Heterogeneous Catalysis |Hot Paper|



Single-Atom Gold Catalysis in the Context of Developments in Parahydrogen-Induced Polarization

Avelino Corma,^[b] Oleg G. Salnikov,^[a] Danila A. Barskiy,^[a] Kirill V. Kovtunov,^{*[a]} and Igor V. Koptyug^[a]

Abstract: A highly isolated monoatomic gold catalyst, with single gold atoms dispersed on multiwalled carbon nanotubes (MWCNTs), has been synthesized, characterized, and tested in heterogeneous hydrogenation of 1,3-butadiene and 1-butyne with parahydrogen to maximize the polarization level and the contribution of the pairwise hydrogen addition route. The Au/MWCNTs catalyst was found to be active and efficient in pairwise hydrogen addition and the estimated contributions from the pairwise hydrogen addition route are at least an order of magnitude higher than those for supported metal nanoparticle catalysts. Therefore, the use of the highly isolated monoatomic catalysts is very promising for production of hyperpolarized fluids that can be used for the significant enhancement of NMR signals. A mechanism of 1,3-butadiene hydrogenation with parahydrogen over the highly isolated monoatomic Au/MWCNTs catalyst is also proposed.

The chemical composition and physical structure of a heterogeneous catalyst, along with its ability to catalyze chemical reactions, are among the main objectives for research on supported metal catalysts. The usefulness of heterogeneous catalysts increases with metal dispersion, and the limit of this is the single atom. Therefore, production of heterogeneous catalysts with single-atom dispersions and maximum atom efficiencies is highly important and of great interest. Many experimental and theoretical studies have demonstrated that subnanometer metal particles may provide better activity and selectivity than nanometer-sized particles in heterogeneous catalytic reactions.^[1] It was recently shown that single Pt atoms could be stabilized on a FeO_x-rich surface support due to electron transfer from Pt to FeO_x, with isolated Pt atoms being able to efficiently catalyze CO oxidation.^[2] Moreover, isolated metal atoms

[a]	O. G. Salnikov, D. A. Barskiy, Dr. K. V. Kovtunov, Prof. I. V. Koptyug Laboratory of Magnetic Resonance Microimaging International Tomography Center SB RAS
	Insitutskaya Street, 3 A, 630090, Novosibirsk (Russia)
	and Novosibirsk State University
	2 Pirogova St., Novosibirsk 630090 (Russia)
	Fax: (+7) 383-3331399
	E-mail: kovtunov@tomo.nsc.ru
[b]	Prof. A. Corma
	Instituto de Tecnologia Quimica UPV-CSIC
	Avda. de los Naranjos, s/n, 46022 Valencia (Spain)

Chem. Eur. J. 2015, 21, 7012 – 7015

Wiley Online Library

may be promising candidates for selective heterogeneous hydrogenation catalysis.^[3] For example, isolated Au^{3+} ions supported on ZrO_2 have been shown to be particularly promising candidates for the selective heterogeneous hydrogenation of 1,3-butadiene.^[4]

One of the main practical advantages of single-site heterogeneous catalysts is the possibility to combine the benefits of homogeneous and heterogeneous catalytic processes.^[5] In particular, the separation of products from reactants and the recyclability of the catalysts are the main advantages of heterogeneous catalysis. In homogeneous catalytic hydrogenations, two atoms of the same H₂ molecule often end up in the same product molecule. As a result, when parahydrogen is used in the reaction, such pairwise hydrogen addition can preserve the quantum correlation of its nuclear spins and the NMR signals of the product molecules may exhibit a very strong signal enhancement, termed parahydrogen-induced polarization (PHIP).^[6] Supposing that the chemical properties of heterogeneous highly isolated monoatomic catalysts and of homogeneous catalysts are close and the reaction mechanisms are similar, one could expect to observe PHIP effects in hydrogenations catalyzed by highly isolated monoatomic catalysts.

