Plasmonic heating using an easily recyclable Pd-functionalized Fe_3O_4/Au core-shell nanoparticle catalyst for the Suzuki and Sonogashira reaction

Amaury De Cattelle[a], Arne Billen[b], Ward Brullot[b], Thierry Verbiest[b], Guy Koeckelberghs[a]*

[a]Laboratory for Polymer Synthesis, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Heverlee, BELGIUM

[b]Laboratory for Molecular Electronics and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200D, B-3001 Heverlee, BELGIUM

* To whom correspondence should be addressed.

E-mail address: guy.koeckelberghs@kuleuven.be (Guy Koeckelberghs)

tel. +32 16 32 74 20

Postal address: Department of Chemistry-Celestijnenlaan 200F - box 2404, 3001 Heverlee, Belgium

Declarations of interest: none

Abbreviations:
PEG: Poly(Ethylene Glycol)
ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy

ABSTRACT

Palladium functionalized gold nanoparticles were used in the past as a catalyst system in light induced cross-coupling reactions, but with a main limitation of the recuperation. To overcome this problem, a palladium functionalized Fe_3O_4/Au core-shell nanoparticle was successfully synthesized with a peak wavelength of 680 nm from the plasmon resonance of the gold shell. By the presence of the magnetite core, the nanoparticle catalyst can easily be removed using magnetic precipitation. This is accompanied with the advantage of having less valuable gold present in the system. The gold shell makes it possible to induce local heating using plasmon resonance. By this combination, it is possible to recuperate the catalyst system using magnetic precipitation and increase the control and safety of the reaction due to the presence of the light-induced plasmonic heating. It was possible to perform light-induced Suzuki cross-coupling reactions using this catalyst system, but with a dependency of the substrate. It was found that an anionic substrate is repulsed from the negatively charged core-shell nanoparticle. The catalyst was examined on its recuperation abilities and could be reused up to 5 cycles. At the catalytic site a temperature was reached between 40 °C and 45 °C. Despite the promising results of the Suzuki reaction, it was not possible to perform light-induced Sonogashira reactions due to the insufficient heat generation at the catalytic site. Nevertheless, these results are promising in the development of an easily recyclable catalyst together with an alternative heating source, resulting in an increase of control and safety.

KEYWORDS: Plasmonic heating, Immobilized catalyst, Magnetically separable, Cross-coupling reaction

1 Introduction

Cross-coupling reactions are powerful pathways in organic synthesis for the formation of mainly carbon-carbon bonds. Homogeneous catalysts resulting in highly efficient cross-coupling reactions have the main drawback of their difficulty in separation.[1–4] On the

2

contrary, heterogeneous catalyst systems have solved this main problem and can be easily separated from the reaction mixture. A lot of efforts have been made to synthesize recoverable catalysts, such as Pd nanoparticles[5–7] and Pd immobilized on silica nanoparticles,[8–11], graphene[12–14], polymers,[15–20], carbon nanotubes,[21,22] and dendrimers[23–26]. Furthermore, Pd has also been immobilized on metal-organic frameworks[27], metal oxides[28–30], metal oxide nanoparticles[31–34] and gold nanoparticles for the use in plasmon-assisted cross-coupling reactions, resulting in localized heating.[35–37] Another type of local heating was recently examined using magnetic induction, resulting in a magnetically recyclable nanoparticle.[38] Despite these advantages, it is hard to use this type of catalyst for industrial applications, due to the presence of the magnetic field. Since a lot of industrial reactors consist (partially) out of steel, it is impossible to use a magnetic field. It should also be mentioned that the reactions were performed on small scale, which means that by upscaling the reaction, the area of the magnetic field also needs to be increased, resulting in an increase of the safety measures. None of these disadvantages are present when plasmon resonances are used to induce local heating, since it is generated by light and can, therefore, be implemented more straightforwardly in (industrial) applications. Localized plasmon resonances can be described as the collective oscillations of electrons in noble metals as a result of the interaction with light. This oscillation of electrons causes a rise in the lattice temperature of the metals, which is thereafter dissipated to the surrounding medium and leads to the plasmonic heating.[39] This type of photothermal conversion has been widely studied in various optical and biotechnological applications.[40–44] For chemical reactions, the plasmonic heating has been utilized using Au or Ag nanocrystals to drive the oxidation of formaldehyde and methanol,[45] the reduction of nitroaromatic compounds,[46] the acceleration of CO oxidation[47] and the ethylene epoxidation.[48] Furthermore, Au nanoparticles or nanorods have been used for photocatalytic Suzuki cross-coupling reactions.[35–37] These results

