

Replies to the comments of Anonymous Referee # 1.

1. Does the paper address relevant scientific questions within the scope of MR?

The authors worked on HET-PHIP which is related to the field of NMR and hyperpolarization and fits the scope of MR.

2. Does the paper present novel concepts, ideas, tools, or data? All submitted papers are assumed to report on new observations and/or new theory; there is no need to draw attention to the novelty in title, abstract, or conclusions.

On the one hand they tested a novel type of bimetallic heterogenous catalyst based on Pd-Ag or Pd-In. On the other hand, the work is embedded in a series of Pd type catalysts these authors used for the same reaction several times. The novelty compared to their former works should be highlighted more in detail.

Authors' response:

We have changed the first sentence of the last paragraph in the introduction to better highlight the novelty of this work. This part now reads:

“However, so far the vast majority of reported HET-PHIP experiments involving supported metal catalysts were performed with monometallic systems, whereas the potential advantages of bimetallic nanoparticles in this context were addressed in only a very few studies. In this work, for the first time we directly compare monometallic and bimetallic Pd-based catalysts in the selective hydrogenation of propyne to propylene with parahydrogen.”

3. Are substantial conclusions reached?

The authors achieved further progress in the field of PHIP employing heterogenous catalyst systems. It is shown that a second metal such as Ag or In acts on the selectivity of the Pd catalyst and let achieve it more selectivity towards pairwise hydrogen transfer which is required to produce PHIP.

4. Are the results sufficient to support the interpretations and conclusions?

In part they are sufficient but a deeper characterization of the system would be helpful. Did the authors obtain molecular bimetallic complexes or did they obtain metallic Pd nanoparticles that are doped with In or Ag to reach the selectivity?

Authors' response:

For the preparation of Pd/Al₂O₃, Ag/Al₂O₃ and Pd-Ag/Al₂O₃, aqueous solutions of Pd(NO₃)₂, AgNO₃ or both were used, respectively. Pd-In/Al₂O₃ was prepared using an aqueous solution of binuclear acetate complex Pd(OOCMe)₄In(OOCMe).

We have added the detailed description of the preparation procedures of catalysts to the revised manuscript.

For convenience, it is repeated here:

1) Pd-Ag/Al₂O₃ catalyst was obtained via incipient wetness impregnation of parent Al₂O₃ (Sasol, specific surface area 56 m²•g⁻¹) preliminarily calcined at 550 °C in flowing air for 3 h with an aqueous solution of Pd(NO₃)₂ and AgNO₃. To prepare this solution, 0.153 g of silver (I) nitrate (Merck, 204390-10G) was dissolved in 0.7059 g of 10 wt.% palladium (II) nitrate solution (Aldrich, 380040-50ML). After that, 0.25 mL of distilled water was added. The resulting solution was used for impregnation of 1.5 g of Al₂O₃. The product was dried overnight at room temperature in air and then reduced in 5 vol.% H₂/Ar flow (~100 mL/min) at 550 °C for 3 h. The temperature was increased from room temperature to 550 °C with a 3.5 °C/min ramp.

2) For preparation of Pd-In/Al₂O₃ catalyst, an aqueous solution of binuclear acetate complex Pd(OOCMe)₄In(OOCMe) was used as a precursor. This complex was synthesized as follows: the reaction between Pd₃(OOCMe)₆ and In(OOCMe)₃ in glacial acetic acid results in the crystalline complex Pd(OOCMe)₄In(OOCMe)•HOOCMe as the crystal solvate with a 49% yield based on Pd. Its subsequent recrystallization from benzene produced the solvent-free complex Pd(OOCMe)₄In(OOCMe) with the yield of 36% based on Pd. More details on its preparation and characterization can be found elsewhere [R1].

