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Pd-based bimetallic catalysts for HET-PHIP

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Abstract. Production of hyperpolarized catalyst-free gases and liquids by heterogeneous hydrogenation with parahydrogen (HET-PHIP) can be useful for various technical as well as biomedical applications, including in vivo studies, investigations
10 of mechanisms of industrially important catalytic processes, enrichment of nuclear spin isomers of polyatomic gases, and more. In this regard, the wide systematic search for heterogeneous catalysts effective in pairwise H_2 addition required for the observation of PHIP effects is crucial. Here in this work we demonstrate the competitive advantage of Pd-based bimetallic catalysts for HET-PHIP. The dilution of catalytically active Pd with less active Ag or In atoms provides the formation of atomically dispersed Pd_1 sites on the surface of Pd-based bimetallic catalysts, which are significantly more selective toward
15 pairwise H_2 addition compared to the monometallic Pd. Furthermore, the choice of the dilution metal (Ag or In) has a pronounced effect on the efficiency of bimetallic catalysts in HET-PHIP, as revealed by comparing Pd-Ag and Pd-In bimetallic catalysts.

1. Introduction

Among the nuclear spin hyperpolarization (HP) techniques that are currently becoming very popular in NMR and MRI,
20 parahydrogen-based approaches such as PHIP and SABRE are of particular interest (Adams et al., 2009; Duckett and Mewis, 2012; Green et al., 2012; Iali et al., 2018; Reineri et al., 2015). They are relatively easy to implement while at the same time they compete successfully with other powerful HP techniques such as DNP (Ardenkjaer-Larsen, 2016; Jannin et al., 2019; Lumata et al., 2015; Rossini, 2018; Zhao et al., 2018). Since the first report of the PHIP effect (Bowers and Weitekamp, 1987), the majority of such studies are based on the homogeneous catalysis by transition metal complexes in solution. Many
25 such catalysts can achieve pairwise addition of H_2 to a substrate and/or to a catalytically active center, which is usually a prerequisite for parahydrogen-based hyperpolarization. At the same time, there are several significant reasons why PHIP via heterogeneous hydrogenations (HET-PHIP) (Kovtunov et al., 2013, 2016, 2020a) can be advantageous. In particular, in vivo applications certainly require catalyst-free hyperpolarized fluids. Removal of potentially toxic transition metal complexes utilized in the homogeneous implementations of PHIP and SABRE, while possible (Cavallari et al., 2020; Kidd et al., 2018;
30 Knecht et al., 2020), still remains one of the primary challenges to be solved. In this respect, solid heterogeneous catalysts

can be filtered out much faster, and thus higher polarization levels can be available upon injection. HET-PHIP is also directly applicable to the production of HP gases (Ariyasingha et al., 2020; Kovtunov et al., 2020b; Salnikov et al., 2019), which appears promising as a means to provide inhalable HP contrast agents for in vivo use in lung MRI. Furthermore, heterogeneous processes are most suited for the production of continuous streams of catalyst-free HP fluids (Kovtunov et al.,

35   2014), which is expected to be useful for various technical as well as biomedical applications.

A separate yet strongly related field of research is the application of HP substances in the studies of chemical processes. In particular, PHIP has proven useful in the mechanistic studies of homogeneous catalytic reactions that involve H_2 (Duckett and Sleigh, 1999). In this respect, extension of the parahydrogen-based NMR signal enhancement to the mechanistic studies of heterogeneous hydrogenations and related processes (Du et al., 2020; Salnikov et al., 2015, 2018;

40   Zhivonitko et al., 2016) is highly desirable. This is because heterogeneous catalysts and processes by far predominate in the modern large-scale industrial catalysis, while at the same time they are significantly more sophisticated by their nature. Developing enhanced analytical tools for such studies is a challenging but rewarding task.

