Nanocluster discovery will protect precious metals

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Scientists have created a new type of catalyst that will lead to new, sustainable ways of making and using molecules and protect the supply of precious metals.

A research team from the University of Nottingham have designed a new type of catalyst that combines features that are previously thought to be mutually exclusive and developed a process to fabricate nanoclusters of metals on a mass scale.

In their new research, published today in *Nature Communications*, they demonstrate that the behavior of nanoclusters of palladium do not conform to the orthodox characteristics that define catalysts as either homogeneous or heterogenous.

Traditionally, catalysts are divided into homogeneous, when catalytic centers are intimately mixed with reactant molecules, and heterogenous, where reactions take place on surface of a catalyst. Usually, chemists must make compromises when choosing one type or another, as homogeneous catalysts are more selective and active, and heterogenous catalysts are more durable and reusable. However, the nanoclusters of palladium atoms appear to defy the traditional categories, as demonstrated by studying their catalytic behavior in the reaction of cyclopropanation of styrene.

Catalysts enable nearly 80 percent of industrial chemical processes that deliver the most vital ingredients of our economy, from materials (such as polymers) and pharmaceuticals right through to agrochemicals including fertilizers and crop protection. The high demand for catalysts means that global supplies of many useful metals, including gold, platinum and palladium, are become rapidly depleted. The challenge is to utilize each-and-every atom to its maximum potential. Exploitation of metals in the form of nanoclusters is one of the most powerful strategies for increasing the active surface area available for catalysis. Moreover, when the dimensions of nanoclusters break through the nanometre scale, the properties of the metal can change drastically, leading to new phenomena otherwise inaccessible at the macroscale.

The research team used analytical and imaging techniques to probe the structure, dynamics, and chemical properties of the nanoclusters, to reveal the inner workings of this unusual catalyst at the atomic level.

The team's discovery holds the key to unlock full potential of catalysis in chemistry, leading to new ways of making and using molecules in the most atom-efficient and energy-resilient ways.

The research was led by Dr. Jesum Alves Fernandes, Propulsion Futures Beacon Nottingham Research Fellow from the School of Chemistry, he said: "We use the most direct way to make nanoclusters, by simply kicking out the atoms from bulk metal by a beam of fast ions of argon—a method called magnetron sputtering. Usually, this method is used for making coatings or films, but we tuned it to produce metal nanoclusters that can be deposited on almost any surface. Importantly, the nanocluster size can be controlled precisely by experimental parameters, from single atom to a few nanometres, so that an array of uniform nanoclusters can be generated on demand within seconds."

Dr. Andreas Weilhard, a Green Chemicals Beacon postdoc researcher in the team added: "Metal clusters surfaces produced by this method are completely 'naked', and thus highly active and accessible for chemical reactions leading to high catalytic activity."

Professor Peter Licence, director of the GSK Carbon Neutral Laboratory at the University of Nottingham added: "This method of catalyst fabrication is important not only because it allows the most economical use of rare metals, but it does it the cleanest way, without any need for solvents or chemical reagents, thus generating very low levels of waste, which is an increasingly important factor for green chemical technologies."

The University is set to embark on a large-scale project to expand on this work with research which will lead to the protection of endangered elements.

Professor Andrei Khlobystov, principal investigator of MASI, said: "Our project is set to revolutionize the ways metals are used in a broad range of technologies, and to break our dependence on critically endangered elements. Specifically, MASI will make advances in: the reduction of carbon dioxide (CO_2) emissions and its valorisation into useful chemicals; the production of 'green' ammonia (NH_3) as an alternative zero-emission fuel and a new vector for hydrogen storage; and the provision of more sustainable fuel cells and electrolyser technologies."

Metal nanoclusters are activated for reactions with molecules, that can be driven by heat, light or electric potential, while tuneable interactions with support materials provide durability and reusability of catalysts. In particular, MASI catalysts will be applied for the activation of hard-to-crack molecules (e.g. N_2, H_2 and CO_2) in reactions that constitute the backbone of the chemical industry, such as the Haber-Bosch process.

More information: Blurring the boundary between homogenous and heterogeneous catalysis using palladium nanoclusters with dynamic surfaces, *Nature Communications* (2021). DOI: 10.1038/s41467-021-25263-6

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