Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Zhang, G. Lu and C. Cai, *Green Chem.*, 2017, DOI: 10.1039/C7GC00818J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/green-chem

Published on 21 April 2017. Downloaded by University of Warwick on 21/04/2017 11:05:55.



Journal Name

COMMUNICATION

Regio- and stereoselective hydrosilylation of alkynes catalyzed by SiO₂ support Pd-Cu bimetallic nanoparticles

Received 00th January 20xx, Accepted 00th January 20xx

Jia-wei Zhang, Guo-ping Lu and Chun Cai*

DOI: 10.1039/x0xx00000x

www.rsc.org/

An efficient, recyclable Pd-Cu bimetallic nanoparticles catalyst has been prepared, which exhibits superior activity and selectivity for the hydrosilylation of internal and terminal alkynes under mild reaction conditions with a low catalyst loading. Distinct enhancement in catalytic performance is observed when compared with traditional monometallic catalysts, and composition of the BMNPs is found to be crucial in both the selectivity and yield. This kind of elevation in catalytic performance can be ascribed to the enrichment of active sites (Pd) on the catalyst surface and a phenomenon collectively referred as "synergistic effects". The successful application of BMNPs as a catalyst in the alkyne hydrosilylation opens new possibilities for the excavation of the value of bimetallic nanoparticles in catalysts development for sustainable chemistry.

Introduction

Vinylsilanes are valuable building blocks and important structural units existing in pharmaceuticals and materials.¹⁻⁷ The carbon-bound silicon in vinylsilanes is readily oxidized, allowing vinylsilanes to serve as masked carbonyl group^{8, 9} which are key intermediates in organic chemistry. Also, vinylsilanes often show properties similar to corresponding organometallic vinyl derivatives, but offer advantages in terms of cost, low molecular weight, low toxicity, functional tolerance and high chemical stability.^{10, 11} Of the available methodologies for the preparation of vinylsilanes, transition metal-catalyzed hydrosilylation of alkynes has been proved to be the most straightforward and convenient method due to the high atom efficiency and low cost of the substrates.¹²⁻¹⁵

During the last decades, plenty of catalytic systems have been developed for the alkynes hydrosilylation reactions. Catalysts based on platinum^{4, 16, 17} and ruthenium¹⁸ have

⁺ Footnotes relating to the title and/or authors should appear here.

emerged as the most popular candidates owing to their high activity. Besides, a number of base-metal complexes which have emerged during the past 5 years offer another alternatives for the hydrosilylation reactions, and this may reduce the reliance on noble metal elements to some extent. ¹⁹⁻²¹ However, albeit these excellent works reported in recent years, the region controlled hydrosilylation of alkynes still remains a major challenge.²²⁻²⁴ What's more, those reported catalysts are mostly homogeneous metal complexes which suffer from catalyst reusability and product purification, so heterogeneous catalysts with low cost and high efficiency are in great demand from a standpoint of green and sustainable chemistry.²⁵⁻²⁸ Quite recently, Buslov and co-workers reported an in-suit formed Ni nanoparticles (NPs) for the hydrosilylation reaction, and they proposed that the homogeneous complexes catalyst were converted into NPs upon reaction with silane, which were responsible for the hydrosilylation activity.²⁹ Since elements like Pt, Ru and Pd are more electronegative than Ni, it's reasonable to propose that reduction of those metal complex may happen upon contact with silane and the in-suit formed NPs maybe the active site for the hydrosilylation reaction.³⁰⁻³²

