Reusable catalyst makes C–H bond oxidation using oxygen easier and more efficient

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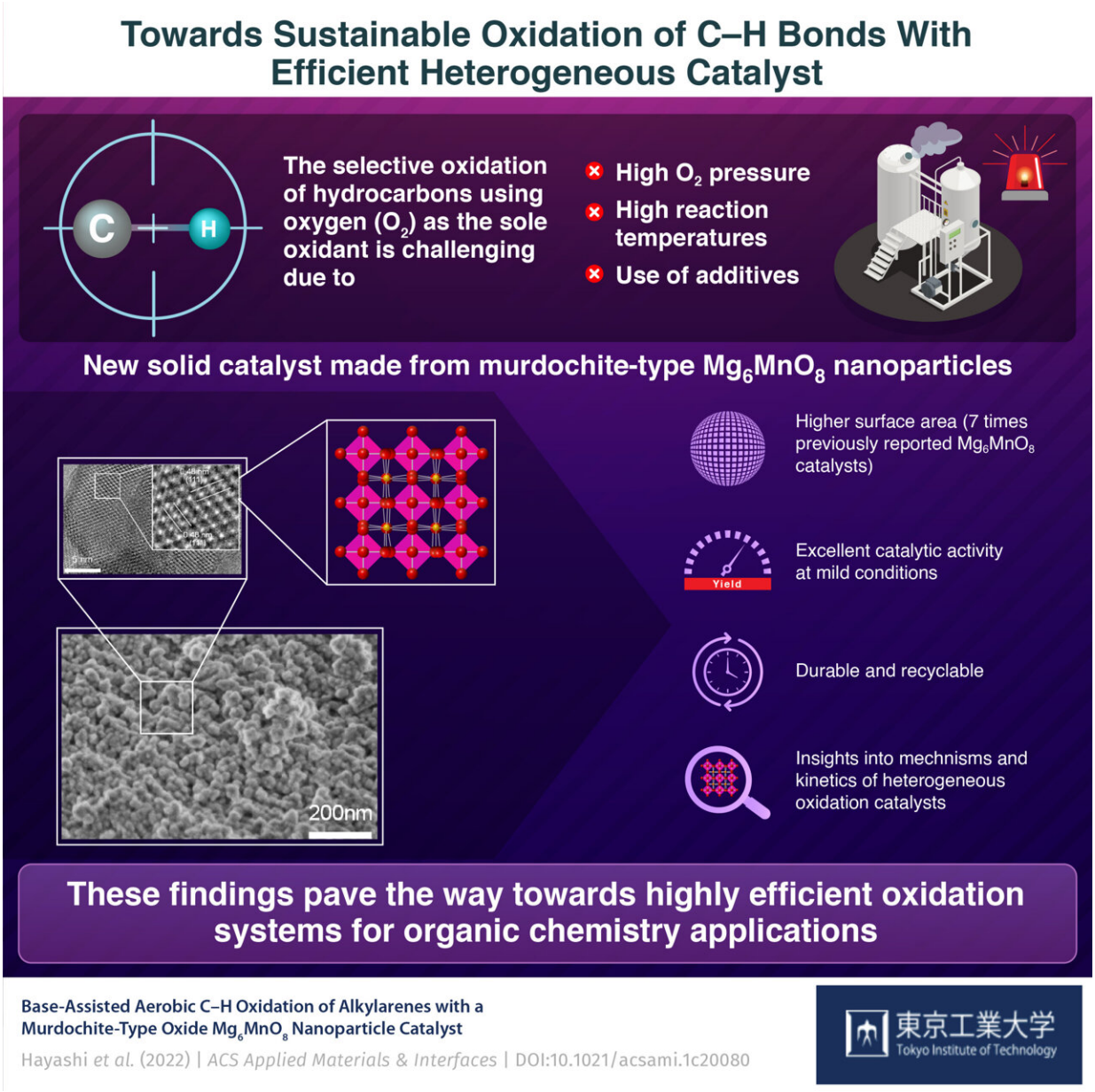

Credit: Tokyo Tech

In the chemical industry, the selective cleavage and oxidation of carbon–hydrogen (C–H) bonds, called "oxidative C–H functionalization" is an essential step in the production of many solvents, polymers, and surfactants, as well as intermediate compounds for agrochemicals and pharmaceuticals. Ideally, one would want to use oxygen (O_2) as the only oxidant in this process to avoid using more expensive and environmentally taxing substances, such as hydrogen peroxide (H_2O_2), chlorine (Cl_2), or nitric acid (HNO_3).

However, using O_2 as the oxidant entails some unresolved problems. While some progress has been made in the field of recoverable and reusable catalysts, most heterogeneous systems require high reaction temperatures, high O_2 pressures, or the use of toxic additives. In turn, this cripples the scope of potential applications, scalability, and efficiency of these catalytic systems.

Against this backdrop, a team of scientists from Tokyo Tech, led by Associate Professor Keigo Kamata, recently found a promising catalyst for oxidative C–H functionalization. As explained in their paper published in *ACS Applied Materials & Interfaces*, they inferred that isolated manganese (Mn) species fixed in a crystalline matrix could constitute a high-performance heterogeneous catalyst even at mild reaction conditions, based on previous knowledge.

Accordingly, they investigated the catalyst murdochite-type Mg_6MnO_8, a rock salt structure of magnesium oxide (MgO) with one eighth of the Mg^{2+} ions replaced with Mn^{4+} ions and another eighth replaced with vacancies, resulting in a crystal with Mn ions and vacancies orderly occupying alternating layers. Using a cost-effective sol–gel method aided

by malic acid, the team prepared Mg_6MnO_8 nanoparticles with a very high surface area. Dr. Kamata elaborates: "The specific surface area of our Mg_6MnO_8 catalyst was 104 m^2/g, about seven times higher than that of Mg_6MnO_8 synthesized using previously reported methods."

The researchers also demonstrated, through numerous experiments, that their Mg_6MnO_8 nanoparticles could efficiently catalyze the selective oxidation of C–H of various alkylarene compounds even under mild reaction conditions, namely 40°C and atmospheric pressure. The yield of the final products was also higher than that obtained using existing Mn-based catalysts. To top things off, the Mg_6MnO_8 nanoparticles could be easily recovered via filtration and then reused without any apparent loss in catalytic activity after multiple cycles.

Finally, the team sought to understand why their proposed catalyst performed so well through a series of kinetic and mechanistic studies. They concluded that the isolation of redox sites (Mn species, in this case) in a crystalline base matrix (MgO) was a particularly important feature to achieve oxidative C–H functionalization using O_2 at mild conditions.

Satisfied with the results and their findings, Dr. Kamata speculates: "Our approach constitutes a promising strategy for the development of highly efficient heterogeneous oxidation systems with wide substrate scopes."

More information: Eri Hayashi et al, Base-Assisted Aerobic C–H Oxidation of Alkylarenes with a Murdochite-Type Oxide Mg6MnO8 Nanoparticle Catalyst, *ACS Applied Materials & Interfaces* (2022). DOI: 10.1021/acsami.1c20080

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