

Acetylene Oligomerization over Pd Nanoparticles with Controlled Shape: a Parahydrogen-Induced Polarization Study

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ABSTRACT: Substantial signal enhancements achieved by using parahydrogen in catalytic hydrogenations are powerful tools for mechanistic studies of chemical reactions involving molecular H₂. Potentially, this technique can be extended to other reaction classes, providing new information about reaction mechanisms. Moreover, this can lead to new substances with highly polarized spins. Here we report strong signal enhancements of oligomerization reaction products observed during the selective acetylene hydrogenation over Pd nanoparticles of different shapes and sizes supported on SiO₂. C₄ oligomeric products (1,3-butadiene, 1-butene, 2-butene)

demonstrated high degree of nuclear spin polarization with the highest degree observed for 1-butene (more than 1.7 % vs 2.4×10^{-3} % at thermal equilibrium), which was an order of magnitude larger compared to that of the triple C-C bond hydrogenation products. No dependence of polarization on the metal surface statistics, and generally on the nanoparticles morphology (cubes, octahedra, cuboctahedra), could be observed. In contrast, the particle size effect was such that larger particles provided higher signal enhancements. This observation is in line with the increased activity over larger Pd nanoparticles observed during the acetylene hydrogenation over the same catalysts.

Keywords: Heterogeneous Catalysis, Parahydrogen, Nuclear Hyperpolarization, Hydrogenation, Oligomerization, Polymerization

1. INTRODUCTION

Parahydrogen-induced polarization (PHIP)^{1,3} is a nuclear spin hyperpolarization technique utilized for NMR/MRI sensitivity boosting.⁴ In particular, it is used for mechanistic studies of chemical reactions consuming H₂ as a reagent. Commonly, PHIP is produced when parahydrogen, the readily available nuclear spin isomer of H₂, participates in chemical processes such as catalytic hydrogenation leading to highly enhanced NMR signals of reaction products.^{5,6} Combined with nuclear spin polarization transfer, chemical interactions can be used to polarize molecules non-hydrogenatively by using the SABRE method.⁷ High NMR signal enhancements were utilized to detect key intermediates and side products of homogeneous hydrogenation processes mediated by transition metal complexes.⁵ The reaction mechanism elucidation using PHIP was attempted also in heterogeneous hydrogenations.^{8,9} The extension of PHIP applications to the studies of chemical reactions other than hydrogenations would open a great perspective for the further development of the technique as a mechanistic tool in chemistry. Only few examples of the PHIP-enhanced NMR signals observation in the hydroformylation reaction,¹⁰

hydrodesulfurization¹¹ and acrolein hydrogenation accompanied by oligomerization¹² have been reported. For instance, polymerization reaction is one of the most important industrial processes, while its mechanism is often debated. Among nuclear spin hyperpolarization techniques, recent achievements of dynamic nuclear polarization (DNP) in homogeneous polymerization reaction studies should be mentioned in this context,^{13,14} while PHIP potential is yet to be recognized.

Herein, we used PHIP to study oligomerization products formation during the heterogeneous hydrogenation of acetylene with molecular hydrogen. Selective hydrogenation of traces of acetylene in ethylene-rich gas streams is the basic approach for the production of polymer-grade ethylene from the products of thermal cracking of petrochemicals.¹⁵ Polymerization and oligomerization processes always accompany the hydrogenation of acetylene performed using conventional industrial catalysts, and lead to deactivation of the hydrogenation catalysts.¹⁶ The minimization of these side reactions is an important practical issue which can be solved by elucidating their mechanisms. In this respect, PHIP can expose the formation of polymers and oligomers present in low concentrations and can provide information about the pairwise route of H₂ addition in the course of the reaction, as it achieves a unique type of labeling for molecules bearing hydrogen atoms from the same H₂ molecule. In the experiments, we used supported Pd nanoparticles which are known to hydrogenate acetylene selectively to ethylene. In addition to the production of ethylene, which has been shown to be important in the context of the production of nuclear spin isomers of polyatomic molecules,¹⁷ the reaction of acetylene with parahydrogen also produced polarized oligomeric C₄ products: 1-butene, 2-butene, 1,3-butadiene and 1-butyne. The observed nuclear polarization and the considerable signal enhancements (up to 700-fold) demonstrated the presence of the pairwise route of H₂ incorporation in the course of the oligomeric products formation. To the best of our knowledge, this is the first example of a systematic study of oligomer formation using PHIP.

2. EXPERIMENTAL METHODS

2.1 Catalysts and reagents

A series of six catalysts containing supported Pd nanoparticles of different shapes and sizes were used in the experiments. Their properties are summarized in Table 1.

Table 1. The properties of the supported Pd nanoparticles used in this work.

Catalyst	Surface characteristics			Surface statistics ^{a,b}		
	wt. Pd	d_{nc}	D^c	X_{100}	X_{111}	X_{edge}
	[%]	[nm]	[%]	[%]	[%]	[%]
Pd ₁₀ /SiO ₂	1.8	10	8.8	97.4 (87.5)	- (-)	2.6 (7.5)
Pd ₁₈ /SiO ₂	5.0	18	5.0	99.2 (96.2)	- (-)	0.8 (2.3)
Pd ₃₇ /SiO ₂	3.6	37	2.8	- (-)	98.8 (95.8)	1.2 (3.4)
Pd ₂₀₂ /SiO ₂	0.4	2.6	34.5	11.2 (4.3)	61.4 (17.0)	27.4 (48.9)
Pd ₃₇ /SiO ₂	0.4	7	13.1	16.8 (7.4)	72.9 (49.0)	9.7 (26.0)
Pd/TiO ₂	1.0	6	15.3	not known ^d	not known ^d	not known ^d

^aSurface statistics estimated for a particle with the specific shape.

