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Study of the catalytic activity of ilmenite obtained from the black sands of Mineros S.A. of Colombia in the oxidation of monoterpenes.

Socialization of the results of the academical practice

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May 17th 2023

Outline

1. Introduction

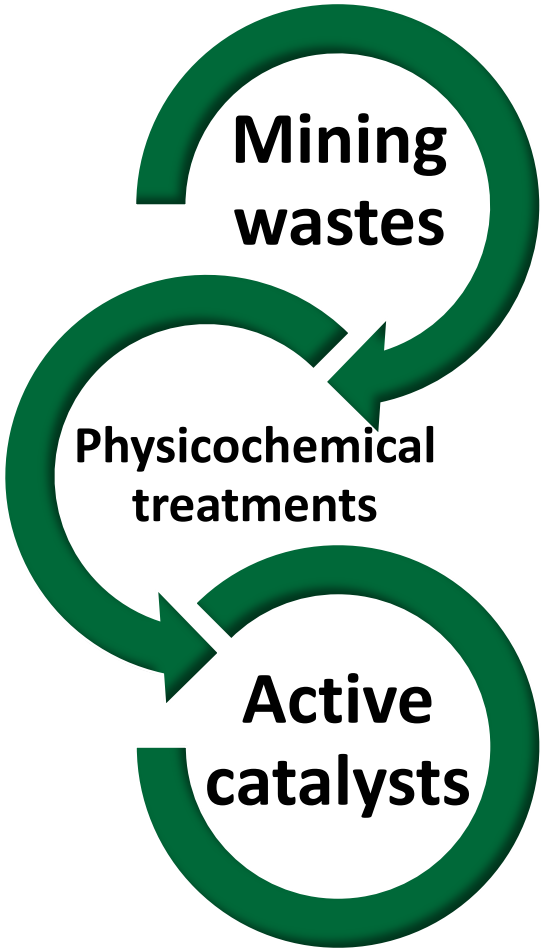
Geo-Catalysis: Valorization of Ilmenite from Mineral Wastes (CODI)

Objective: Evaluation of the catalytic activity of Ilmenite obtained from black sands from Mineros S.A. de Colombia over several heterogeneous catalyzed reactions.

Coordinator: Aída Luz Villa
Research assistant: Luis Valencia
Undergrad student: Daniel Moreno

Research Statement

It is proposed to valorize ilmenite obtained from waste from the company Mineros S.A. of Colombia as a precursor of catalysts in the oxidation of terpenes to produce value-added products in fine chemistry. Physicochemical treatments will be carried out on the recovered material and its catalytic activity in the oxidation of limonene, α and β-pinene will be evaluated. The objective is to determine if ilmenite can be used as a catalyst and what are the best reaction conditions for the 3 terpenes.



Objectives of the project

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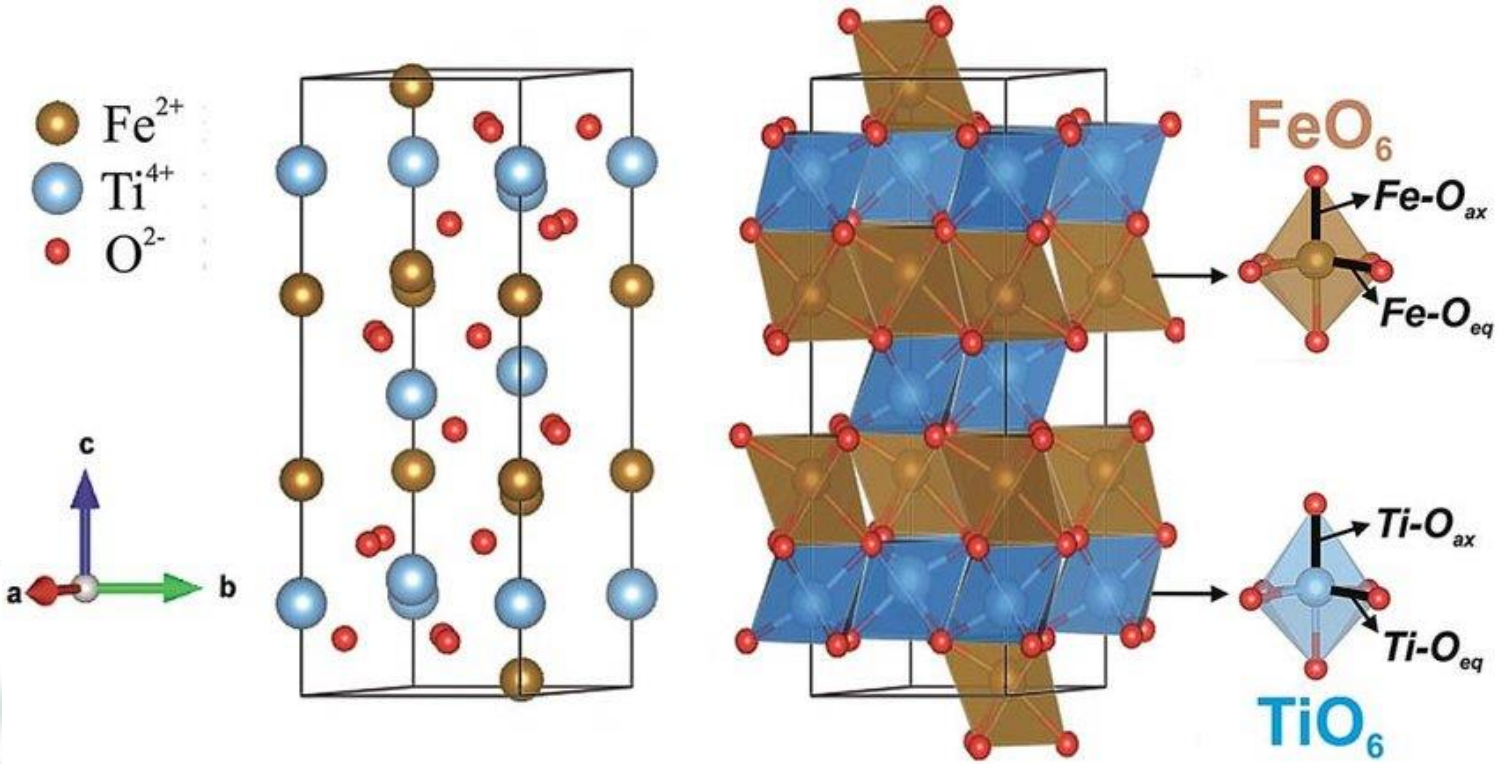
- Develop physicochemical treatments on ilmenite for obtaining active catalysts for monoterpene oxidation.
- Evaluate the catalytic activity of the synthesized materials on the oxidation of α, β-pinene and limonene.
- Characterize promissory materials

2. Ilmenite:

Mixed oxide of iron and titanium of formula $FeTiO_3$, opaque mineral of black iron color and metallic luster, has a hardness between 5 and 6 on the Mohs scale. The iron and titanium oxides of its structure are of interest for their activity as catalysts in redox reactions.



1. Ribeiro, R. A. P., & De Lázaro, S. R. (2014). Structural, electronic and elastic properties of FeBO 3 (B= Ti, Sn, Si, Zr) ilmenite: a density functional theory study. Rsc Advances.

