Teguh Kurniawan <teguh@untirta.ac.id>

Your Submission - [EMID:7c70aa6a7e2a396c]

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Results in Chemistry <em@editorialmanager.com> 15 September 2022 pukul 15.36
Balas Ke: Results in Chemistry <support@elsevier.com>
Kepada: Teguh Kurniawan <teguh@untirta.ac.id>

Ref.: Ms. No. RECHEM-D-22-00711
Catalytic acetalization of glycerol waste over alkali treated natural clinoptilolite
Results in Chemistry

Dear Dr. Kurniawan,

Reviewers have now commented on your paper. You will see that they are advising that you revise your manuscript. If you are prepared to undertake the work required, I would be pleased to reconsider my decision.

For your guidance, reviewers' comments are appended below.

If you decide to revise the work, please submit a list of changes or a rebuttal against each point which is being raised when you submit the revised manuscript.

Your revision is due by Oct 06, 2022.

To submit a revision, go to https://www.editorialmanager.com/rechem/ and log in as an Author. You will see a menu item call Submission Needing Revision. You will find your submission record there.

Yours sincerely

Marta Meazza, Ph.D.
Scientific Editor
Results in Chemistry

Comments from the Editors and Reviewers:

Reviewer #1: The revised paper deals with the modification of natural clinoptilolite and its potential application as catalyst in waste glycerol management. Considering that an increase in biodiesel production brings about an increasing surplus of glycerol, its efficient utilization is very challenging. In the presented paper natural zeolite was treated with the aqueous solution of NaOH (with different concentration). This procedure influenced the textural properties of the studied samples (e.g. crystallinity, surface area, and pore diameter) which enhanced the diffusion properties. A significant increase in glycerol conversion over the modified samples in glycerol acetalization resulted from the easier accessibility of the active sites to reagents due to the formation of mesopores. Although the revised paper deals an interesting topic and the presented results are quite promising, the paper suffers from serious drawbacks which are listed below:

Comments:
1. In the Materials and method section more details should be added, e.g. regarding FT-IR measurements. How the spectra were recorded? There is no information about low temperature N2 adsorption/desorption isotherms.
2. The FTIR analysis is actually not very informative, therefore, this data could be shifted to Supplementary materials (if possible).
3. Section 3.5 in my opinion does not really present the "mechanism", it is rather the graphical presentation of the possible effect of alkaline treatment of clinoptilolite.
4. The caption for Figure 7 is not clear. Again, this is just the graphical presentation of the result of the treatment of natural zeolite with NaOH. Actually, in the figure there is no information about "glycerol conversion".
5. In the paper Author discuss the increase of the "active sites", however, it is not clear what are these "active sites". Actually, there is no information in the text about the nature of the "active sites".
6. In glycerol acetalization reaction the acidic sites of different nature, Broensted and/or Lewis, were indicated as the active one. However, in the revised paper there is no information about the acidic nature of the studied samples. These data should be supplemented in the revised manuscript and it should be discussed along with catalytic results. The

discussion based exclusively on the basis of textural properties of the samples after alkaline treatment is not convincing.
7. What about the selectivity of the studied reaction? Do Authors analyzed the composition of the products?
8. The paper should be carefully corrected by native speaker in order to eliminate numerous grammatical mistakes.

To summarize, the Authors undertook interesting research problem, they present interesting results, however, the paper should be supplement with additional information, the discussion should be widened and English should be carefully corrected before publication in Results in Chemistry.

Reviewer #2: This paper can be published in "Results in Chemistry" after minor revision.
This paper is very interesting due to the extrem importance to improve the economic value of the glycerol.
However, some questions can be raised:
1-It was not understood that the authors did not give any information on the Lewis acid-base priperties of the synthetized catalysts after NAoH treatment.
2-There is no information of the surface properties such as the surface energy and the specific thermodynamic parameters of the new catalysts
3- Why authors stopped on 0.4M NaOH? what will happen if the concentration of NaOH increases from 0.4 to 1M.
4-The mentioned concentration of 4 M of NaOH in literature is it best than the present results.
5-Can authors explain the mechanism of the concentration of NaOH between 0.1M and 5M on the stability of the obtained zeolithe?