We recently described the application of bimetallic nanoparticles (BMNPs) as catalysts in organic chemistry,^{33, 34} in which catalytic performance of a metal can be enhanced by alloying with another metal.³⁵ The BMNPs have emerged as a new platform for developing highly efficient catalysts due to their completely different electronic states and structural conformations.³⁶⁻³⁸ We speculate that the BMNPs may be a better alternative than single metal catalysts to catalyze the hydrosilylation reactions. By coincidence, Shishido and coworkers reported a supported Pd-Au alloy catalysts for the highly efficient and selective hydrosilylation of α , β unsaturated ketones and alkynes.³⁸ Nevertheless, the BMNPscatalyzed hydrosilylations have not been well-studied in the view of sustainable chemistry. Along this line, herein, a series of BMNPs based on Pd and earth-abundant elements were prepared and tested in the alkyne hydrosilylation. Pleasantly, Pd1Cu2/SiO2 BMNPs catalyst show excellent activity and

^a Chemical Engineering College, Nanjing University of Science & Technology, Xiaolingwei 200, Nanjing 210094, P. R. China. E-mail: c.cai@njust.edu.cn

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Entry

1^{*d*} 2 3^e

4

5

6

7

8

9

10

11

12

13

14 15

16

17^{f,g}

18^f

19^{*f,h*}

20^{f, h}

21^f

 Pd_1Cu_2

Pd₁Cu₄

 Pd_1Cu_2

THF

THF

[Bmim]BF₄

COMMUNICATION

selectivity in the hydrosilylation of alkynes under mild reaction conditions with a low catalyst loading. What's more, the catalyst is quite stable during the reaction process, only slight decrease in selectivity was observed after five cycles of the catalyst. Therefore, alloying noble metal with earth-abundant metal elements to upgrade the catalytic performance would be significant with regard to both synthetic and green chemistry.

Results and discussion

At the outset of our study, hydrosilylation of phenylethyne with triethylsilane was chosen as the model reaction to evaluate the catalytic performance of the NPs (Table 1). A very low catalyst loading (0.4 mol %, based on Pd) was employed in the reaction to excavate the catalysts with potential activity. Initially, Pd NPs immobilized on SiO₂ was used as the catalyst, pretty low yield was obtained and the selectivity of product 3 was moderate (Table 1, entry 1). Be mindful of the potential value of alloy NPs in the catalytic field, ³⁹⁻⁴¹ we envisage to alloy Pd with earth-abundant metal elements to heighten the catalytic performance, and as expected, noteworthy enhancement in activity was observed when Pd₁Ni₄ BMNPs was employed as catalyst (entry 1 vs 2). As a benchmark, Ni NPs only show negligible activity in the hydrosilylation of phenylethyne (entry 3), no product was detected in the absence of the catalyst (entry 4).

Generally, amount of the react impact on the reaction process, s influence of silane's dosage was mad (entries 5-8), no distinct difference in y lower the dosage of silane, but the s isomers was relatively low when silane 2 equivalents. Subsequently, we turn of key factor of the chemical reactiondecrease in selectivity was observed when lower the rea temperature (entries 9-10), which may be due to the decrease on transformation from Z isomers to more thermodynamically stable E isomers. Consequently, the room temperature (about 20 °C) was selected as the optimal reaction temperature for energy consideration.

Moreover, composition of the BMNPs was found to be essential for the catalytic property, a series of BMNPs with different metal ratios and components were prepared by a similar preparation procedure and tested in this reaction, Pd₁Cu₂ BMNPs was screened as the optimal catalyst with an extraordinary activity and selectivity (entries 11-16), and the outstanding catalytic performance could be ascribed to copper's good affinity with alkynes. Remarkably, the hydrosilylation reaction could proceed under air (entry 14), which may be a result of the improved stability of Pd-Cu BMNPs. Besides, Cu/SiO₂ was also tested in this reaction (entry 17), and no product was detected. Together with the catalytic performance of single Pd/SiO₂ catalyst, we could proposed that Pd atoms act as the main active site for the hydrosilylation reaction, and Cu may act as a "ligand" in the BMNPs through "electronic effects".⁴² Furthermore, physical mixture of