Obtention of the material

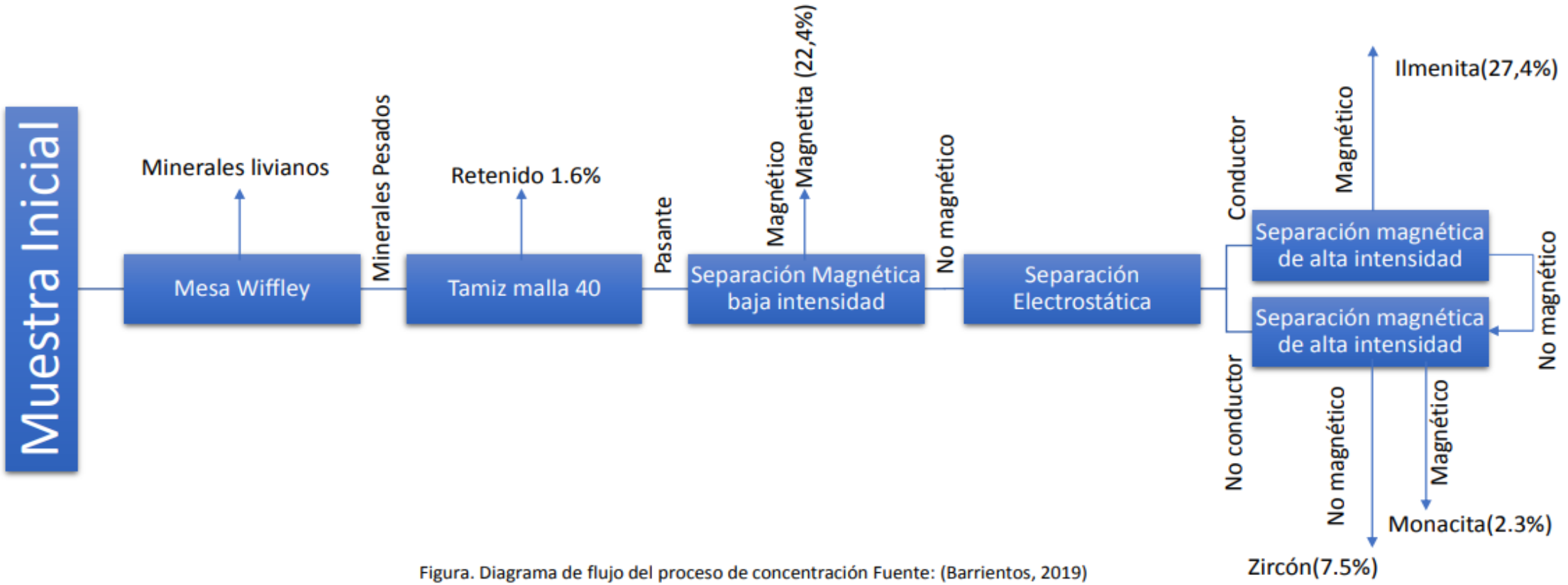


Figura. Diagrama de flujo del proceso de concentración Fuente: (Barrientos, 2019)

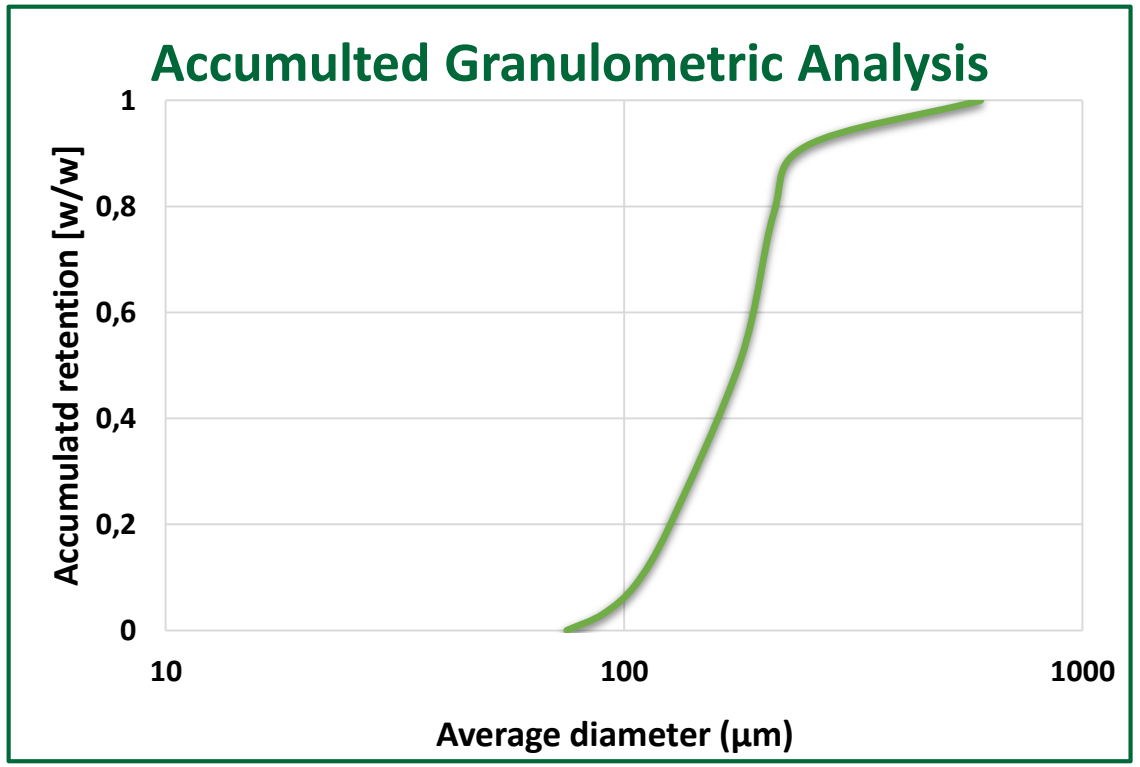
2. Barrientos, S. (2019). Concentración de arenas negras del Bagre Antioquia provenientes de la minería aluvial del oro. In PAE Proyecto académico especial. UN.

4. Methodology

Quartering and sieving

Accumulated granulometric analysis

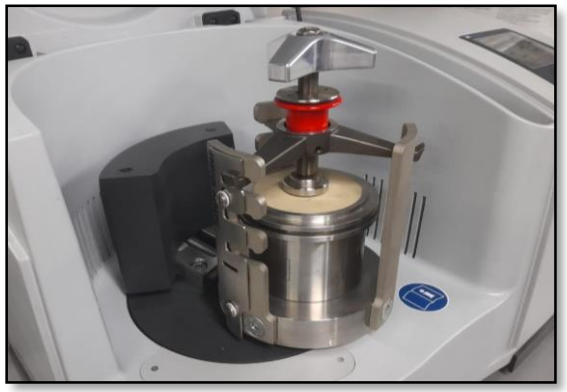
Mesh	Aperture (µm)	Wret (g)	Reten.(%)	Pass. (%)
30	600	0	0.00	100.00
60	250	4.34	8.58	91.42
70	212	6.48	12.81	78.60
80	180	13.82	27.33	51.28
120	125	16.2	32.03	19.24
140	106	5.36	10.60	8.64
170	90	2.81	5.56	3.08
Collector		1.56	3.08	0.00
		50.57	100	



The material has an average particle size of 180 µm; it is required a particle size of 90 µm.

