Synthesis of Single Atom Based Heterogeneous Platinum Catalysts: High Selectivity and Activity for Hydrosilylation Reactions

Xinjiang Cui,† Kathrin Junge,† Xingchao Dai‡, Carsten Kreyenschulte,† Marga-Martina Pohl,† Sebastian Wohlrab,† Feng Shi,‡ Angelika Brückner,‡ and Matthias Beller§,†

†Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Straße 29a, Rostock, 18059, Germany
‡State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No. 18, Tianshui Middle Road, Lanzhou, 730000, China

Supporting Information

ABSTRACT: Catalytic hydrosilylation represents a straightforward and atom-efficient methodology for the creation of C–Si bonds. In general, the application of homogeneous platinum complexes prevails in industry and academia. Herein, we describe the first heterogeneous single atom catalysts (SACs), which are conveniently prepared by decorating alumina nanorods with platinum atoms. The resulting stable material efficiently catalyzes hydrosilylation of industrially relevant olefins with high TON (≥105). A variety of substrates is selectively hydrosilylated including compounds with sensitive reducible and other functional groups (N, B, F, Cl). The single atom based catalyst shows significantly higher activity compared to related Pt nanoparticles.

Olefins hydrosilylation is an important process to form alkylsilanes by catalytic addition of Si–H bonds to olefins.1,2 The resulting products find widespread application in the manufacture of silicone-based aerogels, surfactants, release coatings, lubricants, and adhesives.3,4 Furthermore, organosilicon compounds are of interest for the design of novel catalysts, defense materials and life science products. In general, catalytic hydrosilylations are performed using molecularly defined (pre)catalysts containing mainly Pt,5,6 but also Ru,7,8 Pd,9 and Rh.10,11 In fact, some of these reactions constitute the largest-scale examples of homogeneous catalysis with noble metals. Nowadays, platinum-based complexes such as Speier’s6 and Karstedt’s catalysts formed by reaction of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with chloroplatinic acid and PtCl2(cyclooctadiene) are the most extensively used industrial catalysts, despite the cost of the precious metal. A disadvantage of these platinum catalysts in some applications is that they are trapped in the product and cannot be easily recovered due to the viscous morphology of them. Notably, catalyst costs might account for up to 30% of the cost of silicones.12

Hence, the development of less expensive catalysts is an important and ongoing goal for industrial and academic researchers. Apart from new developments based on common hydrosilylation metals,13,14 in recent years the use of non-noble metals attracted significant interest. In this respect, Chirik and co-workers15 showed that well-defined iron complexes are highly active for the selective anti-Markovnikov addition of silanes to alkenes under mild conditions. Since the original report in 2012, a series of catalysts based on Fe,15−17 Co,12,17−20 Ni,21−23 and B24 were successfully explored in hydrosilylation reactions.

An alternative approach to overcome the drawbacks (vide supra) is the development of highly active supported catalysts. However, most of the known heterogeneous materials are rather inactive. For example, Béland and Pagliaro35 reported small Pt(0) nanoparticles (4−6 nm) encapsulated in a sol−gel derived porous matrix of methyltriethoxysilane for the hydrosilylation of different olefins with triethoxysilane in the presence of 1 mol % catalyst. Simple PtO2 was studied in the hydrosilylation of heptamethyltrisiloxane with n-octene, which revealed that initially Pt(IV) is reduced during the reaction to form the active sites.26 So far, only a silica-supported Karstedt Pt-type catalyst and crystalline Pt nanoparticles embedded into the walls of a mesostructured silica framework showed high catalytic activity on this reaction.27,28 Thus, to the best of our knowledge general heterogeneous Pt-based catalysts with broad substrate scope, high regioselectivity, and high activity comparable to homogeneous systems do not exist.