	22 ^{<i>f</i>}	Pd₁Cu₂	t-BuOH	20
ants may have a huge	23 ^{<i>f</i>}	Pd₁Cu₂	CH_2CI_2	20
o investigation on the	24 ^{<i>f</i>}	Pd₁Cu₂	1,4-ioxane	20
e. As show in the table ield was observed when cereoselectivity to the <i>E</i> 's amount was less than our attention to another temperature, negligible when lower the reaction	[a] Rea on me stirred MS. [d] catalyst as catal	ction condit tal palladiun under argor] 0.4% Pd N t. [f] The rea lyst. [h] 0.3 r	ions: 0.5 mmol n), triethylsilar 1 for 1h. [b] Isol IPs was used a ction was perfo nol % catalyst w	phenyle ne, 0.5 r ated yiel ns cataly ormed un vas used.

Cu/SiO₂ and Pd/SiO₂ do not lead to apparent promotion in catalytic activity, demonstrating that it is the cooperativity of BMNPs, not the simple mixture of Pd and Cu, that account for the elevation of catalytic performance (entry 18). Preliminary attempt to lower the catalyst loading was also made, but conspicuous decrease on the catalytic selectivity was observed (entry 19), and we think this decrease may come from the decreased amount of Cu. To verify our hypothesis, 0.3 mol% Pd₁Cu₄/SiO₂ was employed as a catalyst in the reaction, and the selectivity was relatively better (entry 20). The as prepared Pd_1Cu_2/SiO_2 catalyst was detected by the inductively coupled plasma mass spectrometry (ICP-MS), which confirmed that the Pd/Cu ratio (0.51) was consistent with the designed composition of the Pd1Cu2 BMNPs. In addition, the ICP-MS result showed that the Pd loading of Pd₁Cu₂ BMNPs on the silica gel particles was 1.85wt%, very similar to the theoretical value, indicating that almost no dissipation of metal precursors was observed during the preparation process. Finally, several solvents including [Bmim]BF₄ (1-Butyl-3-methylimidazolium tetrafluoroborate), t-BuOH, CH₂Cl₂, 1,4-dioxane were employed in this reaction, but in all cases the reaction yield was far

+ Et ₃ SiH			► SiEt ₃ + SiEt ₂			
	1	2	Ť	3	4	
	Catalyst	Solvent	T(°C)	Ratio (1 <i>vs</i> 2)	Yield(%) ^b	3/4 ^c
	Pd	THF	40	1:5	24	77/23
	Pd_1Ni_4	THF	40	1:5	96	89/11
	Ni	THF	40	1:5	<5%	90/10
		THF	40	1:5		
	Pd_1Ni_4	THF	40	1:1	91	72:28
	Pd_1Ni_4	THF	40	1:2	94	84/16
	Pd_1Ni_4	THF	40	1:3	96	87:13
	Pd_1Ni_4	THF	40	1:4	95	85:15
	Pd_1Ni_4	THF	20	1:2	96	81/19
	Pd_1Ni_4	THF	30	1:2	94	80:20
	Pd_1Ni_1	THF	20	1:2	87	83:17
	Pd_1Ni_2	THF	20	1:2	98	87:13
	Pd_1Ni_6	THF	20	1:2	99	86:14
	Pd_1Cu_2	THF	20	1:2	98	98:2
	Pd ₁ Fe ₂	THF	20	1:2	98	87:13
	Pd_1Co_2	THF	20	1:2	99	88:12
	Cu	THF	20	1:2		
	Pd+Cu	THF	20	1:2	31	86/14

20

20

20

1:2

1:2

1:2

1:2

1:2

1:2

92

95

63

8

57

34

н

Table 1. Optimization for the hydrosilylation of phenylethyne.^a

н

Published on 21 April 2017. Downloaded by University of Warwick on 21/04/2017 11:05:55.

Journal Name

inferior to that obtained with THF (entries 21-24). Based on the aforementioned results, it can be concluded that the catalytic performance of Pd was greatly enhanced by alloying it as a bimetallic species with Cu, and the Pd-Cu BMNPs show properties superior to both Pd and Cu. Moreover, almost no hydrogenation product of vinylsilanes was detected, which maybe a result of the mild reaction condition and the depression in the hydrogenation activity of BMNPs caused by introducing Cu into Pd.



