

Three ways to rebuild carbon

Besides making defects, the clusters convert one form of carbon into another (Fig. 5a). The researchers found three typical processes (Fig. 5b). In process 1, a Mn cluster pushed its two own carbon shells into the nanotube wall, the first within 148 s and the second within 171 s, so that the lower wall warped; Cr and Fe behaved similarly but less strongly. Process 2 runs the other way: a Ni cluster about 1 nm in size pulled carbon atoms out of the tube wall and grew a new carbon shell 1.18 nm long within 534 s (Video 2), its direction steered by the confining tube. Re, Os, W and Co did the same, Re much faster, forming a long single-walled nanotube, while Mo, Ru and Pd moved carbon onto existing shells. Process 3 combines both: a Pt cluster sitting halfway through a hole in the wall built an inner shell from tube carbon while incorporating its outer shell into the tube, forming a loop-and-hole structure after 86 s that was sealed off at 199 s. At 238 s, the Pt sat inside an internal carbon shell, and a small protrusion had formed on the tube (Video 3).

Clusters that change while they work

Because the HRTEM images show the metal and the carbon at the same time, the researchers could follow the cluster structure during carbon growth. Most of the 14 clusters became more dynamic as soon as they bonded to carbon and started to rebuild the tube. The W and Ni clusters, for example, changed their structure continuously and rapidly while new carbon grew from their surface (Fig. 5b, Videos 2 and 4). This is exactly the key challenge of nanocatalysis, metal clusters changing their atomic structure during the reaction, and it is very similar to what theory had predicted[20],[21]. Such ever-changing clusters also explain why nanotubes of one chirality are hard to grow.

The observations also gave direct evidence of dynamic single-atom catalysis, predicted by theory[22]. In process 3, the Pt cluster behaved like a viscous liquid that dispersed into single

atoms (Fig. 5b, 118 s, green arrow) and later gathered again (238 s). Such single atoms are expected to coexist with nanocatalysts and to play an important role because of their high surface energy[23]. This highly dynamic nature of metal clusters could be harnessed to improve nanocatalysts[24]. Inside the nanotubes, none of the 14 metals showed significant Ostwald ripening or coalescence, two effects that usually limit catalysts in practice, so confinement could lead to more durable and reusable nanocatalysts. The conditions were also milder than in earlier environmental TEM studies of nanotube growth, room temperature and 80 keV, yet small W, Ni and Re clusters were active enough to grow carbon structures, a reminder that the beam cannot be neglected in such experiments.

