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Hydrogen Production by Formic Acid Decomposition with Nanoscale Zero-Valent Iron (nZVI): Effects of nZVI Dosage, Temperature and Time

Siti Aishah Yusuf[1], Siti Nur Syukriena Ismail[1], Meor Saiful Rizal Meor Ahmad Zubairi[2], Govindaraju Muthuraman[3], Siti Fatimah Abdul Halim[1], Siu Hua Chang[1,*]

[1] Waste Management and Resources Recovery (WeResCue) Group, Chemical Engineering Studies, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Malaysia
[2] Graphite Signature Sdn Bhd, 31650 Ipoh, Malaysia
[3] Department of Chemistry, Presidency College, University of Madras, Chennai 600 005, India

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ABSTRACT

Amidst growing interest in renewable hydrogen gas production, this paper examines three important parameters affecting hydrogen production via formic acid decomposition reaction with nanoscale zero-valent iron (nZVI). The study investigates variations in nZVI dosage (200 – 1000 g/L), reaction temperature (25 – 75°C), and reaction time (5 -30 minutes) to identify optimum conditions for maximum hydrogen yield. Results indicate that the maximum hydrogen yield occurred at nZVI dosage, reaction temperature, and time of 800 g/L, 25°C and 30 minutes, respectively, yielding approximately 215 mL of hydrogen at optimal parameter values. The synthesized nZVI was also analysed before and after the reaction, focusing on the specific surface area and pore size of the nZVI. The results from BET characterization regarding specific surface area and pore size are consistent with experimental results, suggesting smaller pores correspond to higher surface area, enhancing reactivity with formic acid to produce hydrogen gas. Conversely, larger pore sizes after the reaction signify reduced surface area and lower reactivity of nZVI.

1. Introduction

Currently, fossil fuels are the primary source of energy for electricity production and are also refined for heating and transportation purposes [1]. Although fossil fuels provide a highly concentrated form of energy, they are responsible for a substantial portion of greenhouse gas emissions. This leads to elevated carbon monoxide levels in the atmosphere, rapid temperature increases, and ozone layer depletion [1]. Moreover, fossil fuels are non-renewable resources with finite reserves [2,3]. In contrast, hydrogen shows great potential as an alternative fuel due to its minimal environmental impact, as it burns cleanly and does not produce greenhouse gas emissions [4].

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[*] *Corresponding author.*
E-mail address: shchang@uitm.edu.my

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Hydrogen is primarily produced through thermochemical, biological, and water splitting processes [5-7]. These methods are typically expensive and require complex, costly equipment to operate under stringent conditions [8]. Additionally, the hydrogen produced is often stored as compressed gas or cryogenic liquid, which raises safety concerns [9]. Therefore, there is an urgent need for a more cost-effective method to produce hydrogen to promote its use as an alternative fuel [10]. Recently, hydrogen storage media such as metal-boron hydrides, ammonia borane, formic acid, hydrazine hydrate, and aromatic compounds have garnered significant attention [11-15]. These media can store hydrogen in liquid form at ambient conditions, offering a safer and more convenient alternative to the traditional storage of hydrogen as compressed gas or cryogenic liquid [16].

Recently, formic acid decomposition has gained significant interest as a method for producing renewable hydrogen gas [17]. Formic acid decomposes at a lower temperature than other simple organic compounds, resulting in reduced production of toxic CO species. Numerous catalysts, both homogeneous and heterogeneous, have been developed for the decomposition of formic acid to generate hydrogen and carbon dioxide under low-intensity conditions [13]. The decomposition of formic acid utilizes various metal-based catalysts, including ruthenium, iridium, copper, iron, palladium, and gold, to produce hydrogen [13]. However, while these metal-based catalysts facilitate hydrogen production from formic acid decomposition, they also generate carbon dioxide and carbon monoxide as by-products, which can make this reaction less favourable. Recently, a new approach utilizes zero-valent iron (Fe^0) as a reactant, not a catalyst, in formic acid decomposition, resulting in the production of hydrogen gas and iron formate salt only, without the emission of greenhouse gases like carbon monoxide and carbon dioxide [18]. This study employs nanoscale zero-valent iron (nZVI) as the reactant for hydrogen production, leveraging its increased reactivity due to its larger surface area at the nano-scale [19]. The reaction of the formic acid decomposition with nZVI for the pure hydrogen production such as [18]:

$$Fe_{(s)} + 2HCOOH_{(\ell)} + 2H_2O \rightarrow H_{2_{(g)}} + Fe(HCOO)_2.2H_2O_{(s)} \quad (1)$$

In this study, various parameters influencing hydrogen production through formic acid decomposition with nZVI were examined, including nZVI dosage, reaction time, and temperature. The research addresses the existing gap in understanding the impact of these parameters on hydrogen production.