Fig. 1 (a) (b) TEM images (c) High-resolution TEM (HRTEM) imagine of the Pd_1Cu_2/SiO_2 catalyst. (d) Size distribution of Pd_1Cu_2 bimetallic nanoparticles

To understand the origin of the enhanced catalytic performance, the BMNPs catalysts were characterized by a series of spectroscopic techniques. Firstly, the morphology of the Pd₁Cu₂/SiO₂ catalyst was directly observed by transmission electron microscopy (TEM). As shown in Fig. 1, the as prepared Pd₁Cu₂ BMNPs have a homogeneous distribution throughout the surface of the SiO₂, the NPs are well proportioned spherical with an average diameter of 2.8 nm, the ultrasmall size means more contact chances between the active sites and substrates were provided. To know the fine structure of the BMNPs, HRTEM study was also undertaken, as shown in Fig. 1c, the BMNPs have a clear crystalline fringe patterns and the lattice fringes align parallel to each other, besides, the interfringe distance is about 0.22 nm, which is between the characteristics of face centered cubic Pd (0.224 nm) and a Cu (0.209 nm) crystal phase in the (111) plane, indicating the formation of Pd-Cu alloys.^{39, 43, 44} A high angle annular dark field (HAADF-STEM) image (Fig. 2a) also indicate that Pd-Cu BMNPs were well dispersed on the matrix, and the EDS elemental maps profile obviously manifested the homogeneous distribution of Pd and Cu in Pd₁Cu₂/SiO₂ catalyst.

Furthermore, to evaluate the surface composition and electronic state of the ${\rm Pd_1Cu_2/SiO_2}$ catalyst, X-ray

View Article Online DOI: 10.1039/C7GC00818J COMMUNICATION

photoelectron spectrum (XPS) was also carried out. The XPS spectra point out that the ratio of the surface concentration between Pd and Cu is 2.94, which is much higher than the result determined by ICP-MS. Such a big difference in atomic ratio may be attributed to that the Pd mainly distributes on the surface of Pd_1Cu_2 BMNPs, which means more contact opportunity between the active site and the reactant molecules. Compared with previous works, in which Pd-Ni ratio was constant throughout the BMNPs³³ and surface composition of the Cu was 2.2 times higher than that in Pd-Cu BMNPs, ⁴⁵ we could conclude that the promotion in catalytic selectivity (Table 1, entry 12 vs 14) can be ascribed to the enrichment of Pd on the catalyst surface.



Fig. 2 a) High-angle annular dark field (HAADF) STEM image of Pd_1Cu_2/SiO_2 . EDS elemental maps for b) Pd and c) Cu.

Fig. 3a depicts the XPS spectra in the Pd 3d region for Pd_1Cu_2/SiO_2 , the intense doublet centering at 335.5 and 340.6 eV belongs to metallic Pd, while the other doublet at 338.1 eV and 343.3 eV is ascribed to the +2 oxidation state of Pd.^{46,47} As illustrated in Fig. 3b, the peaks located at 932.9 and 952.7 eV can be assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, which further confirmed the formation of the Pd–Cu alloy in the Pd₁Cu₂/SiO₂ catalyst.⁴⁸ Besides, peaks at 935.1eV (Fig. 4c) with satellite at about 942.8 eV are indications of copper as CuO which is formed after exposure at air.^{49, 50} Shift (0.2 eV) in the peak positions of Cu $2p_{3/2}$ towards higher BE clearly indicates that electronic structure of Cu was changed upon alloy with Pd.^{48, 50}



Fig. 3 XPS spectrum of Pd_1Cu_2/SiO_2 catalyst: (a) Pd 3d region (b). Cu 2p region.