Recently, heterogeneous catalysts with atomically dispersed active sites were developed as model systems to understand as well as to design such materials at the molecular level and build a bridge between the catalysis subdisciplines.1,2,27,29 In addition to recycling advantages for liquid products, such heterogeneous single atom catalysts (SACs) may display improved activity and selectivity compared to catalysts containing bulk metal or metal nanoparticles. Indeed, SACs based on Pt,34,30−34 Pd,37,38 Ir,39 Rh,40 Co,41−43 and Fe44 were presented in the past 5 years and displayed interesting activity, e.g., in hydrogenations and CO
oxidation. Inspired by these works, we were curious if reducing the size of Pt nanoparticles to single atoms would create improved catalysts for alkene hydrosilylation chemistry. Herein, we present the first heterogeneous SAC for the selective hydrosilylation of all kinds of terminal olefins and show that supported Pt on the surface of specific aluminum oxide nanorods exhibits excellent activity.

To design SACs, it is crucial to select a support which allows creation of defined metal sites on the surface and inhibits the aggregation of the metal atoms toward nanoparticles. In this context, the use of an oxidic support is preferred due to the stronger interaction of unsaturated surface centers with the isolated metal species. Indeed, it has been demonstrated that ZnO, Fe₂O₃, Al₂O₃, and TiO₂ stabilize single noble metal atoms. For our initial catalyst preparation, Al₂O₃ nanorods (NR-Al₂O₃) were selected as carrier because of their high surface area ($S_{BET} = 330 \text{ m}^2/\text{g}$) and controlled pore size ($\approx 12 \text{ nm}$). Deposition of Pt (270 ppm, measured by ICP-AES) onto this support was performed by two different methods, namely, reductive precipitation (RP) and impregnation (IP) (see the Supporting Information).

Figure 1. HRSTEM images of Pt/NR-Al₂O₃-IP (A), Pt LIII edge XANES for Pt/NR-Al₂O₃-IP (B), and k³-weighted Fourier transform of Pt LIII edge EXAFS for Pt/NR-Al₂O₃-IP (C).

When impregnation (IP) was used to deposit Pt on NR-Al₂O₃, TEM images of the resulting material (Pt/NR-Al₂O₃-IP) showed the rodlike morphology of the NR-Al₂O₃ support (Figure S1) and single Pt atoms (white dots in Figure 1A), which are formed exclusively. For comparison, reductive precipitation using NaBH₄ led to the formation of uniform Pt nanoparticles (NPs) of 2−5 nm on NR-Al₂O₃ (Figures S2 and S3). The valence state and environment of Pt were analyzed by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy at the Pt LIII edge. The white line peak of fresh Pt/NR-Al₂O₃-IP in the XANES spectrum is similar to the PtO₂ reference (Figure 1B), indicating the presence of oxidic platinum centers.

To further verify that Pt was dispersed atomically on the support, EXAFS spectra were recorded (Figure 1C and Table S2). The strong peak between 1 and 2 Å is due to a Pt−O shell. No peak in the region of 2−3 Å, which is characteristic for a Pt−Pt shell, is observed, thus confirming the presence of isolated Pt atoms only. The Pt−O coordination number in Pt/NR-Al₂O₃-IP was $\approx 5.0$ considering the fitting error of EXAFS analysis (ca. 20%).

To evaluate the activity of the prepared single atom Pt catalyst and related materials, the hydrosilylation reaction of 1-octene and diethoxymethylsilane under solvent free conditions was chosen as a benchmark test. Obviously, Al₂O₃ nanorods were not active in this reaction (Table 1, entry 1). Platinum nanoparticles (Pt/NR-Al₂O₃-RP catalysts prepared by the reductive precipitation) showed low activity (entry 2). In contrast, the single atom platinum catalyst (SAC) prepared by the impregnation precipitation method showed under optimal conditions high activity achieving the desired product (3a) in 95% yield with $2.06 \times 10^5 \text{ TON}$ (TON = turnover number, moles of product per mole of catalyst; entries 3 and 4). The benchmark reaction occurred with high anti-Markovnikov selectivity and low alkene isomerization compared with previously reported heterogeneous and homogeneous platinum catalysts. Notably, a commercial Pt/Al₂O₃ catalyst showed no activity at all (entry...
7). Meanwhile, the material prepared using commercial Al2O3 instead of Al2O3 nanorods showed significantly lower activity (entry 8). Platinum immobilized on SiO2, CeO2, carbon black (Vulcan XC72), MnO, and ZnO2 formed catalysts, which gave the desired product in no or only low yields (0–26%; entries 9–13). TEM images for Pt/CeO2-IP, Pt/SiO2-IP, and Pt/C showed the formation of Pt nanoparticles on the surface of these materials. These results clearly indicate that the NR-Al2O3 plays a crucial role for the formation of single platinum sites with high activity for the hydrosilylation process. Notably, in terms of activity our Pt/NR-Al2O3-IP is at least comparable to homogeneous state-of-the-art catalysts such as H2PtCl6 and Karstedt’s system (entries 14 and 15).