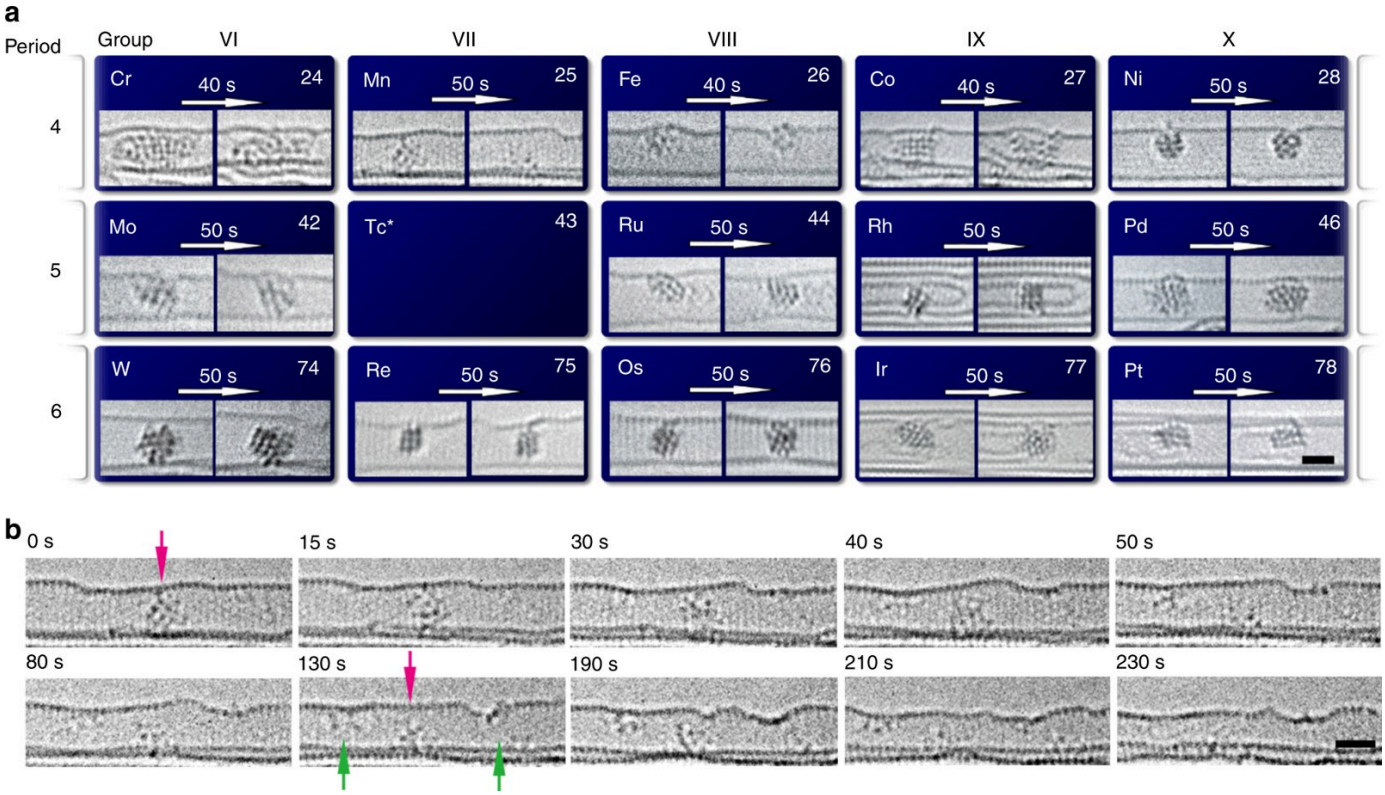

Fig. 2: Cluster dynamics of 14 metals.

Ranking the catalysts

Since all measurements used the same beam energy, dose rate, temperature and pressure, the metals could be compared directly. Measured by how much the carbon structure grew or shrank, the catalytic activities followed a second ranking (series 2):

Pt > Re > Mn > Fe ≫ Ni > Co > Pd > Ru > Mo > W > Os > Cr > Ir = Rh

Pt and Re were the most active, consistent with the importance of Pt–Re catalysts in industrial reforming and other reactions that transform C–C bonds.

A volcano at the nanoscale

If series 1 reflects the bonding energy between cluster and carbon, it should relate to series 2 in a volcano-shaped plot. This is the Sabatier principle: a good catalyst binds neither too strongly nor too weakly[25], so that it holds the reactants and still releases the products. The principle is firmly established in heterogeneous catalysis[26], guides the discovery of new catalysts[27] and also applies to the growth of carbon nanostructures[28]. With their constantly changing surfaces, however, it was uncertain whether nanoclusters would obey it. The 14 metals produced the classic volcano shape (Fig. 6), showing that even clusters of 20 to 60 atoms act more like heterogeneous than like homogeneous catalysts.

Only Ni, Pd and Pt, the three metals of group 10, were more active than the Sabatier principle predicts. They have the most d-electrons of the metals studied, and the filling of the d-orbitals sharply reduces their contribution to metallic bonding[29]. The high d-orbital occupancy allows only transient interactions with carbon and lets carbon atoms diffuse fast through the cluster, so no well-defined interface between metal and carbon can form. This explains why the group 10 metals appear to disobey the rule.

TEM: 14 metals in nano test tubes at 80 kV

Single- and double-walled carbon nanotubes were opened by heating in air at 600 °C or 570 °C. The metals were introduced as small metal-containing molecules: the tubes were sealed with a twofold excess of the compound in an evacuated glass ampoule (10^{-6} mbar) and heated above its sublimation point for three days, then washed with tetrahydrofuran to remove material from the outside. The electron beam broke the molecules down into pure metal clusters; heating to 500 °C under argon gave identical clusters. Energy-dispersive X-ray spectroscopy (EDX) on a JEOL 2100F at 100 kV confirmed the metals.

HRTEM imaging used an image-side C_S-corrected FEI Titan 80-300 (today Thermo Fisher Scientific) at 80 kV, with a modified extraction voltage of the electron source to improve the information limit, and an image-side C_S-corrected, monochromated Zeiss Libra 200MC. Exposure times were 0.2 to 2 s per image at electron fluxes of 0.9 to 1.1 × 10^6 electrons per nm^2 and second, all at room temperature. Reproducibility was checked from area to area and from tube to tube.

