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Beta-Cyclodextrin-Assisted Synthesis of Silver Nanoparticle Network and Its Application in a Hydrogen Generation Reaction

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Abstract: The unsustainable nature of carbon-based fuels has prompted scientists and engineers to investigate alternative sources of energy. Silver nanoparticle networks (AgNPNs) were synthesized using beta-cyclodextrin for applications in hydrogen evolution reactions from sodium borohydride (NaBH_4). The identities of the AgNPNs were confirmed using ultraviolet–visible spectroscopy, X-ray diffraction, and Transmission electron microscopy (TEM). The catalytic activity of the hydrogen evolution reactions was measured using a gravimetric water displacement system. The data collected show an increase in the efficiency of the hydrogen generation reaction with the addition of AgNPN. The silver nanoparticle network catalyst performed best at 22 °C with an increased concentration of NaBH_4 producing hydrogen at a rate of $0.961 \text{ mL} \cdot \text{min}^{-1} \cdot \text{mL}_{\text{cat}}^{-1}$. The activation energy was calculated to be 50.3 kJ/mol.

Keywords: hydrogen generation; silver nanoparticle networks; metal hydrides; hydrogen precursors

1. Introduction

The need for less harmful and more efficient fuel sources has grown rapidly in recent years. The economic and environmental consequences surrounding the use of traditional carbon-based fuels have reached unsustainable levels, prompting a new wave of research within the field of alternative fuels [1]. The burning and harvesting of gasoline are two main sources of excess carbon dioxide in Earth's atmosphere and a direct contributor to the global climate change issue [1–3]. Hydrogen has emerged as one of the more likely candidates for an environmentally friendly fuel alternative. However, there are problems associated with its viability as an alternative fuel. The main sources of hydrogen production today are steam reformation and electrolysis [4]. Steam reformation results in the release of carbon dioxide into the atmosphere because of a reaction between high-temperature steam and fossil fuels [4–6]. Electrolysis, though previously implemented successfully in small-scale systems, is limited on a large scale due to the cost of conducting water-splitting reactions [5]. In addition to the issues surrounding its production, the storage of hydrogen gas also poses a threat to its advancement as an alternative fuel. Hydrogen gas must be stored at high pressures, a requirement which in itself carries risks [7]. The search for a cleaner alternative to fossil fuels has led to the investment in studying new ways to harness hydrogen gas. One possible solution to producing hydrogen can be found in the reduction of hydrogen feedstocks, such as sodium borohydride (NaBH_4) catalyzed by nanoparticles [8].

The study of nanomaterials, specifically nanoparticles (NPs), and their applications have seen a rise in popularity in recent decades within the fields of chemistry, microbiology, medicine, textiles, electronics, and engineering [7,9–17]. Transition metal nanoparticles have been used to promote catalytic

activity in chemical reactions, as an antimicrobial agent, and as an electrodepositing agent [11,15,18–22]. The properties of various metal nanoparticles differ from their bulk metal counterparts; the increased surface area allows for more efficient catalysis of reactions, as well as non-linear optical behavior and different electromagnetic properties [8,23].

Silver is a biologically non-essential metal with a minimal toxicity to humans. However, the extent of the deteriorating effects of silver on biological processes is not completely clear [12]. Studies indicate that the toxicity of silver ions to bacteria correlates with the concentration of silver in the environment, and in larger concentrations, silver nanoparticles can affect mitochondrial function as well as cell membrane permeability [12,24]. Silver nanoparticles (AgNPs) have also been studied in the fields of public health and medicine as an antimicrobial agent—for example, in filter coatings for water treatment and as part of wound dressings to improve recovery time in patients [25]. AgNPs have also been applied in catalysts in many reactions, such as organic reductions, hydrogen generation, and catalytic degradation of hazardous dyes [26–31]. AgNPs were also used in the catalytic oxidation of styrene, which demonstrates its flexibility for both oxidation and reduction reactions [32]. One important feature of nanoparticles, particularly AgNPs, is their high surface area-to-volume ratio. This allows for increased catalysis of reactions and more efficient transformation of reactants to products [11,13,14,20–22]. The aim of this research is to evaluate the ability of silver nanoparticle networks to catalyze a hydrolysis reaction of sodium borohydride and water in order to produce hydrogen gas for application as an alternative fuel system.