Next, we investigated the stability and recyclability of selected catalysts, which are important factors for potential applications in industrial processes. For this purpose, we compared the Pt-SAC and supported Pt-NPss, which both were recycled by centrifugation and reused six times without any reactivation. Gratifyingly, when Pt/NR-Al2O3-IP was used after the sixth recycling, still 92% yield (total TONs of 1.18×105) was achieved (Figure 3). In contrast, a significantly lower activity was observed in the presence of Pt/NR-Al2O3-RP, where almost no product was obtained after the third recycling. These results demonstrate the higher activity of Pt-SAC—which can be anticipated due to the better dispersion of active catalyst centers—compared to Pt nanoparticles. However, contrary to expectations, the former catalyst also showed an improved stability at least on a shorter time scale.

To prove the stability of the SAC, a sample of the recycled material (after 6 runs) was characterized by STEM, XANES, and EXAFS and compared to the fresh one. As shown in Figure 2, no significant differences were observed. For example, the Pt–O coordination number in fresh Pt/NR-Al2O3-IP was approximately 5.0 and did not change much after catalysis (Table S2). Hence, we conclude that single Pt atoms on NR-Al2O3 are stable during the hydrosilylation reactions.

To demonstrate the general synthetic applicability of this single atom catalyst, we explored the hydrosilylation of 1-octene with a variety of tertiary silanes. In all cases we used the active platinum in neat olefin and obtained excellent to quantitative yields of the desired linear products. Hence, hydrosilylations with dimethylphenylsilane (1b) as well as multimiscellaneous containing compounds proceeded smoothly (Table 2). Reaction with 1c is of special interest because the hydrosilylated products have been widely applied in both inorganic chemistry and organic syntheses. In addition, hydrosilylations of the benchmark alkene with silanes containing two Si–H bonds were accomplished, and again, excellent yields were obtained using 1d−1g as starting materials (entries 4–7). In all cases, no side products were observed and the single atom Pt possessed catalytic performance with high turnover numbers.

Furthermore, we tested the hydrosilylation of diverse alkenes using the Pt-SAC. Simple linear and branched aliphatic olefins gave very good yields of the corresponding silylated products (Table 3, entries 1 and 2). More challenging and sensitive oxygen-containing allylic compounds, such as cyclohexyl vinyl

### Table 1. Hydrosilylation of 1-Octene in the Presence of Different Pt Catalysts

| entry | catalyst | time (h) | yield (%) | TON (10^3) | TOF (10^4 h⁻¹) |
|-------|----------|----------|-----------|------------|----------------|
| 1     | NR-Al2O3 | 2        | 0         | 0          | 0              |
| 2     | Pt/NR-Al2O3-IP | 2 | 33       | 7.1        | 3.6            |
| 3     | Pt/NR-Al2O3-IP | 2 | 95       | 20.6       | 10.3           |
| 4     | Pt/NR-Al2O3-IP | 2 | 73       | 31.6       | 15.5           |
| 5     | Pt/NR-Al2O3-IP | 2 | 40       | 8.7        | 4.3            |
| 6     | Pt/NR-Al2O3-IP | 1 | 41       | 8.9        | 4.5            |
| 7     | Pt/Al2O3 | 2 | 0        | 0          | 0              |
| 8     | Pt/Al2O3 | 2 | 57       | 12.2       | 6.1            |
| 9     | Pt/Al2O3 | 2 | 6        | 1.3        | 0.7            |
| 10    | Pt/SiO2-IP | 2 | 26       | 5.6        | 2.8            |
| 11    | Pt/C-IP | 2 | 6        | 2.6        | 1.3            |
| 12    | Pt/MnO-IP | 2 | 0        | 0          | 0              |
| 13    | Pt/ZnO2-IP | 2 | 0        | 0          | 0              |
| 14    | H2PtCl6 | 2 | 46       | 10         | 5.0            |
| 15    | Karstedt catalyst | 2 | 96       | 20.6       | 10.3           |