3

demonstrate clearly the possibility of using plasmonic metal nanocrystals and nanoparticles as energy converters and catalysts to drive chemical reactions at moderate temperatures. However, there is still a lot of improvement potential for this type of reaction. By making use of a novel core-shell nanoparticle catalyst system, consisting out of a magnetite core, surrounded by a gold shell whereupon the palladium catalyst is attached, a lot of the existing drawbacks can be resolved. The implementation of the magnetite core inside the system results in a double advantage compared to the consisting Au nanoparticles. First, it reduces the amount of valuable gold, and by this the price of the catalyst system, because the inner core of the system consists now out of relative cheap magnetite instead of gold. Second, it facilitates the recuperation of consisting Au nanoparticle catalyst systems due to the presence of the magnetite which is superparamagnetic. By using the superparamagnetic character of the magnetite core, the core-shell catalyst system can be removed using a magnet resulting in an easy magnetic precipitation method. This is an advantage compared to existing systems, where the Au nanoparticle catalyst systems are not recovered, resulting in a huge loss of valuable material, or where they can only be recovered using centrifugation. Centrifugation is a less straightforward method and more time consuming compared to magnetic precipitation and often results in unwanted agglomeration of the Au nanoparticle catalyst system. Furthermore, a ligand-free core-shell catalyst system is used, in order to facilitate the catalyst preparation. In this way, an easy and fast synthesized catalyst system is used with an improved recuperation mechanism, resulting in a faster and more straightforward recovery of the catalyst system without the disadvantage of agglomeration. This is combined with the advantages of the plasmonic photothermal catalysis, which are full control of the reaction, the possibility to perform the reaction at moderate temperatures and as a consequence an increase in safety of the reaction. It should be mentioned that plasmonic photothermal conversion has never been performed using this novel $Fe_3O_4/Au/Pd$ core-shell catalyst nanoparticle system, resulting in

an easily recyclable catalyst system and the use of an alternative heating method. This unique combination makes this Pd functionalized core-shell nanoparticle an ideal candidate towards the goal of green chemistry, resulting in an easily synthesized, efficient recyclable catalyst with a high control and safety of the reaction. Not only will the reactions be performed using an easily reusable catalyst combined with an alternative heating source, they will also be executed under air in order to make these reactions more accessible.

2 Experimental

2.1 *Functionalization of the Fe_3O_4/Au/PEG nanoparticles with Pd*

The Fe_3O_4/Au/PEG core-shell nanoparticles were synthesized according to literature.[49] Palladium acetate (50.0 mg, 0.221 mmol) was brought into a 50 mL flask and a dispersion of Fe_3O_4/Au/PEG nanoparticles (50.0 mg) in 1,4-dioxane (10.0 mL) was added to the flask. The reaction mixture was brought under argon atmosphere and stirred for four days. The mixture was transferred to a tarred vial and isolated under the influence of a magnetic field using a magnet. Afterwards, the nanoparticles are washed three times with 1,4-dioxane and dried under reduced pressure. The yield was determined gravimetrically. See supplementary material for more detailed information.

2.2 *General procedure for the Suzuki-Miyaura couplings*

The aryl halide (0.180 mmol), the boronic acid-compound (0.270 mmol), K_2CO_3 (0.360 mmol, 52.5 mg) and 1,3,5-trimethoxybenzene (0.180 mmol, 30.3 mg), as internal standard, were added to a 8 mL glass vial. A dispersion of Fe_3O_4/Au/PEG/Pd nanoparticles made in EtOH was added to the 8 mL glass vial (0.500 mL, 0.400 mg /mL. The reaction mixture was stirred after the addition of 0.500 mL H_2O, while standing in a laser beam with a wavelength of 680 nm and an optical power of 500 mW. After 4 hours, the nanoparticles were isolated from the mixture using a magnet. The conversion, with respect to the desired end-product, was determined by ^{1}H-NMR of the crude reaction mixture, using 1,3,5-trimethoxybenzene as an internal standard. See supplementary material for more detailed information.