3) To obtain the impregnating solution, 0.164 g of Pd(OOCMe)₄In(OOCMe) was dissolved in 4.75 mL of distilled water. After that, 1.45 g of Al₂O₃ (Sasol, specific surface area 56 m²/g) preliminarily calcined in flowing air (550 °C, 3 h) was impregnated by 0.95 mL of the solution followed by overnight drying at room temperature. The impregnation/drying procedure was repeated 5 times to overcome insufficient solubility of the complex and achieve the required metal content with the "dry" impregnation method used. The resulting material was reduced at 600 °C for 3 h in flowing 5 vol.% H₂/Ar (~100 mL/min). The temperature was increased from room temperature to 600 °C with a 3.5 °C/min ramp.

The structure of Pd-Ag/Al₂O₃ was recently characterized in detail by TEM, CO-DRIFTS, H₂-TPR, and H₂-TPD [R2]. The structure of Pd-In/Al₂O₃ catalyst was studied in detail by TEM, CO-DRIFTS, and XPS [R3-R5].

This information on catalysts characterization was added to the revised manuscript.

For convenience, the main findings of the catalysts characterization are repeated here.

The morphology of Pd-Ag nanoparticles was studied by TEM showing spherical PdAg nanoparticles with a relatively narrow unimodal distribution with a maximum at 6–8 nm. The formation of single-atom Pd₁ sites on the surface of supported Pd–Ag bimetallic nanoparticles was proved by infrared spectroscopy of adsorbed CO by disappearance of the signal corresponding to bridged and hollow-bonded CO adsorption and an increase in the intensity of the linearly adsorbed CO band. Additionally it was demonstrated that the structure of Pd₁ single-atom sites is highly stable even under conditions of CO-induced segregation. The H₂-TPR data on PdAg particles clearly show that the reduction of both the Pd and Ag components of bimetallic catalysts occurs at temperatures below 150°C. It should be also noted that the characteristic feature corresponding to PdH decomposition is absent indicating the suppression of the PdH formation in the PdAg alloyed nanoparticles. This data agrees well with that of H₂-TPD analysis.

TEM data demonstrate that Pd-In/Al₂O₃ catalyst contains nearly spherical cuboctahedral nanoparticles [R4]. The particle size distribution is relatively narrow between 2.5 and 6 nm centered at 4.5 nm. Formation of Pd₁ single-atoms isolated by In ones on the surface of the PdIn intermetallic compound was confirmed via CO-DRIFTS by the absence of absorption bands below 2000 cm⁻¹ [R4,R5]. Such structure ensures the formation of isolated active Pd₁ sites on the catalyst surface and explains the absence of multi-point adsorption of CO, which requires the presence of several neighboring palladium atoms. Furthermore, the formation of PdIn intermetallic nanoparticles with Pd₁ isolated sites was shown by XPS [R1,R4]. The characteristic shift of the Pd 3d_{5/2} and In 3d_{5/2} lines was observed from 334.9 to 335.9 eV and from 445.2 to 443.4 eV, respectively. This fact indicates the redistribution of the electron density and formation of PdIn intermetallics. This data agrees well with XRD data [R5]. Thus analysis of XRD patterns reveals the formation of Pd₁In₁ intermetallic phase of cubic structure of the CsCl type, space group Pm-3m, a = 3.23(4) Å (3.246 Å for PdIn 59473-ICSD).