Given that electronegativity of Pd (2.20) is higher than that of Cu (1.90), a charge heterogeneity may occur in the BMNPs, which means that both electron-rich sites and slightly positively charged sites exist on the catalyst surface.^{51, 52} The electron-rich Pd center can active the Si-H bond, generating an electrophilic silicon center, which was responsible for the enhanced catalytic activity.⁵³ In addition, the "synergistic effects" of the BMNPs may partly come from the charge heterogeneity on the catalyst surface, which can accelerate

COMMUNICATION

DOI: 10.1039/C7GC00818J Journal Name

the polarization of the H-Si bond due to the difference in the electronegativity of silicon and hydrogen, allowing the electron-rich hydrogen atom to easily approach the positively charged Cu sites, while the electropositive silicon approach the electron-rich Pd center. Once the alkyne molecules come across to the catalyst surface, addition of H and silicon from one side of the triple bond would happen, affording the *E*-vinylsilanes with high selectivity.



Fig. 4 Recycling of Pd_1Cu_2/SiO_2 catalyst in the hydrosilylation of phenylethyne.

Once the optimal reaction conditions were established, we turn to investigate the reusability of the Pd_1Cu_2/SiO_2 catalyst. The catalyst was recovered by filtration from the reaction described in the entry 14 of Table 1, upon completion of the reaction, the catalyst was washed with water and EtOH, dried under air and then directly reused under the same conditions (Fig. 4). The BMNPs catalyst could be reused up to five times without losing its activity, and only minor decrease in selectivity of *E* isomers might be a result of the mechanical loss.¹¹ The excellent stability of the catalyst could be ascribed to the formation of alloy⁵⁴⁻⁵⁶ and the mild reaction conditions.



Fig. 5 Hot filtration experiments of Pd_1Cu_2/SiO_2 for hydrosilylation of phenylethyne.

Additionally, the heterogeneous nature of the Pd_1Cu_2/SiO_2 catalyst was demonstrated by a hot filtration experiment (Fig. 5). The catalyst was filtered off when the

reaction was proceed for 20 min, and the filtrate was stirred for another 20 min under identical conditions. No further increase in yield was observed after the remove of the catalyst, and addition of the removed catalyst led to resumption of the reaction. These results indicates that metal leaching of the catalyst is negligible during the reaction process, which can be ascribed to the excellent stability of the Pd_1Cu_2/SiO_2 catalyst. Together with the catalyst recycle experiments, we could conclude that the reaction was proceed on the surface of the nanoparticles, not in a molecular way.



^{*a*} Reaction conditions: 0.5 mmol alkynes, 2×10^{-3} mmol catalyst (based on metal palladium), 1 mmol triethylsilane, 0.5 mmol Nal and 1mL solvent was stirred at rt for 1 h. ^{*b*} The reaction temperature was 40 °C ^{*c*} The amount of Et₃SiH was 2 mmol

The scope of alkynes was then examined for this catalytic system using Pd_1Cu_2/SiO_2 as the catalyst, the reactions were performed with 0.4 mol% (based on metal palladium) catalyst loading in THF at room temperature. Generally, arylacetylene with electron withdrawing substituents show better reaction efficiency to that of electron-donating ones. With an electron withdrawing group, the arylacetylene underwent smoothly transformation into vinylsilanes with excellent selectivity under optimized conditions (**3b-3g**). Besides, the halo-substituted alkynes were compatible with the standard conditions, furnishing the halo-substituted vinylsilanes (which are valuable intermediates for further functionalization) with high efficiency (**3b-3d**). In addition, the valuable trifluoro-

methyl group in 1e survived in the present reaction with Et₃SiH. What's more, reducible substituents like nitro and cyano remained unreacted during the reaction process, which may be a result of the mild reaction condition (3f-3g).

