

【水素の電子を常温で抽出・貯蔵して、必要な時に有機合成に利用
～金属廃棄物フリーのクリーンな反応を実現する新しいエネルギーキャリアを開発～】

1. 概要(英文は和文の後に続きます)

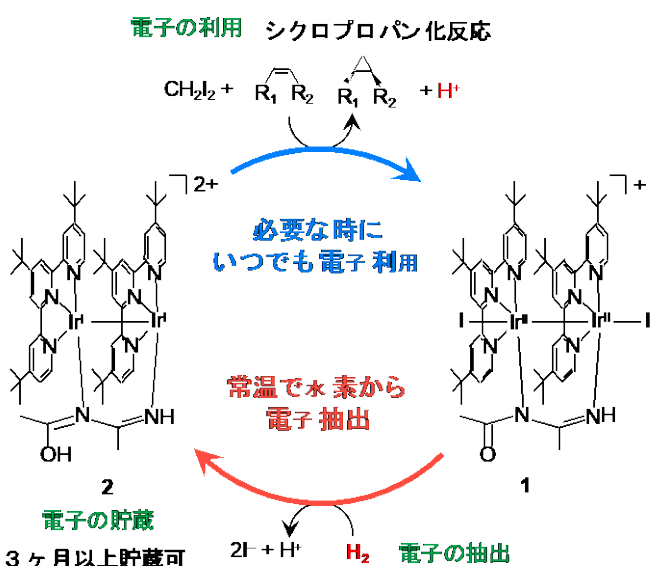
「水素の電子を常温で抽出・貯蔵して、必要な時に有機合成に利用～金属廃棄物フリーのクリーンな反応を実現する新しいエネルギーキャリアを開発～」

水素は利用するとき温室効果ガスを排出しないため、カーボンニュートラル実現のカギとなるクリーンエネルギーとして注目が集まっています。しかし、気体のままでは貯蔵・運搬の効率が低いため、多くのエネルギーを必要とせずに貯蔵・運搬し、そのまま利用できる水素エネルギーキャリアの革新が求められています。

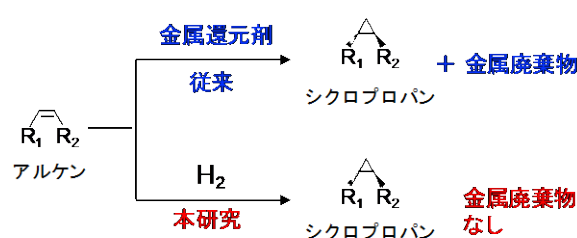
九州大学カーボンニュートラル・エネルギー国際研究所(WPI-I²CNER)／大学院工学研究院の小江 誠司(おごう せいじ)主幹教授らの研究グループは、近畿大学との共同研究により、常温で水素から電子を抽出・貯蔵し、必要な時はいつでもシクロプロパン化反応に利用できる水素エネルギーキャリアとして遷移金属触媒(イリジウム化合物)を開発しました。開発した水素エネルギーキャリアは、水素から「水素ラジカル(H・)」もしくは「ヒドリド(H⁻)」ではなく「電子」を抽出・貯蔵でき、固体状態で、水素の電子を3ヶ月以上保存できます。水素を電子源として使用することで、金属廃棄物を出さずに、有機合成や医薬品合成に重要なシクロプロパン化反応を実現したことは、社会的・学術的に大きな意義があります。水素を電子として貯蔵・運搬する水素エネルギーキャリアの有用性を示せたことは、今後の水素エネルギーキャリアの研究の発展に寄与するものです。将来的には、水素の電子を貯蔵できる貴金属を使用しない水素エネルギーキャリアを開発し、社会実装に向けて企業と連携して研究開発を進めていきます。