Size reduction

Sample received from the Universidad Nacional



Grinding at 250 rpm for 30 min and ball ratio material 1:1 in mass

Ilmenite ground and screened by mesh 200 (75 µm) - Ilmenite

It will be the starting material for the synthesis of catalysts

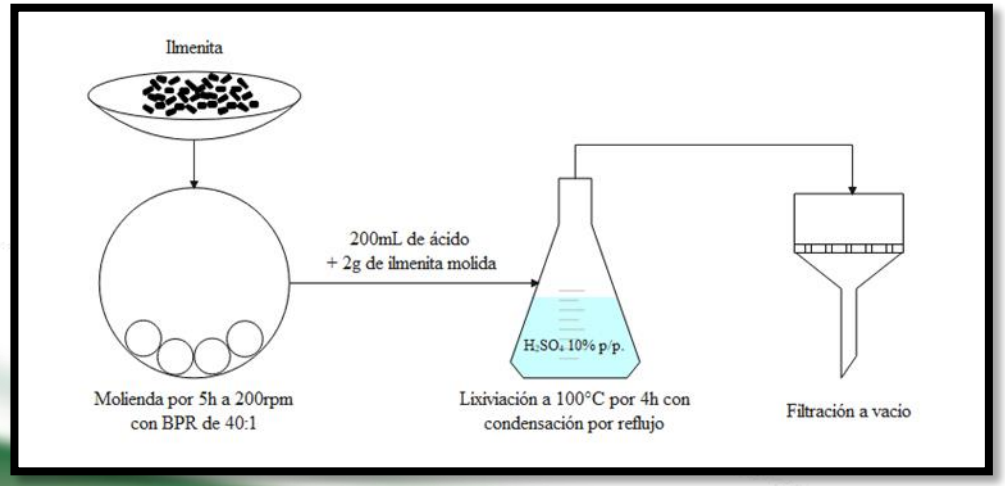
Mechano-chemical treatments

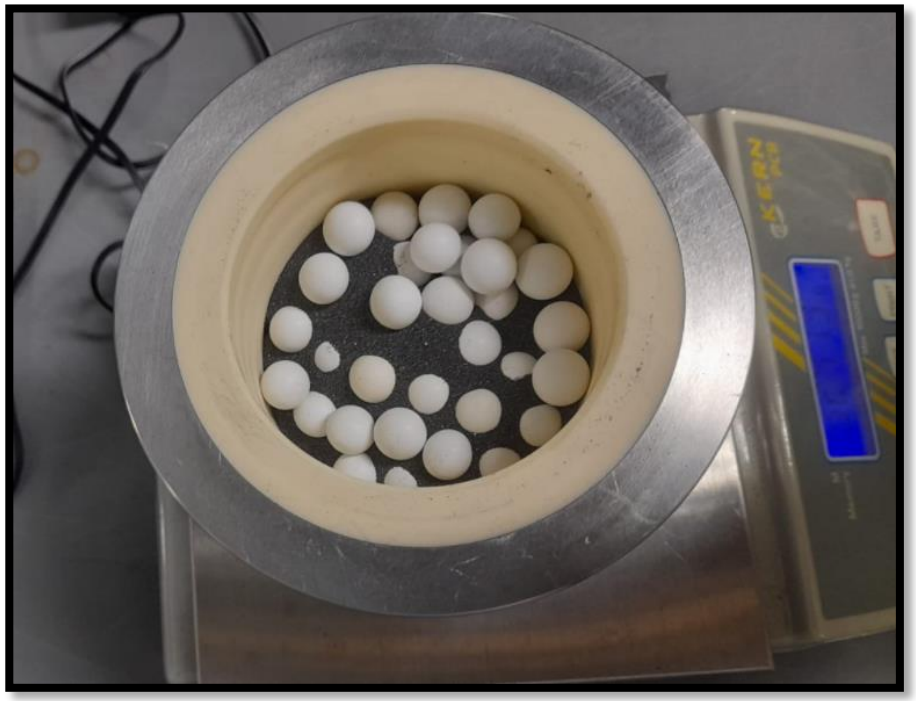
- **Mechanical activation + leaching[8]**

Mechanical activation is performed before leaching by grinding of Ilmenite with a mass ratio of grinding bodies to **ilmenite** of 40:1 (5 h, 200 rpm).

Leaching of 6 g of activated ilmenite is performed using 200 mL of H_2SO_4 at 10% w/w, at 100 ° C with stirring for 4 h.

SL-ilmenite liquid leachate solution is supported by MCM-41 **(LI-MCM-41**).





Equipment: Mill RETSCH PM 100. Corundum glass and balls, 250 mL glass and 1/2 in balls.

8. Li, C., Liang, B., song, H., Xu, J., & Wang, X. (2008). Preparation of porous rutile titania from ilmenite by mechanical activation and subsequent sulfuric acid leaching. Microporous and Mesoporous Materials, 115(3), 293-300.

SL-ilmenite

LI-MCM-41

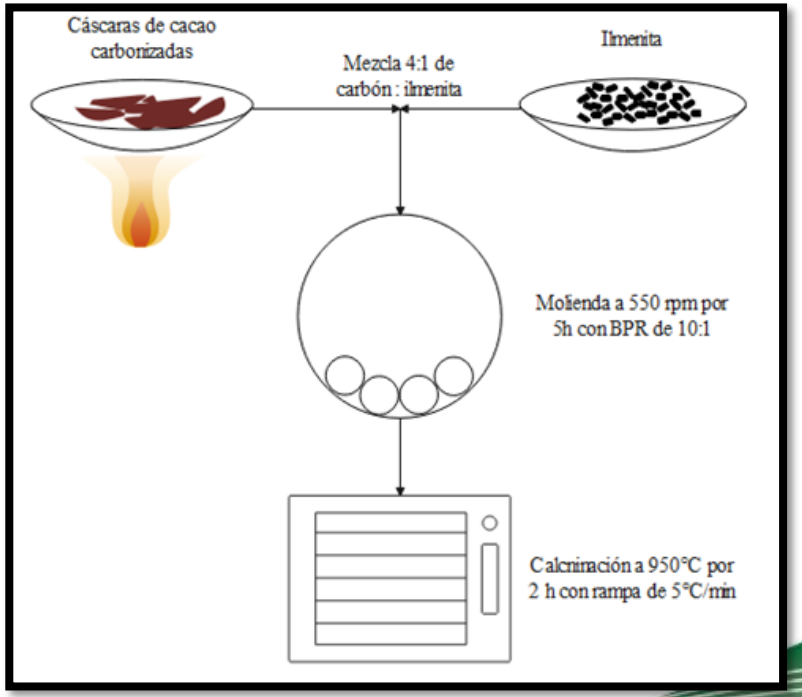
CR-ilmenite

- **Carb-reduced ilmenite[9] (CR-ilmenite):**

A 10:1 ratio of balls to material is used to grind a 1:4 mixture of **Ilmenite** with charcoal obtained from orange peels. The grinding is carried out at 550 rpm for 5 h, the result is a material that has increased its size (agglomeration).

The material is calcined at 950°C for 2 h and sieved with 170 mesh (90µm)

$$FeTiO_3 + C \rightarrow Fe + TiO_2 + CO$$



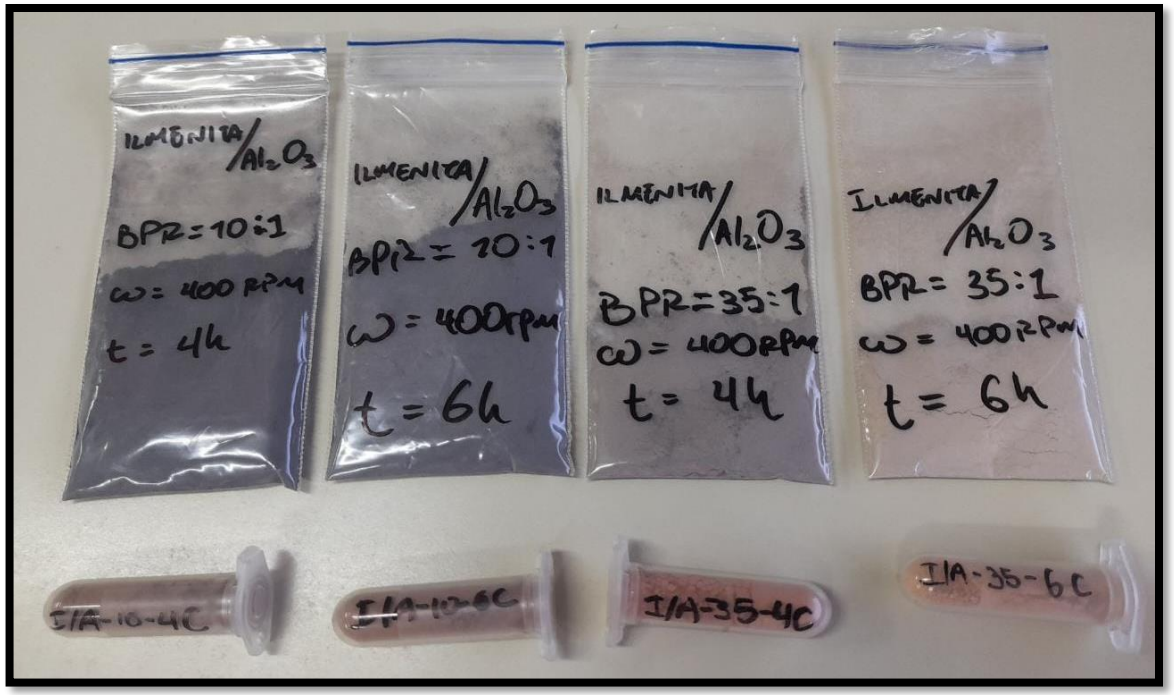
7. Wijewardhana, T. Dilmi. U., Subasinghe, H. C. S., & Ratnayake, A. S. (2021). Value Addition to Ilmenite Using Carbonized Waste Coconut Shells: A Mechanochemical Approach Aided with Powdered Seashells as a Rate Raiser. Mining, Metallurgy & Exploration, 38(3), 1573-1587. https://doi.org/10.1007/s42461-021-00420-z

