

Research Article

Trimetallic PdNiCo nanoparticles encapsulated in NH₂-BDC and UiO-66-NH₂ MOFs for efficient hydrogen production from formic acid

Noor Hayati Ridhwan¹, Najihah Syahbudin¹, Muhammad Shafie Norhisham¹, Norliza Dzakaria^{1,2*}, Nurul Auni Zainal Abidin¹, and Azizul Hakim Lahuri³

¹School of Applied Science and Environment, Faculty of Applied Science, Universiti Teknologi MARA(UiTM), Cawangan Negeri Sembilan, Kampus Kuala Pilah, 72000 Kuala Pilah, Negeri Sembilan, Malaysia

²Advanced Material for Environmental Remediation (AMER), Universiti Teknologi MARA(UiTM), Cawangan Negeri Sembilan, Kampus Kuala Pilah, 72000 Kuala Pilah, Negeri Sembilan, Malaysia

³Department of Science and Technology, Universiti Putra Malaysia Sarawak, Nyabau Road, P.O Box 396, 97008 Bintulu, Sarawak, Malaysia.

*Corresponding author: norliza864@uitm.edu.my

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Abstract

This study reports the synthesis and catalytic evaluation of trimetallic PdNiCo nanoparticles encapsulated within NH₂-BDC and UiO-66-NH₂ metal-organic frameworks (MOFs) for hydrogen production via formic acid dehydrogenation. The catalysts, denoted as PdNiCo-NH₂BDC and PdNiCo-UiO-66-NH₂, were synthesized using solvothermal and post-synthetic impregnation methods. Structural characterization confirmed that PdNiCo-UiO-66-NH₂ exhibited a highly crystalline framework with significantly higher BET surface area (459.79 m² g⁻¹) than PdNiCo-NH₂BDC (14.66 m² g⁻¹). FESEM and TEM analyses revealed improved nanoparticle dispersion and smaller particle size within the UiO-66-NH₂ framework, contributing to enhanced active-site accessibility. Catalytic dehydrogenation experiments demonstrated that hydrogen evolution increased with increasing reaction temperature and formic acid concentration. Under optimum conditions (98 wt% FA, 70 °C), PdNiCo-UiO-66-NH₂ achieved the highest hydrogen production of 0.15334 mmol with no detectable CO formation, indicating high selectivity toward the dehydrogenation pathway. The best catalytic performance was attributed to the synergistic effects of the PdNiCo trimetallic system, high porosity, and strong metal-support interactions provided by the UiO-66-NH₂ framework. These findings highlight the potential of PdNiCo-UiO-66-NH₂ as an efficient catalyst for sustainable hydrogen generation from liquid organic hydrogen carriers.

Keywords: metal organic frameworks, UiO-66-NH₂, trimetallic, dehydrogenation

Introduction

Hydrogen is considered a clean and renewable alternative to fossil fuels, making it a promising energy carrier for future energy systems. Hydrogen storage can generally be divided into physical and chemical methods. Among chemical hydrogen storage materials, liquid organic hydrogen carriers such as formic acid (FA) have attracted significant attention because they are easy to store and transport [1]. However, the development of a hydrogen economy still faces major challenges in hydrogen production, storage, transportation, and efficient utilization. Formic acid is regarded as a suitable hydrogen storage material due to its low toxicity, recyclability, liquid state at room temperature, and high hydrogen content. It can also be produced from biomass processing and CO₂ reduction, making it a renewable and sustainable source. Nevertheless, FA dehydrogenation may

produce carbon monoxide (CO), which can poison fuel cell catalysts and reduce their performance. Therefore, catalysts with high selectivity toward hydrogen production and low CO generation are highly required [2].

Trimetallic catalysts have shown better catalytic performance than monometallic and bimetallic systems because of the synergistic interaction between different metals. Among them, Pd-based catalysts are widely studied for FA dehydrogenation due to their excellent activity toward hydrogen release [3]. However, pure Pd catalysts are expensive and may suffer from particle aggregation and reduced long-term stability. The incorporation of transition metals such as Co and Ni can improve catalytic efficiency while reducing catalyst costs. Co is known to enhance electron transfer and catalytic stability, whereas Ni can

improve hydrogen adsorption and increase the number of active sites during the dehydrogenation process [4]. The combination of Pd, Co, and Ni therefore provides a synergistic effect that enhances catalytic activity, hydrogen selectivity, and catalyst durability [5][2]. In addition, PdCoNi trimetallic systems are more economically viable compared to noble-metal-rich catalysts because Co and Ni are inexpensive and readily available for transition metals.

Studies on FA dehydrogenation have focused on the use of solid supports such as metal oxides, activated carbon, and metal-organic frameworks (MOFs). In this study, MOFs were selected as catalyst supports because of their high surface area, tunable pore structure, and strong metal-support interaction. MOFs are porous crystalline materials composed of metal ions or clusters connected by organic ligands [6]. Their structural diversity, large pore volume, and high porosity make them suitable materials for catalytic and energy-related applications [7].

In catalytic hydrogen evolution, the organic ligands in MOFs help stabilize the framework structure and promote uniform dispersion of metal nanoparticles, resulting in more accessible active sites. The incorporated metal ions such as Pd^{2+} , Co^{2+} , and Ni^{2+} act as catalytic centers that facilitate the breaking of C-H and O-H bonds during FA dehydrogenation, leading to efficient hydrogen production [8]. In UiO-66-based MOFs, the zirconium (Zr) oxo-clusters also play an important role in the proposed dehydrogenation pathway. The $\text{Zr}_6\text{O}_4(\text{OH})_4$ clusters act as Lewis acidic sites that enhance the adsorption and activation of formic acid molecules on the catalyst surface [9, 10]. These clusters facilitate the formation of formate intermediates and promote efficient electron transfer between the MOF framework and the PdCoNi active sites. In addition, the amino ($-\text{NH}_2$) functional groups from the $\text{NH}_2\text{-BDC}$ ligand contribute to improved catalytic performance by increasing the basicity and hydrophilicity of the framework. The $-\text{NH}_2$ groups can strengthen the interaction between FA molecules and the catalyst surface through hydrogen bonding, thereby accelerating formate adsorption and dehydrogenation [11].

Furthermore, the electron-donating nature of the $-\text{NH}_2$ groups can modify the electronic environment of the PdCoNi active centers, enhancing hydrogen selectivity while suppressing undesirable CO formation. The synergistic interaction between the Zr clusters, NH_2 -functionalized ligands, and PdCoNi trimetallic components therefore contributes to enhanced catalytic activity, stability, and hydrogen generation efficiency. Consequently, the development of PdCoNi-supported UiO-66- NH_2 MOF catalysts offers strong potential for efficient and sustainable hydrogen production systems.

