

An exploration of zeolitic octahedral niobium oxide as a catalyst in CO₂ cycloaddition to propylene oxide

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Resumo/Abstract

RESUMO – A conversão do CO₂ para produtos de maior valor agregado é uma das estratégias para reduzir sua concentração na atmosfera. O presente trabalho introduz uma exploração do Óxido de Nióbio Zeolítico Octaédrico como catalisador na cicloadição de CO₂ em Óxido de Propileno, para a formação de Carbonato de Propileno. O catalisador sintetizado foi caracterizado, e concluído como equivalente ao reportado na literatura, com diferenças na estrutura mesoporosa. Quanto ao desempenho reacional, não foi detectada seletividade relevante para a produção do Carbonato de Propileno, após caracterização dos produtos, indicando formação de dióis, devido à interação com água ou a necessidade de nucleofilicidade adicional no meio. Assim, a eliminação da umidade do sistema reacional será explorada no futuro pelos autores, através do refino do processo experimental. Além disso, a cicloadição mencionada necessita de um par de funções ácido e base de Lewis. Portanto, a adição de um co-catalisador será estudada nos próximos passos.

Palavras-chave: dióxido de carbono, catálise heterogênea, ZOMO, nióbio.

ABSTRACT – CO₂ conversion into higher aggregated value products is one of the strategies to reduce its concentration in the atmosphere. The present work introduces the exploration of a Zeolitical Octahedral Niobium Oxide as a catalyst in the cycloaddition of CO₂ to Propylene Oxide, for the formation of Propylene Carbonate. The catalyst synthesized was characterized, and concluded as equivalent to the reported in the literature, with differences in the mesoporous structure. As for the reaction performance, it was not detected any relevant selectivity towards Propylene Carbonate production after characterization of the products, indicating diol formation, due to interactions with water or lack of nucleophilicity in the reaction media. Therefore, the elimination of humidity from the reactional system will be explored in the future by the authors, through refinement of the experimental process. Besides, the cycloaddition mentioned requires a pair of Lewis acid and base functions. Therefore, the addition of a co-catalyst will be studied in the next steps.

Keywords: carbon dioxide, heterogeneous catalysis, ZOMO, niobium.

Introduction

The role of CO₂ gas in climate change and the greenhouse effect has been thoroughly discussed in the literature. An increase from 3.3 °C to 5.7 °C in average global temperature, in relation to the 1850-1900 reference, until 2100 is estimated (1). Therefore, reduction of CO₂ concentration in the atmosphere is an ever more urgent demand. CO₂ conversion to higher value-added products could be one route to contribute to controlling climate change.

Cycloaddition of CO₂ to epoxides has been a prominent study subject on the literature (2-5). In the present work, the product of interest for that reaction is propylene carbonate (PC), with propylene oxide (PO) as the reagent. Adopting conversion and selectivity as performance indicators, their maximization can be obtained with catalysis. Catalytic systems for this reaction require both Lewis acid/base functions (6). The search for catalysts that present both functions, such as metallic organic frameworks (MOFs) (7,8), is a current research trend. However, the use of

materials that present Lewis acid sites, with co-catalysts that present Lewis basic sites, is also a common setup (9).

Zeolitic Octahedral Metal Oxides (ZOMOs) are molecular sieves made of mostly metal oxygen polyhedra with inorganic linkers, presenting crystalline structure (10). The present work aims to introduce the fundamentals for an exploration of Zeolitic Octahedral Niobium Oxide (NbO_x ZOMO) as a catalyst for CO₂ conversion.

Experimental

Catalyst Synthesis

NbO_x ZOMO was synthesized through hydrothermal method of Qiu *et al* (10). Typically, ammonium niobium oxalate was dissolved in deionized water. The solution was introduced into a Teflon liner of a stainless-steel autoclave, which was heated at 175 °C for 72 h. The resulting solid was washed by filtration with distilled water. The final solid was collected by centrifugation and dried at 60 °C overnight.