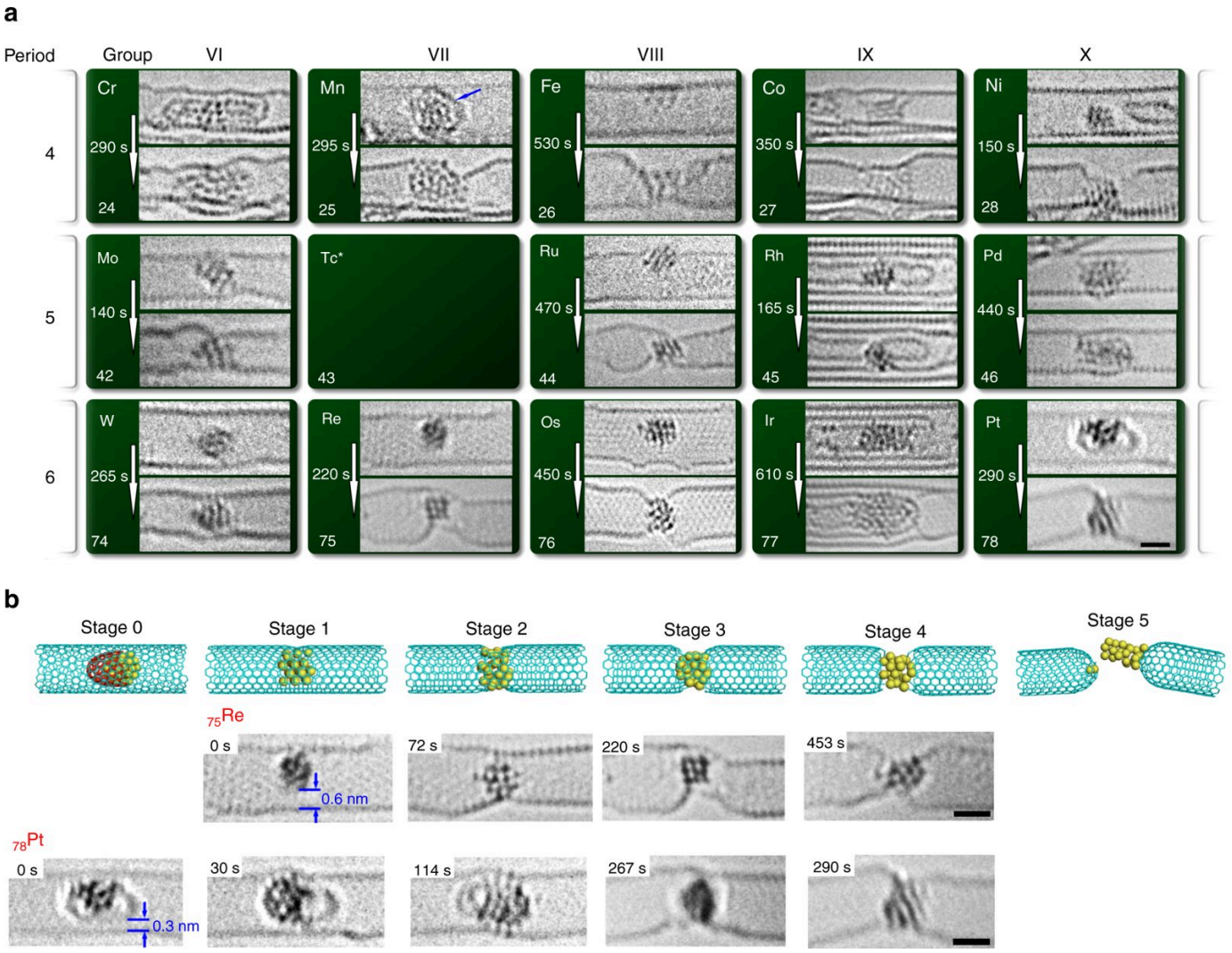

Fig. 3: Defect formation in five stages.

What it opens up

Recent advances in TEM together with nano test tubes offer a new way to study and compare chemical processes at the atomic level[30]. Using a precisely shaped electron beam to drive reactions and record them in real time, combined with a detailed understanding of how the beam interacts with atoms[1],[31],[32], makes it possible to determine thermodynamic parameters[1],[13] and to reveal reaction mechanisms at the single-molecule level[16],[33],[34].