*Reaction conditions: 3 mmol of olefin, 3 mmol of silane, 2 h, N2 (10 bar), 100 °C, isolated yields. IP = impregnation precipitation.  
°Calculated for the total Pt content.  
1Reaction conditions: 3 mmol of olefin, 3 mmol of silane, 2 h, N2 (10 bar), 100 °C, isolated yields. IP = impregnation precipitation.  
2Commercial Pt/C (Vulcan XC72), MnO, and ZnO2 formed catalysts, which gave the desired product in no or only low yields (0–26%; entries 9–13). TEM images for Pt/CeO2-IP, Pt/SiO2-IP, and Pt/C showed the formation of Pt nanoparticles on the surface of these materials. These results clearly indicate that the NR-Al2O3 plays a crucial role for the formation of single platinum sites with high activity for the hydrosilylation process. Notably, in terms of activity our Pt/NR-Al2O3-IP is at least comparable to homogeneous state-of-the-art catalysts such as H2PtCl6 and Karstedt’s system (entries 14 and 15).

### Table 2. Single Atom Pt Catalyzed Selective Hydrosilylation of 1-Octene with Various Tertiary Silanes

| entry | substrate | T (°C) | yield (%) | TON (10^3) |
|-------|-----------|--------|-----------|------------|
| 1     | Me(EO)2SiH (1a) | 100  | 95        | 2.06       |
| 2     | PhMeSiH (1b) | 120  | 94        | 2.04       |
| 3     | HSi(Me)2OSi(Me)2 (1c) | 100  | 95        | 2.06       |
| 4     | HSi(Me)2O(Me)SiH (1d) | 100  | 94        | 1.36       |
| 5     | HSi(OMe)2OSi(OMe)2SiH (1e) | 120  | 93        | 1.35       |
| 6     | HSi(Me)NH(Me)SiH (1f) | 120  | 92        | 1.33       |
| 7     | TDMSS (1g) | 120  | 96        | 0.70       |

*Reaction conditions: 3 mmol of 1-octene, 3 mmol of silane, 2 h, 10 mg of Pt/NR-Al2O3-IP, N2 (10 bar), isolated yields. TON = mol product/mol Pt.  
Discussion of the results is provided in the main text.  
7). Meanwhile, the material prepared using commercial Al2O3 instead of Al2O3 nanorods showed significantly lower activity (entry 8). Platinum immobilized on SiO2, CeO2, carbon black (Vulcan XC72), MnO, and ZnO2 formed catalysts, which gave the desired product in no or only low yields (0–26%; entries 9–13). TEM images for Pt/CeO2-IP, Pt/SiO2-IP, and Pt/C showed the formation of Pt nanoparticles on the surface of these materials. These results clearly indicate that the NR-Al2O3 plays a crucial role for the formation of single platinum sites with high activity for the hydrosilylation process. Notably, in terms of activity our Pt/NR-Al2O3-IP is at least comparable to homogeneous state-of-the-art catalysts such as H2PtCl6 and Karstedt’s system (entries 14 and 15).

Next, we investigated the stability and recyclability of selected catalysts, which are important factors for potential applications in industrial processes. For this purpose, we compared the Pt-SAC and supported Pt-NPs, which both were recycled by centrifugation and reused six times without any reactivation. Gratifyingly, when Pt/NR-Al2O3-IP was used after the sixth recycling, still 92% yield (total TONs of 1.18×105) was achieved (Figure 3). In contrast, a significantly lower activity was observed in the presence of Pt/NR-Al2O3-RP, where almost no product was obtained after the third recycling. These results demonstrate the higher activity of Pt-SAC—which can be anticipated due to the better dispersion of active catalyst centers—compared to Pt nanoparticles. However, contrary to expectations, the former catalyst also showed an improved stability at least on a shorter time scale.

To prove the stability of the SAC, a sample of the recycled material (after 6 runs) was characterized by STEM, XANES, and EXAFS and compared to the fresh one. As shown in Figure 2, no significant differences were observed. For example, the Pt–O coordination number in fresh Pt/NR-Al2O3-IP was approximately 5.0 and did not change much after catalysis (Table S2). Hence, we conclude that single Pt atoms on NR-Al2O3 are stable during the hydrosilylation reactions.