^bThe values in parenthesis correspond to a model *fcc* nanoparticle with one incomplete layer of atoms at the surface, while the values outside the parenthesis correspond to the ideal *fcc* nanostructures.

^cThe dispersion was estimated based on the surface statistics of *fcc* crystals assuming that one face of the nanocrystal was unavailable due to the interaction with the support.

^dThis sample was prepared by a different method compared to the first five samples. The method is not specific to a particular particle shape.

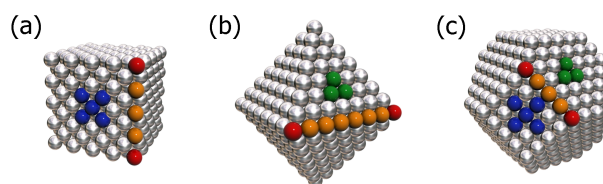


Figure 1. Schematic representation of the differences in Pd metal surface statistics for (a) cubic, (b) octahedral and (c) cuboctahedral shapes of nanoparticles. The colored atoms correspond to (111) faces (green), (100) faces (blue), edges (orange) and corners (red).

The Pd nanocubes, octahedra and cuboctahedra were synthesized according to previously published protocols.^{18,20} The shape and size of the Pd nanocrystals were analyzed by transmission

electron microscopy (TEM). Particle counting allowed determining the average particle size of each sample in which more than 95% of the Pd nanocrystals corresponded to the expected shapes. The full characterization of the nanoparticles can be found in a previous work.²¹ The Pd nanocrystals were subsequently immobilized on commercially available SiO₂ (S5505, Sigma-Aldrich) by wet impregnation.²² Briefly, SiO₂ was dispersed in ethanol and a colloidal solution containing the Pd nanoparticles was added dropwise. The mixture was left under stirring overnight and the final catalyst was then collected by centrifugation. These methods yielded first five catalysts in the table with Pd nanoparticles of cubic (Pd_{c10}/SiO₂, Pd_{c18}/SiO₂), octahedral (Pd_{o37}/SiO₂) and cuboctahedral (Pd_{co26}/SiO₂, Pd_{co7}/SiO₂) shapes. Figure 1 schematically illustrates the Pd surface statistics for the different nanoparticle shapes. Pd/TiO₂ sample as a reference catalyst was prepared as reported elsewhere.²³

The high purity hydrogen (>99.9%) and acetylene (>99.5%) were obtained commercially. The contamination test for acetylene was performed with ¹H NMR spectra, and revealed no C4 hydrocarbons in the gas after extensive scan accumulations.

2.2 NMR experiments

NMR experiments were performed using a Bruker AV 300 SB spectrometer equipped with a 7.05 T superconducting magnet and operating at the proton resonance frequency of 300 MHz. The samples were studied using a 10 mm radio frequency (rf) NMR probe which can accommodate 10 mm o.d. NMR tubes and has an rf coil with a sensitive area which is ca. 20 mm long in the vertical direction. All catalyst samples in the amount of ca. 5 mg were packed between two plugs of glass wool in a quartz tube reactor. The reactor was heated to a desired temperature (85, 125 or 150°C) using a tubular oven around the reactor. In the continuous flow mode, the mixture of parahydrogen and acetylene with a desired acetylene:pH₂ ratio (1:2 or 1:4) was first passed through the reactor, and after that was supplied to the bottom of the 10 mm NMR sample tube inserted in the NMR probe positioned inside the superconducting magnet.

Figure 2b schematically shows the geometry of the experiment. The reaction mixture was supplied through a capillary inserted into the NMR tube at a constant flow rate of approximately 5 scc/s, while ^1H NMR spectra of the reaction gas mixture containing reaction products and unconverted reagents were acquired while the gas was flowing. As the hydrogenation step was performed in the low (Earth's) magnetic field and thereafter the reaction mixture was transferred to the high magnetic field of the NMR instrument, the resulting spectra revealed the ALTADENA-type polarization pattern⁶ (see Figure 2). The 90° rf pulses were used to acquire the NMR spectra in order to maximize the intensity of the observed signals. The thermally polarized spectra were recorded for the relaxed reaction mixture after an abrupt stop of the flow with a valve. The ratio of the hyperpolarized and the equilibrium signal intensities measured experimentally gave the signal enhancement factors provided by PHIP.

The acetylene: $p\text{H}_2$ gas mixture was prepared as follows. Normal hydrogen was passed through the ortho-para conversion catalyst ($\text{FeO}(\text{OH})$) kept at 77 K^{24} to produce a mixture consisting of 50% para- and 50% orthohydrogen isomers, hereafter referred to as parahydrogen ($p\text{H}_2$). Then, $p\text{H}_2$ was collected in a gas bottle charged with 1 bar of acetylene to prepare acetylene: $p\text{H}_2$ mixtures of the desired ratios by volume.

