# **CHEMISTRY** A European Journal



## **Accepted Article** Title: Selective single-site Pd-In hydrogenation catalyst for production of enhanced magnetic resonance signals using parahydrogen Authors: Dudari Burueva, Kirill Viktorovich Kovtunov, Valerii Bukhtiyarov, Andrey Bukhtiyarov, Danila Barskiy, Igor Prosvirin, Igor Mashkovsky, Galina Baeva, Aleksandr Stakheev, and Igor Koptyug This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201705644 Link to VoR: http://dx.doi.org/10.1002/chem.201705644

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## Selective single-site Pd-In hydrogenation catalyst for production of enhanced magnetic resonance signals using parahydrogen

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Abstract: Pd-In/Al<sub>2</sub>O<sub>3</sub> single-site catalyst was able to show high selectivity (up to 98%) in the gas phase semihydrogenation of propyne. Formation of intermetallic Pd-In compound was studied by XPS during reduction of the catalyst. FTIR-CO spectroscopy confirmed single-site nature of the intermetallic Pd-In phase reduced at high temperature. Utilization of Pd-In/Al<sub>2</sub>O<sub>3</sub> in semihydrogenation of propyne with parahydrogen allowed to produce ~3400-fold NMR signal enhancement for reaction product propene (polarization = 9.3%), demonstrating the large contribution of pairwise hydrogen addition route. Significant signal enhancement as well as the high catalytic activity of the Pd-In catalyst allowed to acquire <sup>1</sup>H MR images of flowing hyperpolarized propene gas selectively for protons in CH-, CH<sub>2</sub>and CH<sub>3</sub>- groups. This observation is unique and can be easily transferred to the development of a useful MRI technique for an in situ investigation of selective semihydrogenation in catalytic reactors.

Nuclear magnetic resonance (NMR) phenomenon underlies numerous modern spectroscopic analytical methods and is now routinely used in chemistry, biology, materials science and medicine.<sup>[1-4]</sup> NMR is a highly informative method to study structures, properties and even spatial distribution of various compounds.<sup>[5]</sup> In addition, magnetic resonance imaging (MRI) is a routine instrument for modern medical diagnostics.[6,7] However, the energies of interaction between spins and magnetic field are rather small, which results in the major disadvantage of NMR/MRI methods, namely the low nuclear spin polarization even in relatively high magnetic fields. For example, at 298 K, for <sup>1</sup>H nuclei exposed to a 7.1 T field the polarization in thermal equilibrium is only 2.4×10<sup>-5</sup> (0.0024%). The value of polarization directly determines the signal-to-noise ratio (SNR) in NMR and, among other consequences, limits spatial resolution achievable in MRI.<sup>[8]</sup> In order to overcome this low inherent sensitivity, several methods have been developed to hyperpolarize nuclear spins, i.e., to create a non-Boltzmann

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population of nuclear spin energy levels.<sup>[9]</sup> Nowadays the most popular and common hyperpolarization methods are spinexchange optical pumping of noble gases (SEOP)<sup>[10]</sup>, dynamic nuclear polarization (DNP)<sup>[11]</sup>, chemically induced dynamic nuclear polarization (CIDNP)<sup>[12]</sup>, parahydrogen-induced polarization (PHIP)<sup>[13]</sup> and signal amplification by reversible exchange (SABRE)<sup>[14]</sup> - a form of non-hydrogenative PHIP.<sup>[15]</sup>

The latter approach (PHIP) is based on the conversion of the high spin order of parahydrogen (p-H<sub>2</sub>), a nuclear spin isomer of hydrogen with the total nuclear spin I = 0, into the polarization of target molecules through a catalytic hydrogenation reaction.[16,17] When two hydrogen atoms of p-H<sub>2</sub> molecule are added to an unsaturated substrate as a pair (pairwise hydrogen addition) in magnetically nonequivalent positions, only those nuclear spin levels in the target product molecule get populated that correspond to the symmetry of parahydrogen. In this case, the spin population distribution in the product molecule dramatically deviates from the Boltzmann distribution, leading to significantly enhanced (up to 10<sup>4</sup>-10<sup>5</sup>) absorptive and emissive NMR signals at high magnetic field.<sup>[16]</sup> Depending on the magnetic field in which the catalytic reaction takes place, two types of PHIP experiments are distinguished – PASADENA (parahydrogen and synthesis allow dramatically enhanced nuclear alignment)<sup>[13]</sup> and ALTADENA (adiabatic longitudinal transport after dissociation engenders net alignment)<sup>[18]</sup>. In a PASADENA experiment, the hydrogenation product is formed directly in the high magnetic field of an NMR spectrometer and polarized signals with antiphase patterns are observed. In the case of an ALTADENA experiment, the hydrogenation product is formed in a low (e.g., Earth's, 0.05 mT) magnetic field with a subsequent transfer of the product to the high magnetic field of an NMR spectrometer (several T) for detection. As a result, NMR signals are observed either in net absorption or in emission.

