



Base-free CO₂ hydrogenation to formic acid over Pd supported on defective carbon nitride modified by microwave and acid treatments

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ARTICLE INFO

Article history:

Received 7 November 2020

Revised 7 March 2021

Accepted 9 March 2021

Available online 18 March 2021

Keywords:

Base-free CO₂ hydrogenation to formic acid

Pd/g-C₃N₄

Hybrid microwave annealing

Acid treatments

Defects

ABSTRACT

Graphitic carbon nitride (g-C₃N₄) is synthesized via pyrolyzing urea by hybrid microwave annealing (HMA) to support Pd catalyst for direct CO₂ hydrogenation to formic acid under a base-free condition. The HMA produces fragmented C₃N₄ sheets with abundant defects along their edges, because of the high annealing temperature (>900 °C) in an extremely short time (<5 min). The acid treatment of C₃N₄ further reduces its grain sizes forming additional defect sites to anchor small Pd nanoparticles. The modified C₃N₄ provides ample CO₂ adsorption sites relative to C₃N₄ pyrolyzed by the conventional furnace annealing at 550 °C for 4 h. The Pd catalyst supported on the defective C₃N₄ exhibits the benchmark performance ever reported for base-free CO₂-to-HCOOH conversion in terms of both palladium time yield based on total Pd, and turnover frequency based on exposed surface Pd atoms. The enhanced performance is explained by interplay between small Pd nanoparticles and the abundant CO₂ supply from nearby defect sites along the edges of the modified C₃N₄ sheets.

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1. Introduction

Mitigation of carbon dioxide (CO₂) emission has become an urgent issue to slow down the global climate change [1,2]. Carbon capture and storage (CCS) in underground geological formation has been pursued aggressively as an effective strategy for CO₂ mitigation [3–5], but recently carbon capture and utilization (CCU) is considered a more desirable option in practice, which convert CO₂ to valuable chemicals and fuels [6–10]. Formic acid (HCOOH) is one of those promising chemicals with diverse applications, which can be synthesized from catalytic hydrogenation of CO₂ [7,11]. Recently, it is also receiving attention as an effective liquid H₂ carrier, because it has a high volumetric capacity (53 gH₂/L), low toxicity, and low flammability [7,11–15], and decomposition of HCOOH to CO₂ and H₂ occurs readily on Pd catalysts under mild conditions. It can also serve as a liquid fuel for formic acid fuel cells [16].

Formic acid is industrially synthesized by a two-step process of methanol carbonylation to methyl formate in the presence of a strong base catalyst, followed by hydrolysis [17]. Synthesis by

hydrogenation of CO₂ is thermodynamically unfavourable ($\Delta G^\circ = +32.9 \text{ kJ mol}^{-1}$). The equilibrium limitation could be somewhat mitigated by carrying out the reaction in an aqueous system ($\Delta G^\circ = -4 \text{ kJ mol}^{-1}$) [18], yet more favourable thermodynamics could be realized by performing the reaction in a basic solvent ($\Delta G^\circ = -9.5 \text{ kJ mol}^{-1}$) [19,20]. For example, Filonenko *et al.* applied triethyl amine (NEt₃) as the most effective base for this reaction [21]. However, the reaction forms an adduct of amine and formate (HCOO⁻), and the recovery of HCOOH from the adduct requires several additional processes [18]. To make the separation easier, Upadhyay and Srivastava introduced ionic liquids with a basic amino group [22]. But, the recycling of the expensive ionic liquid is essential, and the separation of this ionic liquid also requires additional processing.

The base-free CO₂ hydrogenation directly to HCOOH can make the product recovery process much simpler without such formate-base adduct formation. Instead, one needs to overcome the kinetic and thermodynamic barriers of the hydrogenation of the stable CO₂ molecule. In the present work, we employ graphitic carbon nitride (g-C₃N₄) as a basic catalyst support for Pd metal to promote adsorption of acidic CO₂ molecules. Carbon materials containing nitrogen are well-known CO₂ adsorbents with the nitrogen acting as a basic site [23–26]. Carbon nitride contains such a high N content, making it well-suited for the purpose [27–29]. In our

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