本研究成果は、アメリカ化学会の雑誌「JACS Au」オンライン版で2024年3月26日(火)午前1時(日本時間)に公開されました。

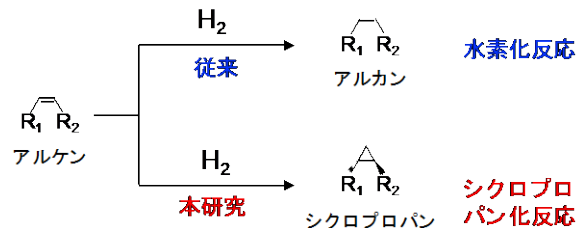
(a) 新発想水素エネルギーキャリアの反応図



(b) 金属廃棄物フリーの反応



(c) アルケンと水素の反応で水素化以外の反応



図(a) 本研究の新発想水素エネルギーキャリアの反応図。(b)(c) 従来法との違い。

「Storing Electrons from Hydrogen for Clean Chemical Reactions」

Fukuoka, Japan—Researchers from Kyushu University have developed a hydrogen energy carrier to address some of the biggest hurdles in the path towards a sustainable hydrogen economy. As explained in a paper published in JACS Au, this novel compound can efficiently “store electrons” from hydrogen in a solid state to use in chemical reactions later.

Hydrogen is a promising source of clean energy with a lot of untapped potential applications in industry and everyday life. Unlike conventional fuels, hydrogen can be used to generate electricity without producing greenhouse gases. It can also be used in various chemical reactions such as hydrogenation, that is, as a source of hydride ion or hydrogen atom electrons. However, storing and transporting hydrogen in either gaseous or liquid states is extremely challenging, requiring expensive equipment and cooling systems.

Professor Seiji Ogo from Kyushu University’s International Institute for Carbon-Neutral Energy Research (WPI-I²CNER) has been developing innovative solutions to these problems. In their most recent study, Ogo and his colleague from Kindai University took inspiration from nature to develop an iridium-based compound with peculiar and remarkably useful properties.

“We have been actively exploring hydrogen energy carriers that can be easily synthesized and used as-is. These compounds are based on the hydrogenase enzyme found in nature, which can catalyze hydrogen into protons and electrons at room temperature,” explains Ogo. “A core idea of our approach that led to a breakthrough was to view hydrogen not as a source of negatively charged hydride ion or hydrogen atom, but as electrons.”

After carefully examining many combinations of metal ions and organic ligands, the research team crafted an iridium-based compound which, when exposed to hydrogen incorporates it into the metal center after losing an iodide ion. In this way, the proposed compound can effectively extract and store electrons from hydrogen.

These changes are readily reversible under the right conditions, and the stored electrons can be easily extracted and used in chemical reactions to synthesize valuable molecules. In this study, the researchers focused on using the electrons stored in the compound to catalyze cyclopropanation reactions.

Cyclopropanes are molecules with a three-membered carbon ring structure and represent important structural units in various pharmaceutical drugs and organic compounds. However, conventional

cyclopropanations have produced large amounts of waste metals as byproducts. The proposed hydrogen energy carrier circumvents this issue entirely.

“The cyclopropanation reactions performed in our study use hydrogen rather than metals as the reductant and thus produce no metal waste. This is a major advantage of the proposed compound over established techniques,” remarks Ogo.

Notably, this study also marks the first time that a reaction between hydrogen and alkenes—hydrocarbons containing a carbon double bond—produces cyclopropanes rather than the much simpler alkanes.

After extensive testing, the team found that the proposed energy carrier can capture electrons from hydrogen and store them for over three months in solid state at room temperature.

In future work, Ogo and colleagues plan to focus on developing a similar energy carrier using iron-group elements, which are cheaper and more abundant than iridium. By promoting industry-academia collaborations, their next efforts will aim to develop scalable solutions for practical problems surrounding upcoming hydrogen economies.

“We sincerely believe that the present achievement will contribute to the realization of a carbon-neutral society,” concludes Ogo.