Since the PHIP technique is based on the catalytic activation and addition of parahydrogen molecule, major emphasis is placed on the screening of catalysts suitable for pairwise hydrogen addition.<sup>[19,20]</sup> The PHIP effect was first observed for homogeneous<sup>[21]</sup> and later for heterogeneous<sup>[22,23]</sup> hydrogenation catalytic systems. However, heterogeneous PHIP (HET-PHIP) catalysts appear most appropriate for the production of hyperpolarized molecules not contaminated with the catalyst, especially in the context of MRI applications.<sup>[24]</sup> The scope of heterogeneous catalysts which are suitable for HET-PHIP increased significantly in the past 10 years. For instance, PHIP was successfully observed over various metal catalysts such as Rh<sup>[25,26]</sup>, Pt<sup>[22,27,28]</sup>, Pd<sup>[29,30]</sup>, Ir<sup>[31,32]</sup>, Au<sup>[33]</sup>, Cu<sup>[34]</sup>, bimetallic systems Pt-Sn<sup>[35]</sup>, Pd-Au<sup>[15]</sup>, Pd-M (M=Sn, Zn, Ag, Mn, Pb, Au)<sup>[36]</sup> supported on support materials such as SiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Al-Si fiberglass<sup>[30]</sup>, chitosan<sup>[26]</sup>, carbon nanotubes<sup>[33]</sup>. Moreover, the PHIP effect was demonstrated for bulk Pt metal<sup>[37]</sup> and several metal oxides (PtO<sub>2</sub>, PdO<sup>[37]</sup> and CeO<sub>2</sub><sup>[38]</sup>).

Utilization of heterogeneous catalytic systems for observation of PHIP effects requires catalysts with a substantial contribution of the pairwise route of hydrogen addition during

catalytic hydrogenation. Although the contribution of the pairwise hydrogen addition in the case of HET-PHIP catalysts does not usually exceed 1-3%<sup>[20]</sup>, the HET-PHIP technique can be successfully applied for the hyperpolarization of prospective contract agents for MRI. For instance, MR visualization of model systems with various geometries was demonstrated with the use of hyperpolarized propane gas produced by heterogeneous hydrogenation of propene with p-H<sub>2</sub> over supported Rh catalysts.<sup>[25,39,40]</sup> As high level of pairwise hydrogen addition corresponds to the high level of NMR signal, synthesis and utilization of new heterogeneous hydrogenation catalysts with significant percentages of the pairwise hydrogen addition level is a highly important task. One of the promising ways is to use catalysts with well-defined single-site structure of active centers.<sup>[33]</sup> These single-site centers behave similarly to the metal centers of homogeneous catalysts<sup>[41-43]</sup> in catalytic reactions and, thus, can be expected to accomplish pairwise addition of H<sub>2</sub> to a substrate. So far the largest contribution of pairwise hydrogen addition (10.9%) was observed with the use of silica-encapsulated Pt-Sn intermetallic nanoparticles<sup>[35]</sup> in propene hydrogenation, but the overall conversion estimated as 0.5% is too low for MRI applications. Here, a Pd-based catalyst with the single-site character of the distribution of active sites was utilized for the production of propene with significant levels of both hyperpolarization and conversion (9.3% (1.7% observable, without corrections) and 20%, respectively) during selective heterogeneous hydrogenation of propyne and for subsequent MR visualization of this hyperpolarized propene.

For the synthesis of palladium catalysts with isolated Pd atoms, one of the promising approaches is the modification of monometallic Pd-based catalysts with another metal (Ag, Cu, Ga) which leads to an intermetallic structure formation.[44-46] It was shown that isolation of Pd atoms on the surface of an intermetallic compound enables significantly improved product selectivity and catalyst stability.<sup>[47,48]</sup> The presence of a second metal in Pd-based catalysts is able to reduce the size of Pd nanoparticles and thus to prevent palladium hydride (PdH<sub>x</sub>) formation.<sup>[49]</sup> The latter is the key to high product selectivity because palladium hydride is the known active species for side reactions such as isomerization or over-hydrogenation.<sup>[50,51]</sup> Pd-In catalyst has been shown to be an effective catalyst for semihydrogenation of a triple to a double carbon-carbon bond in hydrogenation of acetylene,<sup>[52,53]</sup> phenylacetylene, diphenylacetylene and 1-phenyl-1-propyne<sup>[54]</sup>. Moreover, it was established that Pd was present as single atoms.<sup>[52,55]</sup>

