Understanding Hydrogen Production from Formic Acid Decomposition

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ABSTRACT

Hydrogen-based economy aims to make India more energy secure and carbon-neutral. Formic acid (FA) is a potential liquid storage medium combining green hydrogen and CO_2. Catalytic decomposition of FA is a potential reaction for on-site H_2 production due to the renewable sourcing, low toxicity, and high H_2 density. Supported Pd-Ag alloy nanocatalysts are more selective than metals such as Pd, Au, and Ag for H_2 production from FA dehydrogenation than dehydration to H_2O. Furthermore, H_2 production on Pd-based catalysts is a strong function of the supporting material. Our study explains how Ag alloying of Pd and different interfacial sites affect the selective production of H_2 from FA with mechanistic insights for the FA reaction. Supported Pd-Ag nanoparticles (1 wt % loading; 3 – 8 nm) on Al_2O_3, CeO_2, TiO_2, and TiB_2 with varying Pd to Ag atomic ratios (1:0, 20:1, 0.5:1, 0:1) are prepared by incipient wetness co-impregnation. The catalysts were tested in a batch reactor at ambient temperature and pressure in aqueous phase using gas chromatography to quantify products.

Pd-Ag(0.5:1) nanoparticles over Al_2O_3 provide a higher selectivity (98%) to H_2 formation from FA when compared to Pd-Ag(20:1) (38%) and Pd (13%). Similarly, Pd-Ag(0.5:1) nanoparticles

provide higher selectivity (22%) to H_2 formation from FA than Pd-Ag(20:1) (9%) and monometallic Pd (19%) supported on CeO_2. Pd-Ag alloy formation likely disrupts Pd ensembles, modifies the FA adsorption configuration, and favours H_2 formation over H_2O production from FA. Pd-Ag(0.5:1)-TiB_2 maintains a 55% H_2 selectivity for six hours compared to Pd-TiB_2, which primarily dehydrates FA. Pd nanoparticles are electronically modified in the presence of Ag and weakly bind CO, which increases catalyst stability. Overall, combination of electronic and ensemble effects makes Pd-Ag catalysts more selective for H_2 formation from FA reaction than the corresponding monometallic Pd and Ag supported over Al_2O_3, CeO_2, TiO_2, and TiB_2.

Key Words: Alloy, Hydrogen, Interface, In situ spectroscopy, Nanocatalyst