Alumina as support

The planetary ball mill is used to perform the mechanical-chemical mixing of ilmenite (10%) in alumina Al_2O_3 (90%)

Name	BPR	Milling time [h]	Calcination
I/A-10-4	10	4	No
I/A-10-4-C	10	4	Yes
I/A-10-6	10	6	No
I/A-10-6-C	10	6	Yes
I/A-35-4	35	4	No
I/A-35-4-C	35	4	Yes
I/A-35-6	35	6	No

BPR: Ball to powder ratio in the mill**.**



Ilmenite/alumina materials.

The nomenclature of the catalysts is composed of **I/A**: ilmenite on alumina followed by the **BPR**, grinding **time** and **C** is added for calcined materials.

5. Activity Assessment

Catalyst	Conversion [%]	Selectivity to limonene epoxide[%]
I/A-10-4	0	0
I/A-10-6	0	0
I/A-35-4	0	0
I/A-35-6	0	0
I/A-10-4-C	2	10
I/A-10-6-C	<1	23
I/A-35-4-C	10	43
I/A-35-6-C	3	42

Reaction conditions: 0.25 mmol limonene, 0.50 mmol TBHP, 40 mg catalyst, 1 mL acetonitrile, 70°C, 1000 rpm stirring and 24 h. The samples were analyzed by gas chromatography**.**

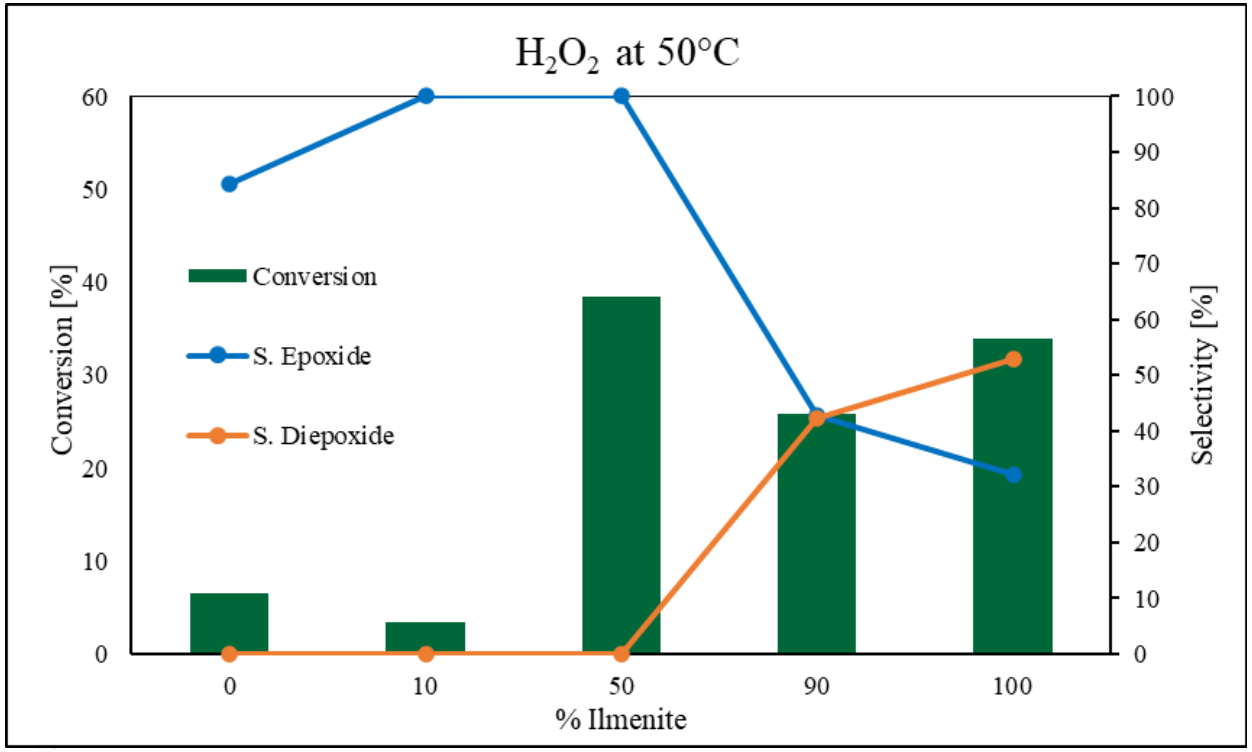
Catalyst	Results
CR-Ilmenite	No activty evidenced
SL-Ilmenite	No activty evidenced
LI-MCM-41	Results not replicable

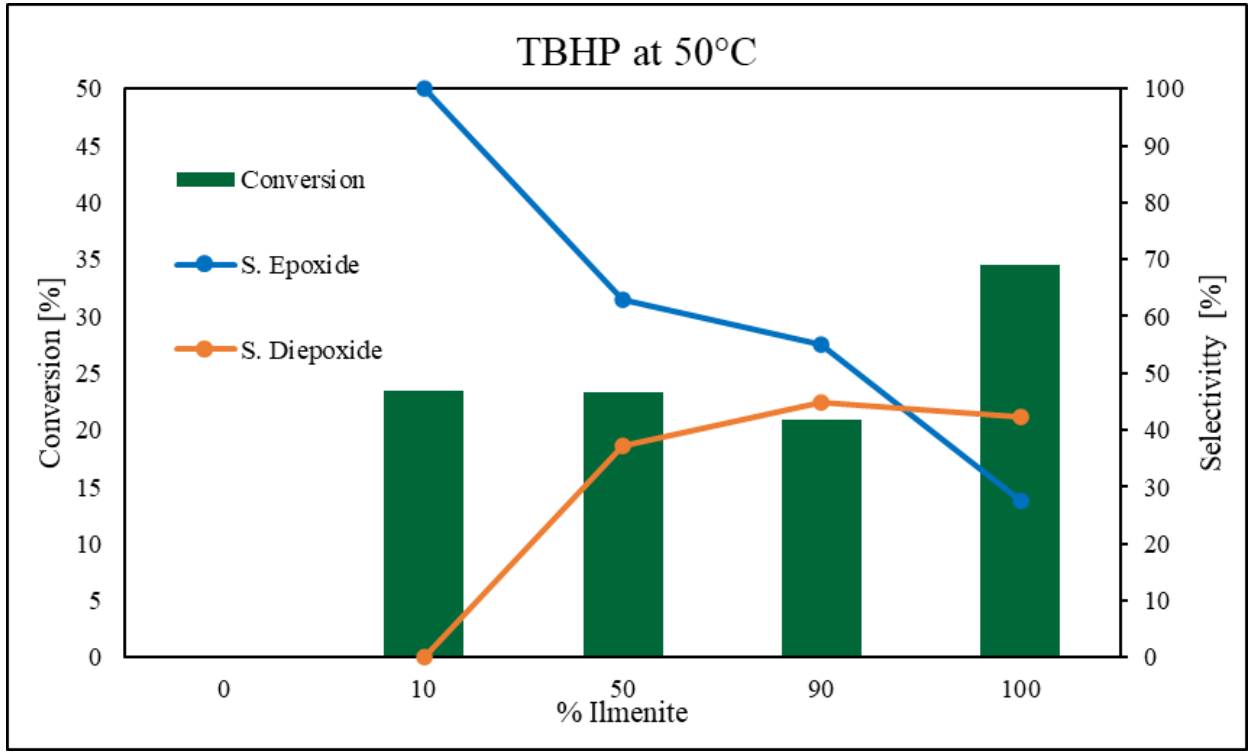
New Supports:
Ilmenite/Alumina

Procedure: 5 g of material mixture of ilmenite + alumina and 175 g of milling bodies (corundum balls) are milled at 400 rpm for 4 h. The material is then calcinated at 550°C with a heat ramp of 10°C/min for 3 h.