Pd-In/Al<sub>2</sub>O<sub>3</sub> single-site catalyst was prepared by incipientwetness impregnation of  $Al_2O_3$  with bimetallic acetate complex PdIn(CH<sub>3</sub>COO)<sub>5</sub> with subsequent reduction (for details, see Supporting Information). Recently it was shown that the use of a bimetallic complex as a precursor of the active component combined with high-temperature reduction enables the formation of bimetallic particles in the catalyst.<sup>[55-57]</sup> The size of Pd-In nanoparticles was determined by TEM after pre-reduction in H<sub>2</sub> atmosphere at 550 °C. TEM images of a reference Pd/Al<sub>2</sub>O<sub>3</sub> sample and Pd-In/Al<sub>2</sub>O<sub>3</sub> sample are shown in Figure S1. TEM experiments show that spherical Pd-In particles with an average size of ~3.5 nm are formed. The dispersion of Pd in the catalysts was determined from the CO uptake in CO chemisorption analysis (assuming a stoichiometry of CO:Pd = 1:1). In particular, for the monometallic Pd/Al<sub>2</sub>O<sub>3</sub> catalyst the dispersion was about ~36%, but for Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst the dispersion value was approximately ~5.6%. This fact indicates direct influence of In

atoms, which do not chemisorb CO, on the nanoparticle surface.<sup>[55,58]</sup> Moreover, FTIR spectrum of CO adsorbed on the reference monometallic Pd/Al<sub>2</sub>O<sub>3</sub> sample exhibits two absorption bands, while the spectrum of CO adsorbed on bimetallic Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits only one intensive band at 2073 cm<sup>-1</sup> attributed to linearly adsorbed CO on metallic Pd (Figure S2). The absence of any other signals within the multi-bonded CO range (2000-1800 cm<sup>-1</sup>) provides the evidence that single Pd atoms are present on the surface of Pd-In nanoparticles and these Pd atoms are able to bind CO in linear form only, without participation of neighboring Pd atoms (the  $\mu$ -bridge form of absorbed CO). The absence of bridged CO species can be the result of the increase in Pd-Pd interatomic distances due to Pd site isolation by In atoms, similar to the Pd-Ga system reported earlier.<sup>[59]</sup>

 $Pd-In/Al_2O_3$  catalyst was tested earlier in the liquid-phase hydrogenation of terminal and internal alkynes (phenylacetylene, diphenylacetylene, and 1-phenyl-1-propyne) and demonstrated high selectivity to the formation of alkenes (up to 98%).<sup>[54]</sup>

In the current study, the catalytic activity of single-site Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst was tested in the gas-phase hydrogenation of propyne gas. To this end, propyne was premixed with parahydrogen in the molar ratio of 1:4. The reaction was conducted in a continuous flow regime at various temperatures  $(m_{cat} = 30 \text{ mg}, \text{ T} = 100\text{-}500 \text{ }^\circ\text{C}, \text{ u} = 0.4\text{-}8.8 \text{ mL/s})$ , with the reactor outflow continuously supplied to the probe of an NMR spectrometer and analyzed by <sup>1</sup>H NMR. The obtained propyne conversion and selectivity to propene are presented in Table 1 and Table S1. At 100 °C, the Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst was inactive and no products could be detected in the thermal <sup>1</sup>H NMR spectra. At 200-300 °C the catalyst activity increased and a 35% conversion was achieved at the gas flow rate of ~0.4 mL/s. The highest conversion levels were observed at 400 °C. Notably, the Pd-In catalyst maintains the high selectivity to propene, up to 98%, over a wide range of temperatures (200-400 °C) even at high propyne conversion (62% yield of propene was observed at 0.4 mL/s gas flow and 400 °C). It is important to note that at 500 °C the conversion to propene dropped down dramatically to ~39% which can be explained by catalyst deactivation and/or propadiene formation (selectivity to allene formation was about ~60%).

**Table 1.** Hydrogenation of propyne with parahydrogen over  $Pd-In/Al_2O_3$  catalyst: propyne conversion, selectivity to propene, <sup>1</sup>H NMR signal enhancements (*SE*) and estimates of percentages of pairwise hydrogen addition calculated for CH and CH<sub>2</sub> protons of propene at 5.1 mL/s

Temperature, °C	100	200	300	400	500
Conversion, %	-	1	7	21	18
Selectivity to propene, %	-	72	95	93	43
SE for CH group of propene	27*	592	214	202	219
SE for CH <sub>2</sub> group of propene	-	429	155	145	159
Percentage of pairwise H <sub>2</sub> addition (CH)	-	1.64	0.59	0.56	0.61
Percentage of pairwise H <sub>2</sub> addition (CH <sub>2</sub> )	-	1.19	0.43	0.40	0.44

\* signal-to-noise ratio was used for SE estimation

High selectivity with respect to the target alkene can be explained by the fact that formation of the Pd-In intermetallic compound considerably decreases the formation of palladium hydrides (PdH<sub>x</sub>), which contain hydrogen source responsible for

complete hydrogenation.<sup>[60]</sup> In our case, the observed high selectivity to propene during gas phase propyne hydrogenation is consistent with the fact that no signals assignable to the decomposition of palladium hydride PdH<sub>x</sub> were observed via TPD analysis of Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>[55]</sup> Furthermore, the catalyst has proven to be able to achieve significant levels of pairwise hydrogen addition.

