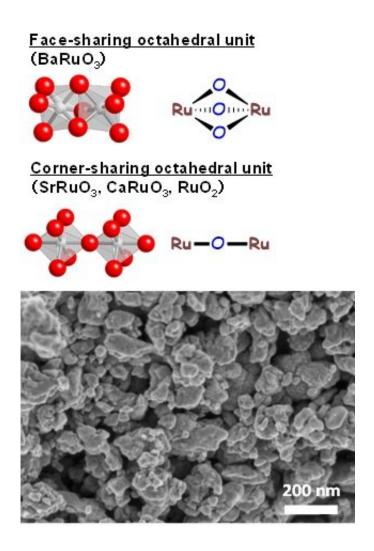


Barium ruthenate: A high-yield, easy-tohandle perovskite catalyst for the oxidation of sulfides

July 16 2018



Top: Schematic representations of the face-sharing unit in rhombohedral BaRuO₃ and corner-sharing unit in tetragonal RuO₂, cubic SrRuO₃, and orthorhombic CaRuO₃. Bottom: Scanning electron microscope (SEM) image of BaRuO₃. Credit: Keigo Kamata



Researchers led by Keigo Kamata and Michikazu Hara of Tokyo Institute of Technology (Tokyo Tech) have developed a ruthenium-based perovskite catalyst that shows strong activity even at low temperatures (down to 313 K). The reusable catalyst does not require additives, meaning that it can prevent the formation of toxic by-products. The oxidation of sulfides is a commercially important process with broad applications ranging from chemicals production to environmental management.

The researchers succeeded in developing a barium ruthenate (BaRuO₃) perovskite—the first catalyst of its kind shown to be capable of the selective oxidation of sulfides under mild conditions, with molecular oxygen (O_2) as the only oxidant and without the need for additives.

Reporting their findings in ACS Applied Materials & Interfaces, the researchers state that BaRuO₃ has three advantages over conventional catalysts.

Firstly, it exhibits high performance even at 313 K, a temperature much lower than the 373 to 423 K range reported in previous systems including other ruthenium- and manganese-based catalysts. Secondly, its high rate of oxygen transfer indicates that it has many potential uses; for example, it is applicable to the oxidative desulfurization of dibenzothiophene, which can produce a 99 percent yield of pure sulfone. Thirdly, the <u>new catalyst</u> is recyclable—the present study showed that BaRuO₃ could be reused at least three times without loss of performance.

The achievement overcomes several classic limitations, such as the need for additives, toxic reagents and high reaction temperatures to achieve good catalytic performance.



The catalyst has a rhombohedral structure (see Figure 1). While other ruthenium-based catalysts investigated to date such as SrRuO₃, CaRuO₃ and RuO₂ can all be described as having corner-sharing octahedral units, BaRuO₃ has face-sharing octahedra. This configuration is thought to be one of the main reasons behind the <u>catalyst</u>'s higher oxygen transfer capability.

The way in which BaRuO₃ was synthesized—based on the sol-gel method using malic acid—was also important. The researchers say: "The catalytic activity and specific surface area of BaRuO₃ synthesized by the malic acid-aided method were higher than those of BaRuO₃ synthesized by the polymerized complex method."

The study highlights the importance of subtle changes in the nanoscale structure of perovskite catalysts, and could provide promising leads for further research on a wide range of perovskite-based functional materials.

More information: Keigo Kamata et al, Heterogeneously Catalyzed Aerobic Oxidation of Sulfides with a BaRuO3 Nanoperovskite, *ACS Applied Materials & Interfaces* (2018). DOI: 10.1021/acsami.8b05343

Provided by Tokyo Institute of Technology

Citation: Barium ruthenate: A high-yield, easy-to-handle perovskite catalyst for the oxidation of sulfides (2018, July 16) retrieved 9 April 2024 from https://phys.org/news/2018-07-barium-ruthenate-high-yield-easy-to-handle-perovskite.html

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