Nowadays, PHIP is a useful tool for studying homogeneous hydrogenation reactions catalyzed by transition metal complexes.^[7] Significant NMR signal enhancement provided by PHIP allows one to determine the nature of intermediate species and to study reaction kinetics for hydrogenation processes.^[8] The observation of PHIP effects is not limited only to homogeneous processes; it has also been demonstrated for heterogeneous catalytic systems in liquid and gaseous phases.^[9] It was shown that the nature of support, the type of metal and the metal particles size can all affect PHIP intensity.^[10] Importantly, for metal catalysts comprising platinum nanoparticles supported on alumina, the efficiency of pairwise hydrogen addition in the heterogeneous hydrogenation of propene to propane increases with decreasing metal particle size.^[9a, 10a] PHIP has been observed in the gas-phase heterogeneous hydrogenations employing various heterogeneous catalysts including supported Au^{III} Schiff-base complexes,^[11] Rh/chitosan,^[12] and metal nanoparticles embedded in supported ionic liquids.^[13] Herein we report the first observation of PHIP effects in hydrogenation products produced using single gold atoms dispersed on multiwalled carbon nanotubes (MWCNTs) as a catalyst and demonstrate that this highly isolated monoatomic heterogeneous catalyst can accomplish pairwise hydrogen addition to a substrate.



CHEMISTRY A European Journal Communication

Isolated gold atoms and dimers were prepared on functionalized multiwalled carbon nanotubes and detected by highangle annular dark field STEM (HAADF-STEM). The synthesis and characterization procedures were described in detail earlier.^[14] This material was previously used in the aerobic oxidation of thiophenol with O₂. In those studies, under the reaction conditions the initially present single gold atoms were found to aggregate to form clusters of 5–10 gold atoms that were highly active for the above-mentioned reaction.^[14] The original material, containing isolated Au atoms and dimers on MWCNTs, has been used here in the heterogeneous hydrogenation of 1,3-butadiene and 1-butyne.

Initially, the monoatomic Au/MWCNTs catalyst was used in the heterogeneous hydrogenation of 1,3-butadiene. The ¹H NMR spectra for 1,3-butadiene hydrogenation with normal hydrogen (ratio of *ortho/para* isomers = 3:1) and parahydrogen (*ortho/para* = 1:1) over the Au/MWCNTs catalyst are presented in Figure 1. It can be seen that all hydrogenation reaction



Figure 1. Reaction mechanism (a) and ¹H NMR spectra (b,c) recorded during 1,3-butadiene hydrogenation with parahydrogen and normal hydrogen over the monoatomic Au/MWCNTs catalyst.

products (1-butene, 2-butene, and butane) exhibit PHIP effects, indicating that they can be formed via the pairwise hydrogen addition route. To estimate the contribution of the latter to the overall reaction mechanism, 1,3-butadiene was also hydrogenated with normal hydrogen. The results (Figure 1) showed that in this case only the NMR signals of 2-butene were possible to detect.