3. RESULTS AND DISCUSSION

Six catalysts differing in the Pd nanoparticle shapes and sizes were used in the experiments (Table 1): 10 nm cubes ($\text{Pd}_{10}/\text{SiO}_2$), 18 nm cubes ($\text{Pd}_{18}/\text{SiO}_2$), 37 nm octahedra ($\text{Pd}_{37}/\text{SiO}_2$), 2.6 nm cuboctahedra ($\text{Pd}_{2.6}/\text{SiO}_2$) and 7 nm cuboctahedra ($\text{Pd}_{7}/\text{SiO}_2$). In addition, a reference catalyst Pd/TiO_2 with Pd nanoparticles of mean diameter ~ 6 nm was used to facilitate a comparison with the results of our previous PHIP studies of heterogeneous hydrogenations over this catalyst.^{17,23} Experiments were performed by passing the acetylene/ $p\text{H}_2$ mixture through the reactor packed with ca. 5 mg of a catalyst at the flow rate of 5 scc/s in the setup shown in Figure 2a. These nanoparticles were previously found to be thermally stable in the hydrogenation of acetylene at

120°C for at least 10 h.²⁵ As the products were formed in the reactor, the product gas flowed through a capillary into the 10 mm glass sample tube in the NMR magnet for analysis, according to the ALTADENA experiment conditions, Figure 2b.⁶ The ¹H NMR spectra acquired in this way revealed the presence of polarized signals corresponding to C4 products of acetylene oligomerization in the presence of p-H₂.

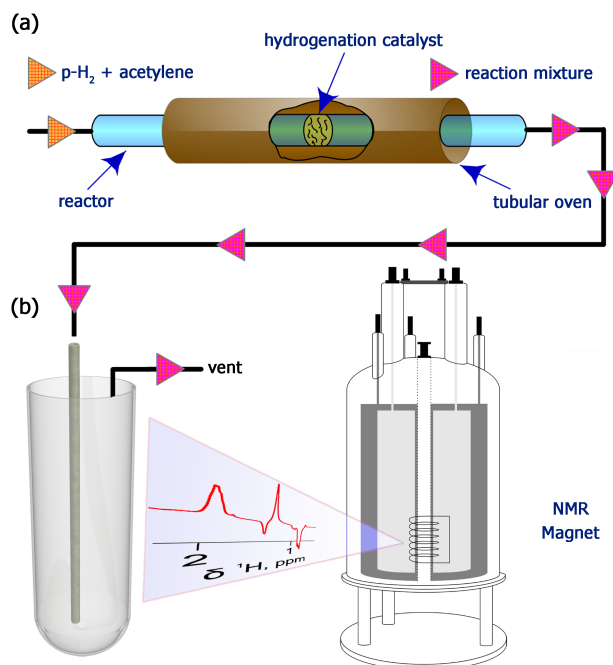


Figure 2. Experimental setup. (a) The p-H₂/acetylene mixture flows through the hydrogenation catalyst layer packed between the plugs of glass wool inside a heated quartz tube. (b) After the hydrogenation reaction, the hyperpolarized gas products flow from the reactor into the sample tube inside the NMR magnet. At the same time, the ¹H NMR spectra of the flowing reaction mixture of polarized products are detected.

As an example, Figure 3b (red trace) shows the ¹H NMR spectrum acquired when Pd_{0.37}/SiO₂ was used as the catalyst in acetylene hydrogenation with parahydrogen at 150°C. Although the main reaction product of acetylene reaction with H₂ was ethylene, the ethylene signal didn't show any noticeable degree of signal enhancement, as expected, because of the magnetic equivalence of all four protons in ethylene, which prevents any manifestation of the nuclear spin polarization. This

observation is consistent with our previous findings, wherein a subsequent chemical reaction was required to break the symmetry and reveal the non-equilibrium spin state of ethylene.¹⁷ At the same time, the NMR signals corresponding to oligomerization products (1,3-butadiene, 1-butene, 2-butene, 1-butyne) were significantly enhanced despite the much lower concentrations of these products compared to ethylene. The signal assignments in the spectrum to particular chemical structures are shown in Figure 3a. For comparison, the spectrum acquired after the relaxation of nuclear spins to thermal equilibrium is shown in Figure 3c (blue trace), revealing the significant extent of polarization in the spectrum of Figure 3b.

