

**A Cheaper Way to Get Energy from Hydrogen
— Inspired by Nature, Developed by Chemists**

Summary

Scientists at Kyushu University (President, Setsuo Arikawa), Japan, have invented a new catalyst that can release electrons from hydrogen gas. The catalyst is a molecule that relies on cheap iron and nickel and works at room temperature and atmospheric pressure. This development is a crucial step in replacing fossil fuels with renewable energy sources. The catalyst was developed by a research collaboration led by Professor Seiji Ogo of the I²CNER (International Institute for Carbon-Neutral Energy Research) (Director, Petros Sofronis) at Kyushu University. The I²CNER is itself a core facility of the WPI (World Premier International Research Center Initiative) established by the MEXT (Ministry of Education, Culture, Sports, Science and Technology).

The catalyst's structure was inspired by natural enzymes called nickel-iron hydrogenases. Chemists have been trying to understand how they work for decades. The first breakthrough came in 2007, when Ogo and coworkers first managed to copy the working of hydrogenases using a nickel-ruthenium molecular catalyst — though ruthenium was more expensive than iron, it pointed the way to a revolution in molecular catalysts for hydrogen splitting. The substitution of iron for ruthenium not only makes the new catalyst four thousand times cheaper, it also forms a crucial model for explaining how some bacteria and algae can harness energy from hydrogen so efficiently. The future development of this catalyst will not only make energy generation cheaper, it will also provide chemists with a whole new way to control reactions that use hydrogen molecules as an important building block.

The group is headed by Kyushu University's Professor Seiji Ogo, and comprises National University Corporation Kyushu University, CROSS (Comprehensive Research Organization for Science and Society), and National University Corporation Ibaraki University. The research was carried out at Kyushu University and the Fias (Fukuoka Industry-Academia Symphonicity). The research subject is part of the CREST (Core Research for Evolutional Science and Technology) of JST (Japan Science and Technology Agency), and is also supported by the grant-in-aid for scientific research on innovative areas of the MEXT.

This research results have been published in the online version of "Science" from Feb. 7, 2013 (U.S. Eastern time zone).

■Background

Supplying safe, clean and sustainable energy is one of the most important challenges of the 21st century. Hydrogen gas is seen as a promising energy carrier for that purpose. Although nickel-iron hydrogenase, an enzyme used by some bacteria and algae, is known to extract electrons from hydrogen gas at normal temperatures and pressures, this has never been achieved by synthetic molecules. Seiji Ogo's research group at Kyushu University previously succeeded in synthesizing a nickel-ruthenium catalyst (Note 2), a synthetic model of nickel-iron hydrogenase (Note 1) (press release on April 25, 2007), which could extract electrons from hydrogen molecules at room temperature and atmospheric pressure (press release on August 9, 2008). This catalyst has already been used to develop a molecular fuel cell (press release on September 6, 2011). However, the use of the expensive precious metal ruthenium was a problem.

(Reference prices: nickel: 1.6 yen/g, ruthenium: 240 yen/g, iron: 0.06 yen/g)

■Content

The research group, headed by Kyushu University, succeeded in developing a new nickel-iron catalyst (Note 3) by studying nickel-iron hydrogenase, a naturally existing hydrogenase enzyme, as a model, and transferring electrons from hydrogen molecules to electron acceptors (ferrocenium ion, methyl viologen, and others) at ordinary temperatures and pressures (Note 4). Elucidation of the crystal structure indicated that the hydride ion (H⁻) produced after activation of the hydrogen molecule is combined with iron, rather than nickel, as had been previously thought. Crucially, the artificial catalyst reproduces all the chemical features of the natural nickel-iron hydrogenase.

■Effect

This research achievement has enabled the elucidation of a hydrogen activation mechanism using nickel-iron hydrogenase, and represents dramatic progress in the study of hydrogen activation using a non-precious metal catalyst. It could lead the way to low-cost hydrogen fuel cell.

■Future Development

It is expected that this research achievement will help advance technology using hydrogen energy in the future, for example, in the development of platinum-free fuel cells. It will also give synthetic chemists the ability to precisely control reactions that use the hydrogen molecule as an important building block.

■Publication

Title : A Functional [NiFe]Hydrogenase Mimic that Catalyzes Electron and Hydride Transfer from H₂
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【Press Contact】

- ◆ Ms. Sonoko Imazu, Public Relations Office, Kyushu University
E-mail: koho@jimu.kyushu-u.ac.jp
- ◆ Public Relation Office, JST (Japan Science and Technology Agency)
TEL : +81-3-5214-8404 FAX : +81-3-5214-8432

【INQUIRIES-Research】

Seiji Ogo, Professor
I²CNER (International Institute for Carbon-Neutral Energy Research)
Department of Chemistry and Biochemistry Graduate School of Engineering
Kyusyu University
TEL : +81-92-802-2818 FAX : +81-92-802-2823
E-Mail : ogolab@mail.cstm.kyushu-u.ac.jp

【INQUIRIES-JST】

(Mr.) Masashi Furukawa
Department of Research Project, JST (Japan Science and Technology Agency)
Tel : +81-3-3512-3531 FAX : +81-3-3222-2066
E-mail : crest@jst.go.jp

【Glossary】

(Note 1) Nickel-iron hydrogenase: This is a naturally occurring enzyme that activates hydrogen gas. The active site has a binuclear structure of nickel (Ni) and iron (Fe) bridged by a sulfur atom (S) of cysteine residue (Cys), as is shown in Figure 1. X indicates H_2O , OH^- or O_2^- in a dormant state, and it also indicates H^- in an activated state.