"For over six centuries scientists have been using laboratory glassware (test tubes, retorts, flasks, beakers etc.) to discover and investigate the properties of chemical elements and the mechanisms of chemical reactions. These traditional methods work well for reactions where the key parameters stay the same, but in nanocatalysis owing to the largely unpredictable and dynamic behaviour of the active centres, new approaches are required," said the senior authors, Ute Kaiser, professor of electron microscopy at Ulm University, and Andrei Khlobystov, professor of chemistry at the University of Nottingham.

"The new study covers the whole block of early and middle transition metals consisting of three periods and five groups, which, for the first time, enabled a detailed analysis of global trends within the family of transition elements," said Kecheng Cao from Ulm University, first author of the study. "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 clusters of metals 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."

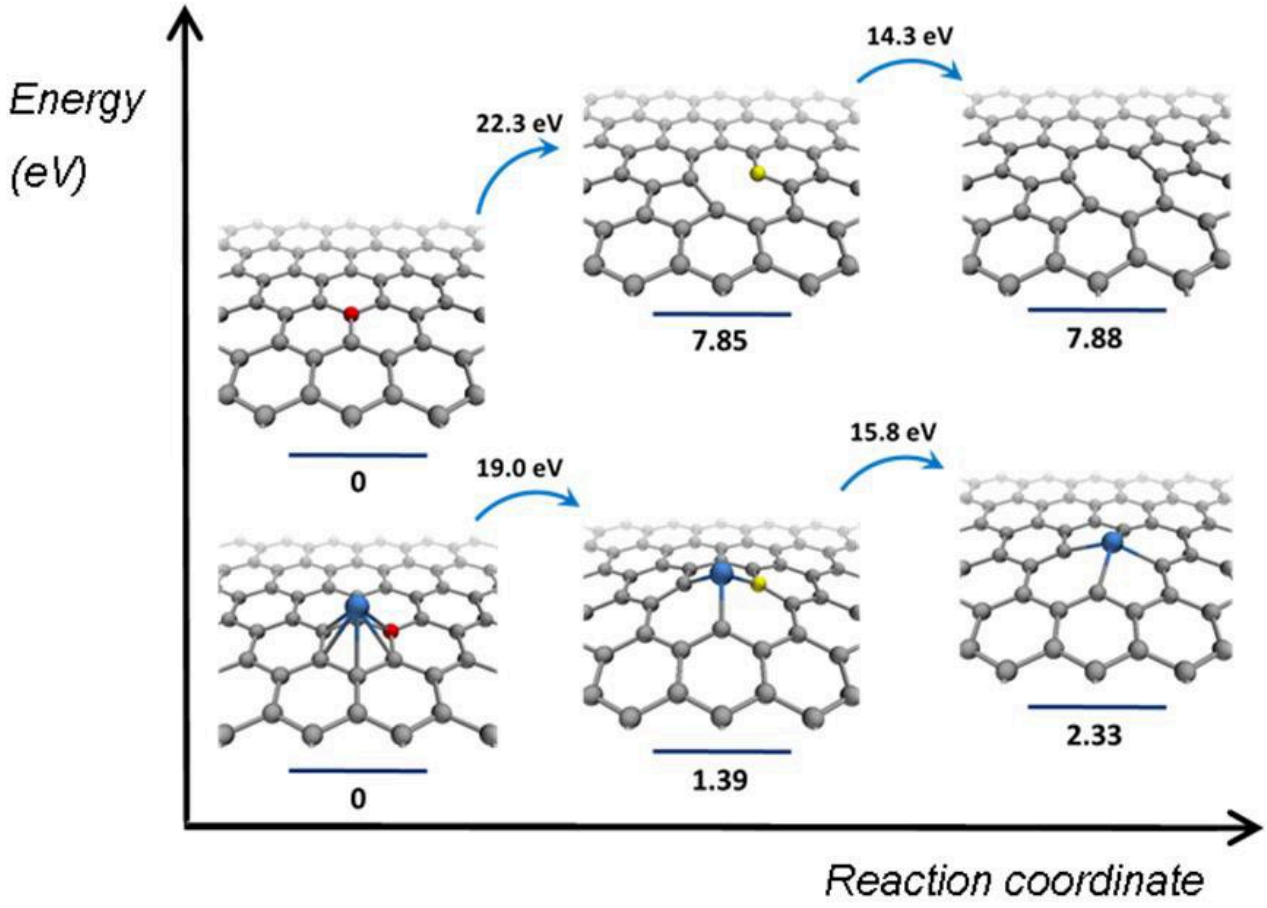

Fig. 4: Ru lowers the knock-out energy.