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Teguh Kurniawan <teguh@untirta.ac.id>

Decision on Your Submission Ms. No. RECHEM-D-22-00711R1 - [EMID:442c6f558e302dd7]

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Results in Chemistry <em@editorialmanager.com> 14 Oktober 2022 pukul 10.39
Balas Ke: Results in Chemistry <support@elsevier.com>
Kepada: Teguh Kurniawan <teguh@untirta.ac.id>

Ref.: Ms. No. RECHEM-D-22-00711R1
Catalytic acetalization of glycerol waste over alkali treated natural clinoptilolite
Results in Chemistry

Dear Dr. Kurniawan,

I am pleased to inform you that your manuscript has now been accepted for publication in Results in Chemistry.

Comments from the Editor and Reviewers can be found below.

Thank you for submitting your work to this journal.

With kind regards

Joyanta Choudhury
Editor
Results in Chemistry

Comments from the Reviewers:

Reviewer #1: The authors have addressed all the comments to the best of their capacity. They have also performed additional experiments which is well appreciated. I would recommend this version is ready to be accepted.

Reviewer #2: The paper is now accepted for publication in "Results in Chemistry".
The response of the authors are well-accepted.

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Teguh Kurniawan <teguh@untirta.ac.id>

RECHEM-D-22-00711 - Confirming your submission to Results in Chemistry - [EMID:5bc6218f55fe3f27]

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Results in Chemistry <em@editorialmanager.com> 12 Agustus 2022 pukul 06.41
Balas Ke: Results in Chemistry <support@elsevier.com>
Kepada: Teguh Kurniawan <teguh@untirta.ac.id>

Dear Dr. Kurniawan,

Your submission entitled "Catalytic acetalization of glycerol waste over alkali treated natural clinoptilolite" has been received by journal Results in Chemistry. It has been assigned the following manuscript number: RECHEM-D-22-00711.

You will be able to check on the progress of your paper by logging on to Editorial Manager as an author. The URL is https://www.editorialmanager.com/rechem/.

Your manuscript will be given a reference number once an Editor has been assigned.

Thank you for submitting your work to this journal.

Kind regards,

Results in Chemistry

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Response to the Referee's comments

Response to the Referee's comments on submitted manuscript.

Journal: Results in Chemistry
ID: **RECHEM-D-22-00711**
Title: **Catalytic acetalization of glycerol waste over alkali treated natural clinoptilolite**

Dear Editor,

Thank you for your useful comments and suggestions on our manuscript.

We have modified the manuscript accordingly, and detailed corrections are listed below:

The authors are appreciative that the referee has reviewed the paper and provided us with some valuable comments. Following are the changes which address the comments of the referees.

These adjustments have been made in the revised version.

The manuscript has been resubmitted to your journal. We look forward to your positive response.

Sincerely,

Associate Professor Dr. Teguh Kurniawan
E-mail: teguh@untirta.ac.id

Chemical Engineering, Universitas Sultan Ageng Tirtayasa

Herewith, an itemized letter answering all the comments made and describing all changes made in response, or the reason why no change should be made. Below, we answer the comments one by one and we indicated clearly where changes have been made to the manuscript in response. Also, we submit our revised manuscript as a copy where the changes have been highlighted using a different color so that they can easily be identified.

Comments from the Editors and Reviewers:

Reviewer #1: The revised paper deals with the modification of natural clinoptilolite and its potential application as catalyst in waste glycerol management. Considering that an increase in biodiesel production brings about an increasing surplus of glycerol, its efficient utilization is very challenging. In the presented paper natural zeolite was treated with the aqueous solution of NaOH (with different concentration). This procedure influenced the textural properties of the studied samples (e.g. crystallinity, surface area, and pore diameter) which enhanced the diffusion properties. A significant increase in glycerol conversion over the modified samples in glycerol acetalization resulted from the easier accessibility of the active sites to reagents due to the formation of mesopores. Although the revised paper deals an interesting topic and the presented results are quite promising, the paper suffers from serious drawbacks which are listed below:

Comments:

1. In the Materials and method section more details should be added, e.g. regarding FT-IR measurements. How the spectra were recorded?

