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Title of work: **Zeolite-amine complex catalysis of Meerwein-Ponndorf-Verley type hydrogen transfer reaction**

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A) EVALUATION OF THE THESIS CONTENT

Scope and relevance of the theoretical introduction, and its alignment with current research	2
Accuracy of the methodology description enabling reproducibility of experiments	1
Presentation of obtained data and interpretation of results	1
Discussion of the conclusions in a broader context	1

This master's thesis investigates the Meerwein-Ponndorf-Verley (MPV) reduction of citronellal, using Lewis acid zeolites (Zr- and Sn-beta) as catalysts. The MPV reaction offers a mild and selective hydrogen transfer process to convert carbonyl compounds into alcohols, but side reactions like cyclization and acetalization can decrease product selectivity. The study examines the role of nitrogen-containing bases, particularly pyridine and its derivatives, in forming zeolite-amine complexes that can enhance selectivity toward citronellol. The study is supported by a detailed characterization of the synthesized zeolites, which differ in their content and source of tetravalent metal atoms (Zr, Sn), using various techniques including FTIR, UV-Vis, SEM, and XRD, as well as by a comprehensive kinetic study of the MPV reduction.

Obtained results show that coordinating bases such as pyridine and 2,5-lutidine significantly increase the yield of citronellol, depending on their molecular size and ability to access Lewis acid sites within the zeolite. Some tested bases, especially bulky ones, showed no effect due to steric hindrance.

Additionally, the thesis explored the potential for inducing stereoselectivity in MPV reductions using chiral amines. Although the chiral bases slowed down the reaction, they did not result in any observable stereoselectivity.

One of the key strengths of this thesis lies in the thorough and well-integrated characterization of the synthesized catalysts. The author not only provides detailed characterization of prepared catalysts but also effectively connects these findings with the catalytic performance and kinetic studies. The level of integration between the characterization results and the kinetic analysis is, in my view, above standard. Furthermore, the experimental section is clearly structured, offering a transparent and systematic description of the catalyst preparation, catalytic testing, and characterization techniques.

On the other hand, the theoretical part of the thesis is somewhat less developed. While the student focuses primarily on characterization methods—which are indeed central to the work—I lack any overview of existing knowledge on MPV reductions using Sn- and Zr-based zeolites or a summary of previously achieved results in this area. The only reference to prior work is the student's own bachelor thesis.

Concerning results of catalytic experiments, the definition of the turnover frequency (TOF) is missing. It would be important to clarify how the number of moles of catalytically active sites

was determined. Equation (4), which describes the yield calculation, refers to the peak area of the substrate in specific time (A_i) and its initial value (A_0). However, in a formula for product yield, one would expect the peak area of the product to be used instead.

I appreciate the thoughtful approach taken in the kinetic study, such as reducing the catalyst amount to obtain reliable kinetic data and adapting a literature-based kinetic model, which was subsequently modified. However, if the final kinetic model is based on equations (9) and (10), then the parameters listed in Table 9— k_1 , k_2 , and k_3 —do not correspond to three rate constants, as K_1 is actually the adsorption equilibrium constant (according to equation 9). If the model is instead a combination of equations (10) and (11), then k_2 appears to be missing. Proposing a kinetic model for such a complex system is undoubtedly a challenging task. The student supports the model's validity by presenting fitted curves generated using the ERA software, which is really helpful. Nevertheless, I would recommend complementing this detailed analysis with a residual distribution assessment using the von Neumann test. Based on the graphical representation, the data suggest a slight positive autocorrelation, which may indicate a suboptimal choice of regression model form.

B) EVALUATION OF THE FORMAL ASPECTS OF THE THESIS

The formal aspects of the thesis show a few minor shortcomings. Locants such as *N* in compounds like *N*-methylpiperidine should be italicized, as should stereochemical descriptors such as *R* and *S* in the case of chiral compounds. Additionally, in Figure 3, one carbon atom is missing in the structure between steps 4 and 5. Aside from these issues, the thesis contains very few typographical errors. These minor formal inconsistencies do not, however, detract from the overall quality of the work.

C) OVERALL RATING

The master's thesis presents a well-executed and methodologically well-grounded investigation of the MPV reduction of citronellal using Lewis acid zeolites. One of its greatest strengths is the thorough characterization of the synthesized catalysts and the effective integration of these findings with catalytic performance and kinetic analysis. The student's thoughtful approach to kinetic modeling, including adaptation from literature and use of the ERA software for data fitting, reflects a high level of scientific insight.

Although the theoretical part could benefit from a more comprehensive review of existing studies on MPV reductions involving Sn- and Zr-based zeolites, this limitation does not significantly diminish the overall quality of the work. Minor shortcomings mentioned above do not detract from the overall impression. The thesis demonstrates a high level of analytical thinking, and experimental proficiency.

D) QUESTIONS

For the discussion during the thesis defense, I suggest:

1. Explanation of the missing definition of the turnover frequency (TOF).

2. On page 35, the student notes: “Zr-beta-A has a lower Si/Zr ratio than expected, suggesting more Zr was incorporated than anticipated.” I would appreciate clarification on how it is possible for more zirconium to be incorporated than initially expected?
3. Furthermore, considering the UV-Vis spectra, would it be possible to quantify the proportion of framework tin atoms (typically associated with an absorption band around 220 nm) versus extra-framework SnO₂ species (260–280 nm)?
4. In the catalytic experiments, the base was added in a 1:10 molar ratio relative to citronellal. Could the student explain how this ratio was chosen? Were other base-to-substrate ratios tested during preliminary experiments or optimization?

In conclusion, this is a very high-quality thesis, and I therefore evaluate it with the grade **“excellent (1)”** and **recommend it for defense.**

In Prague, May 28, 2025



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Signature

