

One-step Synthesis of Core-Gold/Shell-Ceria Nanomaterial and Its Catalysis for Highly Selective Semihydrogenation of Alkynes

Takato Mitsudome,[†] Masaaki Yamamoto,[†] Zen Maeno,[†] Tomoo Mizugaki,[†] Koichiro Jitsukawa,[†] and Kiyotomi Kaneda^{*,†,‡}

[†]Department of Materials Engineering Science, Graduate School of Engineering Science and [‡]Research Center for Solar Energy Chemistry, Osaka University, 1-3, Machikaneyama, Toyonaka, Osaka 560-8531, Japan

S Supporting Information

ABSTRACT: We report a facile synthesis of new core-Au/shell-CeO₂ nanoparticles (Au@CeO₂) using a redox-coprecipitation method, where the Au nanoparticles and the nanoporous shell of CeO₂ are simultaneously formed in one step. The Au@CeO₂ catalyst enables the highly selective semihydrogenation of various alkynes at ambient temperature under additive-free conditions. The core-shell structure plays a crucial role in providing the excellent selectivity for alkenes through the selective dissociation of H₂ in a heterolytic manner by maximizing interfacial sites between the core-Au and the shell-CeO₂.

Metal nanoparticle (NP) catalysts are inevitably employed in refining petroleum, manufacturing petrochemicals and fine chemicals, cleaning exhaust gas, and producing renewable clean energy.¹ Toward more efficient catalysts, the design of metal NPs has become quite sophisticated through controlling the particle sizes and shapes, tuning of electronic states of metals, and modulation of metal-support interactions.² With respect to the metal-support interaction, the supports often play a crucial role in determining the catalytic performance of metal NPs. However, the active perimeter sites at the metal-support interface are a small minority of all metal surface sites, which renders the catalytic activity inadequate. Moreover, the metal-support interaction often weakens during reactions, causing problems of aggregation of active metal species.

The fabrication of core-shell (CS) metal NPs by encapsulation of active metal NPs (core) with a support (shell) is a promising protocol to solve the above metal-support interface issues.^{3,4} The construction of CS NPs entails maximizing the active interfacial area between the core-metal and the shell-support, which would increase the catalytic performance. CS NPs also have a clear advantage in the protection of active metals in the core against aggregation by shell coating. Over the last few decades, CS NP catalysts have been extensively studied. However, the preparation of CS catalysts has become considerably complicated as the design is more precise, often requiring multiple steps⁵ and special techniques.⁶ These elaborate procedures restrict the wide applicability of the CS NPs. Furthermore, core-metal sizes are often relatively large (>10 nm), which is generally not suitable for catalytic applications. A redox-coprecipitation method would be one possibility for the facile synthesis of CS NPs,⁷ where a redox reaction between core and shell precursors allows for the

spontaneous formation of the CS NPs in one step. Advantageously, this straightforward method dispenses with any additional reductants and also provides small NPs suitable for catalytically active metals and the nanoporous shell permitting the diffusion of reactants into the active core-metals.

Here, we report a facile synthesis of new core-Au/shell-CeO₂ NPs (Au@CeO₂) using a redox-coprecipitation method. Au@CeO₂ is composed of Au NPs in the size of sub-10 nm and CeO₂ NPs in a mean diameter of 2 nm, assembling to form the shell structure.^{8,9} Moreover, Au@CeO₂ shows excellent selectivity (near 99% sel.) and high durability for the semihydrogenation of alkynes.

Au@CeO₂ was prepared as follows.¹⁰ Briefly, the reverse micelle solution containing Au(III) and Ce(III) was mixed with NaOH reverse micelle solution under vigorous stirring. During the stirring, the color of the solution became black, indicating the occurrence of the redox reaction between Au(III) with Ce(III) to Au(0) and Ce(IV). The black precipitate was collected by centrifugation and calcined, yielding Au@CeO₂.