Finally, the HET-PHIP approach can prove useful for addressing yet another challenge of modern science, namely the production/enrichment of nuclear spin isomers of polyatomic molecules (NSIM). As mentioned above, the addition of p-H_2

45   to a substrate or intermediate usually has to be pairwise for the correlated spin state of the nascent H atoms to be carried over to a reaction product or intermediate. However, if the two H atoms remain magnetically equivalent there, their correlated spin state, even if preserved, is not immediately revealed as an NMR signal enhancement. This has been demonstrated in numerous studies in solution in the context of the long-lived spin states (Levitt, 2019). Furthermore, hydrogenation of symmetric gaseous substrates is a potential route to the enrichment of their NSIM, as successfully demonstrated earlier for

50   ethylene in a heterogeneous hydrogenation of acetylene with parahydrogen (Zhivonitko et al., 2013). This development is rather significant – while there are several known methods for enrichment or separation of NSIM of polyatomic molecules (Chapovsky and Hermans, 1999; Kilaj et al., 2018; Krüger et al., 2018), to date none of them is able to produce sufficient quantities of an enriched polyatomic gas for NMR signal enhancement applications, including the reported production of the singlet spin state of $^{15}N_2$ by SABRE in solution (Bae et al., 2018). Thus, the work of Zhivonitko et al. (2013) so far remains

55   the only demonstration of NMR signal enhancement derived from a NSIM-enriched polyatomic gas.

Based on the major recent progress achieved in p-H_2-based hyperpolarized NMR, it can be reasonably expected that potential utilization of NSIM-enriched polyatomic molecules can advance this field of research and practice much further, by significantly expanding the scope of reactions and substrates/products for the production of HP agents for in vivo use as well as extending the advanced mechanistic studies to new classes of highly important catalytic processes. This, however, does

60   not exhaust the list of activities that would benefit from the facile production/enrichment of NSIM of polyatomic molecules. In modern science, of significant interest are the properties of NSIM, including their interconversion processes (Chapovsky and Hermans, 1999) and NSIM behavior upon phase transitions (Curl et al., 1966; Hama et al., 2018), the NSIM-related selection rules in molecular spectroscopy (Kanamori et al., 2017; Ozier et al., 1970) and upon chemical transformations (Hu

65 et al., 2020; Kilaj et al., 2018; Oka, 2004), NSIM in astrophysics and astrochemistry research (Hama and Watanabe, 2013; Hily-Blant et al., 2018; Shinnaka et al., 2016; Tielens, 2013), and more.

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). Better heterogeneous catalysts are thus required, something which is constantly searched for in heterogeneous catalysis in general as more active and selective industrial catalysts have a major impact on all areas of our life. One of the powerful recent trends is the
70 exploration of the so-called single-site and single-atom heterogeneous catalysts (Liu et al., 2018; Samantaray et al., 2020), which often outperform other catalyst types in terms of product selectivity and can ensure a much more efficient use of active metals, reducing the costs and contributing to cleaner chemical industry. Selectivity issues are highly important in essentially all catalytic processes; in particular, this includes semihydrogenation of alkynes in the presence of alkenes.

One promising type of catalysts for selective hydrogenation processes are bimetallic systems composed of two
75 different metals either as an alloy or in an intermetallic form. Dilution of a more active metal with a less active one significantly modifies the geometric and electronic structure of an active center, providing isolated active metal atoms at high dilutions (Hannagan et al., 2020). It was demonstrated previously that in addition to an enhanced chemical selectivity to an alkene, Pd site isolation by In in the intermetallic 1 wt.% Pd-In catalyst provides an enhanced selectivity to pairwise addition of H_2 to an alkyne (Burueva et al., 2018).

80 In this work we directly compare monometallic and bimetallic catalysts in the selective hydrogenation of propyne to propylene with parahydrogen. The results clearly indicate that bimetallic Pd-Ag catalyst largely outperforms its monometallic counterparts not only in the overall activity and selectivity toward propylene, but also in the pairwise selectivity of hydrogen addition as revealed by significantly larger NMR signal enhancements for propylene. Furthermore, the choice of the dilution partner has a pronounced effect on the efficiency of bimetallic catalysts in HET-PHIP, as revealed
85 by comparing Pd-Ag and Pd-In bimetallic catalysts.

2. Materials and methods

2.1. Catalyst preparation and characterization

The catalysts were prepared by incipient wetness impregnation of preliminarily calcined Al_2O_3 (Sasol, specific surface area 56 $m^2 \cdot g^{-1}$). Pd-Ag/Al_2O_3 catalyst was prepared using an aqueous solution of $Pd(NO_3)_2$ and $AgNO_3$. Pd-In/Al_2O_3 catalyst was
90 prepared using an aqueous solution of binuclear acetate complex $PdIn(CH_3COO)_5$. The reference catalyst samples (Pd/Al_2O_3 and Ag/Al_2O_3) were also prepared by incipient wetness impregnation with an aqueous solution of the corresponding nitrates. The impregnated samples were dried in air at room temperature overnight followed by the reduction in H_2 (5 vol.% in Ar) flow at 550 °C for 3 h. In case of Pd-In/Al_2O_3 catalyst, the sample was reduced at 600°C. The detailed preparation

procedures of the catalysts used in this work are described elsewhere (Kozitsyna et al., 2008; Markov et al., 2016; Smirnova
95   et al., 2019).

