

Design of heterogeneous nanocatalysts for the synthesis/decomposition of formic acid: a renewable hydrogen storage/delivery mediating carbon dioxide

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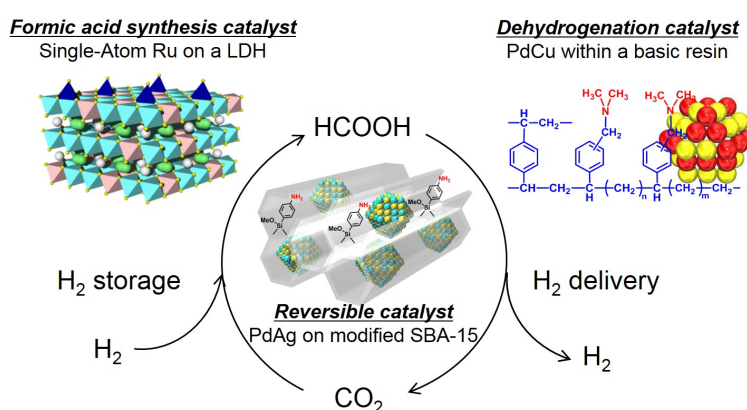
Abstract: Pd-based alloy nanoparticle catalysts were developed for the efficient production of H₂ from formic acid (HCOOH) dehydrogenation. Experimental and DFT calculation studies revealed not only the synergic alloying effect but also cooperative action by the amino-functional groups of the support materials plays crucial roles in achieving exceptional catalytic performances. On the contrary, a stable and well-defined single-atom Ru catalyst on the surface of a layered double hydroxide (LDH) was proven to be efficient for selective hydrogenation of CO₂ to formic acid under mild reaction conditions. Furthermore, a reversible heterogeneous catalyst has been developed for both H₂ delivery and H₂ storage reactions mediated by formic acid and CO₂.

Keywords: Formic acid, Hydrogen storage material, Nanoparticle.

1. Introduction

A considerable amount of research effort is currently devoted to exploring new storage methods.¹ Among investigated, formic acid (HCOOH), which is a liquid at room temperature and contains 4.4 wt% hydrogen, is widely recognized as a convenient hydrogen carrier for fuel cells designed for portable use.^{2,3} Additionally, economical CO₂-mediated hydrogen storage energy cycle can be attained by realizing the regeneration of formic acid through the hydrogenation of CO₂ with H₂.

There have been extensive studies in developing catalysts targeted to either H₂ delivery or H₂ storage mediated by formic acid, independently. Significant progress has been made by using homogeneous catalysts such as Ru and Ir. For the practical reason of on-board application, current research has been focused on the exploitation of efficient heterogeneous catalysts. Bearing this in mind, we present herein the heterogeneous nano-catalysts for the hydrogen production from formic acid and hydrogenation of CO₂ to form formic acid. Furthermore, a reversible heterogeneous catalyst has been designed for the interconversion of H₂ and CO₂ (Scheme 1).



Scheme 1. Nano-catalysts for the use of formic acid as a hydrogen energy storage material.

2. Experimental

Decomposition of formic acid: The catalyst was placed into a reaction vessel with a reflux condenser and equipped with gas burette. After the purging with Ar, HCOOH/HCOONa = 9/1 aqueous solution (1.0 M, 5 mL) was added to the reaction vessel and reacted at 348 K with magnetic stirring.

Hydrogenation of CO₂: The catalyst and 1.0 M NaHCO₃ aqueous solution were loaded into an autoclave, and the pressure was increased to 1.0 MPa of CO₂ and then increased to 2.0 MPa with H₂. The system was heated to 373 K and stirred for 24 h. The yield of formic acid was determined by HPLC.

3. Results and discussion

The catalytic activity of the PdCu/resin with basic $-N(CH_3)_2$ groups in the H_2 production from formic acid was significantly higher than the pure Pd/resin catalyst, while the reaction using pure Cu/resin was seriously sluggish.^{4,5} Surprisingly, PdCu/resin exhibited the considerably high activity compared with the corresponding PdAu and PdAg catalysts. In the investigation of mole fraction of Cu, maximum activity was obtained at Pd:Cu = 50:50. Such volcano type activity order based on the Pd/Cu composition clearly suggests that the formation of uniform PdCu alloy structure within the macroreticular domains of resin and the unusual synergic effect originated from the integration of Pd with Cu.

From the results obtained by kinetic isotope effect (KIE), it is reasonable to determine that cooperative action by the amine functionality as well as synergic catalysis of bimetallic PdCu accounts for its high catalytic activity. The basicity of the resin plays a positive role on the O–H bond cleavage of formic acid and the addition of Cu influence on the rate-determining C–H bond dissociation step from metal-formate intermediate owing to the formation of electron rich Pd species.

Treatment of a LDH, $Mg_{10}Al_2(OH)_{24}CO_3$, with a solution of $RuCl_3 \cdot nH_2O$ in aqueous NaOH solution afforded Ru/LDH. From the Ru K-edge XAFS and the HAADF-STEM results, it can be concluded that a single-atom Ru species with tetrahedral coordination geometry bearing one hydroxyl was grafted onto a triad of oxygen atoms originating from the basic hydroxyl groups on the LDH surface. Ru/LDH is proven to be efficient for selective hydrogenation of CO_2 to formic acid under mild reaction conditions (2.0 MPa, $100^\circ C$).⁶ The electron-donating ability of triads of basic hydroxyl ligands with a particular location is crucial for an active electron-rich Ru center. There is a strong correlation between catalytic activity and adjustable CO_2 adsorption capacity in the vicinity of the Ru center. Such electronic metal-support interactions and a CO_2 concentration effect result in a significant positive influence on the catalytic activity.

Furthermore, PdAg nanoparticle-supported mesoporous silica SBA-15 modified with an amine functional group has been developed as a reversible heterogeneous catalyst for both H_2 delivery and H_2 storage reactions mediated by formic acid and carbon dioxide.⁷ Key to achieve this efficient interconversion of H_2 and CO_2 is the use of a weakly basic phenylamine functional group as a surface modifier, which can allow not only the formation of highly dispersed PdAg nanoparticles, but also the cooperative action between active nanoparticles, such as positive effect on O–H bond cleavage of formic acid, stabilization of formate intermediate, and enhanced CO_2 adsorption property.

4. Conclusions

We successfully designed heterogeneous nano-catalysts for the hydrogen production from formic acid and hydrogenation of CO_2 to form formic acid. The advantages of the present catalytic systems, such as facile preparation method, high durability, and superior catalytic activities compared to the previously reported systems, are particularly desirable for an ideal hydrogen vector in terms of potential industrial application for PEMFCs.

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