References

- [R1] I.P. Stolarov, I.A. Yakushev, A.V. Churakov, N.V. Cherkashina, N.S. Smirnova, E.V. Khramov, Y.V. Zubavichus, V.N. Khrustalev, A.A. Markov, A.P. Klyagina, A.B. Kornev, V.M. Martynenko, A.E. Gekhman, M.N. Vargaftik, I.I. Moiseev, Heterometallic Palladium(II)–Indium(III) and –Gallium(III) Acetate-Bridged Complexes: Synthesis, Structure, and Catalytic Performance in Homogeneous Alkyne and Alkene Hydrogenation, *Inorg. Chem.* 2018, 57, 11482–11491, DOI: 10.1021/acs.inorgchem.8b01313
- [R2] A. V. Rassolov, G. O. Bragina, G. N. Baeva, N. S. Smirnova, A. V. Kazakov, I. S. Mashkovsky, A. V. Bukhtiyarov, Ya. V. Zubavichus, A. Yu. Stakheev, Formation of Isolated Single-Atom Pd₁ Sites on the Surface of Pd–Ag/Al₂O₃ Bimetallic Catalysts, *Kinet. Catal.* 2020, 61 (5), DOI: 10.1134/S0023158420050080
- [R3] I.S. Mashkovsky, N.S. Smirnova, P.V. Markov, G.N. Baeva, G.O. Bragina, A.V. Bukhtiyarov, I.P. Prosvirin, A.Yu. Stakheev, Tuning the surface structure and catalytic performance of PdIn/Al₂O₃ in selective liquid-phase hydrogenation by mild oxidative-reductive treatments, *Mendeleev Commun.*, 2018, 28, 603-605; doi:10.1016/j.mencom.2018.11.013
- [R4] P.V. Markov, A.V. Bukhtiyarov, I.S. Mashkovsky, N.S. Smirnova, I.P. Prosvirin, Z.S. Vinokurov, M.A. Panafidin, G.N. Baeva, Ya.V. Zubaichus, V.I. Bukhtiyarov, A.Yu. Stakheev, PdIn/Al₂O₃ Intermetallic Catalyst: Structure and Catalytic Characteristics in Selective Hydrogenation of Acetylene, *Kinet. Catal.*, 2019, 60 (6), 842–850; doi: 10.1134/S0023158419060065
- [R5] D.B. Burueva, K.V. Kovtunov, A.V. Bukhtiyarov, D.A. Barskiy, I.P. Prosvirin, I.S. Mashkovsky, G.N. Baeva, V.I. Bukhtiyarov, A.Yu. Stakheev, I.V. Koptyug, Selective single-site Pd-In hydrogenation catalyst for production of enhanced magnetic resonance signals using parahydrogen, *Chem. Eur. J.* 2018, 24, 2547-2553, DOI: 10.1002/chem.201705644

When talking about selectivity, what are the byproducts of this reaction?

Authors' response:

The term “selectivity” is used in two different contexts in this work: i) chemical selectivity toward propene in the hydrogenation of propyne; ii) selectivity toward pairwise H₂ addition to a substrate. We believe that this dual use of the term does not create any confusion, as its meaning is explained each time the term is used.

Generally, the only hydrogenation products of propyne are propene and propane. However, at relatively high temperatures (≥ 400 °C) the side reaction can occur – propyne can isomerize to propadiene. The decrease in selectivity to propene at 500 °C for Pd-In catalyst is associated with this side reaction. Therefore, the selectivity toward propene is evaluated as $S_{\text{propene}} =$

$\frac{I_{\text{propene}}}{I_{\text{propene}} + I_{\text{propane}} + I_{\text{propadiene}}}$, where I_{product} is the NMR signal intensity of the corresponding product (propene, propane, or propadiene) normalized by the number of protons contributing to that NMR signal.

Selectivity toward pairwise addition of H₂ is the estimated measure of the contribution of the pairwise H₂ addition to the overall mechanism of hydrogenation which is predominantly non-pairwise. It is evaluated as the ratio of the observed NMR signal enhancement to the largest theoretically possible enhancement under conditions which ensure that H₂ addition is exclusively pairwise.

This information was added in the revised manuscript.

Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists with reasonable effort? Detailed technical and graphical explanations and documentation of limited file size can be provided as supporting information. Access to raw data, processed spectra, and other experimental data must be provided by depositing in a publicly accessible repository or archive as far as practically feasible, and the

DOI provided in the article. Hardware developments need to be documented by photos or equivalent drawings (blueprints with precise dimensions if possible). New software must be accompanied by user instructions. New software should be open source and access to it provided through a software repository if possible.

