Effect of Dry vs. Wet Grinding on the Catalytic Performance of Pyrite (FeS_2) in $NaBH_4$ Methanolysis for Hydrogen Generation

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Abstract. Catalysts play a critical role in hydrogen energy systems, and the development of low-cost, sustainable, and highly active alternatives remains a priority. In this study, pyrite (FeS_2) mineral prepared by dry and wet grinding was investigated as a catalyst for $NaBH_4$ methanolysis. At 30 °C, hydrogen generation rate (HGR) values of 2256 and 3221 $mL \cdot min^{-1} \cdot gcat^{-1}$ were determined for wet-ground (PW1) and dry-ground (PD1) samples, respectively. Characterization results revealed that dry grinding yields a higher BET specific surface area (1.23 vs. 0.61 m^2/g), attributed to the deposition of iron oxyhydroxide species on pyrite surfaces during wet milling through galvanic interactions, which reduce accessible surface area and catalytic activity. Under optimised conditions (0.025 g catalyst, 0.125 g $NaBH_4$, 10 mL methanol, 60 °C), PD1 achieved an HGR of 19990 $mL \cdot min^{-1} \cdot gcat^{-1}$ with an activation energy of 38.07 $kJ \cdot mol^{-1}$, demonstrating that dry grinding preserves chemically reactive fracture surfaces and enhances catalytic performance.

1. Introduction

Growing global energy demand and environmental concerns have intensified research into hydrogen as a clean energy carrier. Among chemical hydrides, $NaBH_4$ offers notable advantages including non-toxic and non-flammable nature, high stability, recyclability, and a theoretical H_2 storage capacity of up to 10.8 wt% [1]. In methanolysis, $NaBH_4$ reacts with methanol to release hydrogen according to Equation (1):

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2 \quad (1)$$

A catalyst is necessary to accelerate this reaction efficiently. With suitable catalysts, high-purity H_2 can be produced from $NaBH_4$ at room temperature [1]. Iron-containing catalysts have shown considerable activity in this context. Fe-B nanoparticles (Fe-B NPs/Ni foam) were supported on porous Ni foam. The catalyst exhibited an activation energy of 7.02 $kJ \cdot mol^{-1}$ at 20–50°C [2]. Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2@NH_2$ nanoparticles were found to be effective catalysts for the methanolysis reaction of $NaBH_4$. The reaction, which takes 30 minutes to complete without a catalyst, was completed in 16, 10, and 20 minutes, respectively, using Fe_3O_4, $Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2@NH_2$ catalysts. Using $Fe_3O_4@SiO_2@NH_2$, a HGR of 13188 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$ and an Ea value of 24.4 $kJ \cdot mol^{-1}$ were calculated in the temperature range of 258–318 K [3].

The use of catalysts, particularly those containing metals, is crucial for controlling and accelerating hydrogen production via the methanolysis of $NaBH_4$ due to their high reactivity and reaction rates; however, their application is limited by cost [4].

Pyrite (FeS_2), one of the most abundant metallic sulfide minerals in the Earth's crust, is the primary gangue mineral in complex sulfide ores; its content in porphyry copper ores ranges from 0.3% to 14.9%[5]. It is commonly found alongside sphalerite, chalcopyrite, galena, and gold-bearing minerals [6]. An important factor affecting the surface properties of pyrite is the grinding environment and the galvanic interactions that occur between minerals [7]. The grinding environment employed in catalyst preparation therefore directly determines the surface chemistry and catalytic potential of pyrite through distinct mechanochemical and electrochemical processes.

Grinding not only reduces particle size but also alters physicochemical surface properties through mechanochemical activation [8]. Secondary processes such as agglomeration and recrystallisation may partially offset these gains over extended milling times [9].

The grinding environment, whether dry or wet, plays a decisive role in determining the extent and nature of these changes. Dry grinding consistently produces deeper structural distortions than wet grinding at equivalent energy input, as the absence of water allows freshly fractured, high-energy surfaces to be preserved rather than immediately passivated. In wet grinding, the aqueous medium promotes surface hydroxylation, which passivates reactive sites and limits the extent of mechanochemical activation [10]. For sulfide minerals, galvanic interactions between steel media and pyrite release Fe^{2+} and Fe^{3+} ions that hydrolyze and precipitate as iron oxyhydroxide species on mineral surfaces, reducing chemical activity [11], [12], [13]. Dry grinding

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eliminates this electrochemical pathway, preserving mechanically activated fracture surfaces [10].

