doi:10.1017/S1431927620024228
Microsc. Microanal. 26 (Suppl 2), 2020

Filming Chemical Reactions at the Single-molecule Level Using Electron Beam

Andrei Khlobystov

University of Nottingham, Nottingham, England, United Kingdom

How do we know that molecules react in one way rather than another? Even in an ideal case, a reaction observed in a laboratory experiment by ensemble-averaging analytical techniques, such as spectroscopy or diffraction, can only support rather than confirm a proposed mechanism, as these macroscopic measurements are unable to rule out that an alternative atomistic mechanism may also exist that results in the same macroscale observation. In practice, definitive information about the mechanisms of intermolecular reactions can be provided only by a direct observation at the single-molecule level of the reactants transforming into products over time.

Transmission electron microscopy (TEM) is one of the most powerful methods to study chemistry of individual molecules as the electron beam enables near-atomic imaging of the molecules and simultaneously provides energy for the reaction. This approach, termed ChemTEM, is based on (i) entrapment of individual molecules in carbon nanotubes that allow control of positions and orientations of the molecules in the e-beam; (ii) direct momentum transfer from fast incident electrons (20-100 keV) to atoms; (iii) stop-frame filming of chemical bond dissociation and formation with spatiotemporal continuity at the single molecule level.

Previously, we demonstrated that kinetic energy transferred directly from the e-beam to atoms of the molecule, displacing them from equilibrium positions, triggers bond dissociation (C-H, C-D, C-C, C-Cl, C-S) and promotes various chemical reactions (halogen elimination, cycloaddition, polycondensation) which can be imaged concurrently with their activation by the e-beam and presented as stop-frame movies. Now we applied ChemTEM to individual metal atoms and small nanoclusters to unveil a number of fascinating phenomena at the atomic scale, including metal-carbon and intermetallic bond dynamics, key for fundamental understanding of atomistic mechanisms underpinning nanocatalysis and crystal formation.

Clear trends in bonding and reactivity between different metals and carbon demonstrated by ChemTEM open doors for studying organometallic reactions with atomic resolution and spatiotemporal continuity, from reactants through intermediates to products. New mechanistic understanding can help to optimise industrial processes involving transition metals, such as chemical vapour deposition, syngas conversion, enabled by ChemTEM which also is becoming a tool for discovery reactions leading to unprecedented products.

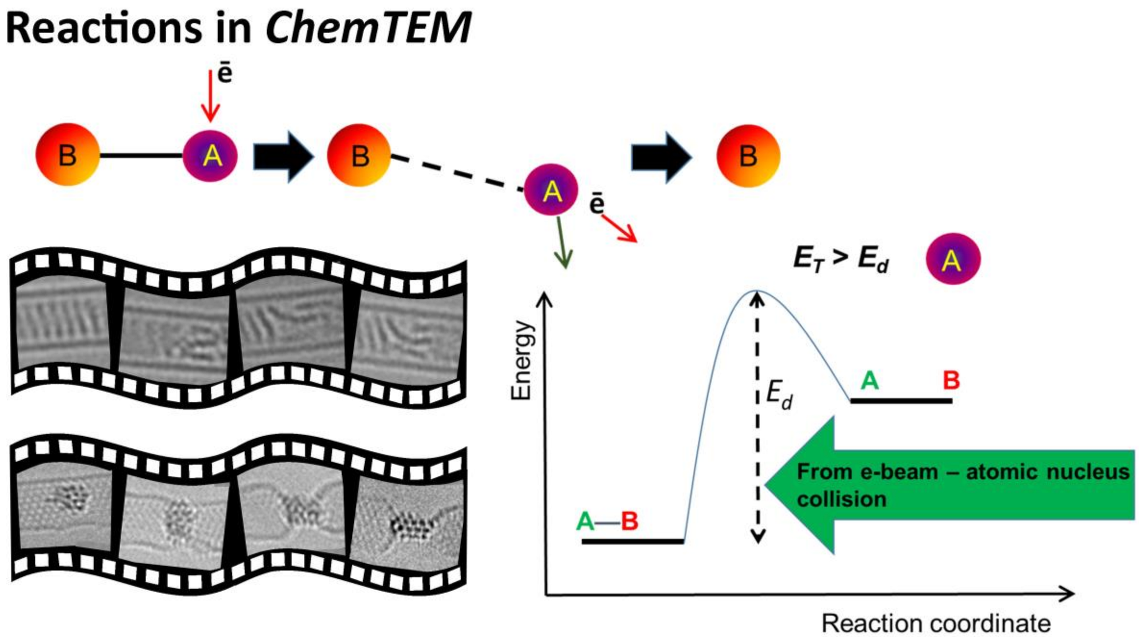

Figure 1. Using the electron beam of TEM as a source of energy and imaging tool at the same time, enables spatiotemporally continuous filming of chemical reactions, at the single-molecule level and in real time.

References

1) *Acc. Chem. Res.*, 2017, **50**,1797;
2) *ACS Nano*, 2017, **11**, 2509;
3) *Nano Lett.*, 2018, **18**, 6334;
4) *Nature Commun*. 2018, **9**, 3382;
5) *Science Adv.* 2020, **6**, eaay5849.

https://doi.org/10.1017/S1431927620024228 Published online by Cambridge University Press