Response:

FTIR spectroscopy was performed using a Shimadzu to evaluate the functional groups of the zeolites with range spectra from 4000-400 cm^{-1}. We used the attenuated total reflectance (ATR) mode with powder samples for the FTIR analysis.

The manuscript has been revised. Please see Section 2.2

There is no information about low temperature N2 adsorption/desorption isotherms.

Response:

The manuscript has been revised. Please see Section 2.2

"Textural properties were examined by nitrogen physisorption technique (Quantachrome TouchWin v1.22) using liquid nitrogen at temperature -196 ^{o}C. Prior to adsorption-desorption analysis, degassing was performed by heating to 200 ^{o}C at 5 ^{o}C/min and dwelled for 10 min, followed by heating to 300 ^{o}C at 10^{o}C/min and dwelled for 60 min."

2. The FTIR analysis is actually not very informative, therefore, this data could be shifted to Supplementary materials (if possible).

Response:

Thank you for your suggestion. The FTIR figure was shifted to supplementary materials.

3. Section 3.5 in my opinion does not really present the "mechanism", it is rather the graphical presentation of the possible effect of alkaline treatment of clinoptilolite.

Response:

Thank you for your comments. We have modified the caption.

4. The caption for Figure 7 is not clear. Again, this is just the graphical presentation of the result of the treatment of natural zeolite with NaOH. Actually, in the figure there is no information about "glycerol conversion".

Response:

The caption has been modified.

5. In the paper Author discuss the increase of the "active sites", however, it is not clear what are these "active sites". Actually, there is no information in the text about the nature of the "active sites".

Response:

The manuscript has been revised. The active sites are Bronsted and Lewis acid sites which located in the pore of zeolites. The acid sites become more accessible after NaOH treatment which removing the amorphous silica blockage as well as creating the mesopore.

6. In glycerol acetalization reaction the acidic sites of different nature, Broensted and/or Lewis, were indicated as the active one. However, in the revised paper there is no information about the acidic nature of the studied samples. These data should be supplemented in the revised manuscript and it should be discussed along with catalytic results. The discussion based exclusively on the basis of textural properties of the samples after alkaline treatment is not convincing.

Response:

Thank you for your comments. We agree with your suggestion that the acidic nature analysis is important to be performed through NH3-TPD and or FTIR-Pyridine. However, currently we do not have access to those devices. To improve the discussion, we add some literature regarding the acidic nature after the NaOH treatment of zeolites, particularly clinoptilolite (Verboekend et al., 2013) and other zeolites type for comparison (Kowalska-Kus et al., 2017).

“The alkali-treated zeolites also improve the micropore and mesopore volume (Table 1), which can be a verdict of high acid sites within the zeolite framework. Kowalska et al. reported that the desilication of MFI, MOR and BEA zeolites using 0.2 M NaOH at 80 oC resulted in the increase of both total acidity and strong acidity using pyridine probe (Kowalska-Kus et al., 2017). The pyridine has diameter kinetic about 0.533 nm. The increase in total acidity of the zeolites contributed by Brønsted acidity and Lewis acidity which could be more accessed by the pyridine after the NaOH treatment. The other groups reported that tandem acid-base created the mesopore while preserved the total acidity by NH3-TPD analysis (Verboekend et al., 2013).”

7. What about the selectivity of the studied reaction? Do Authors analyzed the composition of the products?

Response:

We performed FTIR analysis to identify the solketal in the product. The solketal was identified in the products. Unfortunately, the composition of the products could not be analyzed quantitatively by the FTIR. Hence, the selectivity of the studied reaction is not presented.

8. The paper should be carefully corrected by native speaker in order to eliminate numerous grammatical mistakes.

Response:

The manuscript has been corrected by an English expert.

To summarize, the Authors undertook interesting research problem, they present interesting results, however, the paper should be supplement with additional information, the discussion should be widened and English should be carefully corrected before publication in Results in Chemistry.

Response: Thank you for your comments

Reviewer #2: This paper can be published in "Results in Chemistry" after minor revision. This paper is very interesting due to the extrem importance to improve the economic value of the glycerol.