Although at 100 °C no products were observed in thermally polarized NMR spectra (the spectra acquired after an abrupt interruption of the gas flow and subsequent spin relaxation to thermal equilibrium), the small hyperpolarized signals of CH and CH<sub>2</sub> groups of propene were observed in the <sup>1</sup>H NMR spectra acquired while the gas was flowing (Figure S3). During hydrogenation at 200-500 °C, both PHIP and thermally polarized <sup>1</sup>H NMR signals were detected. The signal enhancement factors and the percentages of pairwise hydrogen addition were estimated by comparing the PHIP <sup>1</sup>H NMR signals with the thermal ones (see SI for details), and the results are shown in Table 1. Importantly, at 400 °C the Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst demonstrated highly intensive PHIP effects along with a relatively high conversion level. Thus, the highest amount of hyperpolarized propene was produced during propyne hydrogenation at 400 °C and the mixture flow rate of ~5.1 mL/s (Figure 1).



Figure 1. (a) Reaction scheme of propyne hydrogenation; (b) <sup>1</sup>H NMR ALTADENA spectra acquired during propyne hydrogenation with parahydrogen at 400 °C over Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst while the gas was flowing with the flow rate of 5.1 mL/s (green line) and after an abrupt interruption of the gas flow and relaxation to thermal equilibrium (purple line). All spectra were acquired with 8 signal accumulations and are presented on the same vertical scale.

The signal enhancements estimated for Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst presented in Table 1 are lower than the actual values because polarization losses caused by nuclear spin relaxation dramatically reduce the intensities of enhanced <sup>1</sup>H NMR signals for propene. Therefore, the percentages of the pairwise hydrogen addition were reevaluated taking due account of spin relaxation effects. The corrected values of signal enhancement

(SE) were obtained by using the approach previously reported for propene hydrogenation (see SI for details).<sup>[61]</sup> Thus, the percentage of pairwise hydrogen addition at 400 °C was found to be 9.3% (Figure S5b). To the best of our knowledge, this is the highest percentage of pairwise addition reported to date for heterogeneous catalytic systems that can achieve significant conversion levels (~20%).

Both high <sup>1</sup>H NMR signal enhancement and high conversion level obtained using Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst during hydrogenation of propyne with parahydrogen allowed us to use MRI for selective visualization of reaction product, propene. For MRI experiments the concentration of protons is critical, and the amount of catalyst was increased 3-fold in order to increase conversion. 2D MR images of propene were acquired using chemical shift selective RF pulses (Figure 2). Selective excitation of different groups of protons overcomes the problem of NMR signals cancelation due to the presence of separate multiplets with opposite phases (ALTADENA experiment). Also, such technique paves the way to determine the spatial distribution of a particular compound in the complex mixture (i.e., reagents and products). For MRI experiments, conventional FLASH<sup>[62]</sup> pulse sequence was modified and used (see SI for details). The results convincingly demonstrate that dramatically enhanced NMR signals of the flowing hyperpolarized propene, produced via propyne hydrogenation with parahydrogen over Pd-In/Al<sub>2</sub>O<sub>3</sub> single-site catalyst, are strong enough for selective <sup>1</sup>H MR imaging, while after an abrupt interruption of the gas flow and relaxation to thermal equilibrium, the NMR signals are not strong enough for acquiring good quality MR images for protons of the CH and CH<sub>2</sub> groups of propene produced in the reaction (Figure 2)

It should be noted that  $Pd-In/Al_2O_3$  catalyst can produce PASADENA polarization at 130 °C (Figure S6) even without pretreatment (high-temperature reduction in  $H_2$  gas) which was used in the experiments described above.

To study the influence of reduction treatment conditions on catalytic activity and the catalyst active sites structure, the chemical state of the catalyst was investigated by X-ray photoelectron spectroscopy (XPS) during the reduction in hydrogen atmosphere at different temperatures (Figure 3). Pd3d and In3d core-level spectra demonstrated formation of different sites on the catalyst surface during reduction. For the fresh catalyst (before reduction treatment), Pd3d XPS spectrum shows the presence of two different Pd states with binding energies of 334.9±0.1 and 335.9±0.1 eV. The peak at 334.9 eV was assigned to the metallic Pd.<sup>[63,64]</sup> According to the literature data, the peak with a higher binding energy (~335.9 eV) could assigned to the indium-palladium be intermetallic compound. [50,65,66] In3d XPS spectrum of non-reduced catalytic sample shows the presence of two indium states with binding energies of 443.4±0.1 eV and 445.2±0.1 eV. The peak at 445.2 eV is assigned to indium in the 3+ state  $(In_2O_3).^{\scriptscriptstyle [50,65,66]}$  The state with a lower binding energy could be related to the presence of Pd<sub>x</sub>In<sub>y</sub> intermetallic compound on the catalyst surface. Thus, we can conclude that for the non-reduced Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst In and Pd are partially present in the form of intermetallic Pd<sub>x</sub>In<sub>y</sub> compound. The rest of palladium is present in metallic form and the rest of indium in the form of In<sub>2</sub>O<sub>3</sub>, which can potentially cover the bimetallic (intermetallic) particles.