The percentage of pairwise hydrogen addition was evaluated by calculating the ratio of the signal enhancement observed experimentally and the maximum signal enhancement predicted theoretically if only the pairwise addition of H₂ to a substrate takes place. This procedure was described in detail previously.^[15] In addition, the influence of the NMR line width on the observed signal enhancement was taken into account here, because line broadening may lead to the loss of observable signal intensity for the antiphase PHIP (PASADENA^[6a]) pattern. As a result, the following theoretical maximum enhancement factors were calculated: 437, 539, and 1090 for the CH₃, CH₂, and vinyl CH₂ groups of 1-butene, respectively; 185 and 244 for the CH₃ and CH₂ groups of butane, respectively; 220 for the CH₃ group of 2-butene. The NMR signal of 2-butene in the spectrum detected using normal hydrogen is clearly observable, therefore the ratio of the PHIP-enhanced and equilibrium signals for this product is straightforward to calculate. The percentage of the pairwise hydrogen addition for the formation of 2-butene was thus estimated as 2%. For other products, the exact determination of the percentage of pairwise addition and/or signal enhancement from our data is not possible, because the NMR signals of 1-butene and butane are not observed at all in the NMR spectrum recorded with the use of normal hydrogen. However, an estimate of the minimum value of signal enhancement that would be consistent with the results obtained is still possible. As the NMR signal intensities of these products in the spectrum obtained using normal hydrogen do not exceed the noise level, the observed signal enhancement cannot be smaller than the ratio of the PHIP-enhanced signal to the level of noise. As a result, for 1-butene formed in the hydrogenation of 1,3-butadiene with parahydrogen, the contribution of the pairwise route was estimated to be not less than 6% from the CH₃ group NMR signal and not less than 3% from the CH₂ group signal. Similarly, the percentage of the pairwise hydrogen addition was found to be not less than 11% and 7% from the NMR signals of the CH₃ and CH₂ groups of butane, respectively. It should be noted that the estimated percentage values are the lower limits for the pairwise addition contributions. Indeed, the intensities of the NMR signals of 1-butene and butane in the NMR spectrum recorded with the use of normal hydrogen are smaller than the noise level, so the actual pairwise percentage values can be larger. In addition, polarization losses caused by nuclear spin relaxation can reduce the intensity of the enhanced NMR signals in the spectra detected using parahydrogen, also potentially leading to the underestimation of signal enhancement and the contribution of the pairwise reaction route.^[10e]

We note that when a fluid (in this case, 1,3-butadiene) rapidly flows into an NMR magnet, its NMR signal is initially much lower than its equilibrium value in the high magnetic field. This incomplete equilibration of the nuclear spin magnetization is carried over to all product molecules when 1,3-butadiene is hydrogenated. As a result, the NMR signal intensities of the products may be significantly suppressed and can lead to a significant over-estimation of the signal enhancements obtained. These effects were not taken into account in a recent report on the heterogeneous hydrogenation of propene over ligand-capped platinum nanoparticles.^[16] In the experiments reported herein, an insert filled with charcoal was placed upstream of the reaction region to accelerate the nuclear spin relaxation of 1,3-butadiene before it enters the reaction, and thus to ensure that the NMR signals of 1-butene, 2butene, and butane are in thermal equilibrium in the strong magnetic field, that is, that they are not artificially suppressed.^[17]

It is quite remarkable that strong PHIP signals are observed for 1-butene and butane produced in the heterogeneous hy-

www.chemeurj.org



drogenation of 1,3-butadiene with parahydrogen, whereas no corresponding signals could be discerned in the spectrum obtained when normal H_2 was used. For 2-butene formation, the situation is different. The NMR signal of the CH_3 group of 2butene is unambiguously observed in the spectrum recorded with the use of normal hydrogen. This result means that the contribution of the non-pairwise hydrogen addition route is much larger for 2-butene than for 1-butene and butane formation. Also from the spectrum recorded when using normal hydrogen, it can be seen that the overall conversion of butadiene is low (the estimated value is about 0.5%).

The contributions of the pairwise hydrogen addition to 1,3butadiene were estimated above as 7-11% and 3-6% for butane and 1-butene, respectively. These values for the highly isolated monoatomic catalyst (or small gold cluster that may be formed during the reaction as it was shown earlier^[14]) are higher than those observed for metal nanoparticles supported on various oxides (0.3-1.2%) in the same reaction.^[17] Moreover, the enhancement factor of 21 for the signal of CH₃ group of butane is five times larger than that obtained for the singlesite rhodium immobilized catalyst.^[18] The result obtained here is unique because even in the case of dissociative chemisorption of hydrogen molecules it can be expected that the hydrogen atoms cannot move freely on the catalyst and thus should not lose the nuclear spin correlation if the highly isolated monoatomic catalyst is used. Here, for the first time, these expectations have been verified experimentally.

The single-atom Au/MWCNTs catalyst was also used for the hydrogenation of 1-butyne. The ¹H NMR spectra detected for 1-butyne hydrogenation with parahydrogen and normal hydrogen over the Au/MWCNTs catalyst are presented in Figure 2. In this case, 1-butene was the only reaction product detected. It can be formed via pairwise hydrogen addition, as confirmed by the successful observation of polarized NMR signals in the experiment with parahydrogen.