Catalyst name	Ilmenite [%]	Alumina [%]
I/A-0	0	100
I/A-10	10	90
I/A-50	50	50
I/A-90	90	10
I/A-100	100	0

Catalytic Assessment Results



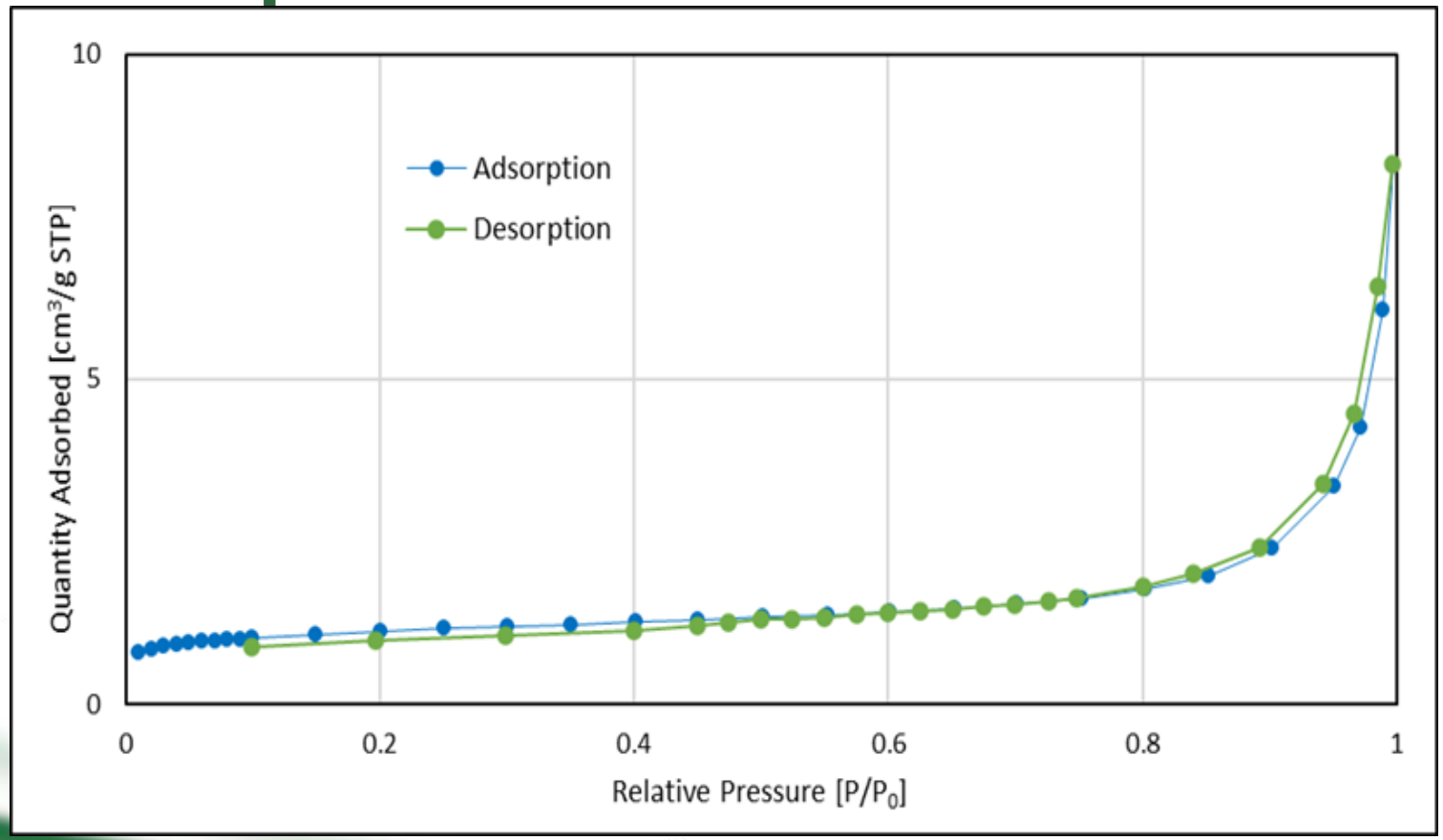


Reaction conditions: 0.25 mmol limonene, 0.50 mmol TBHP or H_2O_2, 40 mg catalyst, 1 mL acetonitrile, 50°C, 1000 rpm stirring and 24 h. The samples were analyzed by gas chromatography**.** The identity of the rest of the should be determined by mass spectrometry.

6. Characterizations

Ilmenite characterizations are performed to evaluate the effect of the modifications on the ilmenite characteristics.

