## Abstract

## [Research Title]

Development of Main-Group-Catalyzed Systems for Hydrogen Purification from Crude Hydrogen Gases / Biogases via Sequential Hydrogenation / Dehydrogenation Reactions of Organic Compounds

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## [Abstract]

Molecular hydrogen (H<sub>2</sub>) is one of the most promising energy carriers for the near future owing to its high gravimetric energy density and the relatively low environmental impact of its combustion products. In the mid-term future, a huge amount of H<sub>2</sub> (>10<sup>12</sup> standard cubic feet/year) is expected to be produced from a wide range of hydrocarbon and renewable resources, including biomass and wastes, via the purification of crude H<sub>2</sub>, which is a gaseous mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, and other components. In this process, the removal of such contaminants before H<sub>2</sub> storage is of paramount importance to prevent the deactivation of expensive metal-based catalysts that are commonly used in fuel cells and the chemical industry. However, such purification processes have a huge impact on the environment and energy consumption (accounting for 10%–15% of the overall consumption), which ultimately increases the cost of the produced H<sub>2</sub>. Therefore, circumventing these purification processes would be highly desirable.

Against this background, we have recently reported a strategy to separate  $H_2$  from a gaseous mixture of  $H_2/CO/CO_2/CH_4$  and simultaneously store it in *N*-heterocyclic compounds acting as liquid organic hydrogen carriers (LOHCs), which can be applied to produce  $H_2$  via subsequent dehydrogenation [*Science Advances* 2022]. Specifically, a newly designed shelf-stable triarylborane was demonstrated to catalyze the hydrogenation of *N*-heteroaromatic compounds in the copresence of substantial amounts of CO, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>O, realizing the simultaneous separation and storage of H<sub>2</sub> with a catalyst turnover number of up to 1520, and to promote the subsequent dehydrogenation for H<sub>2</sub> recovery. Interestingly, both processes proceed *under solvent-free conditions*. The present results demonstrate a proof-of-concept for a LOHC-based H<sub>2</sub> purification technology that goes beyond the well-established use of LOHCs in H<sub>2</sub> storage.

We have also successfully extended this concept for alcohol synthesis via the hydrogenation

of carbonyl compounds directly using crude H<sub>2</sub> and triarylborane catalysts [*Tetrahedron Chem* 2023]. In our system, even in the co-presence of CO and CO<sub>2</sub>, carbonyl groups were selectively hydrogenated without side reactions such as carbonylation, dehalogenation, hydroformylation, and isomerization of olefins.

We strongly believe that our original concept of the direct utilization of crude H<sub>2</sub> using lesstoxic main-group catalysts can connect researchers across diverse disciplines to change the industrial value of crude H<sub>2</sub> containing substantial amounts of CO, CO<sub>2</sub>, and CH<sub>4</sub>, which can be produced from a variety of carbon resources such as biomass and industrial off-gases.

## [References]

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