However, similar to the results obtained in the hydrogenation of 1,3-butadiene, the NMR signals of 1-butene are not observed at all in the spectrum recorded with the use of normal hydrogen. The lower limit for percentage of pairwise hydrogen addition, estimated as explained above, for 1-butene formed in the hydrogenation of 1-butyne with parahydrogen is approximately 2%.

The observation of PHIP effects in hydrogenation reactions heterogeneous over Au/ MWCNTs catalyst allows us to address the reaction mechanism in terms of pairwise hydrogen addition. For 1,3-butadiene hyand drogenation, 1-butene butane are formed to a significant extent via the pairwise route of hydrogen addition, whereas 2-butene is formed mostly via the non-pairwise route. Previously, it was suggested that 2-butene formation



Figure 2. Reaction mechanism (a) and ¹H NMR spectra (b,c) recorded during 1-butyne hydrogenation with parahydrogen and normal hydrogen over the monoatomic Au/MWCNTs catalyst.

in hydrogenation of 1,3-butadiene can proceed via 1-butene isomerization.^[17] Our experimental results confirm this assumption. In the case of the highly isolated monoatomic Au/ MWCNTs catalyst, 1-butene is formed by pairwise hydrogen addition, which isomerizes to the polarized 2-butene, while at the same time the non-polarized 2-butene is formed by direct non-pairwise hydrogen 1,4-addition to 1,3-butadiene. The proposed reaction mechanism for the pairwise hydrogen addition is presented in Scheme 1.

In summary, the hydrogenation of 1,3-butadiene and 1butyne with parahydrogen over single gold atoms and/or possibly small gold clusters that can be formed during the reaction on a heterogeneous Au/MWCNTs catalyst was carried out. The estimated values of pairwise hydrogen addition were at least an order of magnitude higher in the case of hydrogenation of 1,3-butadiene to 1-butene and butane and the hydrogenation of 1-butyne to 1-butene over the highly isolated monoatomic gold catalyst than in the case of supported metal nanoparticle catalysts. Therefore, the use of the highly isolated monoatomic catalysts is very promising for the production of



Scheme 1. Proposed mechanism of 1,3-butadiene hydrogenation with parahydrogen over the monoatomic Au/ MWCNTs catalyst.

www.chemeurj.org



hyperpolarized fluids that can be used for the significant enhancement of NMR signals, and further investigations may increase both the activity and the pairwise-selectivity of these catalysts. The mechanism of 1,3-butadiene hydrogenation over the highly isolated monoatomic Au/MWCNTs catalyst in terms of the pairwise route of hydrogen addition was proposed.

Experimental Section

Commercially available reagents (hydrogen, 1,3-butadiene, 1-butyne) were used. The highly isolated monoatomic catalyst Au/ MWCNTs was prepared by a procedure fully described in a previous report,^[14] starting by wrapping the multiwalled carbon nanotubes with polyallylamine hydrochloride (PAH; 1 mg mL⁻¹) in water at pH 9. After removing excess PAH, MWCNTs were resuspended in water (50 mL) at pH 9, and adequate amounts of an HAuCl₄ aqueous solution and a sodium citrate solution were added (citrate/Au molar ratio = 1700:1). After 3 days of aging at room temperature, citrate ions were removed and the sample dried by lyophilization. The gold content was 0.1 wt%.

¹H NMR spectra were recorded on a 300 MHz Bruker AV 300 NMR spectrometer, with 32 signal averages in the case of 1,3-butadiene and 128 averages in the case of 1-butyne. The catalyst (ca. 0.005 g) was placed in a 10 mm NMR tube positioned inside the magnet bore of the NMR spectrometer and maintained at 130 °C. For PHIP NMR experiments, H₂ was enriched in parahydrogen up to 50% by passing it through FeO(OH) powder (Sigma-Aldrich) maintained at liquid N₂ temperature.^[9a] Four different gas mixtures were used with a 1:4 ratio of the substrate (1,3-butadiene or 1-butyne) to hydrogen (normal or parahydrogen-enriched). The mixture of gases was supplied to the heterogeneous catalyst through a Teflon capillary extended to the bottom of the NMR tube where the catalyst was placed. The reaction was carried out at atmospheric pressure in the high magnetic field of the NMR spectrometer (PASADENA experiment).^[6a] The gas flow rate was 5.1 mL s⁻¹.

