C–H ACTIVATION

Together is better

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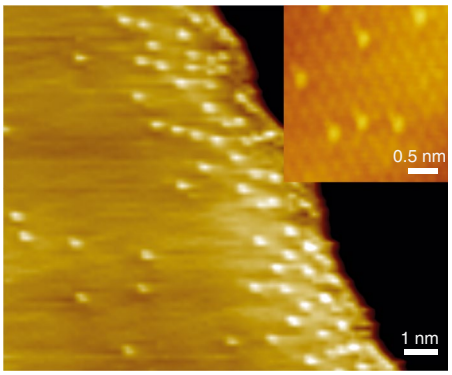

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Light alkanes from natural gas represent an important feedstock for the preparation of valuable chemicals. However, their upgrade is challenging because it requires the activation of relatively inert C–H bonds with expensive metal catalysts such as platinum, which undergo rapid deactivation via coking and the formation of carbonaceous deposits. Now, researchers at Tufts University, University College London, and Argonne National Laboratory have demonstrated that small amounts of platinum alloyed on copper surfaces in the form of single atoms (resulting in single-atom alloys) feature a remarkable resistance to coke formation during C–H activation processes.

To understand this phenomenon, the authors combined surface-science techniques and simulations to compare the catalytic activity of platinum, copper and their respective single-atom alloys during the decomposition of methyl iodide — used as a molecular probe. Temperature-programmed reaction experiments and density functional theory simulations of the energy associated with C–H bond cleavages on the catalyst's surface revealed that platinum–copper single-atom alloys have intermediate barriers for C–H activation, but are remarkably more resistant towards coke formation.

This is explained by the low affinity of copper towards carbon atoms adsorbed on the surface, as well as by its ability to promote C–C coupling reactions; the latter leads to the cleavage of surface-bound activated carbon species and the formation of higher hydrocarbons such as ethene, ethane and propene. Using the dehydrogenation of butane as an example, the researchers showed that the platinum–copper single-atom alloys were stable under realistic reaction conditions for about 50 hours on-stream and avoided the formation of a carbonaceous deposit. Conversely, platinum nanoparticles showed pronounced formation of coke and underwent rapid deactivation even during butane–deuterium isotope scrambling experiments.

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