The rankings give a new guide for better catalysts in processes that break and form C–C bonds, such as the cracking and reforming of hydrocarbons that underpin the petrochemical industry. Such catalysts could be designed rationally and tested in ChemTEM experiments at the atomic scale, and nanotubes that keep clusters from ripening could make them last longer. "This knowledge provides a new guide for the development of better catalysts for important processes involving C–C bond dissociation and formation," the authors conclude.

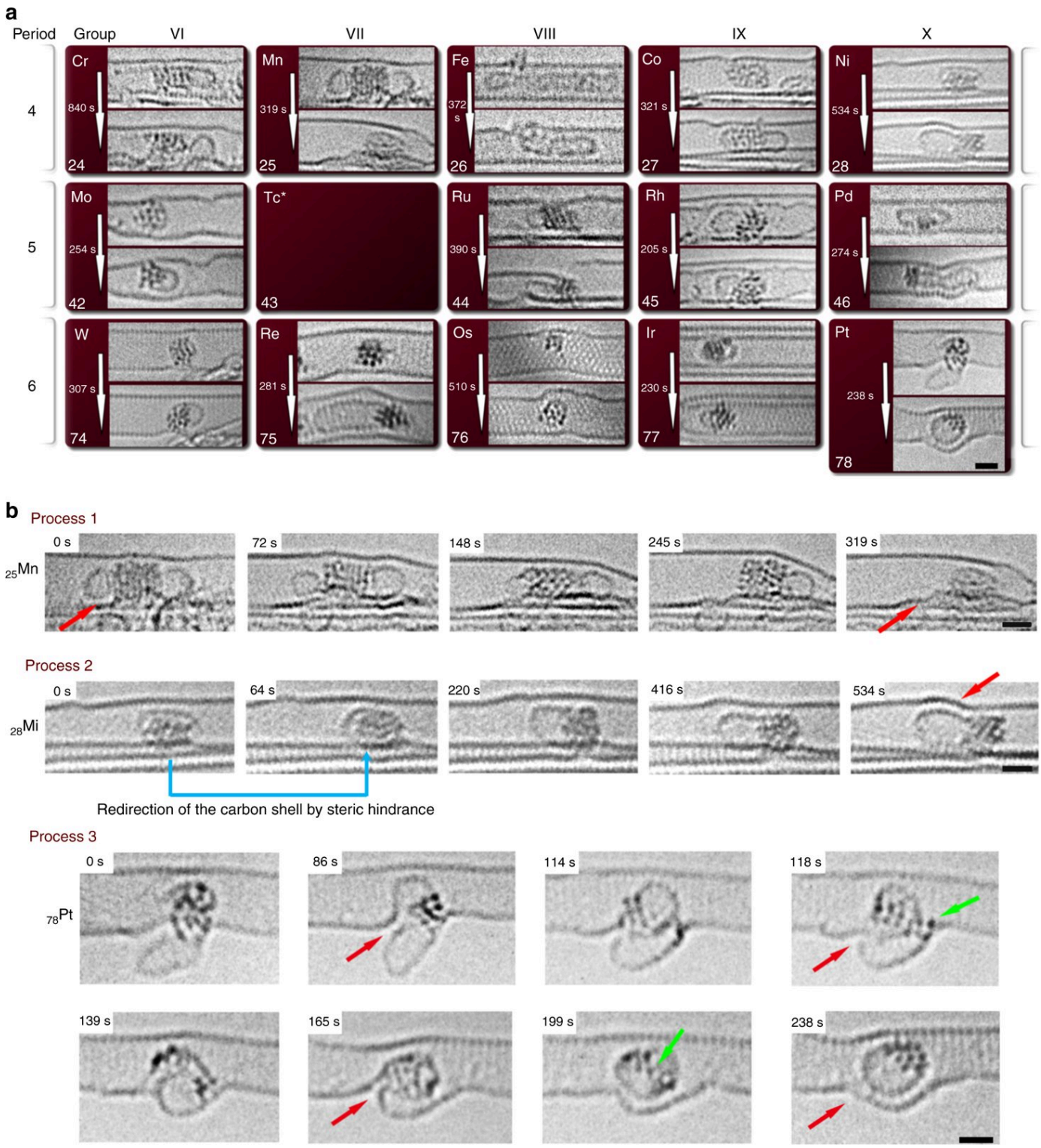

Fig. 5: Catalytic processes 1, 2 and 3.