To demonstrate the general synthetic applicability of this single atom catalyst, we explored the hydrosilylation of 1-octene with a variety of tertiary silanes. In all cases we used the active platinum in neat olefin and obtained excellent to quantitative yields of the desired linear products. Hence, hydrosilylations with dimethylphenylsilane (1b) as well as multimiscellaneous containing compounds proceeded smoothly (Table 2). Reaction with 1c is of special interest because the hydrosilylated products have been widely applied in both inorganic chemistry and organic syntheses. In addition, hydrosilylations of the benchmark alkene with silanes containing two Si–H bonds were accomplished, and again, excellent yields were obtained using 1d−1g as starting materials (entries 4–7). In all cases, no side products were observed and the single atom Pt possessed catalytic performance with high turnover numbers.

Furthermore, we tested the hydrosilylation of diverse alkenes using the Pt-SAC. Simple linear and branched aliphatic olefins gave very good yields of the corresponding silylated products (Table 3, entries 1 and 2). More challenging and sensitive oxygen-containing allylic compounds, such as cyclohexyl vinyl
ether (2d), 1,2-epoxy-4-vinylcyclohexane (2e), and allyl glycidyl ether (2f), were also hydrosilylated with the single atom catalyst to form the corresponding products in high yields (entries 3–5). Notably, the catalyst system even tolerates epoxy rings in allyl glycidyl ether, which is susceptible to various ring-opening reactions. Furthermore, the reaction of 6-chloro-1-hexene (2g) with 1a yielded the desired product and no dehalogenated side product was observed (entry 6). Hydrosilylations of allylbenzene (2h), allyl phenyl ether (2i), and allyl benzyl ether (2j) with 1a also afforded the corresponding hydrosilylated products in quantitative isolated yields with high selectivity (entries 7–9).

N-Allylaniline (2k) and allylpentafluorobenzene (2l) were hydrosilylated smoothly to the desired products in 73% and 91% yields, respectively (entries 10 and 11). Moreover, we performed the hydrosilylation of 1a with vinylsiloxanes such as triethoxysilane (2m), allyltrimethylsilane (2n), vinyltrimethylsilane (2o), and 1,3-divinyltetramethyldisiloxane (2p) and formed the corresponding products in high yields selectively (entries 12–15). For the first time, the boron-containing alkene (2q) was transformed successfully to the hydrosilylated product in 83% yield, which might be interesting for applications in material sciences (entry 16). Moreover, the single atom catalyst showed high activity for the hydrosilylation of renewable substrates with 1a. In this respect, lignin-derived alkenes such as eugenol (2r), 4-allylanisole (2s), 4-allyl-1,2-dimethoxybenzene (2t), and methyl 5-allyl-3-methoxysalicylate (2u) reacted in excellent yields (entries 17–20).

In general, hydrosilylation reactions allow controlling the hydrophilicity/hydrophobicity of a given material/surface. In this respect, such transformations offer interesting possibilities for innovations and find increasing interest for the development of consumer and life science products such as elastic skin. Hence, selective Si–C bond formation in the presence of different functional groups is of increasing concern. For this purpose, the chemoselectivity of the single atom catalyst was tested with substrates including other reducible groups. As shown in Scheme 1, the hydrosilylation of 4-vinyl-1-cyclohexene (2v) took place selectively at the terminal position without hydrosilylation of the internal cyclohexyl group or hydrogenation of the C=CH bonds. Furthermore, (+)-β-citronellene (2w) underwent selective hydrosilylation retaining the internal C=C bond in the substrate. In the case of 5-hexen-2-one (2x), the desired product was obtained in 87% yield without touching the ketone, which easily occurred in the presence of homogeneous Pt and other metal catalysts. In addition, the single site Pt catalyst exhibited good activity in the hydrosilylation of an unsaturated ester affording an ester group tagged silane in 89% yield. Finally, the reaction of 4-allylbenzonitrile (2z) with 1a gave the corresponding nitrile in 57%.