The inductively coupled plasma atomic emission spectra (ICP-AES) were recorded on a Baird Plasma Spectrometer PS-6. According to ICP-AES data, Pd-Ag/Al$_2$O$_3$ catalyst sample contained 2 wt.% of Pd and 6 wt.% of Ag; Pd-In/Al$_2$O$_3$ catalyst contained 2 wt.% of Pd and 2 wt.% of In. The reference catalyst sample Pd/Al$_2$O$_3$ contained 2.5 wt.% of Pd; Ag/Al$_2$O$_3$ catalyst contained 6 wt.% of Ag.

2.2.   Catalytic activity tests

Commercially available hydrogen and propyne gases were used without additional purification. The catalyst (30 mg) was placed in a stainless steel tubular reactor positioned outside an NMR magnet in the ALTADENA experimental protocol (Pravica and Weitekamp, 1988). The bimetallic catalysts were reduced in H$_2$ flow at 550 °C for 1 hour before the catalytic tests. After being cooled to desired temperature, the gas mixture was introduced to the catalyst.

105   ^{1}H NMR spectra were recorded on a 300 MHz Bruker AV NMR spectrometer. For the PHIP experiments, hydrogen gas was enriched with para-isomer up to 87.0-90.5% using Bruker parahydrogen generator BPHG-90.

3. Results and Discussion

Here in this work we studied the catalytic behavior of different Pd-based bimetallic catalysts (Pd-Ag and Pd-In) in the selective gas-phase hydrogenation of propyne with parahydrogen. To this end, propyne was premixed with p-H$_2$ in the molar
110   ratio of 1:4. The reaction was conducted in a continuous flow regime at various temperatures (T = 100-300 °C) with the reactor outflow continuously supplied to the probe of an NMR spectrometer and analyzed by ^{1}H NMR. The conversion and selectivity values were calculated from ^{1}H NMR spectra in thermal equilibrium acquired after complete relaxation of hyperpolarization. The catalytic activity of different catalyst samples in pairwise hydrogen addition was compared using the "apparent signal enhancement" values (SE), evaluated as the ratio between the integral of the enhanced NMR signal of
115   propene CH- group and the integral of the corresponding signal for thermally polarized propene.

First, the synergetic effect of Pd-Ag catalyst in HET-PHIP is addressed, then the behavior of this catalyst is compared to that of Pd-In, and after that factors affecting pairwise H$_2$ addition selectivity are discussed.

3.1.   Synergetic effect of Pd-Ag/Al$_2$O$_3$ catalyst in HET-PHIP

The catalytic activity of the monometallic reference catalysts (6 wt.% Ag/Al$_2$O$_3$ and 2 wt.% Pd/Al$_2$O$_3$) was explored first. It
120   was found that no hydrogenation products were observed in the ^{1}H NMR spectra during the attempted propyne hydrogenation over Ag/Al$_2$O$_3$ catalyst over the entire reaction temperature range, indicating that catalytic activity of Ag/Al$_2$O$_3$ is negligible under the experimental conditions. In contrast, the Pd/Al$_2$O$_3$ catalyst showed an excellent activity –

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even at a relatively low reaction temperature of 100 °C and the flow rate of 1.3 mL·s⁻¹ the propyne conversion reached 100%. However, the monometallic Pd/Al₂O₃ catalyst exhibited a poor selectivity toward propene (Table 1). Slightly higher

125 selectivity values at high gas mixture flow rates is explained by the lower catalyst contact times. In addition, a declining alkene selectivity at higher alkyne conversions is a known problem associated with unmodified Pd catalysts.

Table 1: Hydrogenation of propyne with parahydrogen over Ag/Al₂O₃, Pd/Al₂O₃, and Pd-Ag/Al₂O₃ catalysts: propyne conversion (X) and selectivity to propene ($S_{propene}$) at different gas mixture flow rates and reaction temperature of 200 °C.