In this study, pyrite ore was ground by both methods and used as a catalyst in $NaBH_4$ methanolysis. The surface properties of samples obtained under different grinding conditions were characterized, and the effect on hydrogen production performance was experimentally determined. Although the effects of grinding environment on particle size and surface morphology are well established in ore processing, its impact on catalytic performance in H_2 production remains insufficiently addressed. This study evaluates the potential of natural waste ores as a low-cost and sustainable catalyst alternative.

2. Experimental

2.1 Characterization Methods

The surface areas of the catalysts were calculated using the BET (Brunauer, Emmett and Teller) equation in the relative pressure range of 0.01–1. Crystal structures were determined by XRD analysis using a PANalytical Empyrean device with Cu-Kα radiation (λ = 1.5406 Å) over 2θ = 10°–90°.

2.2. Materials and Chemicals

$NaBH_4$ (99% purity, AFG Bioscience) and methanol (Emsure®) were used without further purification.

2.3. Grinding Methods

Pyrite samples from Central Anatolia were crushed, ground with an agate mortar and pestle, and dry-sieved to below 425 µm. To minimise oxidation, material was sealed and stored at −18 °C. For each experiment, 5 g of pyrite was ground in a stainless steel mill (Ø40 × 75 mm) with 30 steel balls (6 mm diameter) mounted on a Retsch sieve shaker. For wet grinding, 5 ml of distilled water was added. Milling times were established from preliminary experiments to yield comparable product d_{80}, 10 min for dry and 6 min for wet grinding. Particle size distributions were measured by laser diffraction (Malvern Mastersizer Hydro 2000 MU).

2.4. Hydrogen Production

Dry- and wet-ground pyrite samples were designated PD1 and PW1, respectively, and used as catalysts in $NaBH_4$ methanolysis. Specific amounts of $NaBH_4$ and catalyst were placed in a sealed flask in a water bath; methanol at the same temperature was then injected. Released H_2 displaced water in a buret, and the gas volume was recorded over time. The hydrogen generation rate (HGR, $mL \cdot min^{-1} \cdot g\_cat^{-1}$) was calculated from the initial slope of a polynomial fit to the volume–time data using Equation (2):

$$\frac{1}{W_{cat}}\left(\frac{dV_{H_2}}{dt}\right) = r_{H_2} \quad (2)$$

Experiments were conducted under identical conditions for PD1 and PW1. For the superior catalyst, the effects of catalyst amount, $NaBH_4$ amount, and temperature on HGR were then systematically investigated.

3. Results and Discussion

3.1. Characterization of Catalyst

XRD analyses were performed for both samples using Cu Kα radiation (λ = 1.5406 Å) over approximately 5°–90° (2θ). As shown in Figure 1, characteristic diffraction peaks of both samples are consistent with the pyrite phase (ICDD 00-042-1340, FeS_2). Peaks at approximately 2θ = 28.5°, 33.0°, 37.0°, 40.8°, 47.5°, 56.3°, and 61.3° correspond to crystal planes (111), (200), (210), (211), (220), (311), and (222). The absence of secondary phase peaks indicates high purity in both samples.

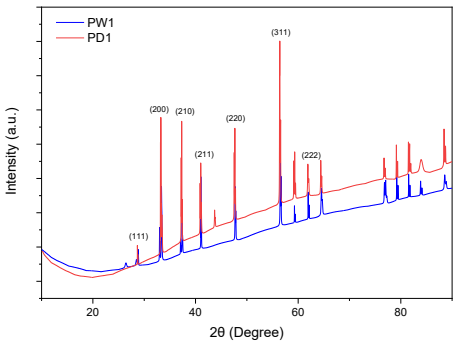

Figure 1. XRD patterns of pyrite samples

Crystallite sizes were approximately calculated using the Scherrer equation ($D = K\lambda / \beta\cos\theta$). In the calculations, K= 0.9 and λ = 1.5406 Å were used, with the peak of highest density, approximately 56.3° (plane 311), used as a reference. Based on the approximate values obtained from the peak widths (FWHM), the crystallite size in the dry-ground sample is approximately in the range of 40–50 nm, while in the wet-ground sample this value decreases to the range of 20–30 nm. This result shows that wet grinding significantly reduces the crystallite size. The peaks appear sharper and more intense in the dry-ground (PD1) sample. This indicates that the crystal structure is better preserved and the crystallite size is larger. In the wet-ground sample (PW1), it was observed that the peaks were wider and their intensities were relatively reduced. The presence of a liquid medium during wet grinding causes interparticle collisions to be more effective and homogeneous, leading to distortions in the crystal lattice and smaller crystallite sizes. However, despite the smaller crystallite size observed in the wet-ground sample, its catalytic activity is lower than that of the dry-ground sample.