Catalyst Evaluation

Propylene Oxide ($\geq 99\%$) was purchased from Sigma-Aldrich. CO_2 was pressurized from an Air Liquide CO_2 cylinder. The catalyst was tested for the conversion of PO and CO_2 to PC in a stainless-steel reactor, with CO_2 fed at an initial pressure of 10 bar, at RT, with a magnetic stir bar spinning at 500 rpm. The reaction was kept at 100°C with an oil bath for 24 h, after which the reactor was lifted, and allowed to cool down to RT, and depressurized. At RT conditions, the possible products are at the liquid state, while both CO_2 and PO are either gases or highly volatile, allowing the assumption that the remaining liquid phase on the reactor represents the products of the reaction. The reactor was washed with acetone, which was filtered through a syringe filter, before being exposed to a vacuum to remove volatile liquids.

Though selectivity and conversion were selected as performance indicators, yield (Y) was measured in this first step as an indirect indicator, calculated as the ratio between the mols of liquid product, while initially estimating 100% selectivity, and the initial mols of PO.

Catalyst initial loading was varied from 50 to 100 mg, and PO initial loading varied from 1.0 to 2.0 mL.

Characterization

The catalyst was characterized through DRX and N_2 adsorption-desorption techniques, to allow for literature comparison and validation of the material, as well as study of porous structure and specific area.

The purified product of the reaction was characterized through GC-MS techniques, to evaluate composition, selectivity and conversion.

Results and Discussion

N_2 adsorption results (Fig. 1a) appear consistent with the literature (10), with an increase width in the observed hysteresis, indicating a possible increase concentration of mesoporosity. BET analysis indicates a surface area of $268\text{ m}^2\cdot\text{g}^{-1}$. DRX results (Fig. 1b) are also consistent with the literature (10).

As for the products, GC-MS results indicate negligible selectivity towards PC, and production of several diol species that result from PO interaction with water and consequent epoxide opening. Therefore, measures of Y also differ from actual results, rendering results null. This indicates a need for refining in the reaction process, in terms of eliminating water from the reactor. Besides, the non-inclusion of a co-catalyst may be causing the low performance.

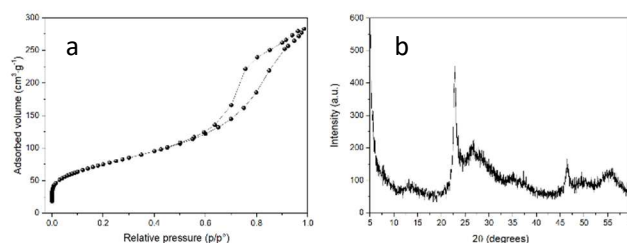


Figure 1. a) N_2 adsorption-desorption isotherm for NbO_x ZOMO; b) XRD pattern for NbO_x ZOMO.

Conclusions

The characterization of the synthesized NbO_x ZOMO indicates that the material matches literature's reports, with some difference in porous structure. The characterization of the reaction products is inconclusive, as for NbO_x ZOMO's performance in the cycloaddition of Propylene Oxide to CO_2 .

The authors intend to continue this study by refining the experimental design, drying the catalyst under vacuum and heating before insertion in the reactor, though understanding that the room humidity content may still impact the results.

Additionally, tetra-n-butylammonium bromide (TBAB) will be studied as a potential co-catalyst.

Acknowledgments

This work was financially supported by the Coordination of Superior Level Staff Improvement (CAPES). The authors extend the acknowledgments to the Federal University of Paraná (UFPR) Chemistry Department's Analytical Central, for the GC-MS characterization.

References

1. International Energy Association. *CO₂ Emissions in 2023, 2024*.
2. Q. T. Nguyen *et al.* *J. CO₂ Util.* **2023**, 70, 102451.
3. Y. Lin *et al.* *J. Nanomater.* **2022**, 12(19), 3442.
4. Y. Ye; Y. Qu; J. Sun, *Catal. Rev.* **2023**, 66(5), 2153-2208.
5. M. Mariyaselvakumar *et al.* *Appl. Catal., A* **2024**, 675, 119634.
6. P. P. Pescarmona. *Curr. Opin. Green Sust.* **2021**, 29, 100457.
7. J. Liang; Y. Huang; R. Cao. *Coord. Chem. Rev.* **2019**, 378, 32-65.
8. S. S. Dhankhar; B. Ugale; C. M. Nagaraja. *Chem. Asian J.* **2020**, 15, 2403.
9. J. Wu *et al.* *ACS Catal.* **2025**, 15, 1305-1340.
10. C. Qiu *et al.* *Nanoscale*. **2021**, 13, 7792-7800.