The goal of this study is to explore the catalytic activity of a network of Ag nanoparticles, and how it compares to previous studies of well-dispersed AgNPs over Multi-walled carbon nanotubes (MWCNTs) [15].

2. Results and Discussion

2.1. Characterization of Catalyst

Figure 1 shows a distribution of network silver nanoparticles within a colloidal solution. Particle size varied throughout the solution ranging from as small as 10 nm up to 100 nm, as depicted in the histogram of 30 randomly selected nanoparticles in Figure 1. The average particle size was 36 ± 21.5 nm.

Beta-cyclodextrin is a commonly used capping agent and was used in the synthesis of the particles, with the goal of restricting this agglomeration. Its unique conformation, consisting of a small primary hydroxyl ring within a larger secondary hydroxyl ring (Figure 2), forms a conical shape, which is useful in exhibiting a level of control over the morphology of the particles by restricting their size and shape within the boundaries of the hydroxyl rings [14,17,20].

The formation of networking was observed in Figure 1, which most likely occurred as a result of the high surface energy of the silver nanoparticle catalysts combined with hydrogen bonding contributed by the structure of beta-cyclodextrin (Figures 2 and 3) [11]. This interaction of silver nanoparticles and beta-cyclodextrin is depicted in Figure 3.

The UV–vis spectrum in Figure 4 shows the absorbance of silver nanoparticles in a colloidal solution. The peak at ~400 nm is characteristic of an aqueous, capped silver nanoparticle suspension, and the shoulder at higher wavelengths (~550 nm) is also commonly reported [26–29,31].

The XRD pattern depicted in Figure 5 reveals a characteristic diffraction pattern at 44.7° . This corresponds to the (200) plane of face-centered cubic silver [26,27,29,31,32]. The other lesser peaks present in the diffraction pattern are attributed to the carbon support. The XRD combined with the UV–vis spectrum indicates that the nanoparticles visualized under TEM microscopy are indeed composed of FCC silver.

Figure 1. TEM micrographs of the Ag nanoparticle network. A silver nanoparticle network (AgNPN) is shown dispersed in solution and is depicted with a scale bar of 50 nm in the bottom left. A Histogram of nanoparticle diameter is inset in the bottom right. Average particle size is 36 ± 21.5 nanometers.

Figure 2. Beta-cyclodextrin depiction identifying the primary (0.78 nm) and secondary hydroxyl ring (1.54 nm) and inner a polar cavity.

Figure 3. Visualization of the concept of networking of AgNPs due to the structure of beta-cyclodextrin. This can explain the morphology in the TEM image. Red, blue and green colors represent AgNPs, beta-cyclodextrin, and the linkers (hydroxyl groups of beta-cyclodextrin), respectively.

Figure 4. UV-vis spectrum of the Ag nanoparticles. Image in the upper righthand corner shows the Ag nanoparticle solution in the test cuvette.

Figure 5. XRD patterns of the AgNPN supported over carbon. * The peak at 44.7° is characteristic of the (200) plane of FCC silver.