Catalyst	Flow rate, mL·s⁻¹	X, %	$S_{propene}$, %
Ag	1.3	0	0
	3.8	0	0
Pd	1.3	100	45
	3.8	92	71
Pd-Ag	1.3	100	75
	3.8	78	86

130 Modification of Pd catalysts with a second metal, which is typically less active or even completely inactive in hydrogenation, leads to synergetic effect in catalytic activity – bimetallic Pd-based catalysts usually demonstrate enhanced selectivity and stability (Bond, 2005). Here we show that the introduction of Ag atoms inactive in propyne hydrogenation to Pd and formation of a bimetallic Pd-Ag catalyst (2 wt.% of Pd and 6 wt.% Ag) dramatically enhances its catalytic behavior. The Pd-Ag catalyst demonstrated a significantly higher selectivity toward propene with a comparable conversion in propyne

135 hydrogenation, e.g. at 100 °C and 1.3 mL·s⁻¹ both Pd and Pd-Ag catalysts showed 100% conversion, but Pd-Ag catalyst showed higher selectivity compared to monometallic Pd catalyst (75 vs. 45%).

Such catalytic behavior is typical for bimetallic catalysts and can be associated with suppression of the formation of palladium hydride phase, which is a known hydrogen source responsible for the undesired unselective hydrogenation of alkynes and alkenes to alkanes (Armbrüster et al., 2012). Nevertheless, the enhanced catalytic performance of Pd-Ag catalyst

140 can be also explained by the fact that atomically dispersed Pd sites (Pd₁) isolated from each other by inactive Ag atoms can be achieved at high dilutions and stabilized during high-temperature pre-reduction in H₂ (400–550°C) (Pei et al., 2015). The authors associate the higher selectivity of isolated Pd₁ sites over Pd-Ag catalyst with the decrease in the heat of adsorption of alkene compared to that on a monometallic Pd catalyst. The differentiation between the effects associated with the formation of isolated Pd₁ sites and the suppression of the formation of palladium hydrides for Pd-Ag catalysts with different Pd/Ag

145 ratio was thoroughly studied in previous works (Rassolov et al., 2020b, 2020a). It was found that an increase in the Ag content in the composition of bimetallic Pd-Ag nanoparticles hinders the formation of palladium hydrides, which is completely suppressed at a ratio of Ag/Pd ≥ 1. Analysis of the structural stability of isolated Pd₁ sites has shown that the stability of such sites can be provided by an increase in the Ag/Pd ratio to ≥ 2.

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The significant dilution of Pd atoms with Ag (Ag/Pd = 3) in this study ensures the formation of isolated Pd_1 sites,

150   which is confirmed by IR spectroscopy of adsorbed CO (Rassolov et al., 2020b). In an analogy with transition metal

complexes in solution, the presence of isolated Pd_1 sites on the Pd-Ag catalyst surface can be expected to result in an

enhanced activity of bimetallic Pd-Ag catalyst in pairwise hydrogen addition. This expectation is indeed borne out by the

experimental observations. Both monometallic Pd and bimetallic Pd-Ag catalysts were active in pairwise H_2 addition in

propyne hydrogenation with parahydrogen (Figure 1). The enhanced NMR signals from CH- (signal # 4 in Figure 1) and