Materials and Methods

Chemicals and Materials

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), palladium(II) nitrate hexahydrate ($\text{Pd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-aminoterephthalic acid (NH_2BDC , $\text{C}_8\text{H}_7\text{NO}_4$, 99%), and zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) were purchased from Sigma-Aldrich. Dimethylformamide (DMF, anhydrous, 99.8%, AR grade), absolute ethanol 99% ($\text{C}_2\text{H}_6\text{O}$), methanol 99% (CH_3OH), formic acid (HCOOH), glacial acetic acid 99% (CH_3COOH), hydrochloric acid (HCl, 37 wt%), and deionized water were purchased from Chemmar.

Synthesis of UiO-66- NH_2

UiO-66s NH_2 was synthesized via a modified solvothermal method. Initially, zirconyl chloride precursor (ZrCl_4 , 0.168 g) and 2-aminoterephthalic acid (NH_2BDC , 0.390 g) were dissolved in 15 mL of N, N-dimethylformamide (DMF). Subsequently, hydrochloric acid (HCl, 1.14 mL) and glacial acetic acid (12 mL) were added as modulators to regulate the crystal growth and framework formation. The resulting mixture was continuously stirred at room temperature until a homogeneous solution was obtained. The solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 110 °C for 3 h under solvothermal conditions. After naturally cooling to room temperature, the suspension was poured into a beaker and allowed to stand undisturbed for 24 h to promote complete precipitation. The resulting white precipitate was collected by centrifugation and repeatedly washed with DMF to remove residual reactants and uncoordinated linker molecules. Finally, the obtained solid was dried at 60 °C for 24 h and labelled as UiO-66- NH_2 .

Preparation of PdNiCo-UiO-66- NH_2

PdNiCo-UiO-66- NH_2 was synthesized via a post-synthetic impregnation-assisted solvothermal method. Initially, UiO-66- NH_2 (0.1788 g, 0.0001 mol) was dispersed in 15 mL of N,N-dimethylformamide (DMF) under continuous stirring. Separately, equimolar amounts of metal precursors consisting of $\text{Pd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0001 mol, 0.0339 g), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0001 mol, 0.0291 g), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0001 mol, 0.0291 g) were dissolved in 15 mL of DMF to obtain a Pd:Ni:Co molar ratio of 1:1:1. The metal precursor solution was subsequently added dropwise into the UiO-66- NH_2 suspension and continuously stirred for 1 h at room temperature to ensure homogeneous metal incorporation within the framework structure. The resulting mixture was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 90 °C for 48 h under solvothermal conditions. After naturally cooling to room temperature, the obtained precipitate was collected by centrifugation at 3000 rpm for 5 min, followed by repeated washing with

DMF and ethanol to remove residual precursors and solvent molecules. The final product was dried overnight and labelled as PdNiCo-UiO-66-NH₂.

Synthesis of PdNiCo-NH₂BDC

PdNiCo-NH₂BDC was synthesized via a modified solvothermal method [4]. Equimolar amounts of metal precursors consisting of Pd(NO₃)₂·6H₂O (0.0005 mol, 0.1693 g), Ni(NO₃)₂·6H₂O (0.0005 mol, 0.1454 g), and Co(NO₃)₂·6H₂O (0.0005 mol, 0.1455 g) were used to obtain a Pd:Ni:Co molar ratio of 1:1:1. The organic linker NH₂BDC (2-aminoterephthalic acid) (0.0005 mol, 0.0906 g) was subsequently added into 15 mL of N,N-dimethylformamide (DMF). The mixture was continuously stirred for 1 h at room temperature until a homogeneous clear solution was obtained. The resulting solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 120 °C for 24 h under solvothermal conditions. After naturally cooling to room temperature, the precipitate formed was collected by centrifugation at 3000 rpm for 5 min and washed several times with DMF and ethanol to remove unreacted precursors and residual solvent. The final product was dried overnight in a hot-air oven and labelled as PdNiCo-NH₂BDC.

Characterization catalysts PdNiCo-NH₂BDC and PdNiCo-UiO-66-NH₂

X-ray Diffraction

The physicochemical properties of the prepared catalyst were characterized by X-ray diffraction (XRD), using the Cu K α X-ray radiation source (40 kV, 40 mA) in the XRD Bruker AXS D8 (Advance type) to record the 2 θ diffraction angle from 5° to 80° at a wavelength (λ = 0.154 nm). The diffractogram was matched with the JCPDS file to identify the crystalline phase composition.

Field Emission Scanning Electron Microscope (FESEM)

To identify the surface micrograph of the prepared catalyst, the ZEISS Supra VP55 type field emission scanning electron microscope (FESEM) was used. This instrument uses a tungsten-type electron gun with a voltage range of 0.1 to 3.0 kV. The microscope has a radiation detector for mapping elements. The sample also underwent EDX analysis to assess the position and distribution of the components within the sample.

Nitrogen Adsorption-Desorption Isotherm

Nitrogen gas isothermal adsorption testing was conducted using the BET method to analyze the physical surface attributes of the prepared catalyst, specifically its nitrogen gas adsorption capacity. Surface area measurements were determined by the Brunauer, Emmett, and Teller (BET) model using a Micromeritics ASAP 2020 analyzer. For the analysis, 0.3-1.0 g of catalyst was degassed in a glass tube under vacuum (20 torr) at 300 °C for 4 hs. Nitrogen gas (N₂) was then adsorbed onto the catalyst surface at -196 °C

(77K), forming monolayers, multilayers, and eventually condensation. The BET model provided the sample surface area (S_{BET}), using the linear portion of the BET plot within the P/P₀ range of 0.05 to 0.30. Additionally, the Barrett-Joyner-Halenda (BJH) method was applied to automatically calculate the pore volume (V_{pore}) and average pore diameter (D_{pore}) using the Micromeritics ASAP 2020 software, which automatically computes these.

Transmission Electron Microscopy (TEM)

The morphology of the prepared catalyst was carried out by transmission electron microscopy (TEM), Thermo Fisher Scientific with Model Talos L120C. 120kV. The prepared catalyst was diluted with ethanol and sonicated in 15 min. The sample was dropped on the copper grid and dried at room temperature for 2 h.

Gas Chromatography-Thermal Conductivity Detector (GC-TCD)

The gaseous products generated during the catalytic dehydrogenation of formic acid were analyzed using an Agilent GC6890 Gas Chromatography system equipped with a Thermal Conductivity Detector (GC-TCD). The evolved gas was collected in an airtight gas bag prior to analysis and manually injected into the GC system. The GC-TCD technique was employed to identify and quantify gaseous species based on their retention times, including hydrogen (H₂), carbon dioxide (CO₂), oxygen (O₂), nitrogen (N₂), methane (CH₄), and carbon monoxide (CO). The chromatographic data obtained were used to evaluate the hydrogen production performance and gas selectivity of the prepared catalysts.