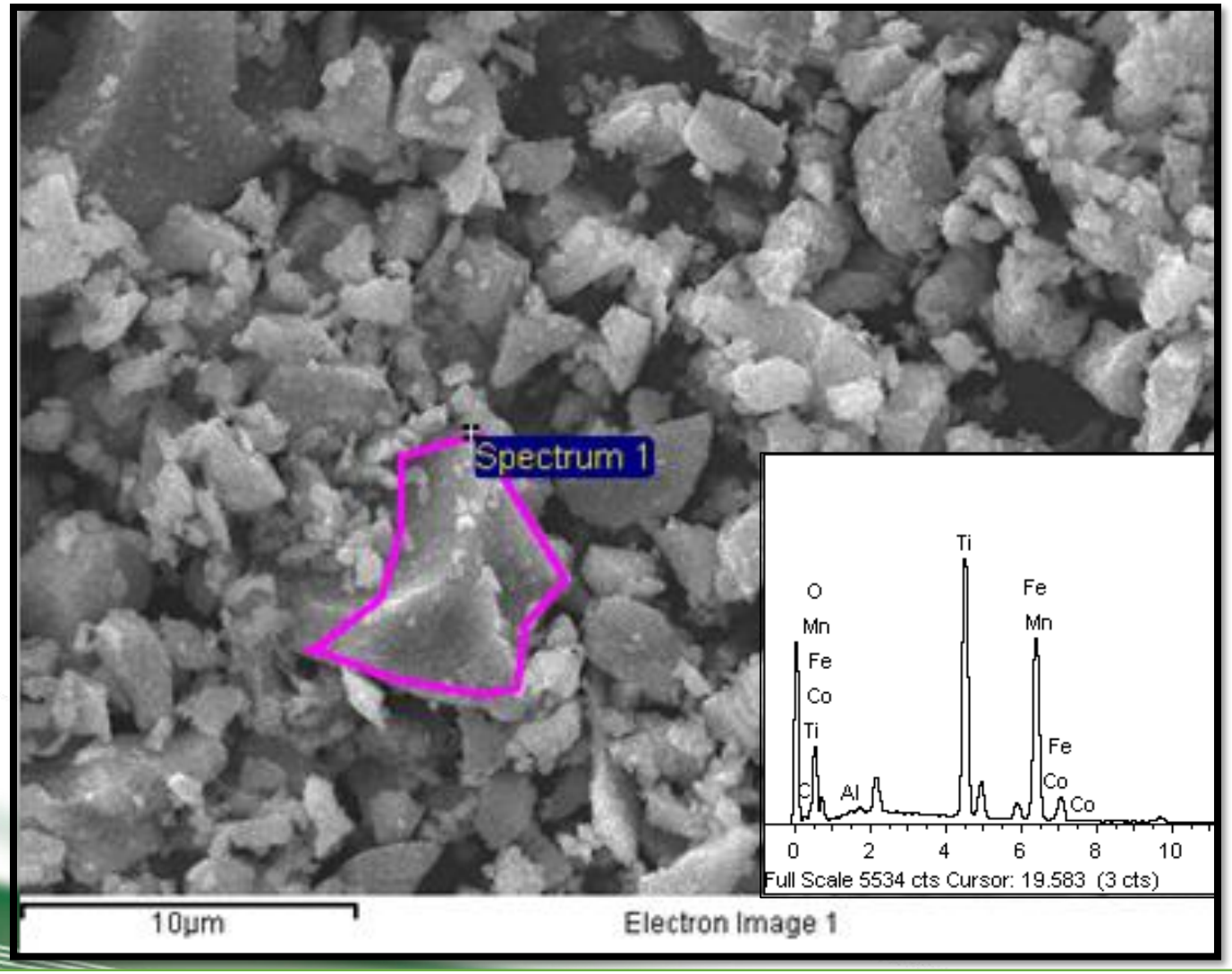
Adsorption isotherm



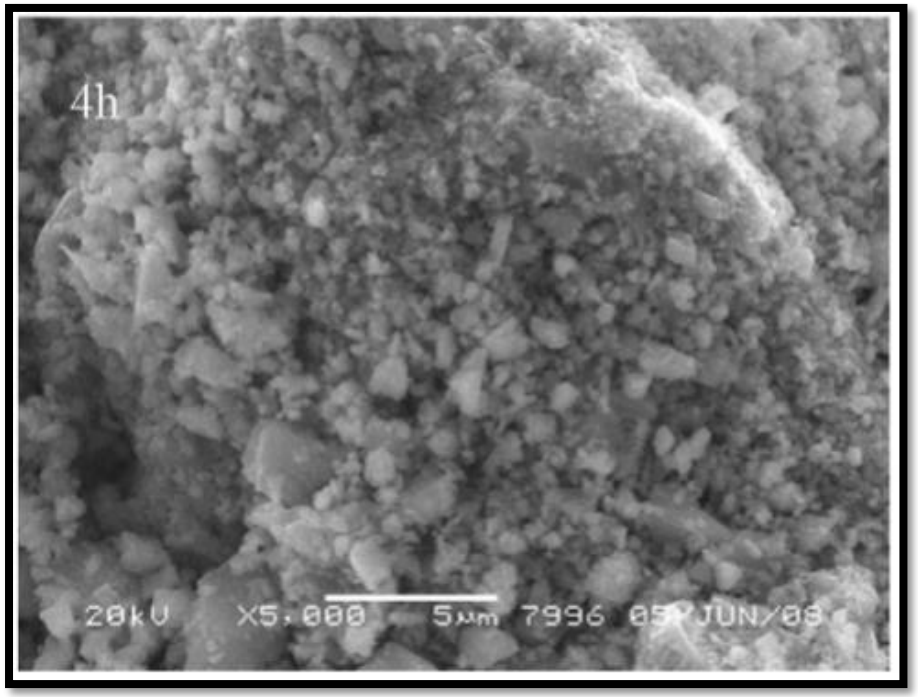
Summary	
Surface area of a point at $P/P_0 = 0.9879$	0.2872 m^2/g
Surface area	3.8971 m^2/g
t-Plot Micropore Area	1.5898 m^2/g
t-Plot External surface area	2.3073 m^2/g
Pore volume at $P/P_0 = 0.9966$	0.01274 cm^3/g

SEM

Ilmenite



Reported[8]



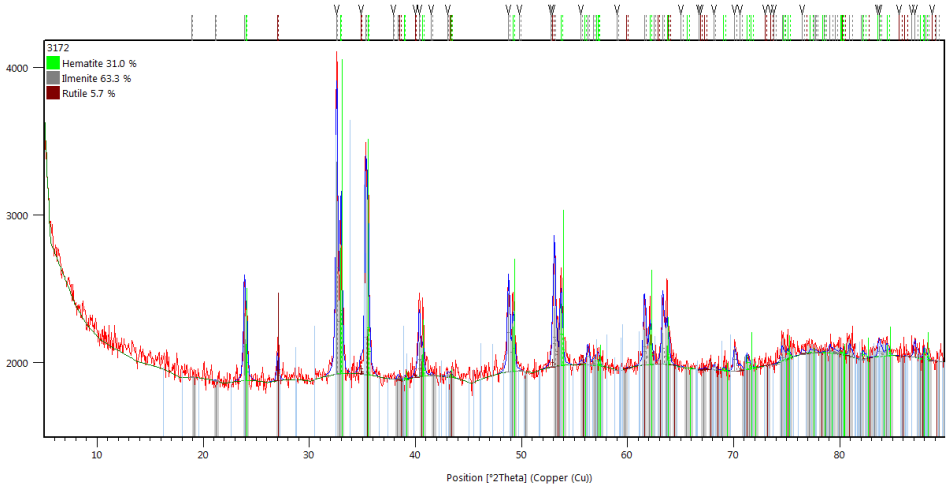
Ilmenite ore reduced in planetary ball mill for 4 hours[8].

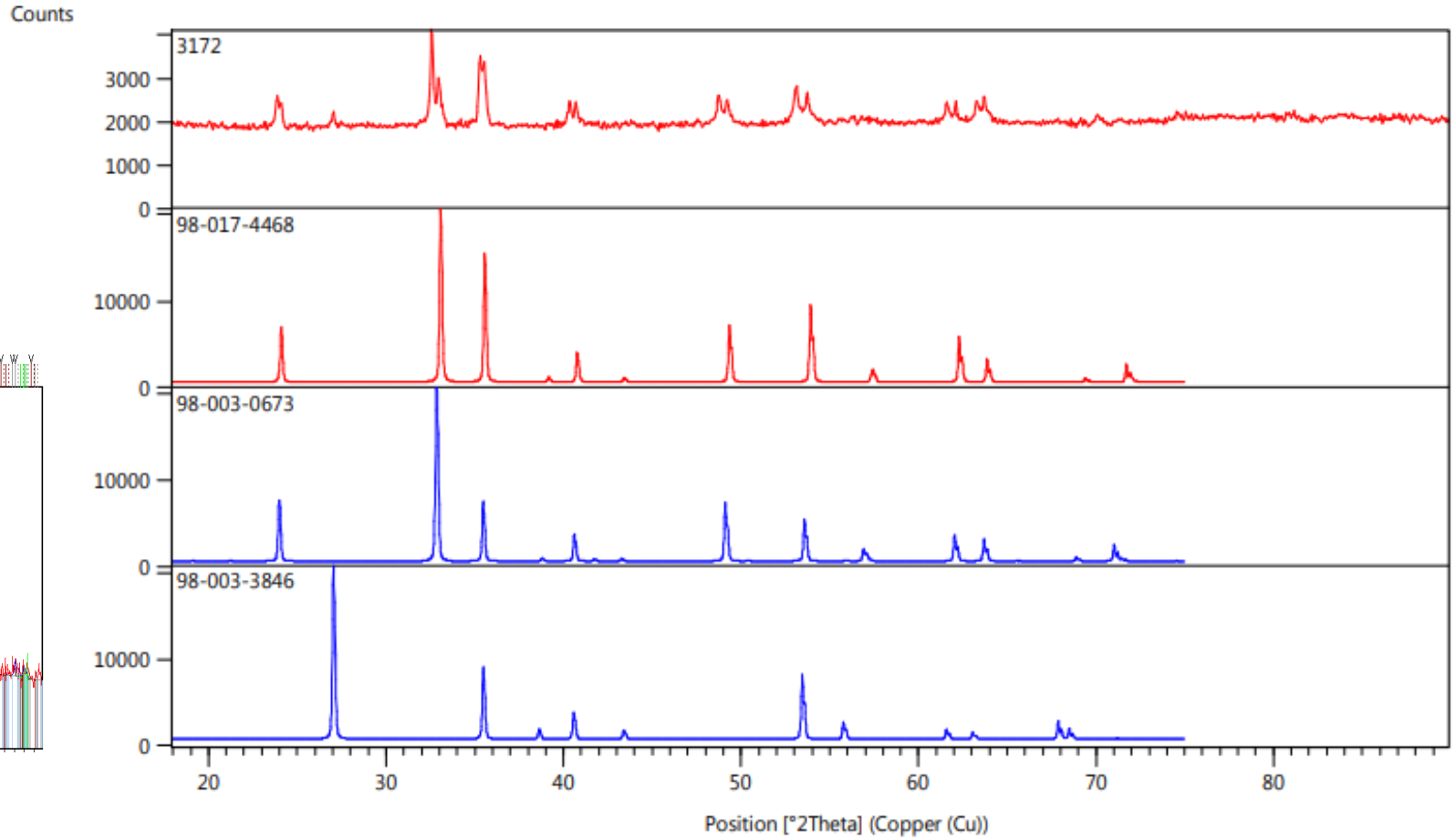
[8] Zhang, L., Hu, H., Wei, L., Chen, Q., & Tan, J. (2010). Hydrochloric acid leaching behaviour of mechanically activated Panxi ilmenite (FeTiO3). *Separation and Purification Technology.*