In part the experiments could be reproduced but I miss more details for the catalyst preparation. Especially amounts of precursors etc. used in the synthesis are missing.

Authors' response:

The details about preparation and characterization of the catalysts were added to the revised manuscript and are also provided above.

Furthermore, details on the catalytic tests are not provided. How did they perform the PHIP experiments? Such details should be provided either in the experimental section or in the ESI.

Authors' response:

Following reviewer's suggestion, we have added in Section 2.2 of the revised manuscript the detailed description of how PHIP experiments were performed.

5. Are numerical data accompanied by error estimates with a description of the methods used to obtain these estimates?

Can the authors provide errors of their calculated enhancement factors?

Authors' response:

The uncertainty in the quantitative analysis of gas-phase NMR spectra was estimated as 10 %. This information was added in the revised manuscript.

6. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

In part. The authors should consider additional citations on HET-PHIP in the introduction

[1] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, J. Phys. Chem. C 2017, 121, 9953-9962.

[2] T. Gutmann, T. Ratajczyk, Y. Xu, H. Breitzke, A. Gruenberg, S. Dillenberger, U. Bommerich, T. Trantzsche, J. Bernarding, G. Buntkowsky, Solid State Nuclear Magnetic Resonance 2010, 38, 90-96.

[3] A. M. Balu, S. B. Duckett, R. Luque, Dalton Transactions 2009, 5074-5076.

Although these works do not name the technique HET-PHIP they show PHIP with heterogeneous catalysts.

Authors' response:

It was an oversight on our part not to cite the work done by others in the introduction.

We have added several relevant references.

In the introduction the authors talked about DNP, but do not specify. When they talk about DNP in general also citations of recent reviews should be included.

[1] A. G. M. Rankin, J. Trebosc, F. Pourpoint, J. P. Amoureux, O. Lafon, Solid State Nuclear Magnetic Resonance 2019, 101, 116-143.

[2] A. S. L. Thankamony, J. J. Wittmann, M. Kaushik, B. Corzilius, Progress in Nuclear Magnetic Resonance Spectroscopy 2017, 102, 120-195.

[3] U. Akbey, W. T. Franks, A. Linden, M. Orwick-Rydmark, S. Lange, H. Oschkinat, in *Hyperpolarization Methods in NMR Spectroscopy*, Vol. 338 (Ed.: L. T. Kuhn), 2013, pp. 181-228.

Authors' response:

We believe the five references that we already have for the DNP technique, covering both MAS DNP and dissolution DNP, to be representative and sufficient, especially given that DNP is not considered and/or used in our work. Besides, at least two of the (solid-state) DNP references suggested by the reviewer are cited in the DNP references provided in our paper.

Line 66-67 “So far, however, most heterogeneous catalysts demonstrated a limited efficiency in the pairwise hydrogen addition, or in some cases the low yields of the desired product, or both (Kovtunov et al., 2013, 2016, 2020a)”

Here also the works of Duckett and of Buntkowsky and co-workers should be considered.

Authors' response:

We have added the relevant references.

7. Does the title clearly reflect the contents of the paper?

Yes

8. Does the abstract provide a concise and complete summary?

Yes

9. Is the overall presentation well-structured and clear?

Yes

10. Is the language fluent and precise?

Yes, but few typos have to be corrected:

Line 199: should be “experimental”

Line 204: should be “hyperpolarized”

Authors' response:

The typos have been corrected and the text spell-checked and proofread once again,

11. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?

In principle table 2 and table 3 can be combined in one table.

Authors' response:

This is certainly possible, but we do not see any real advantage in doing so.

12. Are the number and quality of references appropriate?

In part. See comment 6

Authors' response:

This has been taken care of (see above).

13. Is the amount and quality of the supporting information and supplementary material appropriate?

There is no ESI available