Catalytic Dehydrogenation of FA for H₂ Generation

The catalytic dehydrogenation of formic acid (FA) for hydrogen generation was carried out in a 25 mL two-neck round-bottom flask connected to a rubber tube and gas collection system, as illustrated in Figure 1. In a typical experiment, 0.03 g of catalyst was dispersed in the reaction flask under continuous magnetic stirring at 600 rpm to ensure uniform catalyst suspension and effective mass transfer throughout the reaction. The experiments were conducted under ambient atmospheric conditions without inert gas purging. One neck of the flask was connected to an inverted water-filled measuring cylinder for gas collection via water displacement, while the second neck was used for the controlled addition of FA solution.

PdNiCo-NH₂BDC and PdNiCo-UiO-66-NH₂, were evaluated under identical reaction conditions. Since both catalysts possess different molecular weights and framework compositions, the catalyst loading was standardized on an equivalent molar basis rather than solely by mass to ensure a fair catalytic comparison.

The selected catalyst loading of 0.03 g was determined based on preliminary screening experiments, where the catalyst amount provided stable gas evolution, sufficient active site accessibility, and a suitable solid-to-liquid ratio without causing excessive aggregation or diffusion limitations. The chosen loading was therefore considered appropriate for evaluating the intrinsic catalytic performance of both supported catalysts. FA solutions with nominal concentrations of 50 wt%, 70 wt%, and 98 wt% were investigated to evaluate the influence of FA concentration on hydrogen production efficiency and catalytic activity. The variation in FA concentration was selected to represent diluted, intermediate, and concentrated reaction environments, which may significantly affect proton availability, catalyst surface interaction, and mass transport behavior during FA dehydrogenation. For each reaction, 1 mL of FA solution was introduced into the flask, and the hydrogen evolution profile was monitored for 30 min by recording the displaced water volume at 10 min intervals. The absolute gas volume was determined directly from the measured water displacement after blank correction.

Catalytic reactions were performed at 30 °C, 50 °C, and 70 °C to investigate the temperature-dependent behavior of the catalysts. These temperatures were selected to represent mild, moderate, and elevated reaction conditions while remaining below the boiling point of FA-containing aqueous mixtures. The reaction temperature was maintained using a thermostatically controlled water bath throughout the experiment to ensure thermal stability and reproducibility. Under the optimum catalytic

conditions, the evolved gas was collected in an airtight gas bag for compositional analysis using Gas Chromatography equipped with a Thermal Conductivity Detector (GC-TCD). The airtight gas collection system minimized gas leakage and contamination prior to GC-TCD injection, ensuring reliable determination of hydrogen-containing gaseous products. All catalytic experiments were repeated at least twice, and reproducible hydrogen evolution trends were obtained.

Results and Discussion

X-ray Diffraction (XRD)

The XRD pattern in **Figure 2** revealed distinct differences between the two catalysts. Based on **Table 1**, the PdNiCo-NH₂BDC catalyst showed predominantly amorphous characteristics with a few crystalline peaks with $2\theta = 40^\circ$, 45° and 68° that matched the Pd face-centered cubic (fcc) phase (JCPDS 00-046-1043), while the peaks related to Ni and Co were not clearly distinguished, possibly due to low peak intensity, overlap with Pd peaks, or high metal dispersion in the catalyst structure. In contrast, PdNiCo-UiO-66-NH₂ exhibited well-defined crystalline peaks corresponding to multiple phases: Pd (JCPDS 00-046-1043), Ni (JCPDS 00-001-1260), Co (JCPDS 00-015-0806), and the UiO-66-NH₂ zirconium-based MOF framework (JCPDS 00-015-0667). These results confirm the successful incorporation and crystallization of Pd, Ni, and Co nanoparticles within the crystalline UiO-66-NH₂ structure, which contributes to the catalyst's enhanced stability and activity. These findings are consistent with previous studies [12, 13].

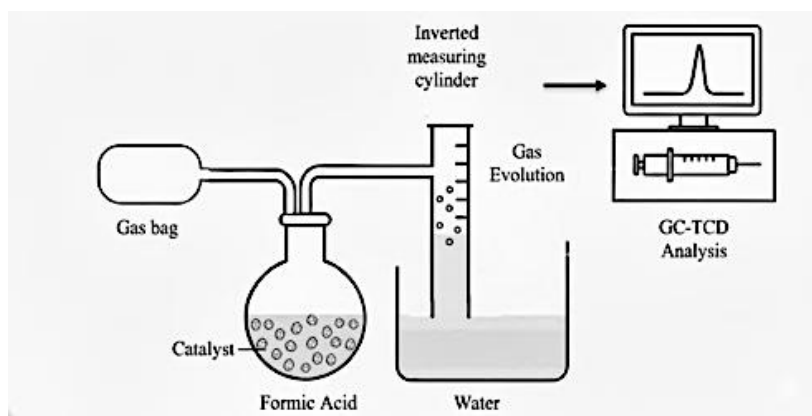


Figure 1. Collection and Analysis of Hydrogen Gases Evolved from FA Dehydrogenation Using GC-TCD

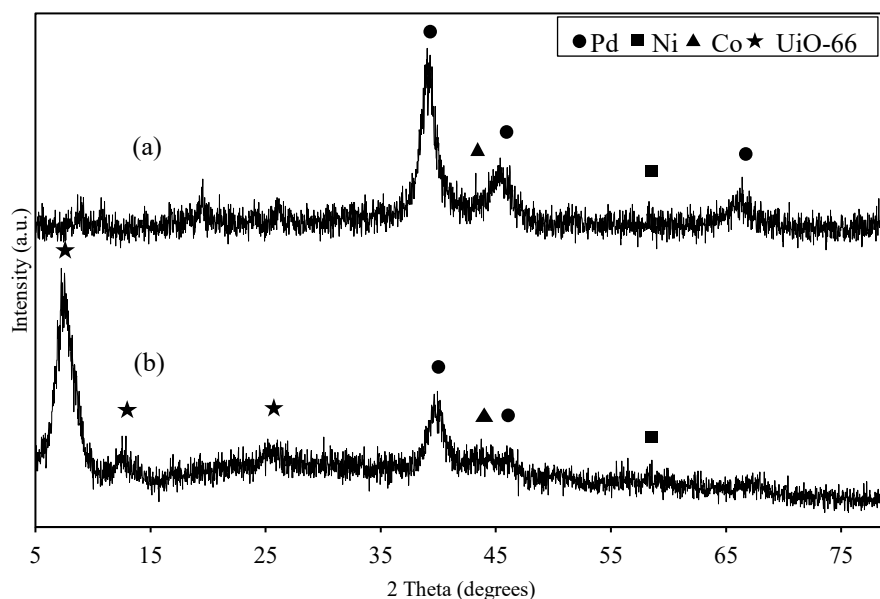


Figure 2. XRD pattern for (a) PdNiCo- NH₂BDC and (b) PdNiCo-UiO-66- NH₂

Table 1. Phase Identification of PdNiCo-Based Catalysts Using JCPDS Standards

Catalyst	JCPDS File No.	Phase / Composition	Notes
PdNiCo-NH ₂ BDC	00-046-1043	Pd (face-centered cubic, fcc)	Only Pd peaks detected; Ni and Co not observed (likely highly dispersed or amorphous)
PdNiCo-UiO-66-NH ₂	00-046-1043	Pd (fcc)	Presence of Pd nanoparticles
	00-001-1260	Ni (fcc)	Ni nanoparticles incorporated
	00-015-0806	Co (fcc)	Co nanoparticles incorporated
	00-015-0667	UiO-66 (Zr-based MOF framework)	Crystalline UiO-66 structure