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For more information about this research, see “Cyclopropanation using Electrons Derived from Hydrogen: Reaction of Alkenes and Hydrogen without Hydrogenation”, Seiji Ogo, Takeshi Yatabe, Keishi Miyazawa, Yunosuke Hashimoto, Chiaki Takahashi, Hidetaka Nakai, and Yoshihito Shiota, JACS Au, DOI: <https://doi.org/10.1021/jacsau.4c00098>

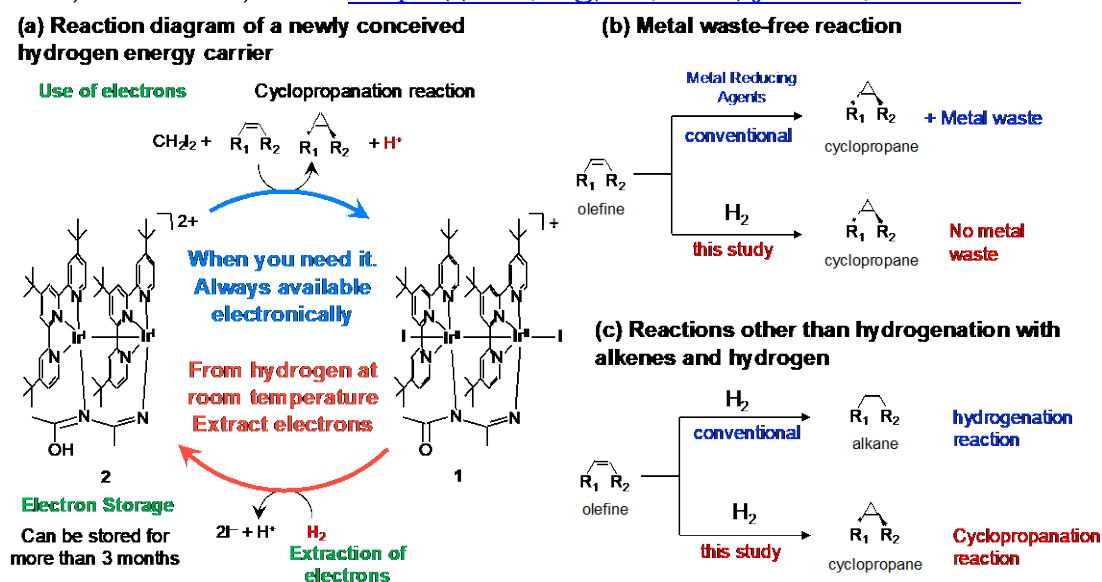


Image title: Reversible extraction and storage of electrons from hydrogen to catalyze cyclopropanation reactions

Image caption: The proposed iridium-based compound can effectively store “electrons” from hydrogen and hold them in solid state at room temperature for months. These stored electrons can then be released to catalyze cyclopropanation reactions that do not produce metal waste.

Image credit: Seiji Ogo from Kyushu University, Japan

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2. 民間企業等との連携実績

社会実装に向けて企業との連携を模索中です。

3. 参考情報

(今回のリリース)

「水素の電子を常温で抽出・貯蔵して、必要な時に有機合成に利用～金属廃棄物フリーのクリーンな反応を実現する新しいエネルギーキャリアを開発～」

<https://www.kyushu-u.ac.jp/ja/researches/view/1062>

<https://www.jst.go.jp/pr/announce/20240326/index.html>

「Storing Electrons from Hydrogen for Clean Chemical Reactions」

<https://www.kyushu-u.ac.jp/en/researches/view/281>

<https://www.eurekalert.org/news-releases/1039405>

(過去のリリース)

「水素を電子として利用する水素エネルギーキャリアの開発」

<https://i2cner.kyushu-u.ac.jp/ja/news/10155/>

「A potentially cheaper and 'cooler' way of hydrogen transport」

<https://www.eurekalert.org/news-releases/1005960>

「水素と酸素から過酸化水素を安全に合成する触媒を開発」

<https://i2cner.kyushu-u.ac.jp/ja/news/9398/>

「A safe synthesis of hydrogen peroxide inspired by nature」

<https://www.eurekalert.org/news-releases/982180>

4. お問い合わせ先 WPI 拠点

九州大学カーボンニュートラル・エネルギー国際研究所(WPI-I²CNER)

[担当]I²CNER・Q-PIT 共通事務支援室 学術支援・渉外グループ

[拠点ウェブページ] <https://i2cner.kyushu-u.ac.jp/ja/>