Exploring iron oxide nanoparticles for the photocatalytic reduction of N_2 in water under simulated solar light

Yasmin S. Casseb[1], Rebeca P. de Oliveira[1], Pietra C.P. Gonçalves[1], Cátia Podence Alves[2], Bruna Pratto[1], Douglas Gouvêa[2], Bruno Ramos[1]

[1]Department of Chemical Engineering - FEI University Center, São Bernardo do Campo, Brazil. [2]Department of Metallurgical and Materials Engineering - Escola Politécnica, University of São Paulo, São Paulo, Brazil

This work presents a comparison of the performance of hematite, goethite and magnetite for the photocatalytic conversion of N_2 into NH_3 in water.

Background: The photoreduction of N_2 to produce ammonia represents a new route in sustainable chemistry, primarily motivated by the need to transition away from the energy-intensive Haber-Bosch process. The photoreduction of N_2 under solar light harnesses renewable energy, offering a greener, less energy-intensive pathway. Iron oxides have been proposed as drivers of photochemical N_2 fixation since the early 1960s [1]. Their ready availability, ubiquity and low toxicity make them an ideal candidate for the development of cost-effective and sustainable processes.

Methodology: The iron oxide varieties were prepared according to well-established methodologies. Hematite was prepared by a modified Pecchini method [2], while goethite and magnetite were prepared by hydrothermal techniques [3][4]. Figure 1 summarizes the synthesis methods. The materials were characterized by XRD and SEM. The photocatalytic tests were carried out in a batch experiment, by adding 100 mL of deionized water in a flask and bubbling N_2 continuously to remove the dissolved oxygen for 20 min. After that period, 10 mg of the catalyst were added under continuous stirring and N_2 bubbling. After 30 min, a UV-A LED (peak emission at 370 nm, irradiance of ca. 4.5 mW/cm^2 at the flask wall) was turned on and the reaction was tracked for 180 min. Samples were collected periodically and treated with a colorimetric ammonia detection kit based on the nitroprusside-phenol method [5]. The ammonia concentration was tracked using the absorption of light at 680 nm following a calibration curve.

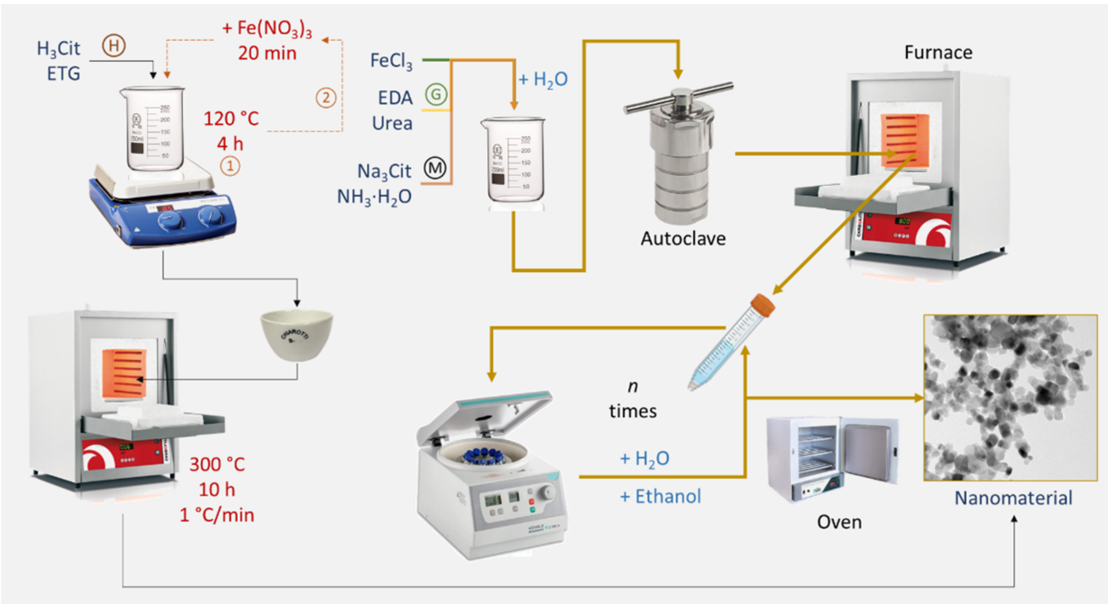

Figure 1. Synthesis routes for hematite (H), goethite (G), and magnetite (M)