Field Emission Scanning Electron Microscopy (FESEM) analysis

FESEM analysis was performed used to determine the morphological and microstructure of the particles. As shown in **Figure 3(a)**, the particles appeared to have an irregular, rough, and spherical shape. It shows the agglomerated catalyst forming a porous network structure. **Figure 3(b)** also shows the rough spherical

but not perfectly spherical spheres, which were also not uniform and agglomerated. Both prepared catalysts show that the morphology is not very different. The reason was mainly due to metal defects in the directly linked with NH₂BDC and the metal was embedded within UiO-66-NH₂, which is not beneficial. The results shows the phenomenon of agglomeration.

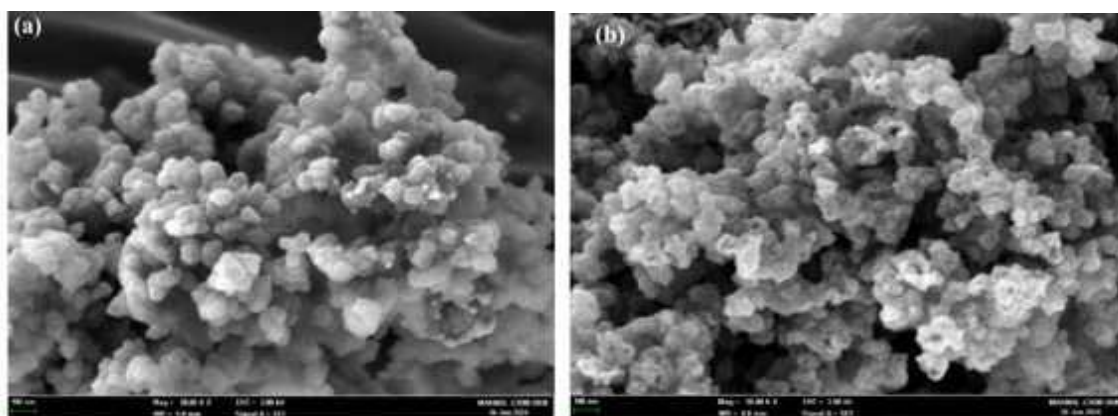
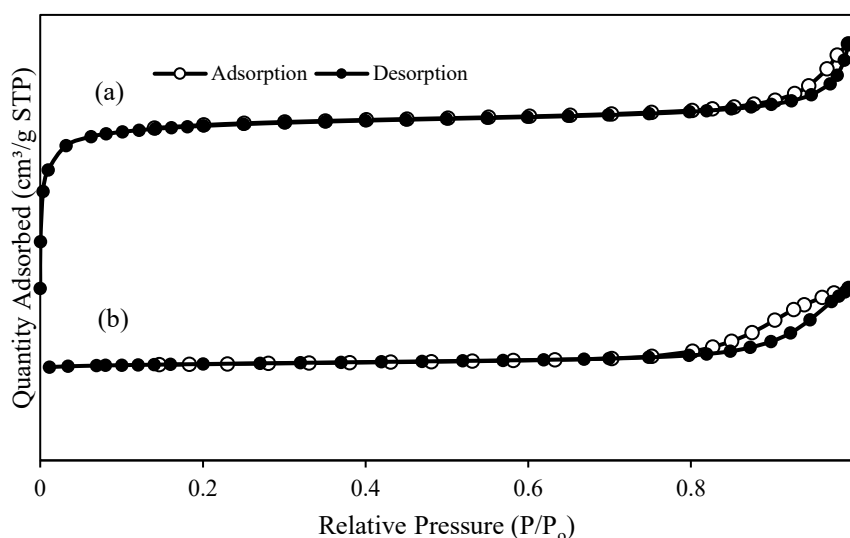


Figure 3. FESEM images for (a) PdNiCo-NH₂BDC and (b) PdNiCo-UiO-66- NH₂

Table 2. BET surface area, pore size and pore volume for PdNiCo-UiO-66-NH₂BDC and PdNiCo-NH₂BDC

Catalyst	BET Surface Area (m ² /g)	Pore Size (nm)	Pore Volume (m ³ /g)
PdNiCo-NH ₂ BDC	14.65610	18.300	18.2998
PdNiCo-UiO-66-NH ₂	459.7890	9.5500	9.54610

**Figure 4.** Nitrogen adsorption-desorption isotherm at 77K for (a) PdNiCo-NH₂BDC and (b) PdNiCo-UiO-66-NH₂

Nitrogen Adsorption-Desorption Isotherm

The nitrogen adsorption-desorption isotherms and corresponding textural properties of PdNiCo-NH₂BDC and PdNiCo-UiO-66-NH₂ are presented in Figure 4 and Table 2, respectively. Both materials exhibited Type IV isotherms with H3-type hysteresis loops, which are characteristic of mesoporous materials with slit-shaped pore structures. This behavior is commonly associated with aggregates of plate-like particles or porous frameworks with non-uniform pore connectivity. Despite their similar isotherm types, a pronounced difference in nitrogen uptake was observed between the two samples. PdNiCo-UiO-66-NH₂ demonstrated a substantially higher nitrogen adsorption capacity at high relative pressure ($P/P_0 \approx 0.95$) compared to PdNiCo-NH₂BDC, indicating a significantly more developed porous structure. This observation is consistent with the BET surface area results summarized in Table 2, where PdNiCo-UiO-66-NH₂ exhibited a remarkably higher specific surface area of 459.79 m²/g, compared to only 14.66 m²/g for PdNiCo-NH₂BDC. The sharp increase in nitrogen adsorption at high relative pressures ($P/P_0 > 0.8$) for PdNiCo-UiO-66-NH₂ confirms the occurrence of capillary condensation within the mesopores, while the broader hysteresis loop suggests improved pore accessibility and connectivity. In contrast, PdNiCo-NH₂BDC showed limited nitrogen uptake, reflecting a poorly developed porous network and restricted surface exposure. Although PdNiCo-NH₂BDC displayed a higher total pore size (18.30 nm) than PdNiCo-UiO-66-NH₂ (9.55 nm), this does not

translate into a higher surface area. This indicates that the pore structure of PdNiCo-NH₂BDC is dominated by fewer but larger or less accessible pores, resulting in inefficient surface utilization. Incorporation of the UiO-66-NH₂ framework significantly enhanced the surface textural properties of the catalyst, particularly by increasing the specific surface area and improving pore accessibility [14]. The substantially higher surface area of PdNiCo-UiO-66-NH₂ provides a greater density of exposed active sites, which is critical for catalytic applications, thereby enhancing catalytic efficiency in reactions such as FA dehydrogenation, gas adsorption, and related surface-driven processes [15].