#### 10.1002/chem.201705644

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**Figure 2.** (a) Reaction scheme of propyne hydrogenation; (b) and (c) <sup>1</sup>H NMR spectra acquired during propyne hydrogenation over Pd-ln/Al<sub>2</sub>O<sub>3</sub> catalyst (b) while the gas was flowing and (c) after an abrupt interruption of the gas flow and the subsequent relaxation of nuclear spins to thermal equilibrium. The spectra are presented on the same vertical scale. The reaction temperature was 400 °C, and the gas flow rate was 8.8 mL/s. (d) MR images of a 10-mm NMR tube filled with gaseous thermal and hyperpolarized propene in the transverse orientation. MR images of hyperpolarized propene were acquired while the gas was flowing. For all MR images, the matrix size and spatial resolution were equal to  $64 \times 64$  and  $0.8 \times 0.8$  mm<sup>2</sup> per pixel, respectively.

The spectra presented in Figure 3 clearly verify that the content of Pd-In intermetallic component increases with the temperature of reduction treatment, while the contents of  $Pd^{0}$  and  $In_2O_3$  decrease.



Figure 3. Pd3d and In3d XPS spectra for the Pd-In/Al<sub>2</sub>O<sub>3</sub> sample reduced in 10 mbar of  $H_2$  at various temperatures.

The atomic concentrations of active sites calculated from XPS data are presented in Table S3. The surface Pd/In atomic ratio of the Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst increases with increasing the temperature of reduction from RT to 250 °C, pointing to a redistribution of both palladium and indium atoms on the catalyst surface (Figure S7b). This increase can be explained by the formation of intermetallic Pd-In sites, diffusion of reduced In into the catalytic particles, and/or Pd isolation by In on the surface of the bimetallic particles. Under higher reduction temperatures (>250 °C), the surface Pd/In atomic ratio remains constant. At the same time, the aggregation of In and Pd sites to intermetallic Pd-In compound still occurs. Moreover, In/Al atomic ratio of

catalyst sample decreases with reduction temperature increase while the Pd/Al atomic ratio remains constant (Figure S7). This represents the direct evidence of indium diffusion from the surface to the bulk of intermetallic particles.

The build-up of the intermetallic state of Pd with the increase in reduction temperature was detected up to 300 °C, and further increase of reduction temperature does not lead to changes in the Pd(Intermetallic)/Pd<sup>0</sup> atomic ratio (see Table S3). At the same time, the In(Intermetallic)/In<sup>3+</sup> ratio gradually increases with reduction temperature increase. It means that indium oxide requires higher temperatures for the reduction and intermetallic compound formation (Figure 3b). Thus, for the intermetallic Pd-In compound formation the reduction of Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst is necessary. The data obtained in this work is in a good agreement with the results reported previously.<sup>[55]</sup>

In conclusion, the single-site Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst was found to be a promising catalyst for the semihydrogenation of propyne, which exhibits up to 98% propene selectivity and the high catalytic activity. The redistribution of both palladium and indium atoms on the catalyst surface associated with the formation of Pd-In intermetallic compounds were observed by XPS during catalyst reduction. It was shown that Pd sites isolation by In atoms leads to improved selectivity of the triple carbon-carbon bond hydrogenation. Moreover, Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst was found to show a unique behavior in PHIP experiments. A ~3400-fold signal enhancement was estimated by taking due account of relaxation processes. This high signal enhancement corresponds to the high percentage (9.3%) of pairwise H<sub>2</sub> addition and represents the highest value reported to date for heterogeneous gas phase hydrogenation with significant conversion (about 20%). The high catalytic activity of Pd-In/Al<sub>2</sub>O<sub>3</sub> single-site catalyst allows one to produce significant amounts of hyperpolarized gas with polarization levels that are unprecedented for heterogeneous PHIP, making it possible to utilize MRI for selective imaging. MR images of flowing hyperpolarized propene were obtained with 0.8x0.8 mm<sup>2</sup> spatial resolution, selectively for each of the three groups of hydrogen

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atoms in propene. The MRI of thermally polarized propene at the same conditions is impossible due to an insufficient concentration of protons. Therefore, these demonstrations of the use of Pd-In/Al<sub>2</sub>O<sub>3</sub> catalyst significantly impact the development of PHIP applications in MRI, and the Pd-In/Al<sub>2</sub>O<sub>3</sub> single-site catalyst can be attractive for both medical and technical MRI applications.

