

Magn. Reson. Discuss., referee comment RC3
<https://doi.org/10.5194/mr-2021-5-RC3>, 2021
© Author(s) 2021. This work is distributed under the Creative Commons Attribution 4.0 License.

Comment on mr-2021-5

Anonymous Referee #2

Referee comment on "Pd-based bimetallic catalysts for parahydrogen-induced polarization in heterogeneous hydrogenations" by Dudari B. Burueva et al., Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2021-5-RC3>, 2021

The authors present PHIP experiments in the gas phase of propyne employing heterogeneous bimetallic catalysts. The study provides useful information for improving HET-PHIP experiments but should be revised with respect to the following specific comments:

- Line 97: "Pd-Ag/Al₂O₃ catalyst sample contained 2 wt.% of Pd and 6 wt.% of Ag; Pd-In/Al₂O₃ catalyst contained 2 wt.% of Pd and 2 wt.% of In". This result in different dilutions of Pd in the other (less catalytically active) metal. Therefore, the amount of catalytically active Pd₁ sites should be different in the two bimetallic catalysts? How does this impact on the comparability of the results for the Pd-Ag and the Pd-In catalyst?
- Very few experimental details are presented in the entire manuscript. Reviewer 1 already asked for more details on the synthesis and analysis of the bimetallic catalysts, which was sufficiently answered by the authors in the revised version of the manuscript. This reviewer is more concerned with the understanding of the NMR experiments and the reaction control of the hydrogenation experiments, which are both not sufficiently described in the experimental section.

Questions on hydrogenation experiments:

- In line 110 the authors mention that "propyne was premixed with p-H₂ in the molar ratio of 1:4". What was the overall pressure of the gas mixture before the reaction?
- The authors performed the hydrogenation experiments at different temperatures, showing how temperature affects the conversion and selectivity of the reaction. It would be also interesting to know how different pressures would affect the reaction. Did the authors ever tried to perform the hydrogenation with different pressures and can give a hint in which way the hydrogenation is affected by different pressures?
- In table 1 the authors provide conversion rates and selectivity values for different flow

rates of the gas mixture and state in line 124-125 that "Slightly higher selectivity values at high gas mixture flow rates is explained by the lower catalyst contact times". However, any information on the design of the tubular reactor for the hydrogenation reaction is missing (i.e. inner diameter and length of the reactor, length of fixed bed containing solid catalyst) that would allow the reader to estimate contact times of the gas stream with the catalyst bed from the provided flow rates.

Questions on NMR experiments and relaxation issues

- Line 111: Were the NMR experiments conducted as continuous flow experiments (i.e. on the flowing gas) (if so, please provide the mean velocity of the flowing sample) or in a stopped flow fashion? Was the used probehead a standard probehead for 5mm NMR tubes? How does the sample container in the NMR probehead looked like? Was it just a tube passed through the NMR coil (if so, please provide the inner diameter of the tube) or a flow cell with a more sophisticated geometry (if so, please provide a description of the geometry)? These points are important for a better understanding of the NMR experiments, as all points have an impact on the SNR of the spectra (i.e. filling factor, outflow effects and line broadening in continuous flow NMR).
- The distance between the tubular reactor and the RF coil of the NMR spectrometer should also be mentioned in the experimental section or even better the transport time (for the two different flow rates) of the hyperpolarized gas from the reactor to the detection site. These times together with the T1 relaxation time of propene (which should also be provided) would help the reader to estimate how severe hyperpolarization loss due to T1 relaxation was. This could also explain the very different SE values for the experiments conducted with 1.3 and 3.8 ml/s flow rates. The authors started a discussion on hyperpolarization losses due to T1 relaxation in chapter 3.3 (line 194-211), but do not provide enough information to understand if the hyperpolarization losses due to T1 relaxation were dramatic (e.g. on the order of 60% of the initial signal enhancement) or minor (e.g. on the order of 10% of the initial signal enhancement) .

Technical comments: Line 199: please correct the wrong spelling of "experimental"

Line 265: add "in" before "order"