The pore size distribution analysis revealed that both catalysts predominantly exhibited mesoporous structures with additional microporous characteristics. A sharp pore distribution peak (Figure 5) below 2 nm indicates the presence of micropores, which contribute significantly to the overall surface area and provide abundant adsorption sites. Meanwhile, the broad pore distribution within the mesoporous region (10–50 nm) facilitates efficient mass transport and improves accessibility of reactant molecules toward the active catalytic centers. Compared to PdNiCo-NH₂BDC, the PdNiCo-UiO-66-NH₂ catalyst displayed a more developed hierarchical porous structure with higher pore volume distribution, suggesting enhanced pore connectivity and greater exposure of catalytic active sites. The incorporation of the UiO-66-NH₂ framework likely contributed to the formation of a

more accessible porous network and improved structural organization. Such structural features are highly beneficial for FA dehydrogenation, as they promote rapid reactant diffusion and efficient hydrogen evolution. In contrast, PdNiCo-NH₂BDC exhibited a relatively lower pore volume distribution and less pronounced porous characteristics, indicating fewer accessible channels for reactant transport. The abrupt increase observed near 100 nm is likely associated with interparticle voids or aggregation effects rather than intrinsic framework porosity.

Transmission Electron Microscopy (TEM) analysis

The morphology of the prepared catalysts was further observed using TEM analysis, as shown in Figures 6(a) and (b). Both particles are spherical but not uniform. In Figure 6(a), the average diameter is 133.30 nm, while in Figure 6(b), the diameter is 128.47 nm. The average diameter of the particle was calculated using the ImageJ software. However, it can also be inferred from the BET results, which show that PdNiCo-UiO-66-NH₂ has a larger surface area compared to PdNiCo-NH₂BDC. It is well recognized in formic-acid dehydrogenation catalysis that smaller

catalyst particle sizes correspond to higher active surface areas and improved hydrogen production performance. Monometallic Pd catalysts with higher Pd loadings tend to form larger particles, which reduces surface availability, thereby lowering the initial hydrogen production rate, even when total hydrogen output remains similar. This indicates that active site accessibility, linked to particle size, governs early activity [16].

Moreover, size effects in FA dehydration with a less desired pathway were distinguished from facet effects using size-controlled Pd/C catalysts, while intrinsic dehydrogenation activity was less size-sensitive (3.0–6.5 nm). Larger particles exhibited faster dehydration rates, leading to deactivation, suggesting that smaller particles help maintain activity by suppressing deactivation pathways [17]. Hence, comprehensive reviews confirmed that particle size is a critical parameter in catalyst performance, often influencing activity more significantly than support or alloy compositions in formic-acid dehydrogenation systems [18]. Therefore, it may be concluded that smaller particle diameter results in a larger surface area.