#### Acknowledgements

D.B.B., K.V.K thank the Russian Science Foundation (grant # 17-73-20030) for the support of MRI and NMR experiments. I.S.M., G.N.B., A.Yu.S. thank the Russian Science Foundation (grant #16-13-10530) for supporting the catalyst synthesis. D.B.B. is also grateful to Haldor Topsøe A/S Ph.D. program for financial support. D.B.B. and K.V.K. thank Alexey Romanov for his contribution to MRI experiments.

Keywords: bimetallic catalysts •heterogeneous hydrogenation • MRI • parahydrogen • parahydrogen-induced polarization

- J. W. Emsley, J. Feeney, Prog. Nucl. Magn. Reson. Spectrosc. [1] **2007**, *50*, 179–198.
- [2] J. J. Ziarek, D. Baptista, G. Wagner, J. Mol. Med. 2017, DOI 10.1007/s00109-017-1560-2.
- [3] V. I. Bakhmutov, Solid-State NMR in Materials Science: Principles and Applications, CRC Press, 2011.
- R. J. Gillies, NMR in Physiology and Biomedicine, Academic Press, [4] 1994
- R. R. Ernst, Angew. Chemie Int. Ed. English 1992, 31, 805-823. [5] [6] S. Posse, R. Otazo, S. R. Dager, J. Alger, J. Magn. Reson. Imaging
- 2013, 37, 1301-1325. [7] E. Van Reeth, I. Tham, Concepts Magn. Reson. 2012, 40A, 306-
- 325
- J. H. Ardenkjaer-Larsen, G. S. Boebinger, A. Comment, S. Duckett, A. S. Edison, F. Engelke, C. Griesinger, R. G. Griffin, C. Hilty, H. Maeda, et al., *Angew. Chemie Int. Ed.* **2015**, *54*, 9162–9185. P. Nikolaou, B. M. Goodson, E. Y. Chekmenev, *Chem. A Eur. J.* [8]
- [9] 2015, 21, 3156-3166.
- [10] T. G. Walker, W. Happer, Rev. Mod. Phys. **1997**, 69, 629–642
- A. Abragam, M. Goldman, Rep. Prog. Phys. 1978, 41, 395-467. [11]
- H. R. Ward, Acc. Chem. Res. **1972**, 5, 18–24. C. R. Bowers, D. P. Weitekamp, J. Am. Chem. Soc. **1987**, *109*, [12] [13]
- 5541-5542. [14] R. W. Adams, J. a Aguilar, K. D. Atkinson, M. J. Cowley, P. I. P.
- Elliott, S. B. Duckett, G. G. R. Green, I. G. Khazal, J. López-Serrano, D. C. Williamson, Science 2009, 323, 1708-1711.
- W. Wang, H. Hu, J. Xu, Q. Wang, G. Qi, C. Wang, X. Zhao, X. Zhou, [15] F. Deng, J. Phys. Chem. C 2018, doi:10.1021/acs.jpcc.7b11801.
- C. R. Bowers, *Encycl. Magn. Reson.* **2007**, *9*, 750–770. R. a. Green, R. W. Adams, S. B. Duckett, R. E. Mewis, D. C. [16] [17]
- Williamson, G. G. R. Green, Prog. Nucl. Magn. Reson. Spectrosc. 2012, 67, 1-48.
- M. G. Pravica, D. P. Weitekamp, Chem. Phys. Lett. 1988, 145, 255-[18] 258
- S. B. Duckett, D. Blazina, Eur. J. Inorg. Chem. 2003, 2003, 2901-[19] 2912.
- K. V. Kovtunov, V. V. Zhivonitko, I. V. Skovpin, D. A. Barskiy, I. V.
   Koptyug, *Top. Curr. Chem.* 2013, 338, 123–180.
   C. R. Bowers, D. P. Weitekamp, *Phys. Rev. Lett.* 1986, 57, 2645– [20]
- [21] 2648.
- K. V. Kovtunov, I. E. Beck, V. I. Bukhtiyarov, I. V. Koptyug, Angew. Chemie Int. Ed. 2008, 47, 1492–1495.
   A. M. Balu, S. B. Duckett, R. Luque, Dalt. Trans. 2009, 5074–5076. [22]
- [23] [24]
- A. M. Bark, G. B. DuCoffey, P. Nikolaou, D. M. Mikhaylov, B. M. Goodson, R. T. Branca, G. J. Lu, M. G. Shapiro, V. Telkki, V. V. Zhivonitko, et al., *Chem. A Eur. J.* 2017, 23, 725–751.
   K. V Kovtunov, D. A. Barskiy, A. M. Coffey, M. L. Truong, O. G. [25]
- Salnikov, A. K. Khudorozhkov, E. A. Inozemtseva, I. P. Prosvirin, V. Bukhtiyarov, K. W. Waddell, et al., Chem. - A Eur. J. 2014, 20, 11636-11639.
- [26] D. A. Barskiy, K. V. Kovtunov, A. Primo, A. Corma, R. Kaptein, I. V.
- Koptyug, *ChemCatChem* **2012**, *4*, 2031–2035. V. V. Zhivonitko, K. V. Kovtunov, I. E. Beck, A. B. Ayupov, V. I. Bukhtiyarov, I. V. Koptyug, *J. Phys. Chem. C* **2011**, *115*, 13386– [27] 13391
- [28] R. Zhou, W. Cheng, L. M. Neal, E. W. Zhao, K. Ludden, H. E.