A TEM image of Au@CeO₂ shows the formation of spherical CS nanocomposites with diameters of 20 nm (Figure 1a). A representative HAADF-STEM image of Au@CeO₂ revealed a NP in an electron-dense core with an 8.6 nm diameter surrounded by spherical NPs with 2 nm diameters assembling to form the shell (Figure 1b). The lattice spacings of the core and shell NPs were determined to be 2.4 and 3.1 Å (Figure 1b, inset), which were in agreement with the values of Au {111} and CeO₂

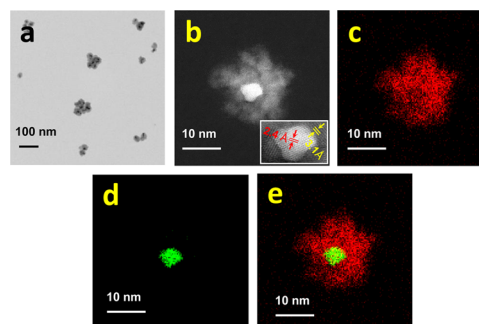


Figure 1. (a) TEM image of Au@CeO₂. (b) HAADF-STEM image of Au@CeO₂ (inset: HRTEM showing the lattice fringes). Elemental mapping images of (c) Ce, (d) Au, and (e) their overlap for Au@CeO₂.

Received: July 18, 2015

Published: October 13, 2015

{111}, respectively. Energy-dispersive X-ray spectroscopy elemental mapping images clearly demonstrated that the Au NP was successfully encapsulated by CeO₂ NPs (Figure 1c–e). The formation of Au(0) and CeO₂ NPs was also supported by XAFS spectroscopy and XRD analyses (Figures S1–S3). The strong interfacial interaction between the core-Au and shell-CeO₂ in Au@CeO₂ derived from its CS structure was confirmed by monitoring the surface plasmon resonance (SPR) absorption of Au NPs (Figure S4).

We next investigated the catalytic potential of Au@CeO₂ in the semihydrogenation of alkynes, which is one of the most important and fundamental reactions in the manufacturing processes of bulk and fine chemicals.¹¹ To date, lead-free environmentally benign semihydrogenation catalyst systems involving Pd,¹² Fe,¹³ Ni,¹⁴ Cu,¹⁵ and Ru¹⁶ metals have been developed as alternatives to the Lindlar catalyst [Pb(OAc)₂-treated Pd/CaCO₃ with large amounts of quinoline].¹⁷ In this context, Au NPs have recently attracted increasing attention due to their high selectivity for alkenes.^{18,19} However, the Au catalyst systems still suffer from limited substrate scope^{18,19b} and the requirements for high temperature,¹⁸ additives,^{19a,d,f} toxic CO reagent,^{19c} and low-atom efficient hydride reagents.^{19a,e,f}

Figure 2a shows the time profile for the hydrogenation of phenylacetylene (1a) using Au@CeO₂ at room temperature (rt)

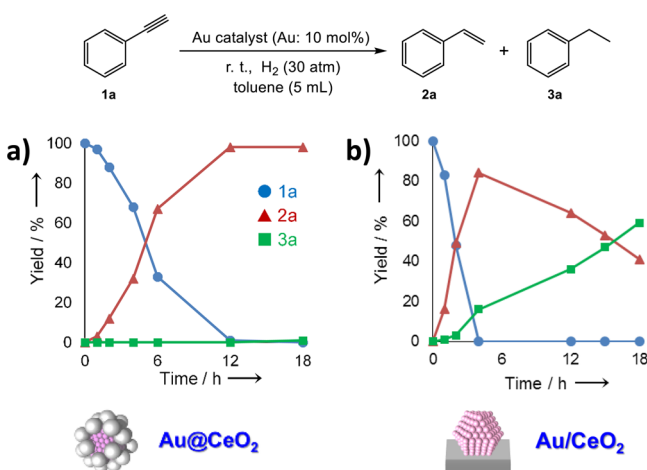
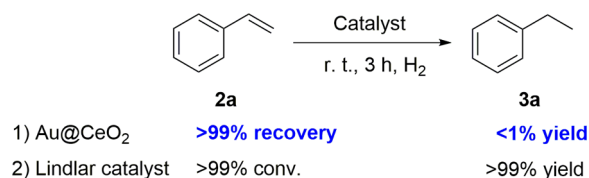