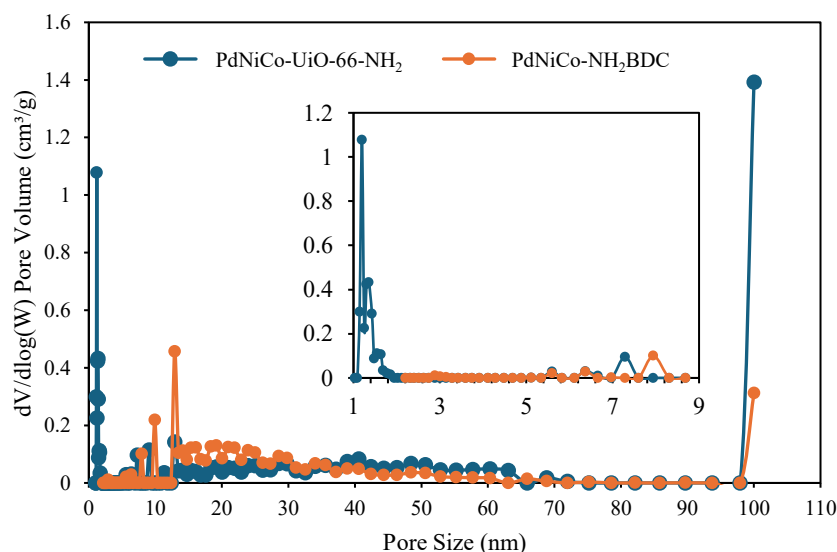


Figure 5. Pore size distribution of (a) PdNiCo-NH₂BDC and (b) PdNiCo-UiO-66-NH₂

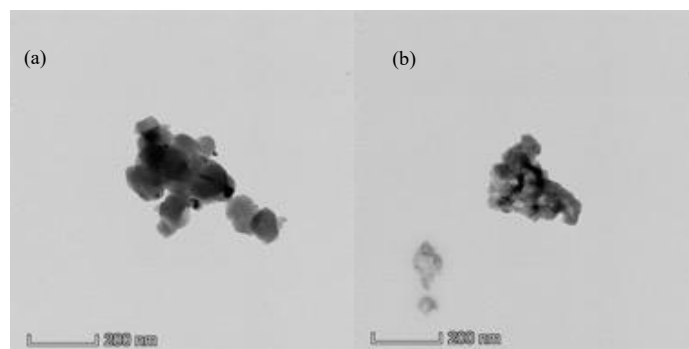


Figure 6. TEM micrograph of (a) PdNiCo-NH₂BDC and (b) PdNiCo-UiO-66-NH₂

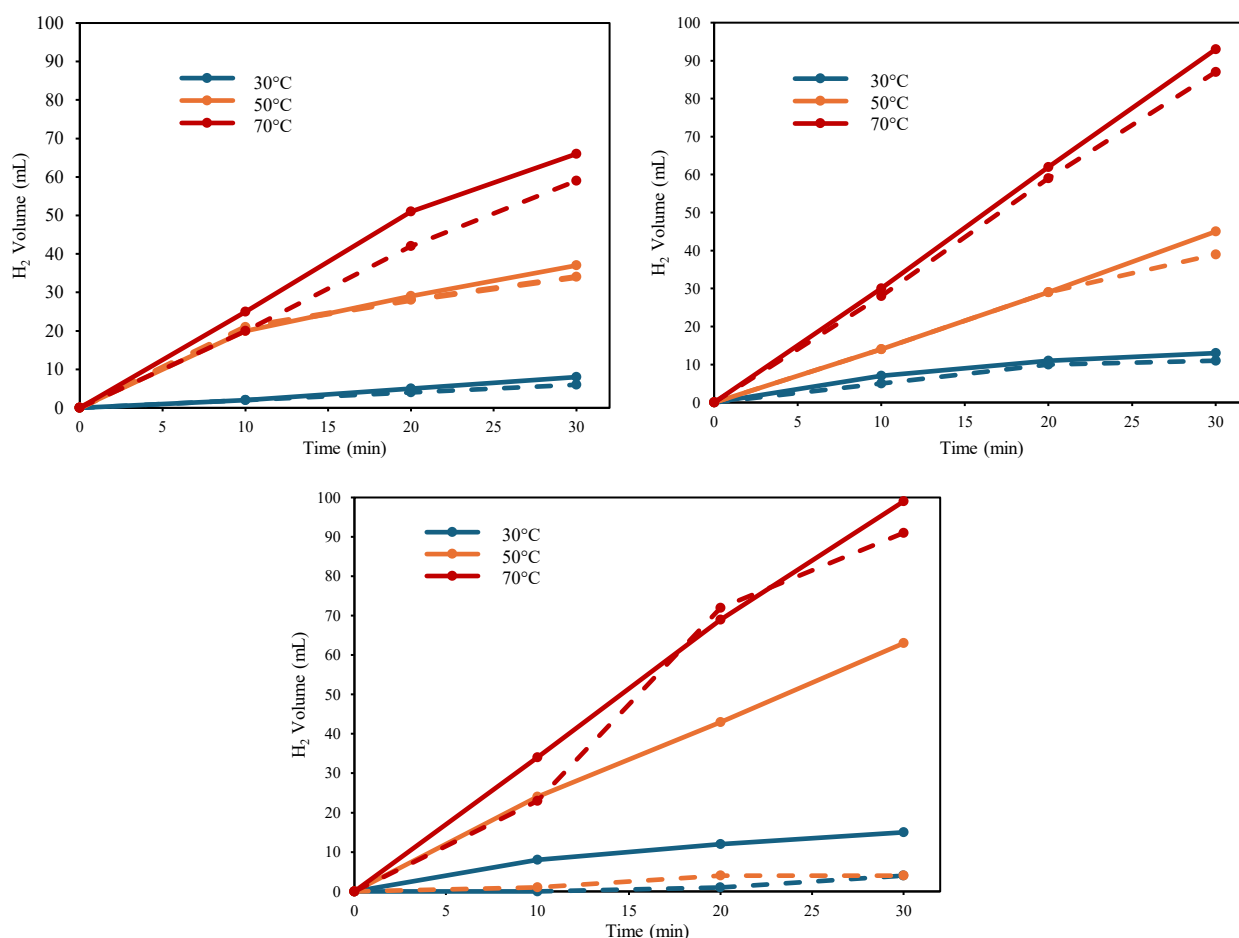


Figure 7. Time-dependent hydrogen evolution profiles during FA dehydrogenation over PdNiCo-NH₂BDC (dashed lines) and PdNiCo-UiO-66-NH₂ (solid lines) catalysts at different temperatures: 30 °C (blue), 50 °C (orange), and 70 °C (red) under (a) 50 wt% FA, (b) 70 wt% FA, and (c) 98 wt% FA conditions.

Catalytic of dehydrogenation of formic acid

Dehydrogenation of FA was performed to evaluate the catalytic activity of the synthesized catalysts, PdNiCo-NH₂BDC and PdNiCo-UiO-66-NH₂. The results are shown in **Figure 7 (a)-(c)**. Both catalysts were employed to dehydrogenate the FA and assess hydrogen efficiency. The FA dehydrogenation equation is shown in Equation 1.



The catalytic activity of PdNiCo-NH₂BDC and PdNiCo-UiO-66-NH₂ was systematically evaluated for hydrogen evolution from FA at three concentrations (50 wt%, 70 wt%, and 98 wt%) and three temperatures (30 °C, 50 °C, and 70 °C), as illustrated in **Figure 7**. The results reveal distinct trends in catalytic performance, highlighting the influence of both the catalyst structure and reaction conditions. For both catalysts, H₂ production increased markedly the temperature at all FA concentrations. At 30 °C, both catalysts showed relatively low H₂ volumes, indicating that FA dehydrogenation is kinetically limited at lower temperatures. As the temperature increased to 50 °C and further to 70 °C,

the rate of hydrogen evolution rose significantly for both catalysts. This is attributed to the enhanced molecular motion and increased energy available to overcome activation barriers, which accelerated the cleavage of C-H and O-H bonds in FA.

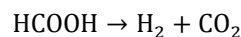
At 50 wt% and 70 wt% FA, both catalysts exhibited similar trends, but PdNiCo-NH₂BDC consistently produced slightly higher or comparable H₂ volumes than PdNiCo-UiO-66-NH₂ at each temperature. For instance, at 70 °C and 70 wt% FA, PdNiCo-NH₂BDC achieved the highest H₂ volume (~ 90 mL), whereas PdNiCo-UiO-66-NH₂ was marginally lower. This suggests that at moderate FA concentrations, PdNiCo-NH₂BDC provides more accessible active sites or more favorable reaction environments, possibly due to its simpler structure and higher initial surface area. At 98 wt% FA, however, a significant performance divergence was observed. PdNiCo-UiO-66-NH₂ demonstrated a pronounced advantage, especially at elevated temperatures. At 70 °C, PdNiCo-UiO-66-NH₂ achieved the maximum H₂ volume (~ 90 mL), while PdNiCo-NH₂BDC lagged at only about 40 mL. Despite some agglomeration observed in the FESEM images, PdNiCo-UiO-66-NH₂ BDC still showed

better catalytic activity and stability under highly concentrated FA conditions. This improved performance may be attributed to the porous UiO-66-NH₂ MOF structure, which facilitated reactant diffusion and provided stronger metal-support interactions that help maintain accessible active sites during the reaction. In contrast, PdNiCo-NH₂BDC likely experienced faster catalyst deactivation or blockage of active sites at high FA concentration, resulting in lower hydrogen production. In contrast, PdNiCo-NH₂BDC appeared to suffer from rapid deactivation or site blockage at high FA concentrations, limiting its effectiveness.

The high surface area, uniform porosity, and strong metal-support interactions provided by the Zr-based clusters facilitated efficient reactant diffusion and stabilized the active metal sites [10]. This is particularly advantageous under demanding conditions, such as high FA concentrations, where conventional supports may fail due to nanoparticle aggregation or pore blockage. The comparative analysis clearly demonstrates that while PdNiCo-NH₂BDC is effective at moderate FA concentrations and temperatures, PdNiCo-UiO-66-NH₂ exhibits higher catalytic activity and stability at high FA concentrations and elevated temperatures. The MOF-supported catalyst leverages the structural advantages of UiO-66-NH₂ to maintain high activity and prevent deactivation, making it a more promising candidate for practical hydrogen generation from concentrated FA. These findings underscore the importance of catalyst support design in optimizing performance for liquid-phase hydrogen storage and release systems.

