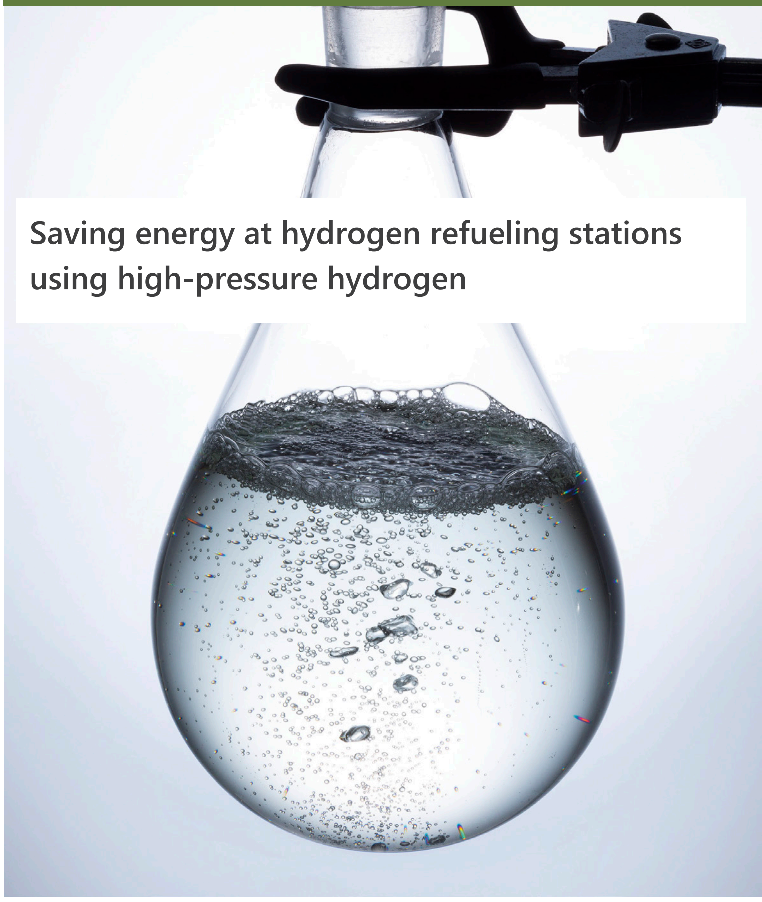
Formic Acid Opens a New Hydrogen Market



Saving energy at hydrogen refueling stations using high-pressure hydrogen

KEY POINTS

Formic acid has attracted attention as **a new hydrogen carrier**. AIST has developed **a high-performance catalyst**, with no known congeners worldwide, which enables **the extraction of hydrogen and carbon dioxide** by simply heating formic acid at a relatively low temperature (see the photo on the left). This process generates **high-pressure hydrogen and carbon dioxide, allowing these two gases to be easily separated**. This research shows high potential for future applications in hydrogen refueling stations.

Safe and easy hydrogen generation by using formic acid as a hydrogen carrier

Using a microspatula, a small amount of catalyst is placed in a flask containing a dilute aqueous solution of formic acid and heated in a water bath. In a second or two, bubbles are generated and move toward the surface, gradually gaining momentum.

“These bubbles are hydrogen. It is quite easy to extract hydrogen from formic acid. This catalyst is highly active, and thus hydrogen generation continues until the formic acid is depleted. Hydrogen generation stops when heating ceases. When diluted with water, formic acid is no longer flammable nor toxic. That is to say, formic acid serves as a safe and easy-to-use hydrogen carrier.” (Note: Formic acid is not subject to the Fire Service Act or the Poisonous and Deleterious Substances Control Act at concentrations below 78% and 90%, respectively).

This was stated by Dr. HIMEDA Yuichiro, Global Zero Emission Research Center, AIST, who has been developing catalysts to synthesize formic acid using carbon dioxide (CO_2) and hydrogen. Currently, he and Dr. KAWANAMI Hajime, Interdisciplinary Research Center for Catalytic Chemistry, AIST, are engaged in developing highly efficient catalysts to generate high-pressure hydrogen and CO_2 from formic acid and in investigating efficient processes for separating hydrogen from CO_2. They regard formic acid as a promising hydrogen carrier that can store surplus energy generated from renewable sources such as hydrogen.

Today ammonia and organic hydrides are regarded as viable hydrogen carriers for use in large-scale plants, where the extraction of hydrogen requires extensive equipment. On the other hand, the use of formic acid does not require specific facilities, making it an attractive hydrogen carrier.

It has been well known since the 1960s that hydrogen can be extracted from formic acid. However, previously used catalysts had poor activity, and hydrogen production from formic acid required heating above 200°C. Under these conditions, carbon monoxide (CO) was generated as a side product during the process, which caused the deterioration of fuel cells. Consequently, further efforts and expenses were required for CO removal and hydrogen purification. Thus, this research had remained stagnant for a long time.