Figure 2. Time course of the hydrogenation of **1a** using (a) Au@CeO₂ and (b) Au/CeO₂.

under 30 atm of H₂. Interestingly, Au@CeO₂ gave styrene (**2a**) in 98% yield with >99% selectivity in 12 h. It is notable that Au@CeO₂ could strictly prevent the overhydrogenation of **2a** and the >99% selectivity for **2a** was maintained even when prolonging the reaction time after full consumption of **1a**. This excellent selectivity is unique and valuable because many conventional catalysts including the Lindlar catalyst cause the rapid overhydrogenation of terminal alkenes into alkanes at a high conversion level, rendering a delicate monitoring of hydrogen-uptake unavoidable. The unique catalysis of Au@CeO₂ was also demonstrated in the hydrogenation of **2a** as a starting material, in which **2a** was not hydrogenated at all and quantitatively recoverable (Scheme 1). In a control experiment, CeO₂-supported Au NPs (Au/CeO₂) having Au NPs similar in size to Au@CeO₂ but without the CS structure were prepared and tested in the hydrogenation of **1a** (Figure 2b). However, Au/CeO₂ resulted in a lower yield of **2a** (84% yield at maximum), which gradually decreased by the overhydrogenation of **2a** to

Scheme 1. Hydrogenation of **2a** Using Au@CeO₂ vs Lindlar Catalyst^a



^aReaction conditions: (1) Au@CeO₂ (Au: 10 mol %), **2a** (0.4 mmol), toluene (5 mL), H₂ (30 atm); (2) Lindlar catalyst (Pd: 0.25 mol %), **2a** (4 mmol), hexane (3 mL), quinoline (0.2 mL), H₂ (1 atm).

ethylbenzene (**3a**). These sharply differing results of Au@CeO₂ vs Au/CeO₂ clearly demonstrate a high catalytic potential of Au@CeO₂ for the semihydrogenation of alkynes derived from its CS structure. This is the first example of Au catalyst for the selective semihydrogenation of alkynes at ambient temperature under additive-free conditions.

Substrate applicability of Au@CeO₂ in the semihydrogenation of alkynes is summarized in Table 1. Aromatic and aliphatic terminal alkynes were transformed into the corresponding alkenes with >99% selectivities at high conversions (Table 1, entries 1, 3–13). Various internal alkynes also gave the alkenes selectively (Table 1, entries 14–17). Reducible moieties including halogeno, methoxy, benzyl, cyano, hydroxyl, and ester groups were not affected in the reaction (Table 1, entries 3–5, 8, and 12–17).

The power of Au@CeO₂ is further demonstrated in the hydrogenation of alkenes with an alkyne moiety as shown in Scheme 2. The selective semihydrogenation of terminal and internal alkyne underwent, whereas alkene moieties in the parent and product molecules were completely intact. Furthermore, Au@CeO₂ was easily recovered after the hydrogenation and reusable without loss of its high efficiency (Table 1, entry 2). Au species in the filtrate were not detected by ICP analysis and no aggregation of Au NPs in the used Au@CeO₂ was observed by TEM images, proving the high durability of Au@CeO₂ (Figure S5).

In order to gain more insight into the origins of the high selectivity of Au@CeO₂ for alkenes, the following experiments were carried out. The investigation of the dependency of the reaction rate on the H₂ pressure in the semihydrogenation of **1a** revealed that the reaction order was first order (Figure 3a), indicating the participation of active polar hydrogen species generated by the dissociation of H₂.²⁰ In a separate experiment using **1m** with an electron-withdrawing substituent (–CF₃) for the hydrogenation, a strong inductive effect on the increase of the reaction rate was observed in the presence of Au@CeO₂ (Figure 3b).²¹ This phenomenon was quite different from the results obtained by Lindlar catalyst, which favored the hydrogenation of 1-phenyl-1-propyne (**1t**) over **1m**.