The surface properties of two different pyrite samples prepared using dry and wet grinding methods were investigated using the Brunauer–Emmett–Teller (BET) method. The grinding process is a critical parameter that significantly affects not only the crystal structure of minerals but also their surface area and pore structure. A regular increase in the amount of adsorbed gas was observed for both samples as the relative pressure increased. It is evident that both samples possess a mesoporous structure. It was observed that the dry-ground sample adsorbed a higher amount of gas compared to the wet-ground sample. This can be explained by effects such as surface rearrangement, agglomeration, or partial pore

blockage that occur during the grinding process in a wet environment. This finding confirms that the dry grinding process provides a higher specific surface area or a more developed pore structure.

BET analysis confirmed that both samples exhibit Type IV isotherm behavior (IUPAC), indicating mesoporous structures. PD1 has a BET surface area of 1.228 m^2/g compared to 0.607 m^2/g for PW1. Since particle size distributions under both conditions are nearly identical (Figure 2), the difference in surface area cannot be attributed to comminution efficiency. Rather, galvanic interactions during wet grinding precipitate iron oxyhydroxide species on freshly formed pyrite surfaces [11], [13], blocking accessible sites for N_2 adsorption and reducing the measured BET surface area. In dry grinding, the absence of an aqueous medium prevents such surface precipitation, preserving clean and reactive fracture surfaces. This interpretation is consistent with previous reports showing that wet-ground pyrite surfaces exhibit higher heterogeneity due to iron hydroxide and oxide deposits, which can be removed by EDTA washing to reveal the underlying sulfur-enriched surface [14].

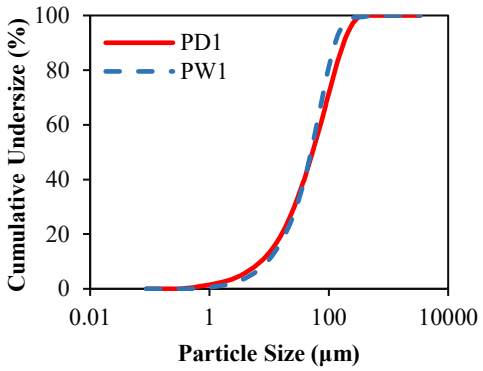

Figure 2. Particle size distributions of ground pyrite samples

3.2. Hydrogen Production Results

The time-dependent hydrogen production rates of the PD1 and PW1 catalysts were compared using 0.05 g of catalyst, 0.125 g of $NaBH_4$, 10 mL of methanol, and at 30°C. Both catalysts produced hydrogen at the theoretical hydrogen volume. However, the highest hydrogen production rate (HGR) was achieved with the PD1 catalyst. PD1 yielded an HGR of 3221 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$, while PW1 yielded 2256 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$. The effects of reaction parameters on the hydrogen production rate were investigated using the catalyst exhibiting higher activity.

The effect of catalyst amount was investigated at 30 °C using 0.125 g $NaBH_4$ in 10 mL methanol with 0.025, 0.05, 0.125, and 0.250 g catalyst (Figure 3). Although increasing catalyst amount raises the absolute reaction rate, HGR (calculated per gram of catalyst) was highest at the lowest catalyst amount (0.025 g). HGR values of 5136 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$, 3221 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$ at, 1381 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$, and 1074 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$ were obtained for catalyst amounts of 0.025 g, 0.05 g, 0.125 g, and 0.250 g, respectively. Based on these findings, 0.025 g was determined to be the optimal catalyst amount to balance reaction efficiency and catalyst quantity in the methanolysis of $NaBH_4$.