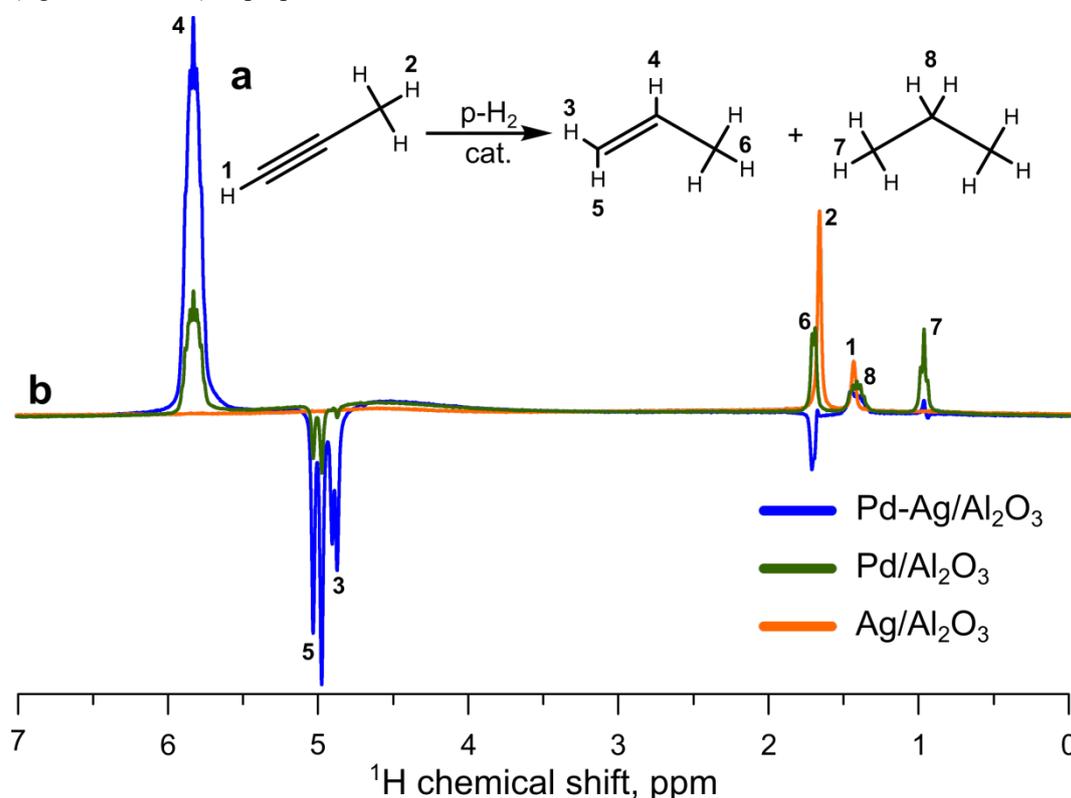155 CH_2-protons (signals # 3 and 5) of propene were observed.

Figure 1: a) Reaction scheme of propyne hydrogenation; b) ^{1}H NMR ALTADENA spectra acquired during propyne hydrogenation with parahydrogen over Pd-Ag/Al₂O₃ (blue line), Pd/Al₂O₃ (green line), or Ag/Al₂O₃ catalyst (orange line). The reaction temperature was 200 °C, the total gas flow rate was 3.8 mL·s⁻¹. All spectra were acquired with 8 signal accumulations and
160   **are presented on the same vertical scale.**

The reference monometallic 2 wt.% Pd/Al₂O₃ catalyst demonstrated very low ^{1}H NMR signal enhancement factors

for CH-proton of propene, with SE values not exceeding 3 over the entire reaction temperature range. However, the dilution

of Pd with Ag atoms allowed a ~4-fold increase in SE (up to 13) for the Pd-Ag catalyst (Table 2). The moderate activity of

bimetallic Pd-Ag catalyst in pairwise H_2 addition may be associated with its tendency to the surface transformations – in an

165   earlier work it was shown that on the surface of Pd-Ag catalyst a transformation of a part of monoatomic Pd_1 centers to

multiatomic Pd_n surface clusters takes place as a result of Pd atoms migration on the surface upon treatment with CO

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(Stakheev et al., 2018) due to adsorbate-induced segregation phenomenon. Most likely, analogous surface transformations are initiated by the strong adsorption of propyne. In the previous study it was found that such surface transformation almost didn't change catalyst selectivity in a liquid-phase hydrogenation process; however, our results clearly show that pairwise

170 hydrogen addition is an extremely sensitive reaction and can be potentially used as a marker of the structural transformations of the catalyst surface.

Table 2: Hydrogenation of propyne with parahydrogen over Ag/Al$_2$O$_3$, Pd/Al$_2$O$_3$ and Pd-Ag/Al$_2$O$_3$ catalysts: propyne conversion (X) and ^{1}H NMR signal enhancement factors (SE) for CH-proton of propene. The p-H$_2$ fraction is 90. 5%.