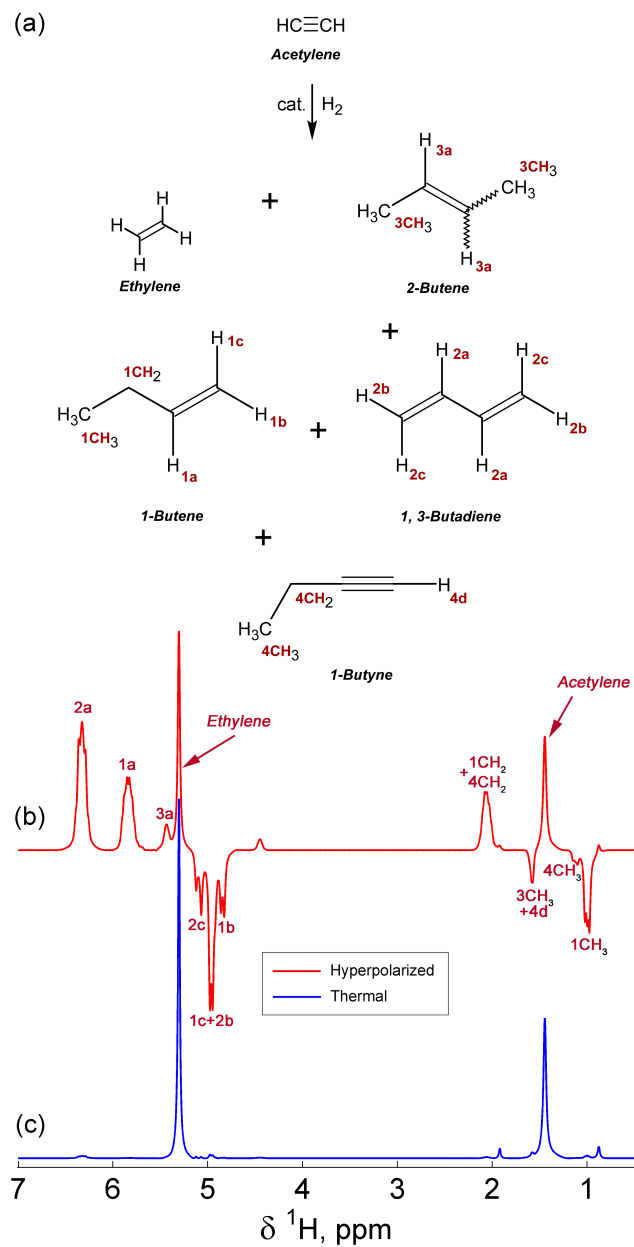


Figure 3. (a) The reaction scheme representing the formation of oligomers in the course of acetylene hydrogenation. (b) ^1H NMR spectra acquired from the flowing hyperpolarized reaction mixture (red trace) and (c) after the relaxation to thermal equilibrium in a stopped-flow experiment (blue trace). The $\text{Pd}_{0.37}/\text{SiO}_2$ catalyst at 150°C (acetylene: $\text{pH}_2 = 1:4$) was used in this particular example. The NMR signals are designated according to the labels shown near the chemical groups of different products in (a).

The enhancements of the NMR signals corresponding to different C4 oligomerization products were calculated for different catalysts to find correlations between the nanoparticle morphology and the nuclear spin polarization stemming from parahydrogen. Figure 4 shows the data obtained for the acetylene:pH₂ = 1:4 mixture at different temperatures. The highest enhancements were observed for 1-butene (the signals 1a, 1b and 1CH₃). Among others, the 1a proton of 1-butene had the strongest polarization corresponding to 200-700-fold signal enhancements depending on the catalyst. Taking into account the surface statistics presented in Table 1, one can find essentially no correlation between the fractions of (100) and (111) Pd metal nanoparticle faces and the observed PHIP effects either for 1-butene or for other oligomerization products. This is visualized in Figure 4g which shows the mean signal enhancement factor for proton 1a against the fraction of (100) faces. The samples with no (100) faces and those with an almost 100% content of (100) faces provide comparable effects, implying no or weak sensitivity toward the nature of exposed faces. Also, the sharp alteration in the number of edge atoms on going from cubes (Pd₁₀/SiO₂, 2.6%) to cuboctahedra (Pd₃₇/SiO₂, 9.7%) of comparable particle sizes does not lead to a strong effect on NMR signal enhancements as well. The graph showing mean signal enhancement factors against the fraction of edge atoms for all shaped catalysts (Figure 4h) demonstrates that the lower content of edge atoms represented essentially by the larger particle sizes (Pd₁₈/SiO₂ – 18 nm, Pd₃₇/SiO₂ – 37 nm) provides larger NMR signal enhancements. The particle size characterizes dimensions, but does not characterize the particular shape. Therefore, we can conclude that the observed PHIP effects reveal the absence of any significant influence of the particle shape (cube, octahedron or cuboctahedron) on the nuclear spin polarization produced in the acetylene oligomerization process over Pd metal nanoparticle catalysts. The similar trend was reported recently by Bowers et al. in propene hydrogenation with parahydrogen when shaped ceria nanocrystals were used as catalysts.²⁶