Arylacetylenes bearing electron donating groups were also applicable, albeit with relatively low selectivity to E isomers (3h-3l). 4-Ethynylaniline (1l), which contain a quite sensitive amino group, could also be transformed into vinylsilanes with high efficiency (3I). Besides, carboxyl group was also compatible with this protocol, producing (E)-4-(2-(triethylsilyl)vinyl)benzoic acid (3m) with high selectivity. Sterically hindered 4-ethynyl-1, 1'-biphenyl and 2-ethynyl-6methoxynaphthalene were also suitable for this transformation (3n-3o). Moreover, the protocol was also effective on heteroaromatic alkynes and aliphatic alkynes, showing a broad-spectrum substrate scope (3p-3s). Since less attention has been paid to the internal alkynes because of the low reactivity and regioselectivity,⁵ preliminary attempts for hydrosilylation of symmetrically substituted internal alkynes have been proved to be successful, furnishing the expected (E)- alkenylsilanes in near quantitative yield and selectivity (3t-3u). However, as to the challenging nonsymmetrical internal alkynes such as 1-phenylprop-1-yne, the reaction was proceed with a poor yield. Finally, this protocol was also suitable for disilylation reaction, the reaction of 1, 4-diethynylbenzene (1v) with Et₃SiH (4.0 equiv) afforded exclusively the para-disilylated product (3v) in 89% yield, only minor monosilylation product was observed during the reaction process. The above result points out that the substrate scope of this reaction is wide, illustrating the good functional group tolerance and potential applications of this protocol.

Conclusions

In summary, a recyclable Pd-Cu bimetallic catalyst has been successfully synthesized, and the catalyst has been applied in alkynes hydrosilylation reactions under ligand-free conditions. Combination of Pd with Cu in an alloy form leads to a considerable improvement of catalytic performance due to the "synergistic effects". The reaction proceeds under mild conditions, furnishing vinylsilanes with excellent yield and selectivity. The enhanced catalytic performance may origin from the ultrasmall size and homogeneous distribution of the BMNPs, the enrichment of Pd at the catalyst surface allow the reaction to proceed with a low catalyst loading. Furthermore, charge heterogeneity exist in the BMNPs due to the difference in electronegativity, which may also contribute to the extraordinary performance of the catalyst. Alloying palladium with the earth-abundant copper not only enhances the catalytic performance (activity, selectivity and stability) but also lowers the cost of catalyst to some extent, and this may be a preferable access for the development of green and sustainable catalysts in the future.

Acknowledgements

Green Chemistry Accepted Manuscript

We gratefully acknowledge Nature Science Foundation of Jiangsu Province (BK 20140776) for financial support. This work was also supported by National Natural Science Foundation of China (21402093, 21476116) and Chinese Postdoctoral Science Foundation (2015M571761, 2016T90465) for financial support. We also gratefully acknowledge Priority Academic Program Development of Jiangsu Higher Education Institutions for financial support.