These results clearly demonstrate that the unique and highly chemoselective catalysis of Au@CeO₂ in the semihydrogenation can arise from in situ formation of a polar hydrogen species through the heterolytic dissociation of H₂. This idea is well supported by the use of 2-propanol as a reductant instead of H₂.²² Au@CeO₂ also showed excellent selectivity toward **2a** in the hydrogenation of **1a** (Scheme 3). In our previous reports, Au or Ag NPs and basic metal oxides can cooperatively dissociate H₂ into polar hydrogen species H^{δ+} and H^{δ-} that straddle the interfacial perimeter sites.^{7c,d,23} It is also reported that polar hydrogen species are favorably reactive to alkynes compared with

Table 1. Selective Semihydrogenation of Various Alkynes to Alkenes Using Au@CeO₂^a

$$\text{R}^1\text{-C}\equiv\text{C-R}^2 \xrightarrow[\text{toluene (5 mL), r. t., H}_2]{\text{Au@CeO}_2} \text{R}^1\text{-C=C-R}^2$$

1 2

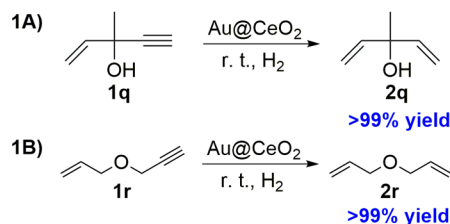
Entry	Substrate	Time [h]	Conv. [%] ^b	Yield [%] ^b
1		12	99	98
2 ^c		12	98	97
3		10	96	96
4 ^d		33	>99	99
5		27	90	89
6		24	>99	>99
7 ^e		45	>99	99
8 ^f		24	95	95
9		24	>99	99
10 ^e		24	96	95
11 ^e		24	72	72
12 ^e		20	98	97
13 ^e		7	>99	>99
14 ^e		18	>99	>99 (>99/<1)
15 ^e		24	>99	>99 (99/1)
16 ^e		20	>99	>99 (>99/<1)
17 ^e		15	93	93 (93/<1)

^aReaction conditions: Au@CeO₂ (Au: 10 mol %), substrate (0.4 mmol), toluene (5 mL), rt, H₂ (30 atm). ^bDetermined by GC using internal standard technique. Values in parentheses are Z/E ratios. ^cReuse. ^dAu: 8 mol %, H₂ (25 atm). ^eAu: 16 mol % H₂ (50 atm). ^fAu: 24 mol %, H₂ (50 atm).

alkenes due to the electrophilicity of alkynes.²⁴ These facts indicate that the excellent selectivity of Au@CeO₂ for alkenes is derived from the selective formation of polar hydrogen species from the heterolytic dissociation of H₂ at the interface between Au and a basic site of CeO₂. The superior selectivity of Au@CeO₂ for alkenes compared with Au/CeO₂ can lie in the CS

Scheme 2. Hydrogenation of Alkynes with Alkene Moieties Using Au@CeO₂. Reaction conditions: 1) Au@CeO₂ (Au: 16 mol %), substrate (0.25 mmol), toluene (5 mL), rt, H₂ (30 atm), 1A) 10 h, 1B) Au: 10 mol %, 30 h, 2) 32 h

1) terminal alkyne vs. terminal alkene



2) internal alkyne vs. terminal alkene

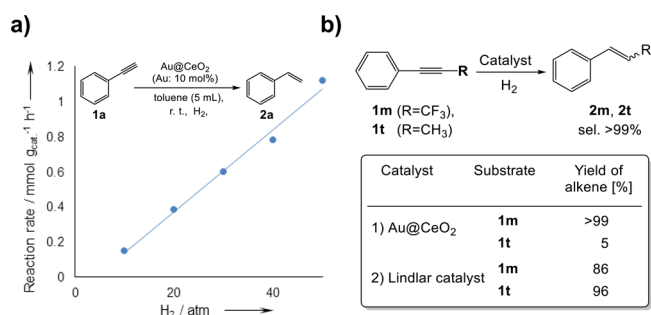
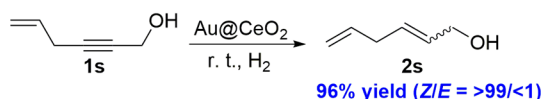
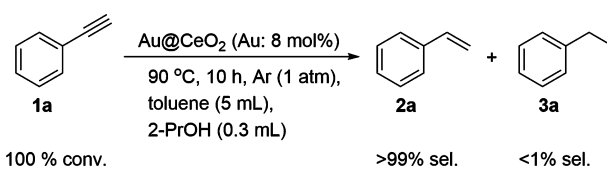