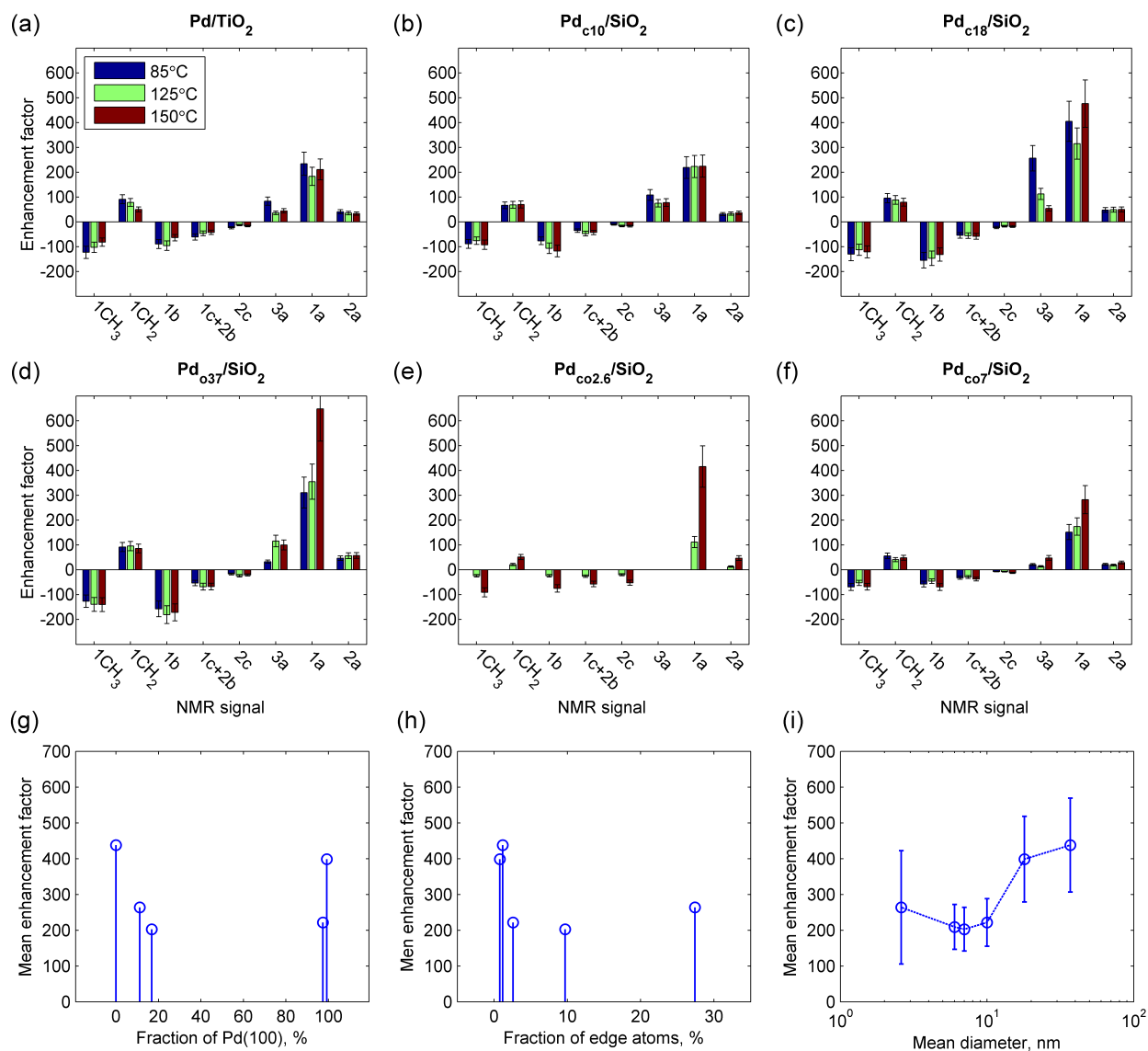


Figure 4. (a)-(f) The bar charts showing the signal enhancement factors obtained in the experiments with the catalysts shown above each chart. The stacks of three bars for different reaction temperatures (85, 125 and 150°C) are shown in each chart for each NMR signal (see Figure 3 for signal assignments). The signal enhancement factors were determined by dividing the integral amplitudes of the hyperpolarized signals by those of the thermally polarized signals. (g)-(i) Summary charts representing mean signal enhancement factors (averaged over temperatures) for 1a proton of 1-butene as a function of (100) face fraction (g), edge atom fraction (h) and mean particle size (i).

There is, however, a clear Pd particle size effect on the polarization observed in the experiments. The studied catalysts can be contingently grouped into three subgroups according to particle size: smaller than 5 nm ($\text{Pd}_{\text{co2.6}}/\text{SiO}_2$), 5-15 nm ($\text{Pd}_{\text{e10}}/\text{SiO}_2$, $\text{Pd}_{\text{co7}}/\text{SiO}_2$, Pd/TiO_2), and larger than 15 nm ($\text{Pd}_{\text{e18}}/\text{SiO}_2$, $\text{Pd}_{\text{oc137}}/\text{SiO}_2$). The general trend that one can spot from PHIP experiments is that larger particles, the third subgroup, provide higher signal enhancements regardless of the particle shape. This trend is explained in the discussion of Figure 4h above, and is visualized specifically by Figure 4i. It should be noted that it is difficult to compare reliably the first and the second subgroups of the catalysts with each other, because of the big uncertainty of the data for $\text{Pd}_{\text{co2.6}}/\text{SiO}_2$ as the reaction yields were very low for this catalyst, which led to the large error in the measured enhancement factors for this catalyst. However, we believe that signal enhancements for these subgroups do not differ significantly and are comparable. The reaction yields of C4 oligomers for different catalysts also reveal similar correlation – the larger the particle size, the higher the C4 yield (see Figure S1 in Supporting Information). Both observations indicate the requirement of multicenter adsorption of acetylene (or more generally sites with multiple surface Pd atoms) for the oligomerization to take place, which is facilitated in the case of larger particles.²⁷