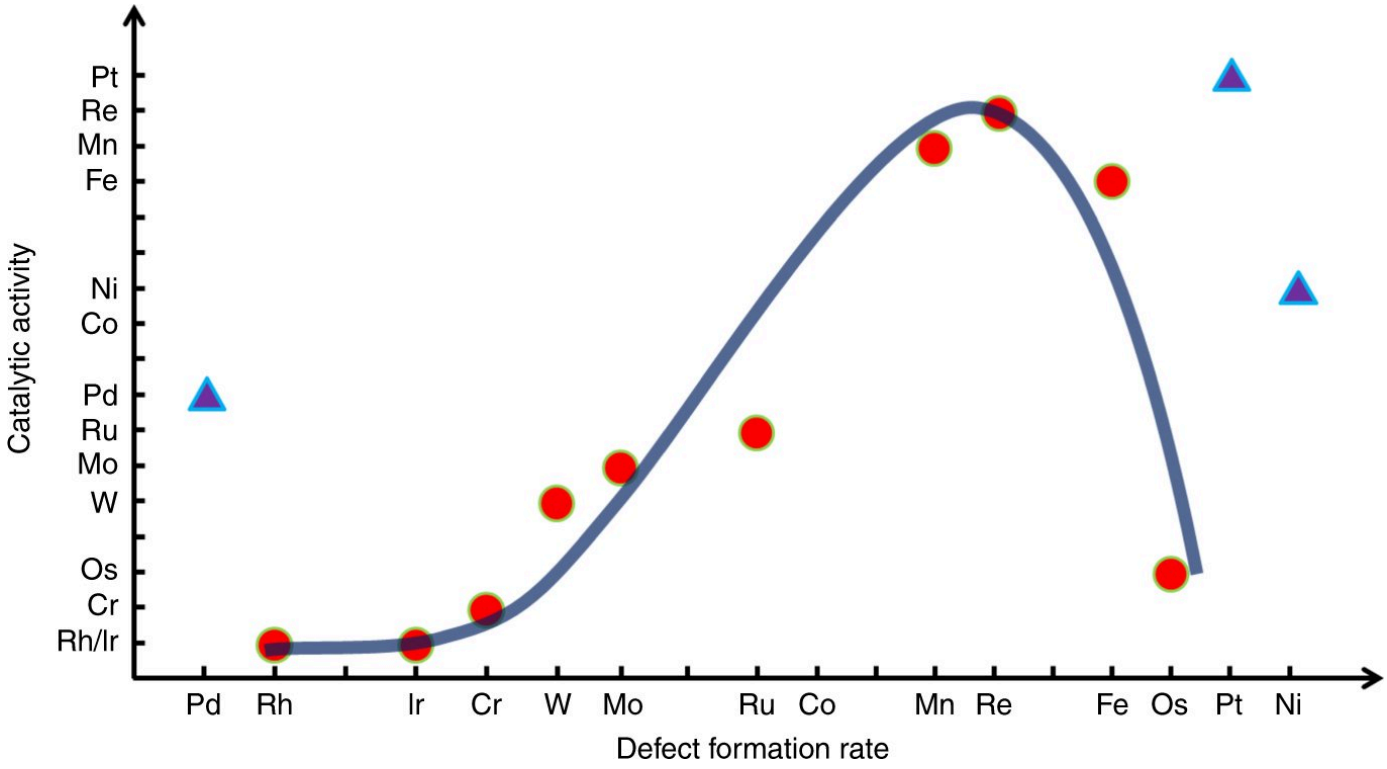

Fig. 6: Activity versus defect formation.

Resource

Cao, K., Zoberbier, T., Biskupek, J., Botos, A., McSweeney, R. L., Kurtoglu, A., Stoppiello, C. T., Markevich, A. V., Besley, E., Chamberlain, T. W., Kaiser, U., Khlobystov, A. N. (2018).
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