Catalyst	T, °C	Flow rate, mL·s^{-1}	X, %	SE
Ag	200	1.3	0	–
		3.8	0	–
Pd	100	1.3	100	-
		3.8	94	3
	200	1.3	100	-
		3.8	92	3
	300	1.3	100	-
		3.8	96	3
Pd-Ag	100	1.3	100	–
		3.8	87	10
	200	1.3	100	–
		3.8	78	13
	300	1.3	96	–
		3.8	77	13

175 ## 3.2. The effect of second metal M (Ag vs. In) on the activity of Pd-M/Al$_2$O$_3$ catalysts in HET-PHIP

As it was shown above, the stability of atomically dispersed Pd$_1$ sites on the surface has a great impact on the efficiency of bimetallic catalysts in HET-PHIP. In order to differentiate the stability effect, Pd atoms were diluted with a different metal, In. The 2 wt.% Pd-In catalyst (Pd/In = 1) was also tested in propyne hydrogenation with parahydrogen. In these experiments,

180 the slightly lower p-H$_2$ enrichment was used; the p-H$_2$ fraction was 87.0% (instead of 90.5% in case of Pd, Ag, and Pd-Ag catalytic activity tests). Therefore, for the sake of comparison, the apparent values of signal enhancement for Pd-In catalyst were extrapolated to 90.5% p-H$_2$ fraction (see column *SE corrected* in Table 3). The Pd-In catalyst clearly demonstrated a higher activity in pairwise hydrogen addition compared to the Pd-Ag catalyst, e.g. at 200 °C and 3.8 mL·s^{-1} the signal

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enhancement was 88, i.e., much larger than for Pd-Ag (13). The comparison of hyperpolarized ^{1}H NMR spectra acquired

185 during propyne hydrogenation over Pd-Ag and Pd-In catalysts is presented in Figure 2; the spectra are presented on the same vertical scale. It is interesting to note that Pd-In catalyst demonstrated also a higher propene selectivity along with higher activity in HET-PHIP – at 200 °C and 1.3 mL·s^{-1} the selectivity toward propene reached 98%, while for Pd-Ag it was 75%. The highest values of SE were observed at 400 °C – at 3.8 mL·s^{-1} the signal enhancement was 113 for Pd-In.

190 **Table 3: Hydrogenation of propyne with parahydrogen over Pd-In/Al$_2$O$_3$ catalyst: propyne conversion (X), selectivity to propene ($S_{propene}$), and ^{1}H NMR signal enhancement factors (SE) for the CH-proton of propene. The p-H$_2$ fraction is 87%. SE values extrapolated to 90.5% p-H$_2$ fraction are provided in the column *SE corrected*.**

Catalyst	T, °C	Flow rate, mL·s^{-1}	X, %	S$_{propene}$, %	SE	SE corrected*
Pd-In	100	1.3	5	94	7	8
		3.8	4	93	59	62
	200	1.3	93	98	4	4
		3.8	63	97	83	88
	300	1.3	89	98	4	4
		3.8	45	96	89	95
	400	1.3	62	94	3	3
		3.8	19	91	**107**	**113**
	500	1.3	24	48	7	8
		3.8	12	47	86	91

* SE values corrected to the 90.5% parahydrogen fraction

3.3. Factors affecting pairwise H$_2$ addition selectivity

The NMR signal enhancements observed in this study are rather moderate, and higher values have been achieved in HET-

195 PHIP experiments with bimetallic catalysts in the past. For instance, higher SE values were observed in the previous work for 1 wt.% Pd-In/Al$_2$O$_3$ catalyst (Burueva et al., 2018), which is likely associated with a different metal loading. Also, substantially higher enhancements were reported for Pt-Sn intermetallic nanoparticles confined within mesoporous silica (Du et al., 2020). However, it should be stressed that the activity of the Pd, Pd-Ag, and Pd-In catalysts is compared here using the "apparent signal enhancement" values. The catalytic tests were carried out under ALTADENA experiemntal protocol

200 (Pravica and Weitekamp, 1988), implying that hydrogenation reaction proceeds outside a NMR spectrometer, with subsequent delivery of catalytic reactor outflow over a substantial distance to the probe of the NMR spectrometer for detection. Hence, the apparent signal enhancements evaluated for Pd-based catalysts presented in Table 2 are lower estimates of the actual values of initial enhancements, underestimated because hyperpolarization relaxation dramatically reduces the intensities of enhanced ^{1}H NMR signals of propene during the transfer. Also, during the delivery of hyperpolazed products to

205   the NMR probe the polarization is redistributed in the Earth's magnetic field, leading to the observation of polarized signal of the CH_3-group of propene (signal #6), which cannot be polarized directly by pairwise hydrogen addition to propyne. In addition, Figure 1 clearly shows that for both Pd and Pd-Ag catalysts the broad signal at 4.5 ppm (from orthohydrogen) emerges in the ^{1}H NMR spectra, meaning that ortho-para conversion of H_2 takes place on these catalysts. The concrete mechanism of this process and its impact on pairwise hydrogen addition is unclear at present, and further detailed

210   investigation is required. Overall, these and other factors lead to the underestimation of the true selectivity to pairwise H_2 addition over the catalysts studied, which can be rahter significant.