2.2. Catalytic Activity with Varied Concentrations of Reactant

It was confirmed that the presence of silver nanoparticle networks in the reaction resulted in an increased production of hydrogen gas by a factor of 53% when compared to the uncatalyzed reaction (Figure 6). For the sodium borohydride-controlled trials, the highest rate at which hydrogen was produced was $0.961 \text{ mL}\cdot\text{min}^{-1}\cdot\text{mL}_{\text{cat}}^{-1}$ for the increased concentration (10.35 mM) of sodium borohydride. This trial outperformed the 6.35 mM ($0.217 \text{ mL}\cdot\text{min}^{-1}\cdot\text{mL}_{\text{cat}}^{-1}$) and 8.35 mM ($0.878 \text{ mL}\cdot\text{min}^{-1}\cdot\text{mL}_{\text{cat}}^{-1}$) of sodium borohydride. Interestingly, the increase in performance between the 10.35 and 8.35 mM trials was not as large as that between the 6.35 and 8.35 mM trials. This suggests that the reaction was approaching saturation at the higher concentrations (8.35 and 10.35 mM). This increase in reaction rate associated with a higher concentration of sodium borohydride is expected and has been observed in various other catalytic studies [11].

Figure 6. Comparison of the volume of hydrogen gas generated versus time by the AgNPN. The reactions were run at $835 \mu\text{mol}$ (8.35 mM), $1035 \mu\text{mol}$ (10.35 mM), and $635 \mu\text{mol}$ (6.35 mM) of NaBH_4 .

2.3. Catalytic Activity Under Varied pH Conditions

Adjusted pH trials revealed that a neutral pH environment is ideal for the hydrolysis reaction of sodium borohydride and water. The reaction produced hydrogen at the highest rate when subjected to a neutral pH of 7— $0.878 \text{ mL}\cdot\text{min}^{-1}\cdot\text{mL}_{\text{cat}}^{-1}$. This reaction outperformed the two other adjusted pH trials, at pH 6 and pH 8, which produced hydrogen at rates of 0.733 and $0.729 \text{ mL}\cdot\text{min}^{-1}\cdot\text{mL}_{\text{cat}}^{-1}$, respectively (Figure 7). In the uncatalyzed reaction, hydroxyl ions (OH^-) shift the equilibrium to favor the reactants, reducing H_2 production— H^+ ions shift the equilibrium toward the products, as per Equation (1) [15]. This shift favors the formation of BO_2^{2-} ions in solution, which, in turn, causes the overall reaction to proceed faster at lower pH.

Based on this theory, it can be concluded from Figure 7 that the catalyst is also susceptible to changes in pH. In previous studies, similar results were observed using MWCNT-supported noble metal nanoparticles [11,15,19].

Figure 7. Comparison of the volume of hydrogen gas generated versus time. Volume of hydrogen gas generated by silver nanoparticle networks under adjusted pH conditions (pH 6–8).

2.4. Catalytic Activity at Varied Temperatures and Activation Energies

Catalysis by the silver nanoparticle network under varying temperatures, as depicted in Figure 8, revealed a non-linear trend. The highest reaction rate achieved was $0.878 \text{ mL}\cdot\text{min}^{-1}\cdot\text{mL}_{\text{cat}}^{-1}$ at 22°C . This significantly outperformed the other two rates achieved by the silver catalyst— 0.586 and $0.086 \text{ mL}\cdot\text{min}^{-1}\cdot\text{mL}_{\text{cat}}^{-1}$, at 30°C and 0°C , respectively. The reduced reaction rate of the silver nanoparticles observed at 30°C can be attributed to an alteration in the capping effect of the beta-cyclodextrin. This effect may increase the ability of other negatively charged species in the reaction, such as nitrate and hydroxyl ions, to block access to the catalytically active sites, which has been reported to decrease catalytic activity [18]. The reaction's activation energy was determined based on the Arrhenius plot shown in Figure 9. The activation energy of the silver nanoparticle networks was calculated to be 50.3 kJ/mol . This compares competitively to literature values for activation energy generated by other known nanocatalysts (Table 1). The proposed mechanism of the AgNPN catalysis is depicted in Scheme 1.

Figure 8. Volume of hydrogen gas produced over time generated by the hydrolysis reaction of sodium borohydride and water, as catalyzed by the produced silver nanoparticle network (0, 22, and 30 °C).