Figure 3. (a) Dependency of the reaction rate on the pressure of H₂. **(b)** Hydrogenation of **1m** and **1t** using (1) Au@CeO₂ or (2) Lindlar catalyst. Reaction conditions: (1) Au@CeO₂ (Au: 16 mol %), substrate (0.25 mmol), toluene (5 mL), rt, H₂ (50 atm), 18 h; (2) Lindlar catalyst (Pd: 0.25 mol %), substrate (4 mmol), hexane (3 mL), quinoline (0.2 mL), rt, H₂ (1 atm), 6 h.

Scheme 3. Semihydrogenation of 1a Using 2-Propanol as a Reductant



structure, which maximizes the Au-CeO₂ interfacial active sites. Concurrently, the CS structure minimizes the exposed surface Au sites. These exposed sites induce the homolytic cleavage of H₂ into nonpolar hydrogen species, resulting in the overhydrogenation of alkenes. Therefore, both maximizing the CS interfacial sites and minimizing exposed surface sites of Au NPs lead to the selective dissociation of H₂ into polar hydrogen species which favor alkynes, thus achieving the highly selective semihydrogenation of alkynes.

In conclusion, we demonstrated a facile synthesis of CS nanocomposite Au@CeO₂ through the spontaneous redox reaction between Au and Ce. Au@CeO₂ acts as an efficient and reusable heterogeneous catalyst for the highly selective semihydrogenation of various alkynes with H₂ at ambient temperature. The CS structure of Au@CeO₂ can effectively exploit the interfacial cooperative catalysis between Au and CeO₂ for the selective dissociation of H₂ in a heterolytic manner by

maximizing interfacial sites between the core-Au and the shell-CeO₂, which provides an excellent selectivity for alkenes. This report demonstrates for the first time a key role of the heterolytic dissociation of H₂ in the Au NP-catalyzed selective semi-hydrogenation.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07521.

Experimental details and characterization of catalysts (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*kaneda@cheng.es.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI grant nos. 26289303, 26630410, 26105003, and 24246129. This work was also supported by the Program for Creating Future Wisdom, Osaka University, selected in 2014. We thank Dr. Uruga, Dr. Nitta, and Dr. Ina (SPring-8) for XAFS measurements. The TEM experiments were carried out at a facility of the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