2. Materials, Equipment and Methods

2.1 Materials

Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), ethanol 99.7%v/v (C_2H_5OH), and formic acid 90%v/v (CH_2O_2) were obtained from R&M Chemicals. Sodium Borohydride ($NaBH_4$) from Bellamy Precision, Malaysia. All chemicals were used as received, without any further modification.

2.2 Equipment

Hotplate (Fisher Scientific) was used to adjust the reaction temperature. The nZVI characterization was measured by using Brunauer-Emmett-Teller (BET) (micromeritics ASAP 2020) for surface area and porosity analyser.

2.3 Preparation of nZVI

The preparation of nanoparticles involved the reduction reaction which has been widely used for the synthesis of nanoparticles as studied by Singh *et al.,* [18] and Shamsuri *et al.,* [20]. The preparation of nZVI involved the reduction reaction of iron chloride [18]. Firstly, 4.45 g of $FeCl_3.6H_2O$ was dissolved in a beaker containing 12.5 ml of 4:1 ethanol to water mixture and 2 g of $NaBH_4$ was dissolved in 55 mL of water in another beaker. The $NaBH_4$ solution was then added drop by drop, at a rate of about 20 drops per minute, into a conical flask filled with the iron chloride solution. The mixture was stirred vigorously at room temperature with a stirring rate of 1200 rpm to minimize particle aggregation during the synthesis of nZVI [18]. The reaction was allowed to process for 10 minutes until nZVI in the form of black particle precipitated. Next, the synthesized nZVI was separated from the solution by using vacuum filtration. The filtered nZVI was then washed with ethanol. This washing step is important to prevent the rapid oxidation of the nZVI particles [18]. The reduction reaction equation for the synthesis of nZVI is as follows [19]:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0_{(s)} + 3H_2BO^-_{3\ (aq)} + 12H^+ + 6H_2 \tag{2}$$

2.4 Hydrogen Production by Formic Acid Decomposition with nZVI

The formic acid decomposition reaction with nZVI for pure hydrogen production was investigated under different operating parameters affecting the hydrogen gas yield. These parameters included different nZVI dosages (200, 400, 600, 800, and 1000 g/L), reaction temperatures (25, 35, 45, 55, 60, 65, 70 and 75°C) and reaction times (5-30 minutes). The experimental setup used as shown in Figure 1, consists of a three-neck round-bottom flask as the reactor, immersed in a water bath beaker. The first neck of the flask is equipped with a thermometer, the second neck connected to a rubber tube linked to an inverted burette submerged in a beaker filled with water, and the third neck is sealed with a rubber stopper and clamped to a retort stand.