5

3   Results and discussion

3.1   *Catalyst preparation*

To produce the catalyst system, a poly(ethylene glycol) (PEG) functionalized Fe_3O_4/Au core-shell nanoparticle was firstly synthesized according to the procedure developed in our group.[49] The reason for the use of a PEG stabilizer is the higher affinity for protic solvents of nanoparticles stabilized with a poly(ethylene glycol) chain, as Suzuki reactions perform better in the presence of water and require protic conditions.[50] The morphology of the Fe_3O_4/Au core-shell nanoparticle is studied using Transmission Electron Microscopy (TEM) (**Error! Reference source not found.**). The mean diameter of the nanoparticles is 100 ± 4 nm. Since the average iron oxide core diameter is known, the average shell thickness can be calculated, which is 40 ± 2 nm. As depicted in **Error! Reference source not found.**, the Fe_3O_4/Au core-shell nanoparticles show a rough surface. This roughness might be an indication of the *in-situ* generation of gold seeds, rather than the direct deposition of a smooth golden shell. This also means that the deposition of the gold does not happen epitaxially. The presence of the golden shell around the magnetite and the presence of the magnetite inside the golden shell was confirmed by TEM-EDX in our previous work.[49] The same Fe_3O_4/Au nanoparticles are used in this work. In addition, to prove the presence of the stabilizer on the nanoparticle, FT-IR spectra are recorded of the PEG stabilized core-shell nanoparticles together with the corresponding stabilizer (**Error! Reference source not found.**). In both spectra, the C-H stretch of the PEG-thiol at 2860 cm^{-1} is strongly present. The O-H and C-O-H stretch at 1094 cm^{-1} is also clearly depicted in the spectra. It should also be mentioned that other less prominent peaks of the PEG-thiol are also present in the functionalized Fe_3O_4/Au core-shell nanoparticles. To have an indication about the presence of iron oxide, the region at 580-600 cm^{-1} and 470-480 cm^{-1} should be examined. Since the spectrum of the functionalized core-shell nanoparticle shows no peaks in this region, there can be concluded that the gold shell is fully closed.

The functionalization of the Fe_3O_4/Au core-shell nanoparticles is performed by stirring the core-shell nanoparticles together with $Pd(OAc)_2$ in 1,4-dioxane for 4 days under argon atmosphere (**Error! Reference source not found.**). It should be mentioned that the synthesis of our catalyst system occurs in the absence of any reducing reagents or without any surface modifications, resulting in an easy and straightforward functionalization of the nanoparticle. Inductive coupled plasma-atomic emission spectroscopy (ICP-AES) is used for the determination of the amount of Pd present on the catalyst system (**Error! Reference source not found.**), resulting in 0.079 mg Pd/mg Fe_3O_4/Au/PEG/Pd nanoparticles.

Since the objective of this study is to induce cross-coupling reactions using plasmonic heating, a UV-Vis spectrum is recorded to study the plasmon resonance of the synthesized core-shell nanoparticles (**Error! Reference source not found.**). As depicted in **Error! Reference source not found.**, the plasmon peak lies at 680 nm.

3.2 *Suzuki cross-coupling reactions*

The cross-coupling of 4-bromoanisol with phenylboronic acid is used as a model reaction for the initial studies and is performed in the presence of K_2CO_3 (**Error! Reference source not found.**). The reason for the use of K_2CO_3 is because it is a base leading to high yields and is applied in many Suzuki reactions.[51–55] As a solvent, an $EtOH/H_2O$ (1:1) mixture was chosen, which according to Zhou *et al.* results in optimal conditions.[50] The reason for the use of PEG stabilized core-shell nanoparticles is the presence of water in the reaction mixture and PEG stabilized nanoparticles results in better dispersion of the nanoparticles in the reaction mixture.