In 2008, however, a highly selective catalyst that functions at a relatively low temperature without generating CO was developed in Europe. Since then, research on formic acid has gained momentum worldwide. Dr. Himeda also conducted experiments using his catalysts and obtained satisfactory results.

"I would like to develop a catalyst that allows us to extract hydrogen very easily from formic acid," thought Dr. Himeda.

He initiated intensive research for the development of catalysts for the dehydrogenation of formic acid as a hydrogen carrier. High-performance catalysts that react at low temperatures are desired for easy-to-use hydrogen carriers without CO contamination. In 2009, he succeeded in developing his own original catalyst, which produced only hydrogen and CO_2 from formic acid at approximately 60°C.

High-pressure hydrogen

Another characteristic of the catalyst developed by Dr. Himeda is that the catalyst generates high-pressure hydrogen from formic acid. By simply heating the system to 60°C in a water bath, the formic acid produces hydrogen at pressures as high as 100 MPa.

Currently, hydrogen refueling stations (HRSs) have mechanical compressors that compress hydrogen to a filling pressure of 82 MPa. The compression of hydrogen gas requires a considerable amount of electricity. Owing to the catalyst developed by Dr. Himeda, the HRSs would be much more compact and energy efficient because high-pressure hydrogen can be supplied by simply heating formic acid in a closed vessel without using mechanical compressors.

"It should lead to good technology," Dr. Himeda instinctively understood. However, he faced difficulties in handling high-pressure gases, which required highly skilled technical expertise as well as conformance to strict legal regulations. He had no prior experience in this field. Therefore, he was unable to proceed to the next step.

A promising opening for him was a meeting with Dr. Kawanami, a specialist in high-pressure chemistry, in 2011. These two researchers began to collaborate in 2012, exploring ways in which formic acid could be used as a hydrogen carrier.

"Initially we estimated that the highest pressure would be around 30–40 MPa, and accordingly, we prepared an apparatus that would accommodate pressures up to 50 MPa. Surprisingly, however, the first trial was far from our expectation. In the experiment, without doing anything special, the pressure rapidly reached and exceeded 50 MPa," Dr. Kawanami recalls. The equipment was then redesigned to withstand a pressure of 100 MPa.

Their collaboration is as follows: Dr. Himeda designed and prepared the catalysts, which were evaluated by Dr. Kawanami through his high-pressure technique. Dr. Kawanami provided feedback on whether the catalyst could withstand high-pressure hydrogen, which part was broken and how, and so on. On the basis of this feedback, Dr. Himeda redesigned the catalyst structure. They repeated this process several times and accumulated considerable expertise in the development of highly efficient catalysts.

"The catalyst we recently developed seems to extract nearly all the potential of formic acid, as it results in a 1000–3000 times faster pressure increase rate and hydrogen generation rate than the previously reported catalysts did," says Dr. Himeda.

Moreover, this catalyst is by far the best catalyst in the world, not only in terms of durability but also in terms of pressure resistance. AIST is currently the only institute with an apparatus capable of withstanding 100MPa pressure. In other words, AIST has the technology to accommodate a high pressure and thus a catalyst with high performance.

Simple separation of hydrogen from CO_2

There is also a reason for the superiority of this technology: it involves not only hydrogen production but also CO_2 capture and utilization.
When the mixture of hydrogen and CO_2 generated from formic acid is cooled under high-pressure conditions during the process, only CO_2 liquefies, and hydrogen is separated as a gas. The simple physical separation of the two products via unique high-pressure phenomena is the technology developed at AIST.

Gaseous CO_2 generated from formic acid is usually discarded. The liquefied CO_2 that is separated from hydrogen has several applications, such as pressured gas for spraying and dry ice.

The international standard for hydrogen-fuel quality stipulates that the purity of hydrogen that is supplied to HRSs should exceed 99.97% (ISO14687-2). At present, the two researchers are exploring ways to produce high-purity hydrogen to meet this stringent standard.

"Electrical generators using formic acid are already sold in Europe and the Middle East. In these, CO_2 generated from formic acid is emitted into the atmosphere. By contrast, our technology can separate CO_2 and recover it in the process. Thus, it is a technology that is one step ahead," says Dr. Himeda.

In collaboration with companies in several fields, they have undertaken research and development to utilize hydrogen energy in daily life in the future. The aim is to make hydrogen-supply technologies safer and easier to implement.

"This new technology using formic acid can complement the part that other energy carriers cannot achieve. We hope the industry will use it together with other energy technologies," says Dr. Himeda.

At present, however, Dr. Kawanami points out that hydrogen gas is still difficult to transport and store using current technologies; thus, there are few successful business endeavors for hydrogen utilization. However, once the technology is developed to make hydrogen safe and easy to use, many interested companies will enter the market.

Dr. Kawanami says, "I think we need to create a new market for hydrogen and make it grow. We are already in an era where hydrogen is used as a fuel to power ships. I believe that as the hydrogen market expands, there will be more opportunities to utilize hydrogen in the future."

The goal of Drs. Himeda and Kawanami is not only to just discover new phenomena but also to develop technologies that can be implemented in society, providing useful practical applications.

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