Hagelin-Weaver, C. R. Bowers, Phys. Chem. Chem. Phys. 2015, 17, 26121-26129

- K. V. Kovtunov, I. E. Beck, V. V. Zhivonitko, D. a. Barskiy, V. I. [29] Bukhtiyarov, I. V. Koptyug, Phys. Chem. Chem. Phys. 2012, 14, 11008
- O. G. Salnikov, D. a. Barskiy, D. B. Burueva, Y. K. Gulyaeva, B. S. Balzhinimaev, K. V. Kovtunov, I. V. Koptyug, *Appl. Magn. Reson.* [30] 2014. 45. 1051-1061
- [31] O. G. Salnikov, D. B. Burueva, E. Y. Gerasimov, A. V Bukhtiyarov, A. K. Khudorozhkov, I. P. Prosvirin, L. M. Kovtunova, D. A. Barskiy, V.
- [32]
- [33]
- [34]
- K. Khudorozhkov, I. P. Prosvirin, L. M. Kovtunova, D. A. Barskiy, V.
  I. Bukhtiyarov, K. V Kovtunov, et al., *Catal. Today* 2017, *283*, 82–88.
  E. W. Zhao, H. Zheng, K. Ludden, Y. Xin, H. E. Hagelin-Weaver, C.
  R. Bowers, *ACS Catal.* 2016, *6*, 974–978.
  A. Corma, O. G. Salnikov, D. A. Barskiy, K. V. Kovtunov, I. V.
  Koptyug, *Chem. A Eur. J.* 2015, *21*, 7012–7015.
  O. G. Salnikov, H.-J. Liu, A. Fedorov, D. B. Burueva, K. V Kovtunov,
  C. Coperet, I. V Koptyug, *Chem. Sci.* 2017, *8*, 2426–2430.
  E. W. Zhao, R. Maligal-Ganesh, C. Xiao, T.-W. Goh, Z. Qi, Y. Pei, H.
  E. Hagelin-Weaver, W. Huag, C. P. Bowers, *Angew, Chemia Int* [35]
- E. Hagelin-Weaver, W. Huang, C. R. Bowers, Angew. Chemie Int. Ed. 2017, 56, 3925-3929.
- O. G. Salnikov, K. V. Kovtunov, D. a. Barskiy, A. K. Khudorozhkov, [36] E. a. Inozemtseva, I. P. Prosvirin, V. I. Bukhtiyarov, I. V. Koptyug,
- ACS Catal. 2014, 4, 2022–2028. K. V Kovtunov, D. a Barskiy, O. G. Salnikov, A. K. Khudorozhkov, V. I. Bukhtiyarov, I. P. Prosvirin, I. V Koptyug, *Chem. Commun.* [37] (Camb). 2014, 50, 875-8.
- [38]
- E. W. Zhao, Y. Xin, H. E. Hagelin-Weaver, C. R. Bowers, *ChemCatChem* 2016, *8*, 2197–2201.
  K. V. Kovtunov, M. L. Truong, D. a. Barskiy, I. V. Koptyug, A. M. Coffey, K. W. Waddell, E. Y. Chekmenev, *Chem. A Eur. J.* 2014, 20 44620, 14620. [39] 20, 14629-14632.
- [40] K. V. Kovtunov, A. S. Romanov, O. G. Salnikov, D. A. Barskiy, E. Y. Chekmenev, I. V. Koptyug, Y. Eduard, Tomogr. A J. Imaging Res. 2016, 2, 49-55.
- S. Zhang, L. Nguyen, J.-X. Liang, J. Shan, J. Liu, A. I. Frenkel, A. Patlolla, W. Huang, J. Li, F. Tao, *Nat. Commun.* **2015**, *6*, 7938. [41]
- [42] B. Han, R. Lang, B. Qiao, A. Wang, T. Zhang, Chinese J. Catal. 2017, 38, 1498-1507.
- Zo T, S, Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, Acc. Chem. Res. 2013, 46, 1740–1748. [43]
- B. Chen, U. Dingerdissen, J. G. E. Krauter, H. G. J. Lansink [44] Rotgerink, K. Möbus, D. J. Ostgard, P. Panster, T. H. Riermeier, S. Seebald, T. Tacke, et al., Appl. Catal. A Gen. 2005, 280, 17-46.
- G. Kyriakou, M. B. Boucher, A. D. Jewell, E. A. Lewis, T. J. Lawton, A. E. Baber, H. L. Tierney, M. Flytzani-Stephanopoulos, E. C. H. [45] Sykes, Science **2012**, 335, 120–1212. M. Armbrüster, R. Schlögl, Y. Grin, *Sci. Technol. Adv. Mater.* **2014**,
- [46] 15, 34803.
- L. Zhang, A. Wang, J. T. Miller, X. Liu, X. Yang, W. Wang, L. Li, Y. Huang, C. Y. Mou, T. Zhang, *ACS Catal.* **2014**, *4*, 1546–1553. X. Cao, A. Mirjalili, J. Wheeler, W. Xie, B. W. L. Jang, *Front. Chem. Sci. Eng.* **2015**, *9*, 442–449. [47] [48]
- [49]
  - J. Osswald, R. Giedigkeit, R. E. Jentoft, M. Armbruster, F. Girgsdies, K. Kovnir, T. Ressler, Y. Grin, R. Schlogl, *J. Catal.* **2008**, *258*, 210– 218
- F. A. Marchesini, S. Irusta, C. Querini, E. Miró, Appl. Catal. A Gen. [50] 2008, 348, 60-70.
- M. García-Mota, B. Bridier, J. Pérez-Ramírez, N. López, J. Catal. [51] 2010. 273. 92-102.
- Q. Feng, S. Zhao, Y. Wang, J. Dong, W. Chen, D. He, D. Wang, J. Yang, Y. Zhu, H. Zhu, et al., *J. Am. Chem. Soc.* **2017**, *139*, 7294– [52] 7301.
- Y. Cao, Z. J. Sui, Y. Zhu, X. Zhou, D. Chen, ACS Catal. 2017, 7, [53] 7835-7846.
- P. V. Markov, G. O. Bragina, G. N. Baeva, O. P. Tkachenko, I. S. [54] Mashkovskii, I. A. Yakushev, M. N. Vargaftik, A. Y. Stakheev, Kinet. Catal. 2016, 57, 625-631.
- P. V. Markov, G. O. Bragina, G. N. Baeva, O. P. Tkachenko, I. S. [55] Mashkovskii, I. A. Yakushev, M. N. Vargaftik, A. Y. Stakheev, Kinet. Catal. 2016, 57, 617-624.
- [56] P. V. Markov, G. O. Bragina, A. V. Rassolov, G. N. Baeva, I. S. Mashkovsky, V. Y. Murzin, Y. V. Zubavichus, A. Y. Stakheev, Mendeleev Commun. 2016, 26, 502-504
- P. V. Markov, G. O. Bragina, A. V. Rassolov, I. S. Mashkovsky, G. N. Baeva, O. P. Tkachenko, I. A. Yakushev, M. N. Vargaftik, A. Y. [57]
- Stakheev, *Mendeleev Commun.* **2016**, *26*, 494–496. Z. Wu, E. C. Wegener, H.-T. Tseng, J. R. Gallagher, J. W. Harris, R. E. Diaz, Y. Ren, F. H. Ribeiro, J. T. Miller, *Catal. Today* **2016**, *6*, [58] 6965-6976.
- K. Kovnir, M. Armbrüster, D. Teschner, T. V. Venkov, F. C. Jentoft, [59] A. Knop-Gericke, Y. Grin, R. Schlögl, Sci. Technol. Adv. Mater. 2007. 8. 420-427.
- M. Armbrüster, M. Behrens, F. Cinquini, K. Föttinger, Y. Grin, A. [60] Haghofer, B. Klötzer, A. Knop-Gericke, H. Lorenz, A. Ota, et al., ChemCatChem 2012, 4, 1048–1063.
- [61] D. a. Barskiy, O. G. Salnikov, K. V. Kovtunov, I. V. Koptyug, J. Phys. Chem. A 2015, 119, 996-1006.