The signal enhancements of C4 oligomeric products didn't exhibit a significant dependence on the reaction temperature (see Figure 4). The three bars corresponding to the particular signals represent signal enhancements measured at 85, 125 and 150°C are of the same order of magnitude, albeit with some exceptions in Figure 4d and 4e, suggesting that in most cases PHIP was virtually independent of temperature. In turn, the catalytic activity was not also significantly influenced by the temperature (see Figure S1 in Supporting Information). Only the $\text{Pd}_{\text{co2.6}}/\text{SiO}_2$ sample didn't show a considerable activity at 85°C, which increased upon the temperature increase to 150°C. At the same time, both the catalytic activity and the signal enhancements were dependent on the reactants composition. Raising the concentration of acetylene from 20 vol% (1:4 mixture) to 33 vol% (1:2 mixture) led to a slight decrease in the yields of the C4

oligomerization products and ethylene with concomitant decrease of the signal enhancements (see Figures S2 and S3 in Supporting Information). The Pd_{co2.6}/SiO₂ sample was practically inactive with the 33 vol% reagent mixture, and thus, the corresponding data are not presented here. It is worth noting that the reliable determination of the signal enhancements to have a meaningful quantification of PHIP effects is impossible without knowing the amplitudes of thermal NMR signals. Hence, the mixtures with acetylene concentrations below 20 vol% were not used in this study because a reliable quantification of very weak thermal ¹H NMR signals of C4 products that are present in very low concentrations would be difficult to achieve.

Although addressing a detailed mechanism of the oligomerization is beyond the scope of this work, we intended to show that PHIP can provide mechanistic information about heterogeneous catalytic reactions other than a hydrogenation. As mentioned in the introduction, the signal enhancement provides unique information about the fraction of H₂ molecules transferred to a substrate in a pairwise manner in the course of a hydrogenation process. In this study, the hydrogenation is accompanied by the substrate oligomerization, thus the signal enhancements shed light on the formation of the oligomers as well. For instance, among all C4 oligomerization products observed, 1-butene has the highest enhancement factors for vinyl protons (compare signals 1a, 2a and 3a in Figure 4). This result is in noticeable contrast to the reported acetylene oligomerization mechanism,²⁸⁻³¹ where the oligomerization results first in the formation of 1,3-butadiene, while 1-butene is assumed to be produced upon the subsequent hydrogenation of 1,3-butadiene. Such a mechanism implies that the nuclear spin polarization carried by the vinyl group of 1,3-butadiene would be inherited by the vinyl group in the 1-butene, and thus cannot be much lower than the nuclear spin polarization carried by the vinyl group of 1-butene. Likely, the reaction mechanism leading to the formation of 1-butene and 1,3-butadiene includes separate routes of production of these two C4 hydrocarbons, and 1-butene can be produced from adsorbed acetylene and H₂ on an active catalytic center through some intermediates without the indispensable formation of 1,3-butadiene as a precursor to 1-butene. Such a process, for instance, could be mediated by the surface vinyl or vinylidene,²⁸⁻³³ typically considered in acetylene

literature, just by a formal addition of an extra H₂ molecule to the adsorbed C4 intermediate in the 1,3-butadiene formation. We should note that reference experiments performed on 1,3-butadiene hydrogenation with pH₂ (see Figure S6 in Supporting Information) have shown that the signal enhancements exhibited by 1-butene produced in this process are two orders of magnitude lower (4-fold enhancement) as compared to those observed for the same product in the acetylene hydrogenation, confirming that the high polarization of 1-butene rather cannot be produced directly from 1,3-butadiene.

It should be noted that under ALTADENA conditions, a considerable polarization sharing can take place as a result of the nuclear spin dynamics in produced molecules at the low magnetic field. Such an effect can lead to an induced hyperpolarization of some other nuclear spins in a molecule which do not originate from pH₂.^{34,35} To test the importance of the polarization sharing under our experimental conditions, we performed reference experiments with acetylene hydrogenation under PASADENA conditions, wherein the polarization sharing does not take place. The PASADENA experiments indicated the presence of characteristic antiphase NMR signal patterns for all protons that appeared polarized in the ALTADENA experiments, with comparable amplitudes of polarizations observed with these two different methods (see Figure S7 in Supporting Information). This means that polarization sharing did not significantly alter the polarization patterns observed in our ALTADENA experiments. Most importantly, this implies that assuming the product distribution was the same for PASADENA and ALTADENA experiments, the large hyperpolarization of vinyl protons in 1-butene was not the result of polarization transfer from the ethyl protons of 1-butene after its formation upon the addition of pH₂ molecule to 1,3-butadiene in the low magnetic field. The latter conclusion was additionally confirmed by numerical simulations (see Figure S9 in Supporting Information).