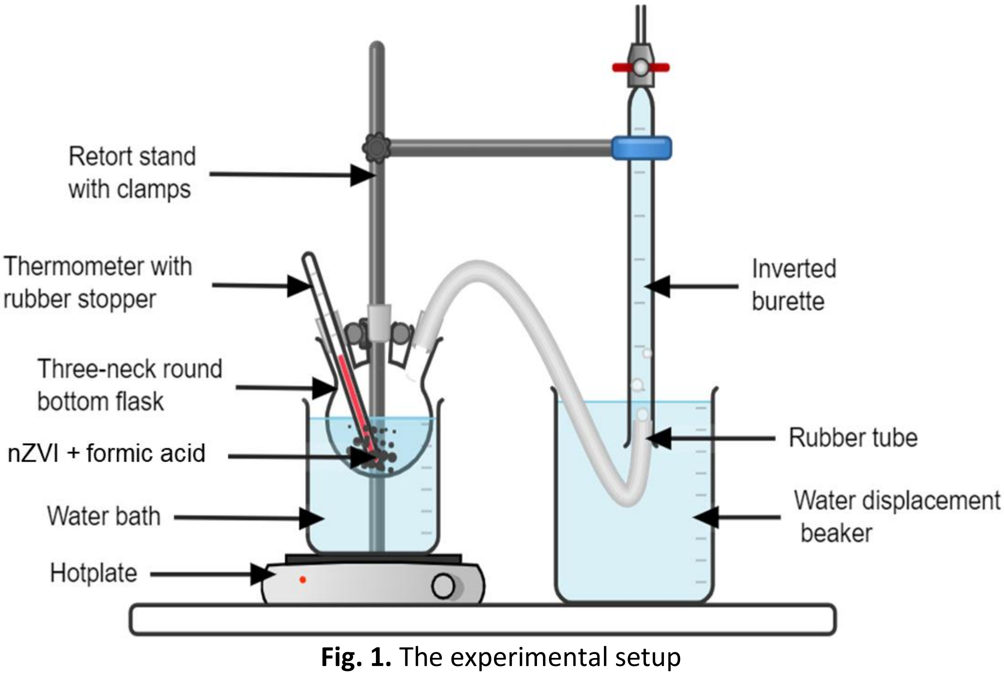

Fig. 1. The experimental setup

To study the effect of nZVI dosage, the reaction temperature was kept constant at room temperature (25°C). Then, a known amount of nZVI dosage was added into the round bottom flask, and the stopwatch was started. The hydrogen gas produced from the reaction was collected in the inverted burette and recorded from the burette scale after 30 minutes.

For the study of reaction temperature, formic acid solution in the round bottom flask was gradually heated to the desired temperature. Next, a specific dosage of nZVI was added to the flask to initiate the reaction with formic acid. The quantity of hydrogen gas produced from the reaction was then measured after 30 minutes.

To study the effect of reaction time, a procedure similar to the previously described procedures for the studies of nZVI dosage and reaction temperature was used. However, in this case, the volume of hydrogen gas produced was measured every five minutes throughout a 30-minute reaction period. A consistent volume of 10 mL of formic acid solution at a concentration of 50% v/v was utilized in all of these experiments.

3. Result and Discussion

3.1 Effects of nZVI Dosage

The hydrogen yield was studied at different dosage of nZVI at 200, 400, 600, 800, and 1000 g/L. The hydrogen yield from the reaction is as shown in the Figure 2.

