

Magnetite as a catalyst for the partial oxidation of glycerol through heterogeneous photo-Fenton reactions

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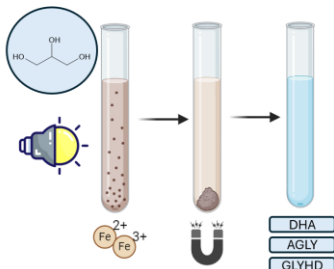
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Partial catalytic glycerol oxidation was analyzed through the photo-Fenton process using magnetite as a catalyst. The experiments were carried out by varying the H₂O₂ concentration while keeping constant the catalyst loading and glycerol concentration. The results show an increasing conversion of glycerol as a function of the amount of H₂O₂ and reaction time. Complete glycerol conversion was achieved using the maximum amount of oxidant at 8 h. Also, regardless of the H₂O₂ concentration, selectivity remains unaffected, yielding dihydroxyacetone (DHA) as the major product, with minor proportions of glyceraldehyde (GLYHD) and glyceric acid (AGLY).

Introduction

The increase in glycerol production as a byproduct in biodiesel manufacturing has generated both environmental and economic challenges due to its underutilization. Hence, efforts to valorize glycerol by transforming it into higher-value products [1] have been widely analyzed. One of them is the use of glycerol as raw material to produce dihydroxyacetone (DHA), glyceric acid (AGLY), and glyceraldehyde (GLYHD). These products have potential applications in the cosmetic, polymer, and pharmaceutical industries.

Catalytic processes involving oxidizing agents are required to achieve glycerol oxidation. However, these processes have certain drawbacks, including the need to use strong alkaline reagents that can corrode the reactors, high energy consumption due to elevated temperatures, and low selectivity toward desired products. Therefore, photocatalytic processes have been explored taking advantage of the use of light to activate the catalyst, generating oxidation reactions at ambient temperature and natural pH. These processes can employ iron-based catalysts to carry out Fenton and photo-Fenton reactions. One of the catalysts that have been explored is magnetite, which possesses ferromagnetic properties [2, 3].

Nevertheless, the use of iron also presents challenges related to the selectivity and catalyst stability against oxidation [3]. Therefore, this study aims to investigate the photocatalytic oxidation of glycerol using hydrogen peroxide as an oxidant and magnetite as a catalyst under various experimental conditions.

Material and Methods

For the synthesis of magnetite, 13 mmol of FeSO₄·7H₂O and 35 mmol of FeCl₃·6H₂O were dissolved in 15 mL of H₂SO₄ 0.5 M. Subsequently, the two solutions were mixed and diluted to 50 mL with the acid solution. The mixture was heated to 70 °C, and then 43% KOH solution was added at a flow rate of 500 μL/min for 30 minutes, followed by a

change to 100 μL/min for 30 min to obtain a final pH of 9.15. Finally, the magnetite crystals were aged for 24 hours at 70 °C, washed with deionized water to a pH of 7.0, and dried at 60°C for 24 h. All experiments were conducted using deionized water.

The crystalline phases were identified via powder X-ray diffraction using a XRD 7000 MAXima instrument (Shimadzu Scientific Instruments), scanning from 5° to 70° 2θ with a step size of 0.02°, and operated with a Cu anode (Kα: 1.5406 Å). Raman spectra were recorded at room temperature using a ThermoScientific DXR Raman microscope with a 532 nm laser at 8 mW power and a 50 μm slit.

The catalytic activity was evaluated through the photo-Fenton reaction. 100 mg of the prepared catalyst and 20 g of a 0.1 M aqueous glycerol (GLY) solution were mixed with constant air bubbling. The reaction was assisted by a commercial white LED light (1.8 W) and a 30% H₂O₂ commercial solution, adding 100, 250, and 500 μL/h until 8 hours. Afterwards, the solution was filtered and analyzed via high-performance liquid chromatography (HPLC) Shimadzu Prominence) with a Shodex ® SH1821 column (300 mm x8.0 mm) from Phenomenex, with UV/Vis (210 nm) and refractive index detectors. An aqueous solution of H₂SO₄ 3.3 mM was used as eluent (mobile phase), with a 0.5 mL min⁻¹ flow rate and a column temperature of 60 °C.