All experiments were carried out with a charcoal insert placed upstream of the catalyst to promote the relaxation of nuclear spins of reactants to thermal equilibrium in the strong magnetic field, even at a relatively high velocity of gas flow.^[17]

Acknowledgements

This work was supported by a grant from the Russian Science Foundation (project no. 14–13–00445).

Keywords: gold • heterogeneous catalysis • hydrogenation • NMR spectroscopy • signal enhancement

a) S. Vajda, M. J. Pellin, J. P. Greeley, C. L. Marshall, L. A. Curtiss, G. A. Ballentine, J. W. Elam, S. Catillon-Mucherie, P. C. Redfern, F. Mehmood, P. Zapol, *Nat. Mater.* 2009, *8*, 213–216; b) A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon, G. J. Hutchings, *Science* 2008, *321*, 1331–1335; c) K. Judai, S. Abbet, A. S. Worz, U. Heiz, C. R. Henry, *J. Am. Chem. Soc.* 2004, *126*, 2732–2737; d) Y. Lei, F. Mehmood, S. Lee, J. Greeley, B. Lee, S. Seifert, R. E. Winans, J. W. Elam, R. J. Meyer, P. C. Redfern, D. Teschner, R. Schlögl, M. J. Pellin, L. A. Curtiss, S. Vajda, *Science* 2010, *328*, 224–228.