Gas Chromatography-Thermal Conductivity Detector (GC-TCD)

GC-TCD analysis as shown in **Figure 8** was conducted to evaluate the gaseous products generated during FA dehydrogenation under different reaction temperatures and FA concentrations. Based on **Table 3 and 4**, the results demonstrated that the reaction mainly produced H₂ and CO₂, while no detectable CO peak was observed in all chromatograms, confirming that the reaction predominantly proceeded through the dehydrogenation pathway rather than the undesirable dehydration pathway.



At a constant FA concentration of 98%, increasing the reaction temperature from 30 °C to 70 °C significantly enhanced hydrogen production. The H₂ yield increased from 0.00394 %mol at 30 °C to 0.15335 %mol at 70 °C, indicating that elevated temperatures accelerated the dehydrogenation of FA and improved catalytic activity. Higher reaction temperatures provide sufficient activation energy for the cleavage of the O-H and C-H bonds in FA, thereby promoting hydrogen release. In addition, the H₂ selectivity increased from 0.89% to 8.55% when the temperature increased from 30 °C to 70 °C, suggesting that higher temperatures favor the dehydrogenation reaction pathway.

The effect of FA concentration was also observed by comparing 70% and 98% FA at 70 °C. The catalyst exhibited higher hydrogen yield at 98% FA compared to 70% FA, where the H₂ yield increased from 0.01134 %mol to 0.15335 %mol. This behavior indicates that a higher concentration of FA provides more reactant molecules available for catalytic dehydrogenation, resulting in greater hydrogen generation. The higher H₂ selectivity obtained at 98% FA further confirms that concentrated FA enhances catalytic dehydrogenation efficiency. Although H₂ formation was confirmed in all samples, CO₂ remained the dominant detected product gas. The relatively high CO₂ selectivity compared to H₂ may be associated with differences in detector sensitivity, gas diffusion behavior, partial hydrogen loss during sampling, or atmospheric contamination introduced during gas collection and injection. This observation is supported by the presence of O₂ and N₂ peaks in the chromatograms, which originated from residual air contamination rather than catalytic reaction products.

The results clearly demonstrate that reaction temperature and FA concentration strongly influence hydrogen generation performance. Among all tested conditions, 98% FA at 70 °C exhibited the highest hydrogen yield and H₂ selectivity, indicating that higher temperature and concentrated FA are favorable conditions for efficient catalytic hydrogen production through FA dehydrogenation.

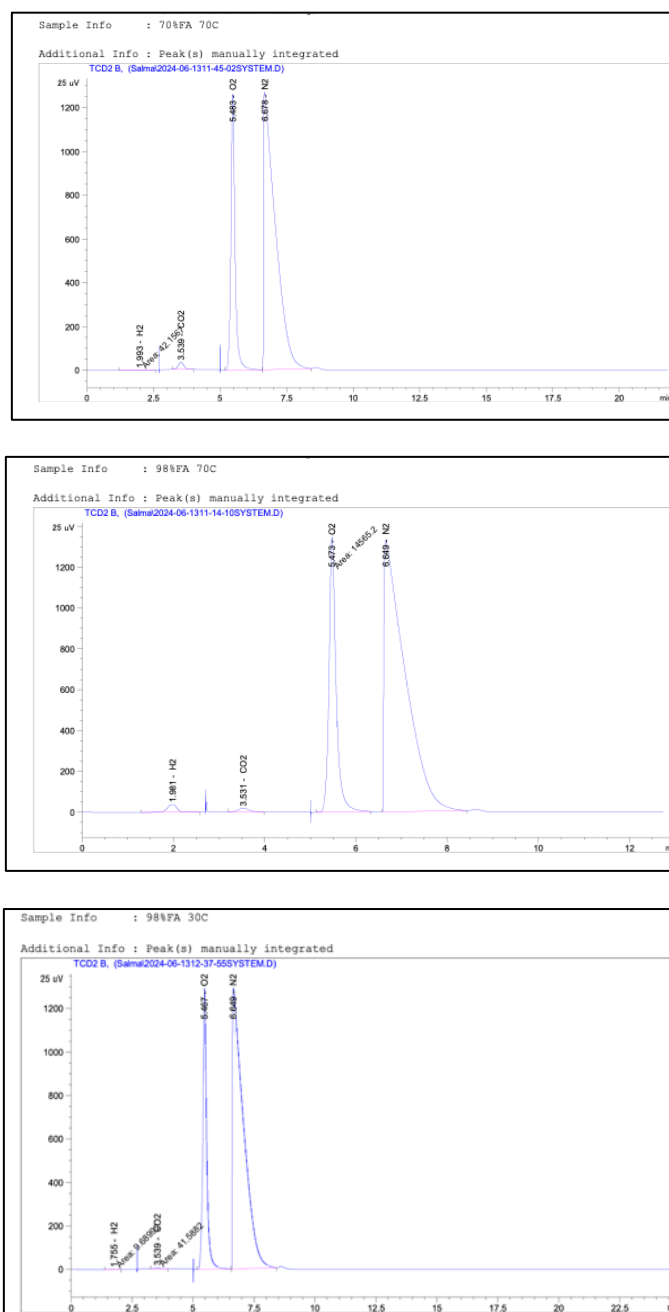
Table 3. Quantitative Analysis of Gas Components by GC-TCD for PdNiCo-UiO-66-NH₂

Retention Time (min)	Peak Area (μV·s)	Identified Gas	Amount (mmol)
1.981	570.0899	H ₂	0.15334
3.531	267.5284	CO ₂	0.03640
5.473	4.5156	O ₂	0.00058
6.649	4.2171	N ₂	0.03993

Table 4. Effect of reaction conditions of PdNiCo-UiO66-NH₂ on gaseous product selectivity during FA dehydrogenation

FA Concentration (%)	Temperature (°C)	H ₂ Produced (mmol)	H ₂ Selectivity (%)	CO ₂ Selectivity (%)	CO Detection
98	70	0.15334	8.55	91.45	Not detected
70	70	0.01134	0.38	99.62	Not detected
98	30	0.00394	0.89	99.11	Not detected

Reaction Conditions: 0.03 g catalyst, 1 mL FA, reaction performed under catalytic dehydrogenation conditions followed by GC-TCD analysis.

**Figure 8.** Chromatogram and Quantitative Analysis of Gas Sample Using Gas Chromatography with Thermal Conductivity Detector (GC-TCD) for PdNiCo-UiO-66-NH₂.