Among the industrially applied silanes, there is a substantial interest in the reaction of 2,4,6,8-tetramethylcyclotetrasiloxane: The derived products find widespread applications in cosmetic ingredients due to their excellent spreading, lubrication properties, and unique volatility characteristics. Thus, the hydrosilylation of different alkenes such as 1-octene, allyl glycidyl ether, and 6-chloro-1-hexene with 2,4,6,8-tetramethylcyclotetrasilox-
ane was done in the presence of the single atom Pt catalyst (Scheme 2).

Scheme 2. Selective Hydrosilylation of Cyclostetrasiloxane and POSS Derivatives

To our delight, in all experiments the products were obtained in good yields as colorless fluids with high selectivity and low alkene isomerization. Furthermore, polyhedral oligomeric silsesquioxanes (POSS) have attracted attention as precursors to ceramic materials and nanocomposites. Traditionally, substituted POSS derivatives are prepared by hydrolysis of organotrichlorosilanes where large amounts of HCl are formed. Complementarily, the cross-coupling of 1-octene and POSS-SiH proceeded in the presence of Pt-SAC with excellent yield.

To demonstrate the utility of our catalyst, two industrially relevant reactions of polysilanes with olefins were studied. The resulting materials exhibit distinctive optical and electrical properties, and some of them constitute important precursors for novel materials such as nanostructured silicon carbide. Hence, the hydrosilylation of 1-octene with PMHS and PL6020 proceeded smoothly in the presence of the single atom Pt catalyst (Scheme 3). Finally, the cross-coupling of PL6020 and vinyl-trimethylsilane gave 3c, which represents an example for cross-linked silicone polymers.

Scheme 3. Cross-Linked Silicone Fluids Prepared Using Single Atom Pt Catalyst 4c

“270 mg of PMHS (Sigma-Aldrich, MFC00084478), 3 mmol of 1-octene. 270 mg of SL6020 (Sigma-Aldrich, MFC01325013), 2 mmol of olefin.

In summary, we present the first heterogeneous single atom Pt catalyst, which allows for efficient and selective Si–C bond formation. Contrary to all previously known heterogenized catalysts for hydrosilylation, the prepared Pt/NR-Al2O3/IP offers high activity as well as wide substrate scope and excellent chemoselectivity. In a more general sense, this example demonstrates the superiority of SAC compared to more common heterogenized nanoparticles.
(12) Schuster, C. H.; Diao, T. N.; Pappas, I.; Chirik, P. J. Bench-Stable, Substrate-Activated Cobalt Carboxylate Pre-Catalysts for Alkene Hydrosilylation with Tertiary Silanes. ACS Catal. 2016, 6, 2632–2636.

(13) Marko, I. E.; Sterin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J. P. Selective and efficient platinum(0)-carbon complexes as hydrosilylation catalysts. Science 2002, 298, 204–206.

(14) Du, X. Y.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. ACS Catal. 2017, 7, 1227–1243.

(15) Tondreau, A. M.; Atienza, C. H.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Chirik, P. J. Iron Catalysts for Selective Anti-Markovnikov Alkene Hydrosilylation Using Tertiary Silanes. Science 2012, 335, 567–570.

(16) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. Preparation and molecular and electronic structures of iron(0) dinitrogen and silane complexes and their application to catalytic hydrogenation and hydrosilylation. J. Am. Chem. Soc. 2004, 126, 13794–13807.

(17) Node, D.; Tahara, A.; Sunada, Y.; Nagashima, H. Non-Precious-Metal Catalytic Systems Involving Iron or Cobalt Carboxylates and Alky Isocyanides for Hydrosilylation of Alkenes with Hydrosiloxanes. J. Am. Chem. Soc. 2016, 138, 2480–2483.

(18) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. Rapid, Regioconvergent, Solvent-Free Alkyl Isocyanides for Hydrosilylation of Alkenes and Alkynes. Chem. Rev. 2013, 113, 585–624.

(19) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. Rapid, Regioconvergent, Solvent-Free Alkyl Isocyanides for Hydrosilylation of Alkenes and Alkynes. Chem. Rev. 2013, 113, 585–624.

(20) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. J. Am. Chem. Soc. 2014, 136, 14714–14717.