The signal enhancements observed for C4 oligomers varied depending on the molecule. Taking as a reference the proton labeled “a” in the methine (-CH=) fragment which is present in all C4 products, we noted that the signal enhancements exhibit the following trend: 1-butene (200-700)

> 2-butene (50-100) > 1,3-butadiene (20-50). At the same time, the signal enhancements of C4 oligomerization products are considerably larger as compared to those of the triple bond hydrogenation products. A reliable determination of the enhancement would not be possible for ethylene produced in acetylene hydrogenation because the polarization is not visible for ethylene due to the symmetry of this molecule.¹⁷ Instead, we performed propyne and 1-butyne hydrogenations with $p\text{H}_2$ as reference processes and estimated the signal enhancements of the triple bond hydrogenation products using produced propene and 1-butene, respectively (see Supporting Information). It was found that signal enhancement factors for propyne hydrogenation over Pd catalysts hardly exceed an order of magnitude (Figure 5), meaning that C4 products accumulate stronger polarization, especially considering a 700-fold enhancement observed for 1-butene in acetylene hydrogenation. The signal enhancement factors (c.a. 10, see Figure S5 in Supporting Information) obtained for 1-butene in 1-butyne hydrogenation confirmed this conclusion.

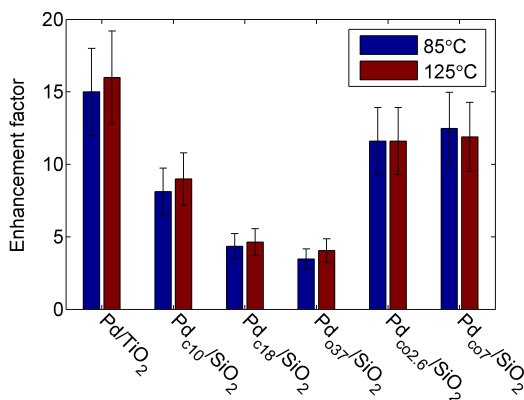


Figure 5. The bar chart of signal enhancement factors obtained in the propyne hydrogenation experiments. The data are presented in stacks of two bars for different temperatures (85 and 125°C). The absolute average value over the three ^1H NMR signals of the vinyl fragment of product propene is presented. The enhancement factors were determined by using the analysis described in Supporting Information.

The signal enhancement is a direct measure of the pairwise H_2 addition,³⁶ and can be converted into the fraction of the pairwise addition in the overall reaction process. Indeed, formally, the conversion of the measured signal enhancement factors into fractions of pairwise H_2 addition in the overall hydrogenation leads to characteristic values of 5.1% for 1-butene in the acetylene oligomerization (assuming that only one pH_2 was added per oligomeric product), 0.5% for propene in propyne hydrogenation and 0.1% for 1-butene in 1-butyne hydrogenation (see Supporting Information). Thus, the observations indicate the differences in the mechanisms of the products formation, and phenomenologically imply that the pairwise addition of H_2 in the case of acetylene hydrogenation accompanied by the oligomerization is at least an order of magnitude more probable as compared to that of the triple bond hydrogenation. It is worth to note that the presented fractions of pairwise H_2 addition give the lowest estimates because nuclear spin relaxation destroys the nuclear polarization in time, thus the “true” fraction values must be higher.^{37,38} The nuclear spin relaxation times for different species formed in the reactions (for protons labeled “a”: 1-butene (1.5 s), 2-butene (1.4 s), 1,3-butadiene (1.0 s), propene (0.6 s)³⁹) are not dramatically varying, and thus there shouldn’t be any major errors while comparing the fractions for different products. We understand, however, that it is hard to present a reliable chemical reaction mechanism based on the observed signal enhancement differences without confirmations by other physical methods. Mechanistic studies of the oligomer formation in acetylene hydrogenations over Pd nanoparticles are rather controversial, providing no clear picture. Typically, it is assumed that oligomers are formed as a result of subsequent transformations of 1,3-butadiene which is produced in the interaction of an adsorbed acetylene π -complex with vinyl intermediate ($-CH=CH_2$).^{28-30,32} In some publications, it was also proposed that 1,3-butadiene forms in the interaction of acetylene π -complex and surface vinylidene ($=C=CH_2$).^{31,33} An alternative mechanism presumes participation of vinyl radical in the oligomerization ($\cdot CH=CH_2$).^{39,40} However, none of these mechanisms can explain the nuclear polarization effects presented here for C4 hydrocarbons, for the reason described above that 1-butene has an order of magnitude higher enhancement factors as compared to 1,3-butadiene, one

concludes that the former cannot be produced from the latter. There are also other critical reasons to consider the current mechanistic views on the oligomerization as oversimplified. Indeed, the polarization labels a pair of hydrogen atoms stemming from the same H_2 molecule. These atoms must be incorporated into the product molecule somehow through the above-mentioned intermediates. The PASADENA signal pattern reveals such pairs of H atoms chiefly in the vicinal positions of all C4 oligomers, which are easily seen from the J-coupling splittings in the polarized NMR spectra (see Figure S7 and Figure S8 in Supporting Information for details). This implies that either the C2 surface intermediates must bear the vicinal pair of H atoms from pH_2 already before the oligomerization, or the pH_2 incorporation to vicinal positions occurs after the oligomerization. The former hypothesis, in turn, supports the vinyl intermediate or the vinyl radical as active species in the oligomerization, because they have vicinal H atoms, whereas vinylidene does not. Furthermore, the vinyl radical route is less probable compared to the vinyl intermediate, because the presence of the free radical center would dramatically increase nuclear spin relaxation leading to a rapid decay of the nuclear spin polarization. The vinyl intermediate was also proposed to be a key species in oligomerization processes observed during acrolein hydrogenation studied earlier by using PHIP.¹² The incorporation of the vicinal pair of H atoms into the surface vinyl intermediate requires hydrogen abstraction from acetylene adsorbed on Pd nanoparticles, which was actually observed earlier under the chemisorption of acetylene on metal surfaces at 100-200°C.^{22,41,42} This process leads to the formation of carbon (carbide) species prone to reduction under H_2 atmosphere,⁴² which, inter alia, can result in the formation of oligomeric butyl species. Therefore, it seems that the observed polarization effects can be explained both in terms of the necessary hydrogen abstraction/addition steps for vicinal H atoms on the catalyst surface either before the oligomerization in C2 species produced from acetylene, or after the oligomerization in C4 species. We note that a similar kind of H atom pair chemical exchange was proposed as a mechanism of PHIP for the reagent molecules in some heterogeneous catalytic systems.⁴³⁻⁴⁵ The formation of 1-butyne detected in the experiments (Figure 3b) could support the presence of the hydrogen abstraction/addition step for 1-butene. However, the signal