DRX

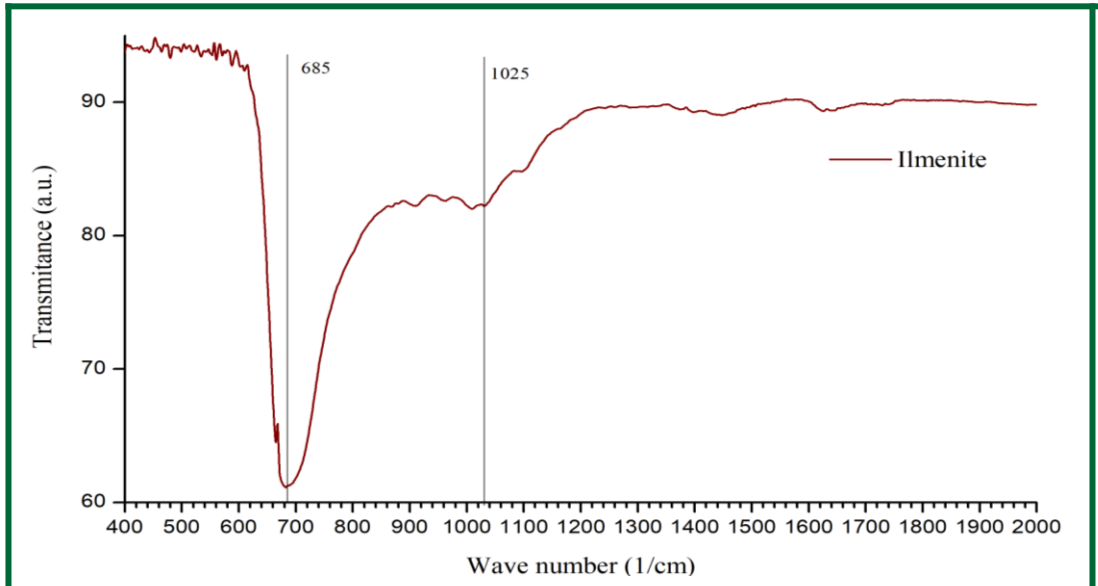
Conditions: Malvern-PANalytical X-ray Diffractometer (XRD) Model Empyean 2012, with Pixel 3D detector and Cu source (λ = 1.541874 Å) at 45kV and 40mA; Goniometer: Omega/2 theta and platform configuration: Spinner transmission reflection with 4s rotation. Step of 0.05° and time per step of 52s.

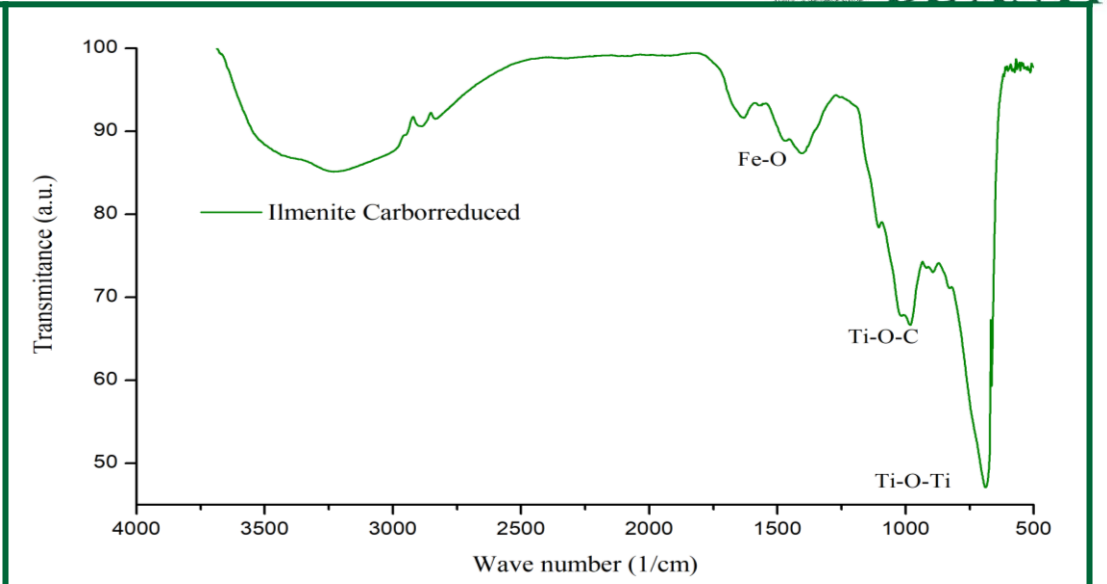
Composition [%]	
Ilmenite	63.3
Hematite	31
Rutile	5.7