REFERENCES

- 1 S. Ding, L. J. Song, L. W. Chung, X. Zhang, J. Sun and Y. D. Wu, J. Am. Chem. Soc., 2013, 135, 13835-13842.
- S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima, J. Am. Chem. Soc., 2007, 129, 12650-12651.
- C. Thiot, M. Schmutz, A. Wagner and C. Mioskowski, Chem. Eur. J., 2007, 13, 8971-8978.
- D. A. Rooke and E. M. Ferreira, Angew. Chem. Int. Ed., 2012, 4 51. 3225-3230.
- A. Garcia-Rubia, J. A. Romero-Revilla, P. Mauleon, R. Gomez 5 Arrayas and J. C. Carretero, J. Am. Chem. Soc., 2015, 137, 6857-6865.
- B. M. Trost and Z. T. Ball, Synthesis, 2005, 2005, 853-887.
- H. F. Sore, W. R. Galloway and D. R. Spring, Chem. Soc. Rev., 7 2012. 41. 1845-1866.
- J. R. McAtee, S. B. Krause and D. A. Watson, Adv. Synth. 8 Catal., 2015, 357, 2317-2321.
- 9 G. R. Jones and Y. Landais, Tetrahedron, 1996, 52, 7599-7662
- 10 J. J. Pérez-Torrente, D. H. Nguyen, M. V. Jiménez, F. J. Modrego, R. Puerta-Oteo, D. Gómez-Bautista, M. Iglesias and L. A. Oro, Organometallics, 2016, 35, 2410-2422.
- 11 W. Guo, R. Pleixats, A. Shafir and T. Parella, Adv. Synth. Catal., 2015, 357, 89-99.
- 12 A. Rivera-Hernandez, B. J. Fallon, S. Ventre, C. Simon, M. H. Tremblay, G. Gontard, E. Derat, M. Amatore, C. Aubert and M. Petit, Org. Lett., 2016, 18, 4242-4245.
- 13 W. Wu and C.-J. Li, Chem. Commun., 2003, 14, 1668-1669.
- 14 B. M. Trost and Z. T. Ball, J. Am. Chem. Soc., 2005, 127, 17644-17655.
- 15 Y. Corre, C. Werlé, L. Brelot-Karmazin, J.-P. Djukic, F. Agbossou-Niedercorn and C. Michon, J. Mol. Catal. A: Chem., 2016. 423. 256-263.
- 16 D. A. Rooke and E. M. Ferreira, J. Am. Chem. Soc., 2010, 132, 11926-11928.
- 17 L. Ortega-Moreno, R. Peloso, C. Maya, A. Suarez and E. Carmona, Chem. Commun., 2015, 51, 17008-17011.
- 18 M. Zaranek, B. Marciniec and P. Pawluć, Org. Chem. Front., 2016. 3. 1337-1344.
- 19 Du and Z. Huang, ACS Catalysis, 2017, 7, 1227-1243.
- 20 B. Raya, S. Jing, V. Balasanthiran and T. V. RajanBabu, ACS Catalysis, 2017, 7, 2275-2283.
- 21 J. Wenz, H. Wadepohl and L. H. Gade, Chem. Commun., 2017, 53, 4308-4311.
- 22 S. Nakamura, M. Yonehara and M. Uchiyama, Chem. Eur. J., 2008. 14. 1068-1078.
- 23 J. Gu and C. Cai, Chem. Commun., 2016, 52, 10779-10782.
- 24 D. Do Van, T. Hosokawa, M. Saito, Y. Horiuchi and M. Matsuoka, Appl. Catal. A-Gen., 2015, 503, 203-208.
- 25 F. Alonso, R. Buitrago, Y. Moglie, J. Ruiz-Martínez, A. Sepúlveda-Escribano and M. Yus, J. Organomet. Chem., 2011, 696. 368-372.
- 26 F. Alonso, R. Buitrago, Y. Moglie, A. Sepúlveda-Escribano and M. Yus, Organometallics, 2012, 31, 2336-2342.
- 27 R. Cano, M. Yus and D. J. Ramón, ACS Catalysis, 2012, 2, 1070-1078.

Published on 21 April 2017. Downloaded by University of Warwick on 21/04/2017 11:05:55.

Published on 21 April 2017. Downloaded by University of Warwick on 21/04/2017 11:05:55.

