Sustainable Hydrogen Generation via Continuous Dehydrogenation of Biomass-derived Formic Acid

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Abstract

Hydrogen generation from biomass waste offers a sustainable alternative to fossil-based energy and complements intermittent solar and wind power. Today's technologies for biomass-derived H_2 production, e.g. gasification, require harsh reaction conditions. An efficient alternative involves the conversion of wet biological waste to aqueous formic acid (e.g. so called OxFA process), followed by its dehydrogenation. Temperatures below 150 °C are sufficient to release hydrogen and carbon dioxide, enabling decentralized applications[1]. Heterogeneous Pd-based catalysts show high activity for formic acid (FA) dehydrogenation, but poisoning by the side-product carbon monoxide causes catalyst deactivation[2].

In this study, Pd/C catalysts were evaluated in continuous aqueous formic acid dehydrogenation under different process conditions. In the gas-phase reaction, a mean formic acid conversion of 52 % and productivity of 2.8 $g_{H2}\ g_{Pd}^{-1}\ min^{-1}$ were achieved at 150 °C (see Fig. 1). Despite the formation of CO in an average concentration of 1269 ppm, the catalyst shows stable activity over 24 h. Catalyst deactivation was not observed, even at temperatures ranging from 130 °C to 175 °C. Thus, gas-phase reaction conditions enable stable formic acid dehydrogenation, providing a promising basis for biogenic hydrogen generation at a technical scale. Further catalyst systems will be developed, including nickel phosphides and Pd supported on carbon nitride. The aim is to achieve higher H_2 release rates and improve selectivity for dehydrogenation to minimize product purification for fuel cell applications.

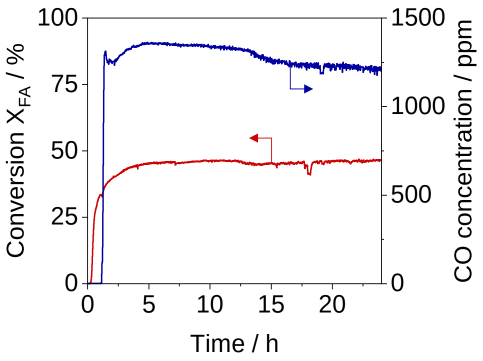

Fig. 1: Formic acid conversion and CO concentration versus time in continuous dehydrogenation. Reaction conditions: 0.1 g Pd/C (1 wt.% Pd), 150 °C, 7500 $g_{FA}\ g_{Pd}^{-1}\ h^{-1}$, 25 wt.% FA.

For the process efficiency, the liquid-phase reaction is advantageous due to lower temperatures. But Pd/C showed significant deactivation in formic acid dehydrogenation at 50 °C. Therefore, alternative and modified catalyst systems will be investigated with a focus on enhanced CO tolerance. In addition, process parameters will be adjusted, including temperatures above 100 °C and pressures exceeding vapor pressure. The objective is to identify reaction conditions that suppress deactivation and enable stable formic acid dehydrogenation for sustainable hydrogen generation.

[1] Preuster, P.; Albert, J. *Energy Tech* **2018**, 6 (3), 501–509.
[2] Kosider, A. et al. *Catal. Sci. Technol.* **2021**, 11 (12), 4259–4271.