Figure 9. Arrhenius plot used to determine the activation energy of the silver nanoparticle network (50.3 kJ/mol).

Table 1. Reported activation energies for NaBH₄ hydrolysis by catalyst.

Catalyst	E _a (kJ/mol)	Temperature (°C)	Reference
Co nanoparticles	35.0	29–59	[33]
ZrCo/C	34.8	10–50	[34]
Ru nanoclusters	41.0	25–45	[21]
Ni nanoclusters	54.0	25–45	[22]
Pt/C	45.0	15–75	[35]
Au/MWCNTs	21.1	0–30	[11]
Pd/MWCNTs	62.66	0–30	[19]
Ag/MWCNTs	44.5	0–30	[15]
AgNPNs	50.3	0–30	This Work

Scheme 1. Proposed mechanism of the hydrolysis of sodium borohydride, as catalyzed by the silver nanoparticle network.

3. Materials and Methods

3.1. Synthesis

Silver nitrate was used to create a 1 mM aqueous precursor solution for the synthesis of silver nanoparticles in this experiment. The precursor solution was reduced using 250 μL of a fresh aqueous solution of 180 mM sodium borohydride (NaBH_4) in the presence of the capping agent beta-cyclodextrin. The resulting 134.5 μM silver solution was stirred for two hours to facilitate the formation of silver nanoparticles. The 200 μL aliquots of the resulting solution were used for catalytic activity measurements. All materials were purchased from Sigma Aldrich with high purity, unless otherwise specified.

3.2. Characterization

Transmission electron microscopy (TEM) confirmed the presence of silver nanoparticles in the sample. TEM further revealed the size, shape and network of the particles.

Ultraviolet–visible spectroscopy further confirmed the successful synthesis of silver nanoparticles. Nanoparticle solutions were characterized in quartz cuvettes using a Shimadzu UV-2600 UV–VIS Spectrophotometer.

3.3. Catalysis

A gravimetric water displacement system was used to measure the amount of hydrogen generated by the hydrolysis reaction of sodium borohydride and water in the presence of the silver nanoparticle network (AgNPN) catalyst [11,15,19]. The system consisted of a sealed reaction chamber, which vented into a reservoir vessel. The reservoir vessel would then displace its liquid into a third container placed on a microbalance which recorded data every 3 s using data-logging software. The reaction was

conducted at various pH (6–8), amounts of reactant (6.35, 8.35, and 10.35 μmol), and temperatures (0, 22, and 30 $^{\circ}\text{C}$). The change in pH was obtained using HCl and NaOH buffer solutions, while temperature was varied using hot and ice water baths. Standard reactions took place in 100 mL of deionized water with a concentration of 8.35×10^{-4} NaBH_4 at room temperature (20–22 $^{\circ}\text{C}$).

4. Conclusions

The silver nanoparticle network produced via controlled reduction was applied as a catalyst in the hydrolysis reaction of sodium borohydride. Beta-cyclodextrin was used as a capping agent for the synthesis of the nanoparticles resulting in round, fairly uniform-shaped particles. The particles functioned well as catalysts, effectively increasing the rate of the hydrogen generation reaction to as much as $18.967 \text{ mL} \cdot \text{min}^{-1} \cdot \text{mL}_{\text{cat}}^{-1}$ at an increased concentration of NaBH_4 at room temperature (22 $^{\circ}\text{C}$). The activation energy of the reaction was 50.3 kJ/mol, which compares favorably with known literature values for hydrolysis catalysts. Sodium borohydride is an attractive hydrogen feedstock for portable fuel cell applications due to its high specific hydrogen capacity (10.4 wt%) and low environmental toxicity. Silver nanoparticles have shown promise as a useful catalytic material for the generation of hydrogen gas for application in a fuel cell system, and further investigation of capping agents and nanoparticle networks can further optimize their performance.

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