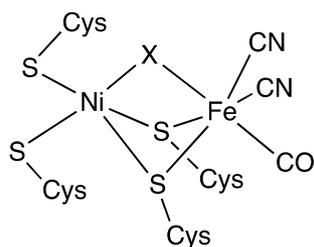


Figure 1. Active site structure of nickel-iron hydrogenases (Cys = cysteine residue)

(Note 2) Nickel-ruthenium catalyst: This is an artificial model catalyst of a nickel-iron hydrogenase, which was developed by the research group headed by Seiji Ogo of Kyushu University in 2007. (Figure 2) This artificial model catalyst uses ruthenium (Ru) instead of iron (Fe), and activates hydrogen at normal temperatures and pressures. (Published in Science 315, 585-587, 2007, Press release on April 25, 2007)

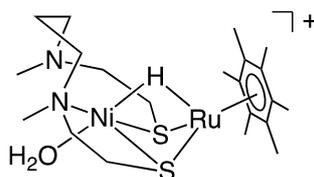


Figure 2. Structure of the nickel-ruthenium catalyst

(Note 3) Nickel-iron catalyst: This is an artificial model catalyst of nickel-iron hydrogenase, which has now been developed by the research group headed by Seiji Ogo of Kyushu University (published in Science 2013). Like the nickel-iron hydrogenase that naturally occurs in nature, it activates hydrogen using nickel (Ni) and iron (Fe) at ordinary temperatures and pressures. The group revealed the structure of the artificial model catalyst using X-rays and neutron diffraction. (Figure 3)

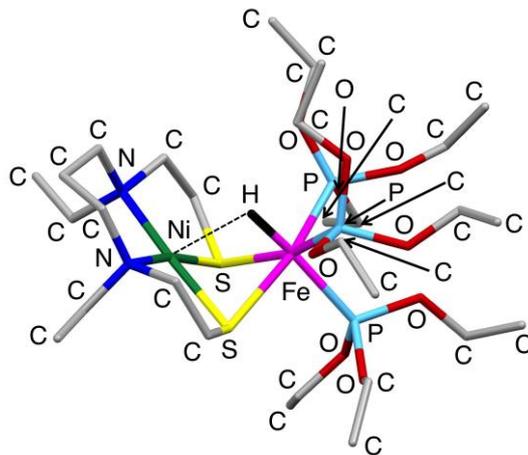


Figure 3. X-ray structure of the nickel-iron catalyst (this work)

(Note 4) Extraction of electrons from hydrogen molecules at room temperature and atmospheric pressure: Specifically, this refers to a catalytic cycle as shown in Figure 4. Catalyst 1 activates hydrogen molecules, and then becomes Catalyst 2, where iron (Fe) is combined with hydride ion (H^-). Catalyst 2 provides electrons to electron acceptors and then returns to being Catalyst 1.

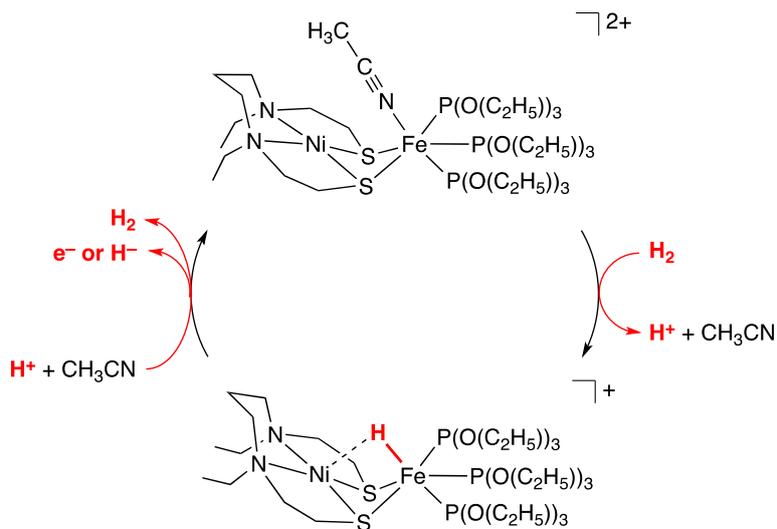


Figure 4. Electron extraction from hydrogen gas with the nickel-iron catalyst (this work)