The Pd-In bimetallic catalyst is shown to provide a significantly more pronounced PHIP effect compared to the Pd-Ag system. One potential reason for the inferior behavior of the Pd-Ag catalyst is already mentioned earlier, namely the restructuring of the surface under reactive conditions in the presence of adsorbates such as propyne and H_2. In contrast to

215   Pd-Ag solid solution alloy, Pd-In surface structure is more stable owing to the high formation enthalpy of the Pd-In intermetallic compound, which prevents surface segregation even in the presence of adsorbates.

However, there are potentially other contributing factors. While the Ag/Al_2O_3 catalyst was completely inactive in propyne hydrogenation, this does not mean that hydrogenation cannot proceed on the Ag atoms of the Pd-Ag catalyst. Indeed, the primary reason of the inactivity of metals such as Ag and Au in catalytic hydrogenations is known to be their

220   inability to efficiently activate H_2 due to a large activation energy barrier for dissociative H_2 chemisorption on these metals. In bimetallic catalysts containing Ag or Au in combination with a platinum group metal such as Pd, a new reaction channel becomes available. It involves dissociative and often essentially barrierless chemisorption of H_2 on a Pd atom/cluster followed by spillover of the resulting hydrogen atoms to the other metal (e.g., Ag or Au) which can then efficiently incorporate atomic hydrogen into the hydrogenation product (Hannagan et al., 2020). As hydrogen spillover tends to

225   randomize hydrogen atoms on the catalyst surface, such hydrogenation mechanism cannot achieve pairwise H_2 addition to a substrate. This may be an additional reason why Pd-Ag combination is inferior to Pd-In in the production of HET-PHIP. Furthermore, in addition to the ensemble effects associated with the isolation of individual Pd atoms as catalytically active centers when Pd is diluted with a less active metal, the electronic structure of Pd is altered upon dilution, and this alteration will significantly depend on the electronic (e.g., electron -donating or -withdrawing) properties of the added metal.

230   Importantly, in the current study we show that Pd-containing bimetallic catalysts significantly outperform monometallic Pd catalysts in terms of the achievable NMR signal enhancements in heterogeneous hydrogenations of unsaturated compounds with parahydrogen, while at the same time maintain very high activity as well as hydrogenation selectivity toward semihydrogenation of alkynes. This is in contrast to the behavior of Pt-based catalysts reported earlier (Du et al., 2020), which demonstrated a significant decline in activity upon progressive dilution with Sn, combined with usually

235   lower selectivity of Pt in the hydrogenation of alkynes to alkenes compared to compared to Pd. This is in agreement with the fact that Pd-based catalysts are preferred in industrial hydrogenations to achieve high reaction yields and product selectivities. Furthermore, the results presented above clearly show that the choice of the dilution metal for bimetallic catalysts has a pronounced effect on their efficiency in HET-PHIP. This efficiency is governed by multiple factors, including