- 28 Y. Ishikawa, Y. Yamamoto and N. Asao, *Catal. Sci. Technol.*, 2013, **3**, 2902.
- 29 I. Buslov, F. Song and X. Hu, Angew. Chem. Int. Ed., 2016, 55, 12295-12299.
- 30 T. Galeandro-Diamant, M. L. Zanota, R. Sayah, L. Veyre, C. Nikitine, C. de Bellefon, S. Marrot, V. Meille and C. Thieuleux, *Chem. Commun.*, 2015, **51**, 16194-16196.
- 31 T. Galeandro-Diamant, R. Sayah, M. L. Zanota, S. Marrot, L. Veyre, C. Thieuleux and V. Meille, *Chem. Commun.*, 2017, 53, 2962-2965.
- 32 M. Chauhan, B. J. Hauck, L. P. Keller and P. Boudjouk, J. Organomet Chem., 2002, 645, 1-13.
- 33 J.-w. Zhang, Y. Cai, G.-p. Lu and C. Cai, Green. Chem., 2016, 18, 6229-6235.
- 34 J.-w. Zhang, G.-p. Lu and C. Cai, Catal. Commun., 2016, 84, 25-29.
- 35 G. Schmid, H. West, M. H. and L. A., Inorg. Chem., 1997, 36, 891-895.
- 36 M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kiely and G. J. Hutchings, *Chem. Soc. Rev.*, 2012, **41**, 8099-8139.
- 37 D. Wang, Q. Peng and Y. Li, *Nano Research*, 2010, **3**, 574-580.
- 38 H. Miura, K. Endo, R. Ogawa and T. Shishido, ACS Catalysis, 2017, 7, 1543-1553.
- 39 Y. L. Junjie Mao, Zheng Chen, Dingsheng Wang and Yadong Li, *Chem. Comm.*, 2014, **50**, 4588-4591.
- 40 D. Wang and Y. Li, Adv. Mater., 2011, 23, 1044-1060.
- 41 R. K. Rai, D. Tyagi, K. Gupta and S. K. Singh, *Catal. Sci. Technol.*, 2016, **6**, 3341-3361.
- 42 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Chem Soc Rev*, 2012, **41**, 8075-8098.
- 43 D. Sengupta, J. Saha, G. De and B. Basu, *J. Mater. Chem. A*, 2014, **2**, 3986-3992.
- 44 S. F. Ho, A. Mendoza-Garcia, S. Guo, K. He, D. Su, S. Liu, O. Metin and S. Sun, *Nanoscale*, 2014, 6, 6970-6973.
- 45 S. Jung, S. Bae and W. Lee, Environ. Sci. Technol., 2014, 48, 9651-9658.
- 46 J. Xia, Y. Fu, G. He, X. Sun and X. Wang, *Appl. Catal. B* Environ., 2017, **200**, 39-46.
- 47 X. Jiang, N. Koizumi, X. Guo and C. Song, *Appl. Catal. B* Environ., 2015, **170-171**, 173-185.
- 48 E. B. Fox, S. Velu, M. H. Engelhard, Y.-H. Chin, J. T. Miller, J. Kropf and C. Song, *J. Catal.*, 2008, **260**, 358-370.
- 49 A. Kandory, H. Cattey, L. Saviot, T. Gharbi, J. Vigneron, M. Frégnaux, A. Etcheberry and G. Herlem, *J. Phys. Chem. C*, 2017, **121**, 1129-1139.
- 50 C. Trapalis, G. Kordas, P. Osiceanu, A. Ghita, M. Anastasescu, M. Crisan, C. Anastasescu and M. Zaharescu, *Plasma Process* and Polym., 2006, **3**, 192-196.
- 51 S. Sarina, H. Zhu, E. Jaatinen, Q. Xiao, H. Liu, J. Jia, C. Chen and J. Zhao, J. Am. Chem. Soc., 2013, 135, 5793-5801.
- 52 H. Zhang, T. Watanabe, M. Okumura, M. Haruta and N. Toshima, *Nat. Mater.*, 2011, **11**, 49-52.
- 53 M. C. Lipke, A. L. Liberman-Martin and T. D. Tilley, Angew. Chem. Int. Ed., 2017, 56, 2260-2294.
- 54 W. Albrecht, J. E. van der Hoeven, T. S. Deng, P. E. de Jongh and A. van Blaaderen, *Nanoscale*, 2017, 9, 2845-2851.
- 55 47. X. Liu, A. Wang, X. Yang, T. Zhang, C.-Y. Mou, D.-S. Su and J. Li, *Chem. Mater.*, 2009, **21**, 410-418.
- 56 48. A. Cao and G. Veser, Nat Mater, 2010, 9, 75-81.