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- [62] A. Haase, J. Frahm, D. Matthaei, W. Hanicke, K.-D. Merboldt, J.
- Magn. Reson. 1986, 67, 258–266.
  W. Ju, M. Favaro, C. Durante, L. Perini, S. Agnoli, O. Schneider, U. Stimming, G. Granozzi, *Electrochim. Acta* 2014, *141*, 89–101. [63]
- Stimming, G. Granozzi, *Electrocnim. Acta* 2014, 147, 89–101.
  A. K. Khudorozhkov, I. A. Chetyrin, A. V. Bukhtiyarov, I. P. Prosvirin, V. I. Bukhtiyarov, *Top. Catal.* 2017, 60, 190–197.
  I. A. Witońska, M. J. Walock, P. Dziugan, S. Karski, A. V. Stanishevsky, *Appl. Surf. Sci.* 2013, 273, 330–342.
  C. Rameshan, H. Lorenz, L. Mayr, S. Penner, D. Zemlyanov, R. Arrigo, M. Haevecker, R. Blume, A. Knop-Gericke, R. Schlögl, et al., Lorder 2022, 2023. [64]
- [65]
- [66]
- J. Catal. 2012, 295, 186-194.

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Selective single-site Pd-In hydrogenation catalyst for production of enhanced magnetic resonance signals using parahydrogen