■ REFERENCES

- (1) (a) Hagen, J. *Industrial Catalysis: A Practical Approach*; Wiley-VCH: Weinheim, 1999. (b) Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J. *Handbook of Heterogeneous Catalysis*, 2nd ed.; Wiley-VCH: Weinheim, 2008. (c) Astruc, D. *Nanoparticles and Catalysis*; Wiley-VCH: Weinheim, 2008.
- (2) (a) Tauster, S. J.; Fung, S. C.; Baker, R. T.; Horsley, J. A. *Science* **1981**, *211*, 1121. (b) Schubert, M. M.; Hackenberg, S.; van Veen, A. C.; Muhler, M.; Plzak, V.; Behm, R. J. *J. Catal.* **2001**, *197*, 113. (c) Bell, A. T. *Science* **2003**, *299*, 1688. (d) Tian, N.; Zhou, Z.-Y.; Sun, S.-G.; Ding, Y.; Wang, Z. L. *Science* **2007**, *316*, 732. (e) Somorjai, G. A.; Park, J. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 9212.
- (3) (a) Aiken, J. D.; Finke, R. G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 1. (b) Zhong, C.; Maye, M. *Adv. Mater.* **2001**, *13*, 1507. (c) Li, G.; Tang, Z. *Nanoscale* **2014**, *6*, 3995.
- (4) (a) Alayoglu, S.; Nilekar, A. U.; Mavrikakis, M.; Eichhorn, B. *Nat. Mater.* **2008**, *7*, 333. (b) Joo, S. H.; Park, J. Y.; Tsung, C.-K.; Yamada, Y.; Yang, P.; Somorjai, G. A. *Nat. Mater.* **2009**, *8*, 126. (c) Mazumder, V.; Chi, M.; More, K. L.; Sun, S. *J. Am. Chem. Soc.* **2010**, *132*, 7848.
- (5) (a) Cargnello, M.; Wieder, N. L.; Montini, T.; Gorte, R. J.; Fornasiero, P. *J. Am. Chem. Soc.* **2010**, *132*, 1402. (b) Zhou, H.-P.; Wu, H.-S.; Shen, J.; Yin, A.-X.; Sun, L.-D.; Yan, C.-H. *J. Am. Chem. Soc.* **2010**, *132*, 4998.
- (6) (a) Dravid, V. P.; Host, J. J.; Teng, M. H.; Hwang, B. E. J.; Johnson, D. L.; Mason, T. O.; Weertman, J. R. *Nature* **1995**, *374*, 602. (b) Lu, J. F.; Kung, B. M. C.; Xiao, G.; Elam, J. W.; Kung, H. H.; Stair, P. C. *Science* **2012**, *335*, 1205.
- (7) (a) Yeung, C. M. Y.; Yu, K. M. K.; Fu, Q. J.; Thompsett, D.; Petch, M. I.; Tsang, S. C. *J. Am. Chem. Soc.* **2005**, *127*, 18010. (b) Kayama, T.; Yamazaki, K.; Shinjoh, H. *J. Am. Chem. Soc.* **2010**, *132*, 13154. (c) Mitsudome, T.; Mikami, Y.; Matoba, M.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 136. (d) Mitsudome, T.; Matoba, M.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Chem. - Eur. J.* **2013**, *19*, 5255.
- (8) For previous methods for the synthesis of Au@CeO₂ in multistep processes, see: (a) Cargnello, M.; Gentilini, C.; Montini, T.; Fonda, E.;

Mehraeen, S.; Chi, M.; Herrera-Collado, M.; Browning, N. D.; Polizzi, S.; Pasquato, L.; Fornasiero, P. *Chem. Mater.* **2010**, *22*, 4335. (b) Zhu, F.; Chen, G.; Sun, S.; Sun, X. *J. Mater. Chem. A* **2013**, *1*, 288. (c) Wei, Y.; Zhao, Z.; Yu, X.; Jin, B.; Liu, J.; Xu, C.; Duan, A.; Jiang, G.; Ma, S. *Catal. Sci. Technol.* **2013**, *3*, 2958. (d) Li, B.; Gu, T.; Ming, T.; Wang, J.; Wang, P.; Yu, J. *ACS Nano* **2014**, *8*, 8152.

(9) There is only one report on the one-step synthesis of Au@CeO₂ for CO oxidation with a mean diameter of 17 nm of Au NPs in the core and a CeO₂ shell with 100 nm thickness, see: Qi, J.; Chen, J.; Li, G.; Li, S.; Gao, Y.; Tang, Z. *Energy Environ. Sci.* **2012**, *5*, 8937. However, the Au@CeO₂ material did not show any catalytic activity for the semi-hydrogenation of **1a**, see Supporting Information.

(10) See Supporting Information for details.

(11) (a) Derrien, M. L. *Catalytic Hydrogenation; Studies in Surface Science and Catalysis*; L. Červený, Ed.; Elsevier: Amsterdam, 1986; Vol. 27, p 613. (b) Piringer, O. G.; Baner, A. L. *Plastic Packaging: Interactions with Food and Pharmaceuticals*, 2nd ed., Wiley-VCH: Weinheim, 2008.