(21) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. ACS Catal. 2016, 6, 290–300.

(22) Liu, J. L.; Lucchi, F. R.; Yang, M.; Lee, S.; Marcinkowski, M. D.; Therrien, A. J.; Williams, C. T.; Sykes, E. C. H.; Flytzani-Stephanopoulos, M. Tackling CO Poisoning with Single-Atom Alloy Catalysts. J. Am. Chem. Soc. 2016, 138, 6396–6399.

(23) Dvorak, F.; Camellone, M. F.; Tovt, A.; Tran, N. D.; Negreros, F. R.; Vorokhta, M.; Skala, T.; Matolinova, I.; Myslivecek, J.; Matolin, V.; Fabris, S. Creating single-atom Pt-ceria catalysts by surface step decoration. Nat. Commun. 2016, 7, 10801–10807.

(24) Liu, J. Y.; Wang, A. Q.; Qiao, B. T.; Liu, J. Y.; Liu, J. Y.; Zhang, T. Single-atom catalysis of CO oxidation using Pt1/FeOx. Nat. Chem. 2011, 3, 634–641.

(25) Wei, H. S.; Liu, X. Y.; Wang, A. Q.; Zhang, L. L.; Qiao, B. T.; Yang, X. F.; Huang, Y. Q.; Miao, S.; Liu, J. Y.; Zhang, T. FeOx-supported platinum single-atom and pseudo-single-atom catalysts for chemoselective hydrogenation of functionalized nitriles. Nat. Commun. 2014, 5, 5634–5640.

(26) Yang, S.; Kim, J.; Tak, Y. J.; Soon, A.; Lee, H. Single-Atom Catalyst of Platinum Supported on Titanium Nitride for Selective Electrochemical Reactions. Angew. Chem., Int. Ed. 2016, 55, 2058–2062.

(27) Zhang, B.; Asakura, H.; Zhang, J.; Zhang, J. G.; De, S.; Yan, N. Stabilizing a Platinum(1) Single-Atom Catalyst on Supported Phosphomolybdic Acid without Compromising Hydrogenation Activity. Angew. Chem., Int. Ed. 2016, 55, 8319–8323.

(28) Moses-DeBusk, M.; Yoon, M.; Allard, L. F.; Mullins, D. R.; Wu, Z. L.; Yang, X. F.; Veith, G.; Stocks, G. M.; Narula, C. K. CO Oxidation on Supported Single Pt Atoms: Experimental and ab Initio Density Functional Studies of CO Interaction with Pt Atom on theta-Al2O3(101) Surface. J. Am. Chem. Soc. 2013, 135, 12634–12645.

(29) Wang, J.; Zhao, X. C.; Lei, N.; Li, L.; Zhang, L. L.; Xu, S. T.; Miao, S.; Pan, X. L.; Wang, A. Q.; Zhang, T. Hydrogenolysis of Glycerol to 1,3-propanediol under Low Hydrogen Pressure over WOs-Supported Single/Pseudo-Single Atom Pt Catalyst. ChemSusChem 2016, 9, 784–790.

(30) Dvorak, F.; Camellone, M. F.; Tovt, A.; Tran, N. D.; Negreros, F. R.; Vorokhta, M.; Skala, T.; Matolinova, I.; Myslivecek, J.; Matolin, V.; Fabris, S. Creating single-atom Pt-ceria catalysts by surface step decoration. Nat. Commun. 2016, 7, 10801–10807.

(31) Liu, J. Y.; Wang, A. Q.; Qiao, B. T.; Allard, L. F.; Jiang, Z.; Cui, Y. T.; Liu, J. Y.; Zhang, T. Single-atom catalysis of CO oxidation using Pt1/FeOx. Nat. Chem. 2011, 3, 634–641.

(32) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. Rapid, Regioconvergent, Solvent-Free Alkyl Isocyanides for Hydrosilylation of Alkenes and Alkynes. Chem. Rev. 2013, 113, 585–624.

(33) Yang, S.; Kim, J.; Tak, Y. J.; Soon, A.; Lee, H. Single-Atom Catalyst of Platinum Supported on Titanium Nitride for Selective Electrochemical Reactions. Angew. Chem., Int. Ed. 2016, 55, 2058–2062.