- [2] B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, Nat. Chem. 2011, 3, 634–641.
- [3] 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. Sykes, *Science* 2012, 335, 1209–1212.
- [4] X. Zhang, H. Shi, B.-Q. Xu, Angew. Chem. Int. Ed. 2005, 44, 7132–7135; Angew. Chem. 2005, 117, 7294–7297.
- [5] J. M. Thomas, R. Raja, D. W. Lewis, Angew. Chem. Int. Ed. 2005, 44, 6456-6482; Angew. Chem. 2005, 117, 6614-6641.
- [6] a) C. R. Bowers, D. P. Weitekamp, J. Am. Chem. Soc. 1987, 109, 5541–5542; b) M. G. Pravica, D. P. Weitekamp, Chem. Phys. Lett. 1988, 145, 255–258; c) T. C. Eisenschmid, R. U. Kirss, P. P. Deutsch, S. I. Hommeltoft, R. Eisenberg, J. Bargon, R. G. Lawler, A. L. Balch, J. Am. Chem. Soc. 1987, 109, 8089–8091.
- [7] a) J. Natterer, J. Bargon, Prog. Nucl. Magn. Reson. Spectrosc. 1997, 31, 293–315; b) S. M. Oldham, J. F. Houlis, C. Sleigh, S. B. Duckett, R. Eisenberg, Organometallics 2000, 19, 2985–2993; c) P. Hübler, R. Giernoth, G. Kümmerle, J. Bargon, J. Am. Chem. Soc. 1999, 121, 5311–5318; d) D. Blazina, S. B. Duckett, J. P. Dunne, C. Godard, Dalton Trans. 2004, 2601–2609; e) T. Trantzschel, J. Bernarding, M. Plaumann, D. Lego, T. Gutmann, T. Ratajczyk, S. Dillenberger, G. Buntkowsky, J. Bargon, U. Bommerich, Phys. Chem. Chem. Phys. 2012, 14, 5601–5604.
- [8] a) S. B. Duckett, R. E. Mewis, Acc. Chem. Res. 2012, 45, 1247–1257;
 b) R. A. Green, R. W. Adams, S. B. Duckett, R. E. Mewis, D. C. Williamson, G. G. R. Green, Prog. Nucl. Magn. Reson. Spectrosc. 2012, 67, 1–48.
- [9] a) K. V. Kovtunov, I. E. Beck, V. I. Bukhtiyarov, I. V. Koptyug, Angew. Chem. Int. Ed. 2008, 47, 1492–1495; Angew. Chem. 2008, 120, 1514–1517; b) A. M. Balu, S. B. Duckett, R. Luque, Dalton Trans. 2009, 5074–5076; c) I. Koptyug, V. Zhivonitko, K. Kovtunov, ChemPhysChem 2010, 11, 3086–3088; d) K. V. Kovtunov, D. A. Barskiy, A. M. Coffey, M. L. Truong, O. G. Salnikov, A. K. Khudorozhkov, E. A. Inozemceva, I. P. Prosvirin, V. I. Bukhtiyarov, K. W. Waddell, E. Y. Chekmenev, I. V. Koptyug, Chem. Eur. J. 2014, 20, 11636–11639; e) K. Kovtunov, M. Truong, D. Barskiy, I. Koptyug, K. Waddell, E. Chekmenev, Chem. Eur. J. 2014, 20, 14629–14632.
- [10] a) V. Zhivonitko, K. Kovtunov, I. Beck, A. Ayupov, V. Bukhtiyarov, I. Koptyug, J. Phys. Chem.C 2011, 115, 13386–13391; b) K. Kovtunov, I. Beck, V. Zhivonitko, D. Barskiy, V. Bukhtiyarov, I. Koptyug, Phys. Chem. Chem. Phys. 2012, 14, 11008–11014; c) O. Salnikov, K. Kovtunov, D. Barskiy, A. Khudorozhkov, E. Inozemtseva, I. Prosvirin, V. Bukhtiyarov, I. Koptyug, ACS Catal. 2014, 4, 2022–2028; d) K. Kovtunov, D. Barskiy, O. Salnikov, A. Khudorozhkov, V. Bukhtiyarov, I. Prosvirin, I. Koptyug, Chem. Commun. 2014, 50, 875–878; e) D. Barskiy, O. Salnikov, K. Kovtunov, I. Koptyug, J. Phys. Chem. A 2015, 119, 996–1006.
- [11] K. V. Kovtunov, V. V. Zhivonitko, L. Kiwi-Minsker, I. V. Koptyug, Chem. Commun. 2010, 46, 5764-5766.
- [12] D. A. Barskiy, K. V. Kovtunov, A. Primo, A. Corma, R. Kaptein, I. V. Koptyug, *ChemCatChem* **2012**, *4*, 2031–2035.
- [13] K. Kovtunov, V. Zhivonitko, A. Corma, I. Koptyug, J. Phys. Chem. Lett. 2010, 1, 1705–1708.
- [14] A. Corma, P. Concepcion, M. Boronat, M. Sabater, J. Navas, M. Yacaman, E. Larios, A. Posadas, M. Lopez-Quintela, D. Buceta, E. Mendoza, G. Guilera, A. Mayoral, *Nat. Chem.* **2013**, *5*, 775–778.
- [15] K. V. Kovtunov, I. V. Koptyug in Magnetic Resonance Microscopy. Spatially Resolved NMR Techniques and Applications (Eds.: S. Codd, J. Seymour), Wiley-VCH, Weinheim, 2008, pp. 101–115.
- [16] R. Sharma, L.-S. Bouchard, Sci. Rep. 2012, 2, 277.
- [17] K. V. Kovtunov, V. V. Zhivonitko, I. V. Skovpin, D. A. Barskiy, I. V. Koptyug, *Top. Curr. Chem.* **2013**, *338*, 123–180.
- [18] S. Abdulhussain, H. Breitzke, T. Ratajczyk, A. Grünberg, M. Srour, D. Arnaut, H. Weidler, U. Kunz, H. J. Kleebe, U. Bommerich, J. Bernarding, T. Gutmann, G. Buntkowsky, *Chem. Eur. J.* 2014, *20*, 1159–1166.

Received: December 29, 2014 Published online on March 6, 2015

www.chemeurj.org