enhancement factors measured for 1-butene were two orders of magnitude larger than in the experiments with 1-butyne hydrogenation performed purposely to have an independent measure for polarization levels in the triple bond hydrogenation with pH_2 (see Figure S5 in Supporting Information). The reference experiment with 1,3-butadiene hydrogenation also resulted in a much lower signal enhancement for 1-butene, meaning that hydrogen abstraction from 1-butene leading to 1-butyne or 1,3-butadiene and followed by pH_2 addition cannot explain the high signal enhancements observed in acetylene hydrogenation. Therefore, we believe that hydrogen abstraction takes place before the oligomerization step at the stage of the C2 surface intermediates. Further elucidation of mechanistic details requires extensive systematic studies, which are ongoing. However, the current results already provide useful insight into the mechanistic details of oligomer formation during the acetylene hydrogenation.

4. CONCLUSIONS

Mechanistic studies play an important role in modern heterogeneous catalysis as the activity and selectivity may crucially depend on experimental conditions since the reaction mechanism changes. Nowadays, nuclear hyperpolarization techniques find more and more applications in mechanistic studies of chemical processes. PHIP technique was extensively used for investigations of homogeneous hydrogenation reactions for decades.^{5,46-48} This technique has been recognized to provide valuable information about heterogeneous hydrogenations,^{8,9,49} and metal-free catalysis.^{50,51} This work presents the first example of PHIP applied to study catalytic oligomerization taking place during acetylene hydrogenation. This process is considered highly undesirable because it leads to deactivation of catalysts.¹⁶ The suppression of the oligomerization can result in significant economic effects as selective acetylene hydrogenation is used in ethylene purification, with an annual production of more than 100 million tons.¹⁵

We show that the use of parahydrogen in acetylene hydrogenation leads to the strong signal enhancements of C4 oligomerization products, with the largest enhancements observed for 1-butene (700-fold). This fact suggests that the latter product cannot be produced (at least

exclusively) from 1,3-butadiene as proposed in the literature, because 1,3-butadiene shows an order of magnitude lower signal enhancements. The evaluation of polarization levels obtained in the triple bond hydrogenations (propyne to propene and 1-butyne to 1-butene) and 1,3-butadiene hydrogenation showed that the signal enhancements are two orders of magnitude lower as compared to those of oligomerization products. This observation suggests substantial differences in the mechanisms of these catalytic processes.

The variation of Pd nanoparticle shapes didn't reveal any significant sensitivity to the number of (100), (111) and edge Pd atoms, whereas the larger particles produced larger quantities of C₄ oligomers and generally led to higher NMR signal enhancements. With the signal enhancements approaching three orders of magnitude, the oligomers formation can be used as a method for the production of highly hyperpolarized substances.

ASSOCIATED CONTENT

Supporting Information. Reaction yields of different products in the hydrogenation with 1:4 (acetylene:pH₂) reagent mixture; signal enhancements and reaction yields for different products in the hydrogenation with 1:2 (acetylene:pH₂) reagent mixture; description of propyne, 1-butyne and 1,3-butadiene hydrogenation reference experiments; PASADENA acetylene hydrogenation reference experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

ACKNOWLEDGMENT

The financial support by the grants from the Council on Grants of the President of the Russian Federation (MK-1329.2014.3), RFBR (14-03-93183-MCX-a, 16-33-60198 mol_a_dk) is acknowledged. VVZ, IVS and IVK thank RSF (grant #14-13-00445) for the support of the experiments of 1-butyne hydrogenation with parahydrogen. This work was also funded by the Russian Science Foundation (Grant 15-19-20023). The authors would like to thank Prof. Mingshang Jin (Xi'an Jiaotong University) for providing the shape-controlled Pd nanocrystals.

We thank Prof. V. I. Bukhtiyarov and his group (Boreskov Institute of Catalysis) for providing the Pd/TiO₂ catalyst sample used in this work.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ABBREVIATIONS

PHIP, parahydrogen-induced polarization; ALTADENA, Adiabatic Longitudinal Transport After Dissociation Engenders Nuclear; PASADENA, Parahydrogen And Synthesis Allows Dramatically Enhanced Nuclear Alignment; SABRE, Signal Amplification by Reversible Exchange; pH₂, parahydrogen; rf, radio frequency; DNP, dynamic nuclear polarization.

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