Results and Discussion

Figure 1 shows the characteristic diffraction peaks of magnetite. All indexed diffraction planes indicate the formation of a spinel-type structure. The absence of the signals of crystalline hematite and iron hydroxides indicates the successful synthesis of the desired crystalline phase. However, complementary analysis conducted via Raman spectroscopy (Figure 2) indicates the formation of other species, such as hematite and maghemite, likely present on the surface passivating the magnetite (Fe₃O₄), which undergoes oxidation processes under ambient conditions, especially when exposed to oxygen and atmospheric moisture [4].

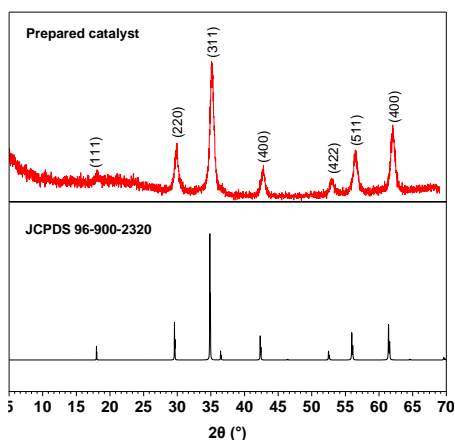


Figure 1. Diffraction pattern of the prepared catalyst and the magnetite pattern (cubic, JCPDS 96-900-2320).

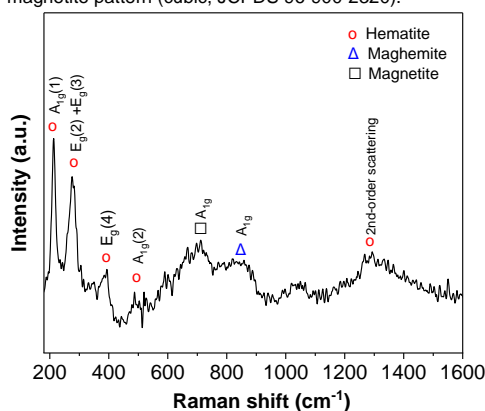


Figure 2. Raman spectrum of the prepared catalyst.

The catalytic evaluation in Figure 3 demonstrates an increasing glycerol conversion over time and

Conclusions

The partial oxidation of glycerol was successfully achieved using magnetite as a catalyst in photo-Fenton processes at the natural pH of the solution 6.4 and using a low wattage and visible light irradiation. Under reaction conditions, the conversion of glycerol shows a strong dependence on the concentration of hydrogen peroxide. Additionally, regardless of the amount of oxidizing agent, the higher selectivity to dihydroxyacetone was obtained.

Acknowledgments

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References

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peroxide concentration. After 8 hours of reaction, complete conversion is achieved using 500 $\mu\text{L/h}$. These results indicate that magnetite is active in the photo-Fenton reaction and is significantly dependent on the concentration of the oxidizing agent used. Regarding selectivity, the results show that regardless of time and peroxide concentration, the major product obtained is dihydroxyacetone (DHA), followed by the formation of glyceraldehyde (GLYHD). The high selectivity toward dihydroxyacetone indicates that glycerol is selectively oxidized by the dehydrogenation of the hydroxyl group of the secondary carbon. However, a small amount of glyceraldehyde was also obtained, showing that the dehydrogenation of the hydroxyl group of the primary carbon also occurs.

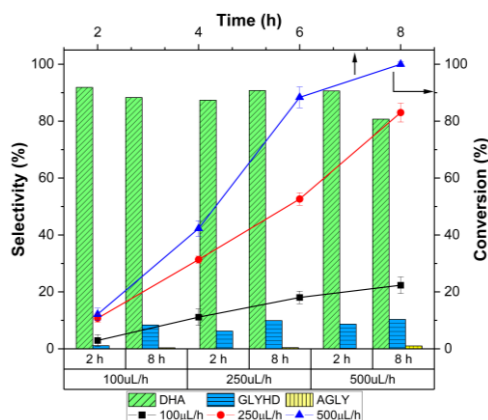


Figure 3. Catalytic activity and selectivity under visible light irradiation and different H_2O_2 concentration. The lines correspond to the catalytic activity and the bars to the selectivity towards the products.