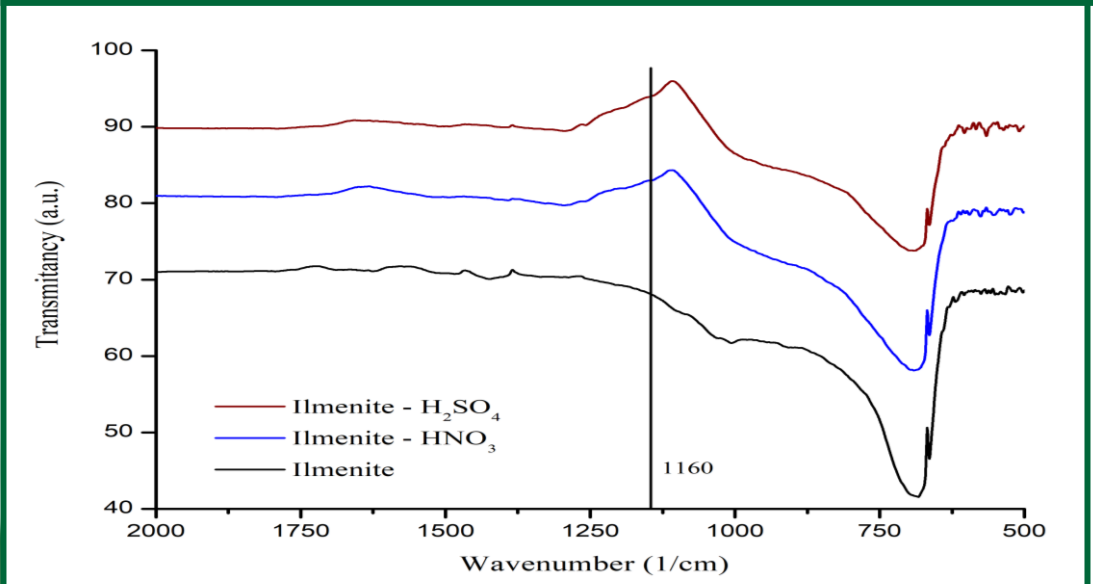


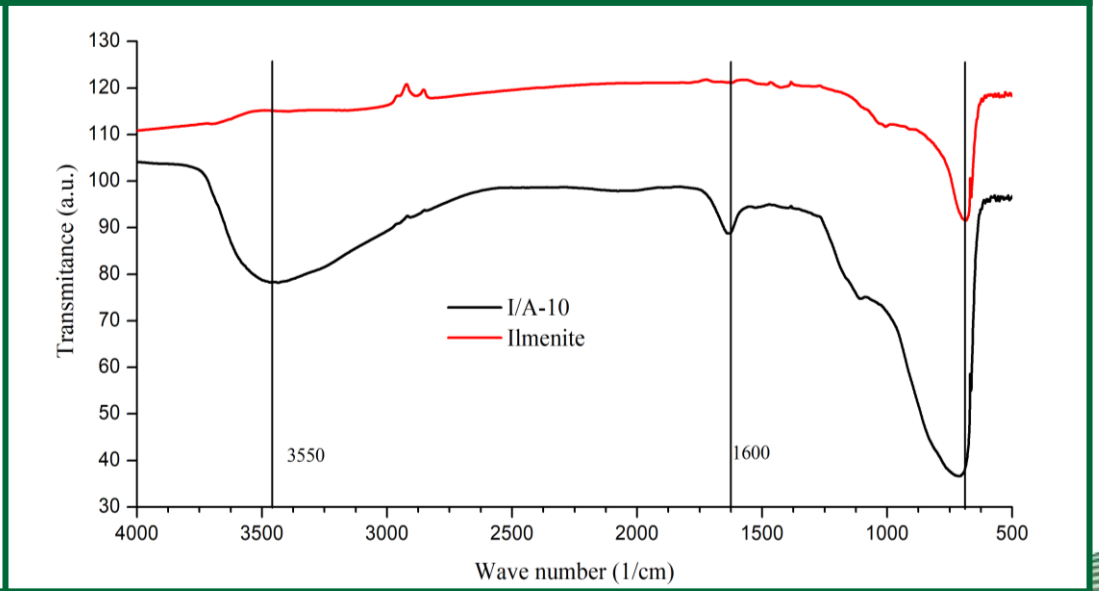


DRIFT









11. Chukanov, N. V., & Chukanov, N. V. (2014). IR spectra of minerals and reference samples data. Infrared spectra of mineral species: Extended library, 21-1701.

7. Analysis

Presence of metal oxides

The raw mineral obtained from Mineros is a mixture of mainly ilmenite and hematite. Which are metal oxides of iron and titanium. Those oxides have been reported as active phases in the oxidation of monoterpenes[4 5].

Low activity

The material has a very low Surface area and low porosity. The material has also too much more active phase in comparison to the reported catalysts in which iron and titanium oxides have a low composition of the material

3. A. Wróblewska, et al., «Fe/Nanoporous Carbon Catalysts Obtained from Molasses for the Limonene Oxidation Process», Catal. Lett., vol. 147
4. A. Gawarecka y A. Wróblewska, «Limonene oxidation over Ti-MCM-41 and Ti-MWW catalysts with t-butyl hydroperoxide as the oxidant», React. Kinet. Mech. Catal.

8. Conclusions

Characterizations suggest that the material is non-porous or microporous material mainly composed by ilmenite, hematite, and rutile.

The DRIFT of the materials suggest that the physicochemical treatments modify in the functional groups on the surface of ilmenite

Catalysts prepared with the mechanochemical support methodology exhibit activity in the oxidation of limonene.

9. References

1. Ribeiro, R. A. P., & De Lázaro, S. R. (2014). Structural, electronic and elastic properties of FeBO 3 (B= Ti, Sn, Si, Zr) ilmenite: a density functional theory study. Rsc Advances.

2. Barrientos, S. (2019). Concentración de arenas negras del Bagre Antioquia provenientes de la minería aluvial del oro. In PAE Proyecto académico especial. UN.

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5. P. Oliveira, et al.,, «Limonene oxidation over V2O5/TiO2 catalysts», Catal. Today

6. A. Wróblewska, «The Epoxidation of Limonene over the TS-1 and Ti-SBA-15 Catalysts», Molecules

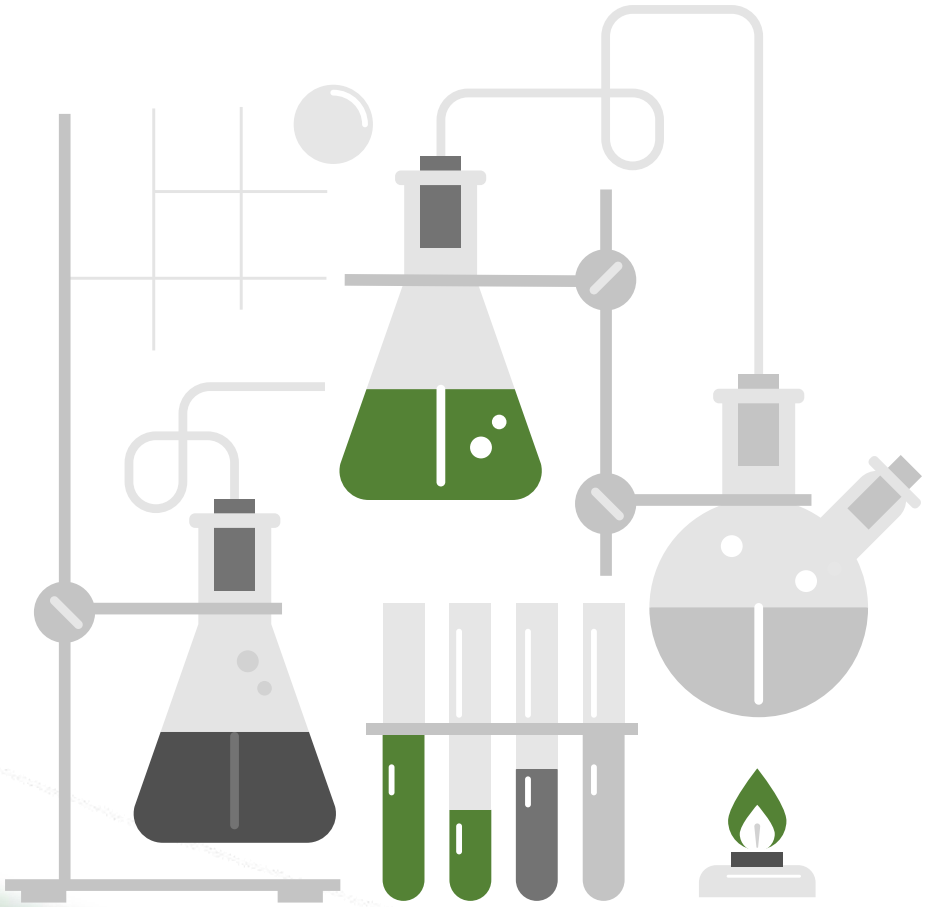
7. J. A. Becerra, et al., «A bio-inspired heterogeneous catalyst for the transformation of limonene from orange peel waste biomass into value-added products», Catal. Today.

8. Li, C., Liang, B., song, H., Xu, J., & Wang, X. (2008). Preparation of porous rutile titania from ilmenite by mechanical activation and subsequent sulfuric acid leaching. Microporous and Mesoporous Materials, 115(3), 293-300.

9. Wijewardhana, T. Dilmi. U., Subasinghe, H. C. S., & Ratnayake, A. S. (2021). Value Addition to Ilmenite Using Carbonized Waste Coconut Shells: A Mechanochemical Approach Aided with Powdered Seashells as a Rate Raiser. Mining, Metallurgy & Exploration, 38(3), 1573-1587. https://doi.org/10.1007/s42461-021-00420-z

10. Ramakrishnan, C., Mani, R., & Babu, D. S. (1997). Ilmenite from the Chavara deposit, India: a critical evaluation. Mineralogical Magazine.

11. Chukanov, N. V., & Chukanov, N. V. (2014). IR spectra of minerals and reference samples data. Infrared spectra of mineral species: Extended library, 21-1701.



Thanks!