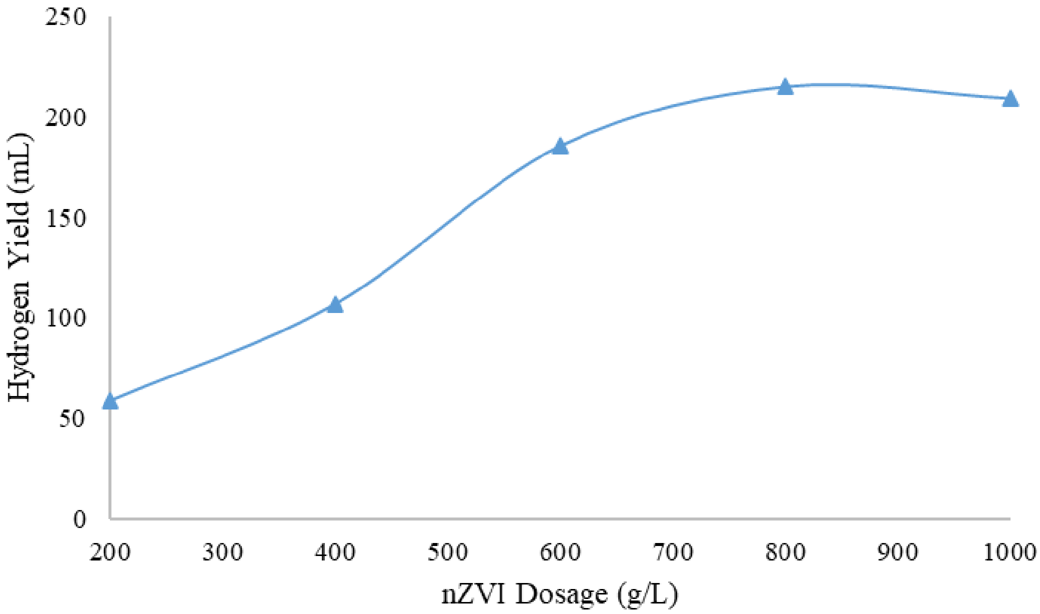

Fig. 2. Effects of nZVI dosage on hydrogen yield

Figure 2 shows the hydrogen yield at different nZVI dosage for the formic acid decomposition starting from the nZVI dosage of 200 g/L until 1000 g/L. The result shows that the hydrogen gas yield increased gradually along with the increment of nZVI dosage from 200 g/L until 800 g/L with the hydrogen yield of ~59 mL until ~215 mL, respectively. The graph was then showing a decreasing pattern as the nZVI dosage was further increased to 1000 g/L, where the hydrogen yield recorded was ~209 mL. The result for the effects of the nZVI dosage on the hydrogen yield depicts that the reaction system may have reached a plateau as the nZVI dosage for the reaction were further increased more than 800 g/L. This can be seen as the hydrogen yield shows a very significant rises from 200 g/L until 800 g/L of nZVI dosage which prove that the formic acid molecules have sufficient amount of nZVI to react with. However, as the nZVI dosage was further increased, the hydrogen yield decreases which may suggest that the reaction system may have reached a point of diminishing returns, where all available formic acid molecules may have reacted with the nZVI particles, resulting in excess nZVI particles without sufficient remaining formic acid for further reactions.

This result may also due to the agglomeration factor of nZVI at higher dosages, which reduces the available reactive surface area. Study by Ibrahim *et al.,* [21] also discussed on the agglomeration and aggregation tendency in bare nZVI without any support materials. Thus, explains on the decreasing pattern after the dosage was increased higher than 800 g/L. Since the effects of the nZVI dosage on the hydrogen yield for the formic acid decomposition reaction is still new and limited, there is lack of study for comparison. However, a relatively similar pattern can be seen in the study by Chen *et al.,* [22] on the water decomposition by nZVI reaction for hydrogen production. From the study, the hydrogen production shows a slightly decrease pattern as the nZVI dosage were increases. The findings suggested that this might be due to the formation of hydroxide ion during the reaction which leads to the accumulation of the iron hydroxide on the surface of the particle which reduces the reaction area, leading to a lower hydrogen yield [22]. Thus, the maximum hydrogen yield for the effect of nZVI dosage is at 800 g/L at 215 mL.

3.2 Effects of Reaction Temperature

The hydrogen yield was studied at different reaction temperature for the formic acid decomposition by nZVI such as at 25, 35, 45, 55, 60, 65, 70 and 75°C. The hydrogen yield from the reaction is as shown in the Figure 3.

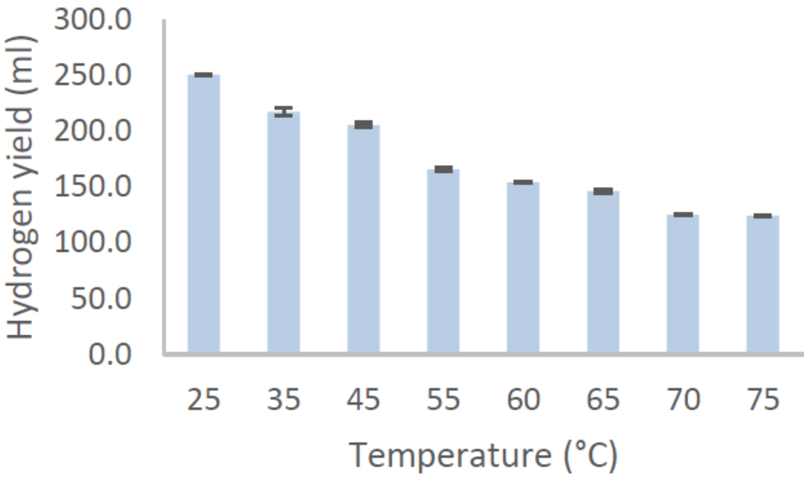

Fig. 3. Effects of reaction temperature on hydrogen yield

Figure 3 illustrates a gradual decrease in hydrogen yield with increasing temperatures from 25°C to 75°C. This trend suggests that higher temperatures may lead to formic acid degradation, as observed in previous studies by Arts *et al.,* [23], resulting in reduced hydrogen production efficiency. The degradation of formic acid diminishes its reactivity with nZVI, thereby lowering hydrogen yield. Therefore, based on these findings, the optimal temperature for maximizing hydrogen production from formic acid decomposition with nZVI appears to be 25°C.