Conclusion

The intercorrelation between the structural, surface, and morphological properties of the synthesized catalysts and their catalytic performance in FA dehydrogenation demonstrated the superiority of PdNiCo-UiO-66-NH₂ over PdNiCo-NH₂BDC. The XRD analysis confirmed that PdNiCo-UiO-66-NH₂ possessed a more crystalline structure with distinct Pd, Ni, Co, and UiO-66 peaks, while PdNiCo-NH₂BDC exhibited predominantly amorphous characteristics. The BET analysis showed that PdNiCo-UiO-66-NH₂ has a significantly higher surface area, providing more accessible active sites and improved pore accessibility for catalytic reactions. FESEM and TEM analyses revealed that both catalysts consisted of agglomerated particles, although PdNiCo-UiO-66-NH₂ exhibited slightly smaller and better-dispersed nanoparticles compared to PdNiCo-NH₂BDC. These structural properties directly influenced the catalytic performance during FA dehydrogenation. Both catalysts showed increased hydrogen production with increasing temperature and FA concentration; however, PdNiCo-UiO-66-NH₂ demonstrated superior catalytic activity under highly concentrated FA conditions. Under the optimum condition of 98 wt% FA at 70 °C, PdNiCo-UiO-66-NH₂ achieved the highest hydrogen yield (0.15334 mmol H₂) with no detectable CO formation compared to PdNiCo-NH₂BDC, confirming selective dehydrogenation performance. Therefore, the integration of PdNiCo nanoparticles within the UiO-66-NH₂ framework successfully enhanced the structural properties, catalyst stability, and hydrogen production efficiency, making PdNiCo-UiO-66-NH₂ a promising catalyst for sustainable hydrogen generation from FA.

For practical application, further studies are still required to develop low-cost and highly efficient catalysts for hydrogen generation from liquid-phase chemical hydrogen storage materials. In this study, the possible influence of air contamination during gas collection and handling may have affected the purity and accuracy of the hydrogen analysis. Therefore, future work should focus on improving the gas collection system and ensuring an inert or airtight reaction environment to minimize contamination and enhance the reliability of catalytic performance evaluation.

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References

- Schlapbach, L., and Züttel, A. (2010). Hydrogen-storage materials for mobile applications. *Nature*, 414, 353–358.
- Grasemann, M., and Laurenczy, G. (2012). Formic acid as a hydrogen source - Recent developments and future trends. *Energy & Environmental Science*, 5(8), 8171–8181.
- Santos, J.L., Megías-Sayago, C., Ivanova, S., Centeno, M.Á., and Odriozola, J.A. (2021). Functionalized biochars as supports for Pd/C catalysts for efficient hydrogen production from formic acid. *Applied Catalysis B*, 282, 119615.
- Chen, H. Y., Huo, Y. Q., Cai, K. Z., Teng, Y. (2021). Controllable preparation and capacitance performance of bimetal Co/Ni-MOF. *Synthetic Metals*, 276, 116761.
- Ruan, L., Pei, A., Liao, J., Zeng, L., Guo, G., Yang, K., Zhou, Q., Zhao, N., Zhu, L., Chen, B.H. (2021). Nitrogen-doped carbon nanotubes-supported PdNiCo nanoparticles as a highly efficient catalyst for selective hydrogenation of furfural. *Fuel*, 284, 119015.
- Duan, S., Hou, P., Yuan, X., Habuda Stanić, M., Qiang, Z., Dong, H. (2020). Homogeneous activation of bisulfite by transition metals for micro-pollutant degradation: Mn(VII) versus Cr(VI). *Chemical Engineering Journal*, 394, 124814.
- Wang, Q., and Astruc, D. (2020). State of the art and prospects in metal-organic framework (MOF)-based and MOF-derived nanocatalysis. *Chemical Reviews*, 120(2), 1438–1511.
- Bawornruttanaboonya, K., Devahastin, S., Mujumdar, A.S., and Laosiripojana, N. (2018). Comparative evaluation of autothermal reforming of biogas into synthesis gas over bimetallic Ni–Re/Al₂O₃ catalyst in fixed-bed and coated-wall microreactors: A computational study. *International Journal Hydrogen Energy*, 43, 13237–13255.
- Wang, J., Liu, C., Feng, J., Cheng, D., Zhang, C., Yao, Y., Gu, Z., Hu, W., Wan, J., and Yu, C. (2020). MOFs derived Co/Cu bimetallic nanoparticles embedded in graphitized carbon nanocubes as efficient Fenton catalysts. *Journal of Hazardous Materials*, 394, 122567.
- Yang, G., Gao, M., Lv, J., Ding, Y., He, L., Hao, D., Tang, X., and Wang, Q. (2025). Breaking base dependence: Solar-boosted CO₂ hydrogenation to formic acid over confined PdAg@NH₂-UiO-66. *ACS Sustainability Chemical Engineering*, 13, 19573–19585.
- Li, Z., and Xu, Q. (2017). Metal-Nanoparticle-Catalyzed Hydrogen Generation from Formic Acid. *Acc. Chemical Research*, 50, 1449–1458.
- Guan, Q., Wang, B., Chai, X., Liu, J., Gu, J., Ning, P. (2017). Comparison of Pd-UiO-66 and Pd-UiO-66-NH₂ catalysts performance for

- phenol hydrogenation in aqueous medium. *Fuel*, 205, 130–141.
13. Nie, M., Sun, H., Lei, D., Kang, S., Liao, J., Guo, P., Xue, Z. and Xue, F. (2020). Novel Pd/MOF electrocatalyst for hydrogen evolution reaction. *Materials Chemistry and Physics*, 254, 3481.
14. Kandiah, M., Usseglio, S., Svelle, S., Olsbye, U., Lillerud, K.P., and Tilset, M. (2010). Post-synthetic modification of the metal-organic framework compound UiO-66. *J. Mater. Chem.* 20, 9848–9851.
15. Cisneros, S., Chen, S., Fauth, C., Abdel-Mageed, A.M., Pollastri, S., Bansmann, J., Olivi, L., Aquilanti, G., Atia, H., Rabeah, J., Parlinska-Wojtan, M., Brückner, A., and Behm, R.J. (2022). Controlling the selectivity of high-surface-area Ru/TiO₂ catalysts in CO₂ reduction - modifying the reaction properties by Si doping of the support. *Applied Catalyst B*, 317, 121748.
16. Ribota Peláez, M., Ruiz-López, E., Domínguez, M.I., Ivanova, S., Centeno, M.A. (2023). Formic acid dehydrogenation over a monometallic Pd and bimetallic Pd:Co catalyst supported on activated carbon. *Catalysts*, 13, 977.
17. Meng, Q., Wang, X., Xiao, M., Jin, Z., Ge, J., Liu, C., and Xing, W. (2023). Revealing the true origin of size-dependent Pd/C catalytic behavior towards formic acid decomposition. *Chinese Chemical Letters*, 34, 026.
18. Kim, Y., and Kim, D.H. (2019). Understanding the effect of Pd size on formic acid dehydrogenation via size-controlled Pd/C catalysts prepared by NaBH₄ treatment. *Applied Catalyst B*. 244, 684–693..