Main-Group Catalysis for H_2 Purification Based on Liquid Organic Hydrogen Carriers

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Abstract

We demonstrate a strategy to separate H_2 from a gaseous mixture of $H_2/CO/CO_2/CH_4$ that can include an excess of CO and CO_2 relative to H_2 and simultaneously store it in *N*-heterocyclic compounds that act as liquid organic hydrogen carriers (LOHCs), which can be applied to produce H_2 by subsequent dehydrogenation. Our results demonstrate that LOHCs can potentially be used for H_2 purification from CO- and CO_2-rich crude H_2 in addition to their well-established use in H_2 storage.

1. Introduction

Molecular hydrogen (H_2) is an essential reductant and one of the most promising energy carriers of the future. Thus, it can be expected that a huge amount of H_2, on a magnitude of more than 10^{12} standard cubic feet/year, will be produced from a wide range of hydrocarbon and renewable resources.[1] The predominant contemporary route to H_2 production includes the intensive purification of crude H_2, which is a gaseous mixture of H_2, CO, CO_2, and other components that is produced by gasification, reforming, and/or water-gas shift (WGS) (process I in Fig. 1). Purification processes such as pressure swing adsorption (PSA), membrane separation, and cryogenic separation critically determine the purity of the H_2 and influence the total energy consumption of the H_2 production process, making it cost-inefficient. Thus, although H_2 can currently be stored after or during the process I in Fig. 1, we envisaged a solution where H_2 could be stored in its carrier directly from crude H_2, which often includes more CO than H_2, *without* the requirement for any of the aforementioned shift and purification processes (process II in Fig. 1).[3] Moreover, the recovery of H_2 after our proposed path ultimately leads to the production of highly pure H_2.

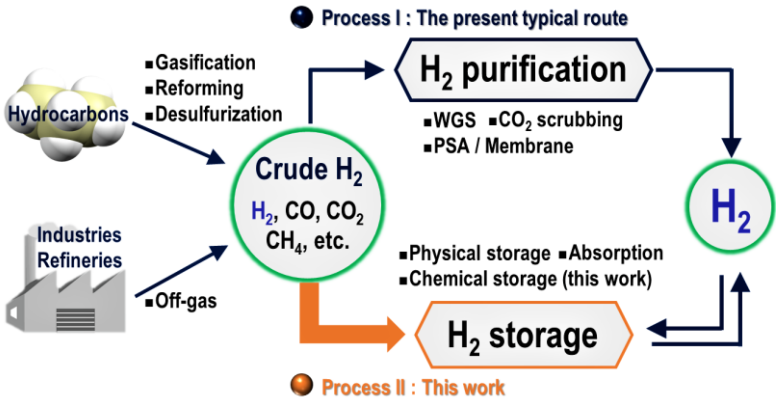

Fig. 1 Research background and concept of this work.

2. Experiment

A 30 mL autoclave was charged with 2-methylquinoline and triarylborane. Once sealed, the

autoclave was pressurized with $H_2/CO/CO_2$ (4 atm each) and heated to 100 °C for 2 h. After cooling to room temperature, all volatiles were removed *in vacuo*. Then, the reaction mixture was transferred into a 10 mL two-neck flask. The reaction mixture was then stirred at 200 °C for 3 h.

3. Results and discussion

In the presence of catalytic amount of our original triarylborane catalyst, the hydrogenation of 2-methylquinoline proceeded effectively (upto 1520 turnover) at 100 °C under the solvent-free, mixed-gas ($H_2/CO/CO_2$; 1/1/1 molar) conditions (Fig. 2). After degasification to remove CO and CO_2, dehydrogenation from the tetrahydroquinoline was carried out at 200 °C, which afforded H_2 of >99.9% purity with the regeneration of 2-methylquinoline.

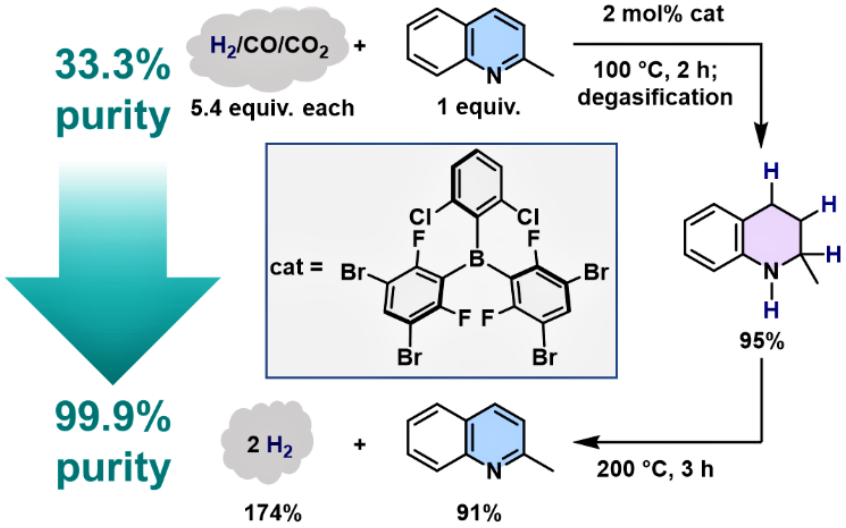

Fig. 2 H_2 purification based on the borane-catalyzed hydrogenation of 2-methylquinoline under mixed-gas conditions and subsequent catalytic dehydrogenation.

4. Conclusions

The present results demonstrate a proof-of-concept for a H_2-purification technology based on LOHCs that goes beyond their well-established use in H_2 storage. This technology can be expected to change the industrial value of crude H_2 containing substantial amounts of CO, CO_2, and CH_4, which can be produced from a variety of carbon resources such as biomass and industrial off-gases. Moreover, this work demonstrates a new aspect of main-group catalysis beyond its application as a simple alternative to well-established transition-metal-catalyzed processes, i.e., the main-group-catalyzed hydrogenation of unsaturated molecules under mixed-gas conditions.

References

1) K. Liu, C. Song and V. Subramani, Eds., *Hydrogen and Syngas Production and Purification Technologies*. (Wiley, 2010).

2) T. Hashimoto, T. Asada, S. Ogoshi and Y. Hoshimoto, Main-group catalysis for H_2 purification based on liquid organic hydrogen carriers, Science Advances, 8, eade0189 (2022). DOI: 10.1126/sciadv.eade0189