3.3 Effects of Reaction Time

The hydrogen yield was studied at different reaction time for the formic acid decomposition by nZVI from 5 to 30 minutes. The hydrogen yield from the reaction is as shown in the Figure 4.

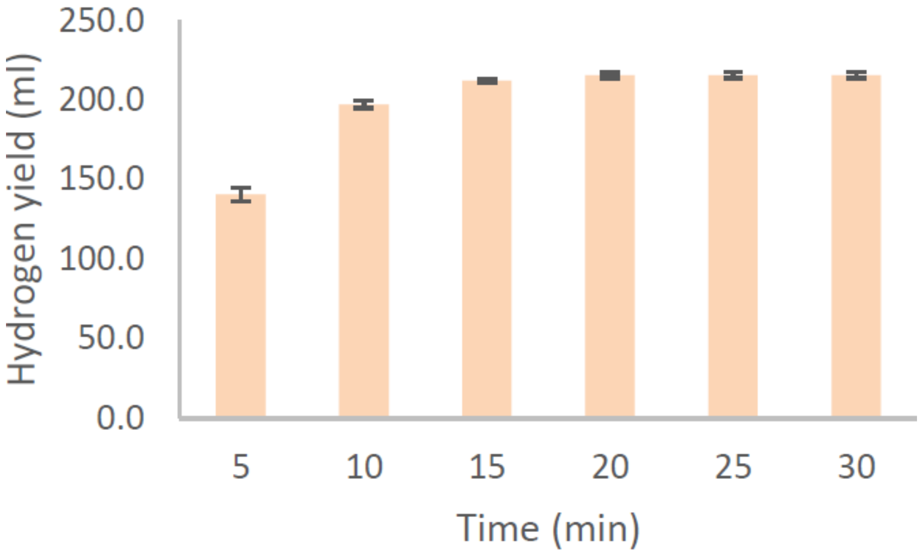

Fig. 4. The effects of hydrogen yield on the reaction time

Figure 4 demonstrates a significant increase in hydrogen yield as reaction time progresses from 5 to 15 minutes, using nZVI dosage at 800 g/L and a temperature of 25°C. Subsequently, between 15 and 25 minutes, the hydrogen yield shows a marginal increment before stabilizing from 25 to 30 minutes. This pattern indicates that initially, nZVI particles react rapidly with formic acid, benefiting from abundant reactant availability and heightened kinetics. However, as time progresses, the incremental increase in hydrogen yield slows, suggesting nearing completion of the reaction due to reduced formic acid availability [24]. The reaction concludes after 30 minutes when all available formic acid has reacted with the excess nZVI. Therefore, these findings suggest that a reaction time of 30 minutes optimally ensures completion for hydrogen production via formic acid decomposition with nZVI.

3.4 Specific Surface Area and Pore Size of nZVI

The specific surface area and pore size of nZVI were characterized before and after the hydrogen production reaction by using Brunauer-Emmett-Teller (BET) (micromeritics ASAP 2020). The specific surface area of nZVI before and after the reaction are as shown in Figure 5.