Results and Discussion : Figure 2a shows the XRD data of the catalysts, and their microstructures as seen by SEM analysis is given in Figs 2b,c,d. The preliminary data shows that, except for goethite, the desired species were obtained successfully following the methodologies used. A Rietveld refinement of the diffractograms shows that the prepared materials exhibit average crystallite sizes of 37 nm and 32 nm for hematite and magnetite, respectively. After the analysis, the goethite sample was found to contain only 0.4% of the desired product, with the majority being assigned to hematite, as can be seen from the diffraction pattern. The SEM images show that the nanoparticles form agglomerates of average diameter (or length) of 98 nm, 70 nm, and 49 µm, with 2D platelet-like shape for hematite, and nano- and micro-spherical shapes for the goethite and magnetite samples, respectively. The hematite sample was tested for NH_3 production, resulting in the kinetics shown in Fig 2e. The preliminary data show that the amount of dissolved ammonia increases with time, with an apparent rate of 3.63×10^{-2} mmol NH_3 (mol N_2)$^{-1}$ min^{-1}. After 180 minutes of reaction, the final concentration of ammonia was measured at 4.46 µmol/L, well below the theoretical maximum of ca. 1.4 mmol/L, estimated from N_2 solubility limits at the experimental conditions. Further tests will be carried out in an optimized reactor including the remaining materials and shall be presented at the conference.

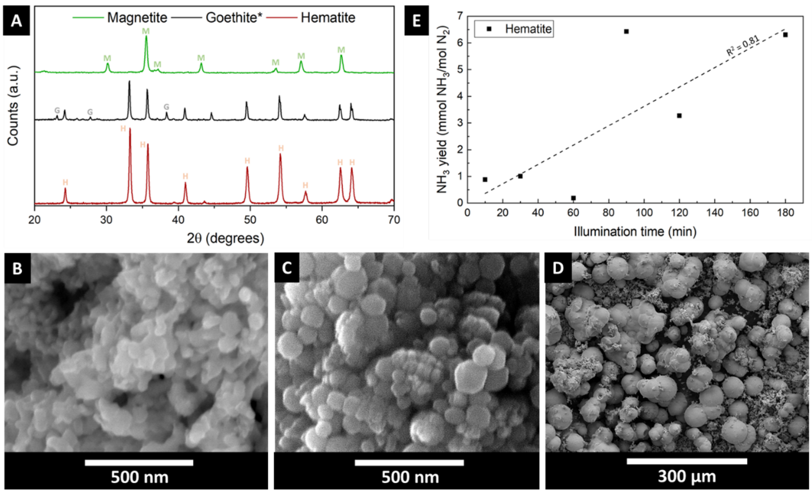

Figure 2. Characterization of the iron oxides. (A) X-ray diffraction patterns of the synthesized samples; (B-D) SEM micrographs of hematite, goethite and hematite; and (E) photocatalytic production of ammonia under simulated sunlight using hematite.

Conclusions

The preliminary results show that the synthesis methodologies yielded crystalline materials with high purity. The goethite sample yielded highly crystalline nano-spherical hematite, requiring adjustments in the synthesis procedure. Ammonia production was confirmed using hematite, achieving a yield of ca. 6 mmol NH_3/mol N_2 after 180 min of continuous illumination. Further experiments will be carried out using the other varieties of iron oxides in an optimized experimental system to be presented.

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References

[1] G.N. Schrauzer, N. Strampach, L.N. Hui, J. Salehi, PNAS 80 (1983) 3873.
[2] C.A.P Alves, MSc Thesis, University of Sao Paulo, 2021.
[3] R. Zamiri, H. A. Ahangar, A. Zakaria et al., J Nanopart Res 16 (2014) 2333.
[4] C. Han, D. Zhao, C. Deng, K. Hu, Mat Lett 70 (2012) 70.
[5] J.E. Harwood, A.L. Kühn, Water Res 4 (1970) 805.