(12) For examples of Pd-catalyzed semihydrogenation of alkynes, see: (a) van Laren, M. W.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3715. (b) Yabe, Y.; Yamada, T.; Nagata, S.; Sawama, Y.; Monguchi, Y.; Sajiki, H. *Adv. Synth. Catal.* **2012**, *354*, 1264. (c) Mitsudome, T.; Takahashi, Y.; Ichikawa, S.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 1481.

(13) (a) Armbrüster, M.; Kovnir, K.; Friedrich, M.; Teschner, D.; Wowsnick, G.; Hahne, M.; Gille, P.; Szentmiklósi, L.; Feuerbacher, M.; Heggen, M.; Girgsdies, F.; Rosenthal, D.; Schlögl, R.; Grin, Yu. *Nat. Mater.* **2012**, *11*, 690. (b) Torres Galvis, H. M.; Bitter, J. H.; Khare, C. B.; Ruitenbeek, M.; Dugulan, A. I.; de Jong, K. P. *Science* **2012**, *335*, 835.

(14) (a) Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553. (b) Studt, F.; Abild-Pedersen, F.; Bligaard, T.; Sørensen, R. Z.; Christensen, C. H.; Nørskov, J. K. *Science* **2008**, *320*, 1320. (c) Carenco, S.; Leyva-Pérez, A.; Concepción, P.; Boissière, C.; Mézailles, N.; Sanchez, C.; Corma, A. *Nano Today* **2012**, *7*, 21.

(15) Semba, K.; Fujihara, T.; Xu, T.; Terao, J.; Tsuji, Y. *Adv. Synth. Catal.* **2012**, *354*, 1542.

(16) Niu, M.; Wang, Y.; Li, W.; Jiang, J.; Jin, Z. *Catal. Commun.* **2013**, *38*, 77.

(17) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446.

(18) For gas-phase semihydrogenation of alkynes using gold catalysts, see: (a) Bond, G.; Sermon, P. *J. Chem. Soc., Chem. Commun.* **1973**, 444. (b) Jia, J.; Haraki, K.; Kondo, J. N.; Domen, K.; Tamaru, K. *J. Phys. Chem. B* **2000**, *104*, 11153. (c) Azizi, Y.; Petit, C.; Pitchon, V. *J. Catal.* **2008**, *256*, 338.

(19) (a) Yan, M.; Jin, T.; Ishikawa, Y.; Minato, T.; Fujita, T.; Chen, L.-Y.; Bao, M.; Asao, N.; Chen, M.-W.; Yamamoto, Y. *J. Am. Chem. Soc.* **2012**, *134*, 17536. (b) Shao, L.; Huang, X.; Teschner, D.; Zhang, W. *ACS Catal.* **2014**, *4*, 2369. (c) Li, S.-S.; Liu, X.; Liu, Y.-M.; He, H.-Y.; Fan, K.-N.; Cao, Y. *Chem. Commun.* **2014**, *50*, 5626. (d) Li, G.; Jin, R. *J. Am. Chem. Soc.* **2014**, *136*, 11347. (e) Vasilikogiannaki, E.; Titilas, I.; Vassilikogiannakis, G.; Stratakis, M. *Chem. Commun.* **2015**, *51*, 2384. (f) Wagh, Y. S.; Asao, N. *J. Org. Chem.* **2015**, *80*, 847.

(20) Kluwer, A. M.; Koblenz, T. S.; Jonischkeit, T. T.; Woelk, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 15470.

(21) Polar hydrogen species preferentially react with alkynes with electron-withdrawing substituents compared to alkynes without the substituents, see: Vianello, R.; Peran, N.; Maksić, Z. B. *J. Phys. Chem. A* **2006**, *110*, 12870.

(22) Mitsudome, T.; Noujima, A.; Mikami, Y.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5545.

(23) Noujima, A.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 2986.

(24) For electrophilicity of alkynes, see: (a) Miller, S. I. *J. Org. Chem.* **1956**, *21*, 247. (b) Dale, J. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1969. (c) Yu, J.; Spencer, J. B. *J. Org. Chem.* **1997**, *62*, 8618.