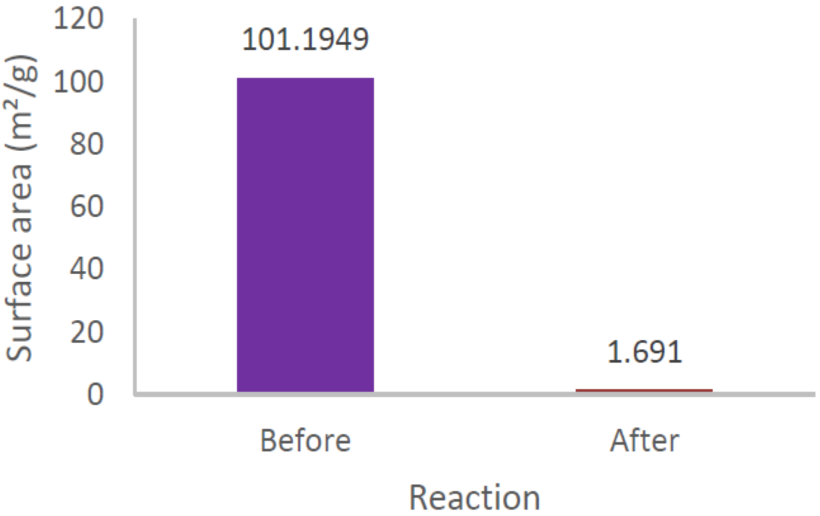

Fig. 5. Specific surface area of the nZVI before and after reaction

The specific surface area of the nZVI particles experienced a significant reduction, decreasing from 101.1949 m²/g before the reaction to 1.691 m²/g after the formic acid decomposition. This substantial decrease underscores the extensive consumption of nZVI particles during the reaction, resulting in a significant reduction in their surface area. As nZVI served as the reactant in this study, it underwent chemical transformation and interaction with formic acid molecules, leading to the depletion of its surface-active sites [25]. This phenomenon is consistent with the observed decrease in specific surface area after the reaction, highlighting the dynamic changes in particle morphology and surface properties induced by the formic acid decomposition process [18]. This also why the hydrogen yield decreases over time in the reaction, as shown in Figure 4. As the reaction progresses, the surface area of the nZVI particles decreases, leading to a slower rate of hydrogen production. This reduction in surface area reduces the availability of active sites for the reaction, thereby slowing down the overall reaction rate.

Figure 6 illustrates the pore size of nZVI particles characterized by BET, with pore sizes measured as 131.774 Å before the reaction and 330.271 Å after. The results indicate a significant increase in pore size after the reaction compared to before. Pore size directly influences nZVI reactivity: smaller pores correspond to higher surface area, enhancing reactivity with formic acid to produce hydrogen gas [26]. Conversely, larger pore sizes after the reaction signify reduced surface area and lower reactivity of nZVI [25]. This correlation explains the observed slowdown in hydrogen production over time, as nZVI particles are consumed and react during the process, leading to reduced reactivity and slower reaction rates.

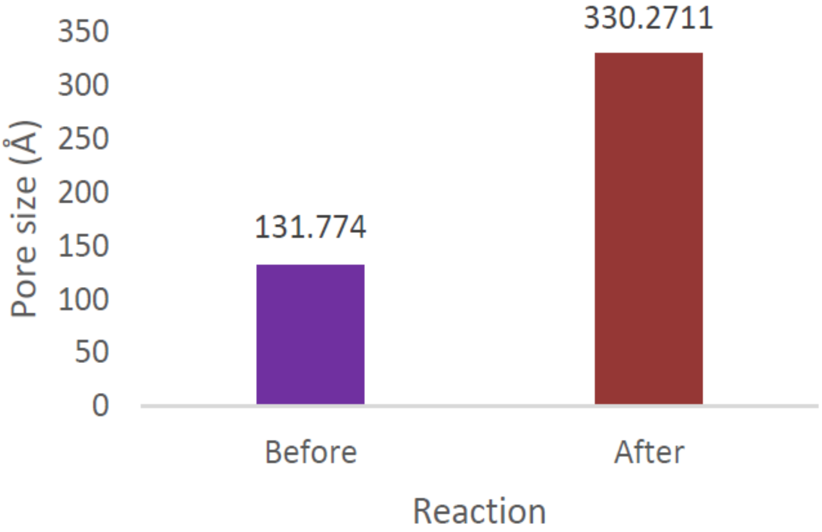

Fig. 6. nZVI pore size before and after the reaction

4. Conclusions

It can be concluded that nZVI dosage, reaction temperature, and reaction time had significant effects on the hydrogen yield from the formic acid decomposition reaction with nZVI. The maximum hydrogen yield achieved was 215 mL at 800 g/L of nZVI dosage, 25°C of reaction temperature, and 30 minutes of reaction time. The results from BET characterization regarding specific surface area and pore size are consistent with experimental results, suggesting smaller pores correspond to higher surface area, enhancing reactivity with formic acid to produce hydrogen gas. Conversely, larger pore sizes after the reaction signify reduced surface area and lower reactivity of nZVI. This correlation explains the observed slowdown in hydrogen production over time. Further studies on formic acid decomposition for hydrogen production should focus on exploring different other operating parameters like formic acid concentration and stirring speed that influence hydrogen yield in formic acid decomposition with nZVI.

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