Response:

Thank you very much for your comments.

However, some questions can be raised:
1-It was not understood that the authors did not give any information on the Lewis acid-base priperties of the synthetized catalysts after NAoH treatment.

Response:

Thank you for your comments. The Lewis acid analysis is important to be performed. However, currently we do not have access to the device. To improve the discussion, we add some literature regarding the acidic nature after the NaOH treatment of zeolites (Verboekend et al., 2013) and (Kowalska-Kus et al., 2017).

"The alkali-treated zeolites also improve the micropore and mesopore volume (**Table 1**), which can be a verdict of high acid sites within the zeolite framework. Kowalska et al. reported that the desilication of MFI, MOR and BEA zeolites using 0.2 M NaOH at 80 ^{o}C resulted in the increase of both total acidity and strong acidity using pyridine probe (Kowalska-Kus et al., 2017). The pyridine has diameter kinetic about 0.533 nm. The increase in total acidity of the zeolites contributed by Brønsted acidity and Lewis acidity which could be more accessed by the pyridine after the NaOH treatment. The other groups reported that tandem acid-base created the mesopore while preserved the total acidity by NH3-TPD analysis (Verboekend et al., 2013).

2-There is no information of the surface properties such as the surface energy and the specific thermodynamic parameters of the new catalysts

Response:

Thank you for your comments. We did not study the surface properties for current work. It is valuable suggestion for our next catalyst research development.

3- Why authors stopped on 0.4M NaOH? what will happen if the concentration of NaOH increases from 0.4 to 1M.

Response:

From our previous work, high concentration of NaOH solutions (0.8 M and 1.0 M) led to a decrease in peak intensity (Irawan et al., 2021), which suggested that the crystallinity of zeolite was decrease. That is the reason why we stopped on 0.4 M NaOH.

4-The mentioned concentration of 4 M of NaOH in literature is it best than the present results.

Response:

"Jha and Hayashi reported that the natural clinoptilolite remained intact after 4 M NaOH treatment at room temperature with time variation from 24-72 h (Jha & Hayashi, 2009)".

The temperature was at room temperature instead of the present work at 60 ^{o}C. That's why the natural clinoptilolite remained intact even though the concentration 4 M NaOH. Here, we want to explain that at room temperature NaOH treatment did not destroyed the zeolite framework.

5-Can authors explain the mechanism of the concentration of NaOH between 0.1M and 5M on the stability of the obtained zeolithe?

Response:

The explanation has been incorporated in the manuscript please see section 3.5 and Figure 6. At harsh NaOH treatment, the crystallinity decreases as more silica from the zeolite framework extracted. It also creating the mesopore and at the same time demolishing the micropore. The total surface area would decrease significantly as reported in our previous work (Irawan et al., 2021).

References

Irawan, A., Bindar, Y., Kurniawan, T., Alwan, H., Rosid, & Fauziah, N. A. (2021). Bayah natural zeolites to upgrade the quality of bio crude oil from empty fruit bunch pyrolysis. *Journal of Engineering and Technological Sciences*, *53*(3), 210308. https://doi.org/10.5614/j.eng.technol.sci.2021.53.3.8

Jha, V. K., & Hayashi, S. (2009). Modification on natural clinoptilolite zeolite for its NH4+ retention capacity. *Journal of Hazardous Materials*, *169*(1), 29–35. https://doi.org/https://doi.org/10.1016/j.jhazmat.2009.03.052

Kowalska-Kus, J., Held, A., Frankowski, M., & Nowinska, K. (2017). Solketal formation from glycerol and acetone over hierarchical zeolites of different structure as catalysts. *Journal of Molecular Catalysis A: Chemical*, *426*, 205–212. https://doi.org/https://doi.org/10.1016/j.molcata.2016.11.018

Verboekend, D., Keller, T. C., Milina, M., Hauert, R., & Pérez-Ramírez, J. (2013). Hierarchy Brings Function: Mesoporous Clinoptilolite and L Zeolite Catalysts Synthesized by Tandem Acid–Base Treatments. *Chemistry of Materials*, *25*(9), 1947–1959. https://doi.org/10.1021/cm4006103