possible catalyst surface restructuring under reactive conditions, electronic effects exerted by the secondary metal on the
240 catalytically active component, and involvement of additional reaction pathways such as "metal-ligand cooperation" when
both metals are involved in the hydrogenation event. Further detailed studies are required to establish which factors are the
most relevant, which will eventually provide guidance to achieving the ultimate NMR signal enhancements in HET-PHIP
experiments.
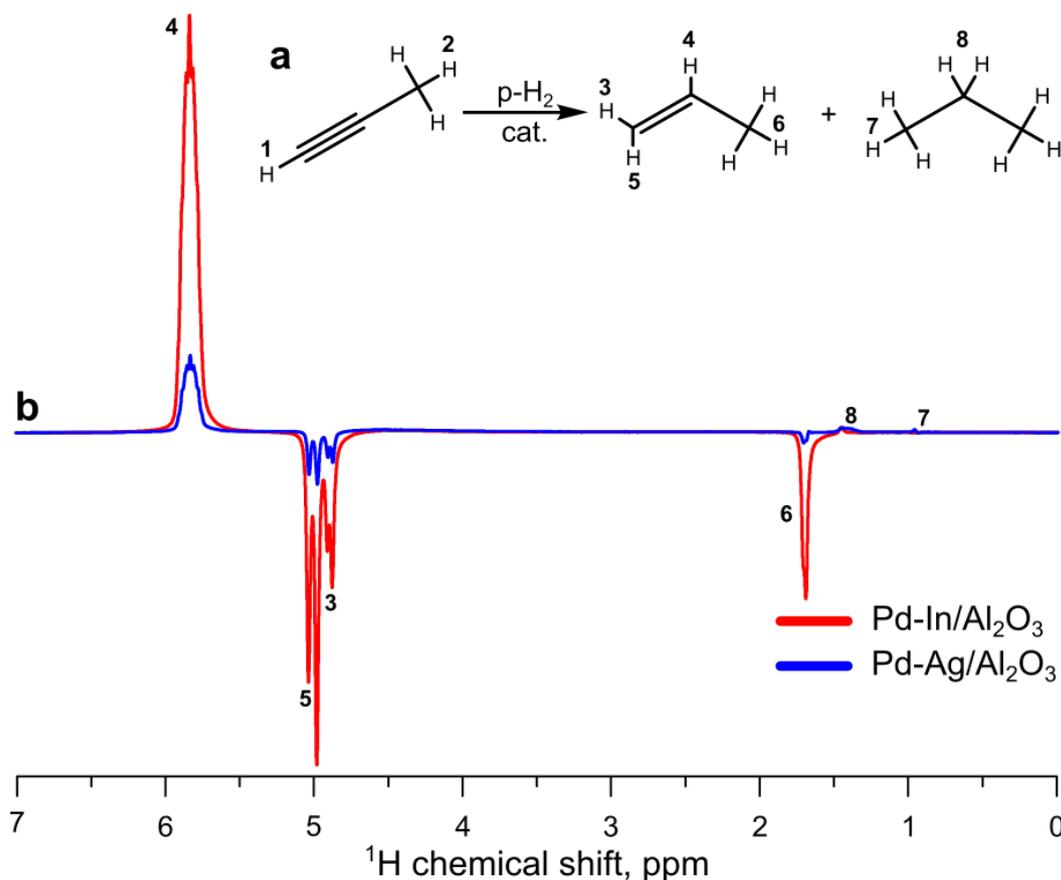
245 **Figure 2: a) Reaction scheme of propyne hydrogenation; b) ^{1}H NMR ALTADENA spectra acquired during propyne hydrogenation with parahydrogen over Pd-In/Al$_2$O$_3$ (red line) or Pd-Ag/Al$_2$O$_3$ (blue line) catalysts. The reaction temperature was 200 °C, the total gas flow rate of 3.8 mL·s^{-1}. All spectra were acquired with 8 signal accumulations and are presented on the same vertical scale.**

4. Conclusions

250 Further progress in the development of parahydrogen-induced polarization in heterogeneous hydrogenation reactions is beneficial for multiple fundamental and practical applications. These include facile production of catalyst-free hyperpolarized liquids and gases (including their continuous production) for numerous purposes including in vivo studies, a possibility to gain deeper insight into the detailed mechanisms of industrially important catalytic processes, enrichment of

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255   nuclear spin isomers of polyatomic gases, and more. All this requires novel advanced strategies for increasing efficiency of heterogeneous catalysts in the pairwise H_2 addition to unsaturated substrates. One such strategy addressed here is the use of heterogeneous bimetallic catalysts in which a more active metal is diluted by a less active one, thereby providing the structure reminiscent of single-metal-atom catalytic centers of homogeneous transition metal complexes. Indeed, it is demonstrated that the high hydrogenation activity of Pd metal is largely retained upon dilution in the Pd-Ag and Pd-In

260   catalysts, while at the same time the selectivity toward pairwise H_2 addition to propyne is measurably enhanced compared to the monometallic Pd system. Furthermore, In is shown to be a better choice compared to Ag as the secondary metal in bimetallic Pd-M compositions, which is likely associated with differences in the tendency toward surface restructuring, the potential involvement of additional non-pairwise reaction channels, and differences in ensemble effects and electronic structures of active centers in the two compositions. While the exact reasons factors that govern pairwise efficiency in bimetallic structures are yet to be fully established, the results demonstrate that further search for more efficient bimetallic

265   catalysts is warranted order to advance this field of research.

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