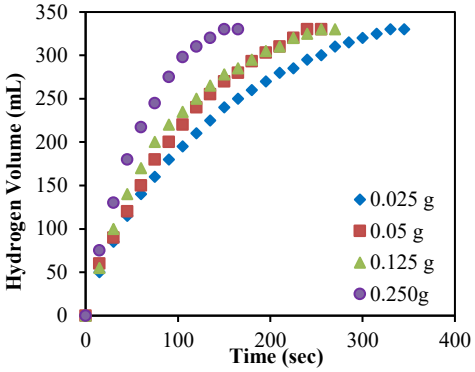

Figure 3. Effect of catalyst amount

To investigate the effect of the $NaBH_4$ amount, methanolysis reactions were carried out using 0.05 g, 0.100 g, 0.125 g, and 0.150 g of $NaBH_4$. These experiments were conducted in 10 mL of methanol solution in the presence of 0.025 g of catalyst at 30 °C. The results are presented in Figure 4. HGR values of 2207, 3855, 5136, and 10503 $mL \cdot min^{-1} \cdot g$ were obtained, respectively. 0.125 g of $NaBH_4$ was considered the most suitable reactant amount.

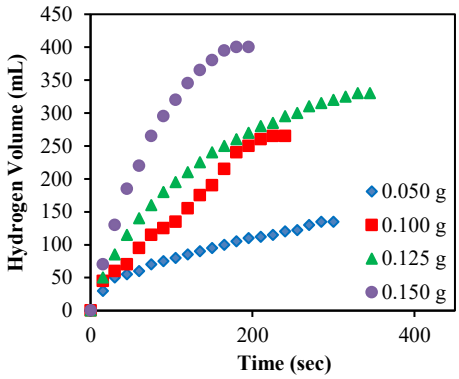

Figure 4. Effect of $NaBH_4$ amount

The effect of temperature was investigated at 25, 30, 40, 50, and 60 °C with 0.025 g catalyst, 0.125 g $NaBH_4$, and 10 mL methanol (Figure 5). HGR values increased with temperature: 2634, 5136, 11353, 12835, and 19990 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$ at 25, 30, 40, 50, and 60 °C, respectively. Activation energy was calculated from the Arrhenius equation (Equations 3):

$$lnk = lnA - Ea/RT \quad (3)$$

Here, k represents the reaction rate constant, The Arrhenius constant, Ea the activation energy, R the gas constant, and T the absolute temperature in Kelvin.

Ea is calculated as 38.07 $kJ \cdot mol^{-1}$. This relatively low Ea indicates that the catalyst may allow for efficient hydrogen production under suitable conditions by reducing the energy barrier for the methanolysis reaction of $NaBH_4$. Under optimised conditions (0.025 g catalyst, 0.125 g $NaBH_4$, 10 mL methanol, 60 °C), PD1 achieved an HGR of 19990 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$. This compares favourably with pyrite modified with polyethylenimine (PEI), which yielded 2883 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$ [15]; CS/FeS_2 composites, which achieved 8000 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$ at 25

°C [16]; and Fe_3O_4/FeS_2 hybrid structures at 8480 $mL \cdot min^{-1} \cdot g_{cat}^{-1}$ at 20 °C [17].

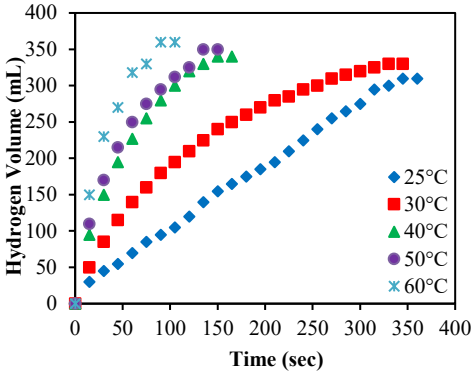

Figure 5. Effect of temperature

4. Conclusions

This study demonstrated the feasibility of using dry- and wet-ground pyrite (FeS_2) as a catalyst for $NaBH_4$ methanolysis. At 30 °C, dry-ground PD1 significantly outperformed wet-ground PW1.

The superior performance of dry-ground pyrite is attributed to the preservation of chemically reactive, high-energy fracture surfaces in the absence of aqueous passivation and galvanic interactions with steel grinding media. Characterization confirmed that the grinding environment alters mineral surface properties and that these changes directly influence catalytic performance. These findings establish the grinding environment as a critical parameter in mineral-based catalyst preparation for hydrogen generation. Furthermore, naturally occurring minerals offer a low-cost and earth-abundant alternative to synthetic catalyst systems. From a mineral processing perspective, dry grinding presents an additional advantage for sustainable operations in water-scarce regions.

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