The reason for the use of 4-bromoanisol in the model reaction is twofold. First, it consists of an electron-donating group and consequently this results possibly in a lower conversion. As such, there is still a large improvement potential if other substituents (poorly donating or even electron-withdrawing) are used. Second, this substrate cannot be deprotonated by the presence

7

of K_2CO_3. Due to this precaution, it cannot affect the conversion by the interaction with the nanoparticle. This possible influence on the conversion can be explained by an attraction/repulsion between the compound and the catalyst system, which was observed in our previous studies.[38]

First, the proof-of-principle is given using the light-induced model reaction together with the corresponding thermal reaction. This corresponding thermal reaction is a reaction performed using identical conditions as the light-induced reaction and at the same temperature as that of the bulk during the light-induced reaction in function of time (**Error! Reference source not found.**). The light-induced reaction is performed using a pulsed laser at a wavelength of 680 nm with an optical power of 500 mW (maximal power). This is the wavelength corresponding to the plasmon resonance of the Pd functionalized Fe_3O_4/Au core-shell nanoparticles (**Error! Reference source not found.**).

According to **Error! Reference source not found.**, the reaction tends to stop after 4 hours, and a difference of 52 % of conversion is observed between the light-induced reaction and the thermal contribution. The temperature in the reaction vial of the light-induced reaction is around 23 °C after 4 hours of reaction time and was measured using a thermal couple. To obtain a stronger evidence of the proof-of-principle of the light-induced Suzuki reaction, the same study was performed in triplo (**Error! Reference source not found.**). According to these results, an average difference of 54 % of conversion is observed after a reaction time of 4 hours.

It was demonstrated that the irradiation of light indeed has an influence on the conversion and knowing that the Suzuki reaction is largely affected by the amount of catalyst, the reaction is further optimized by varying the amount of nanoparticles, and by this varying the catalyst loading. The amount of nanoparticles is changed, while the wavelength and intensity of the light beam are kept the same. (**Error! Reference source not found.**)

8

As depicted in **Error! Reference source not found.**, increasing the catalyst loading increases the conversion. It should be mentioned that this is not only a trend that is observed for the light-induced reaction, but also for the thermal contribution reaction. When the conversion of the thermal contribution is abstracted from the conversion obtained during the light-induced reaction, it can be concluded that the optimal amount of nanoparticles is 0.2 mg, since the conversion difference was the largest (52 %). The reaction tends to stop after 4 hours, which was not only observed using 0.2 mg of Fe_3O_4/Au/PEG/Pd nanoparticles but also for 0.1 mg and 0.4 mg of nanoparticles. Therefore, there can be concluded that optimal results were obtained using a catalyst loading of 0.2 mg of Fe_3O_4/Au/PEG/Pd nanoparticles with a reaction time of 4 hours.

Knowing the optimal conditions for the model Suzuki reaction, the light-induced reaction performance using Fe_3O_4/Au/PEG/Pd as catalyst system is investigated for various substrates. The results are summarized in **Error! Reference source not found.**.

As can be derived from **Error! Reference source not found.** all substrates lead to conversion to the end-product except for the chlorinated compounds (**Error! Reference source not found.**; Entry 5 and 6). By introducing more steric hindrance on the aryl bromide the conversion decreases (**Error! Reference source not found.**; Entry 7 and 8). This is also observed for the introduction of a strong electron-donating amine-group on the aryl bromide (**Error! Reference source not found.**; Entry 11). The use of electron-withdrawing groups (**Error! Reference source not found.**; Entry 10 and 13) on the other hand, result in an increase in conversion compared to the model reaction, as expected. Very interesting results are observed by comparing entry 4 with 9 and entry 12 with 13. It is observed that although an approximately equal electron-donating (**Error! Reference source not found.**; Entry 4 and 9) or electron-withdrawing (**Error! Reference source not found.**; Entry 12 and 13) effect is present, they result in total different conversion. This can be explained by the presence of the

9

base and the zeta-potential of the core-shell nanoparticle. Due to the presence of K_2CO_3 in the reaction mixture, 4-bromobenzoic acid (**Error! Reference source not found.**; Entry 12) and 4-bromophenol (**Error! Reference source not found.**; Entry 4) are deprotonated, resulting in a negative charge. Knowing that the zeta-potential of the Fe_3O_4/Au/PEG/Pd nanoparticle equals -14.0 mV (Supplementary Information S8), the anionic compound is repulsed from the negatively charged nanoparticle as it approaches. In this way, the compound remains further away for the heating source and the catalytic site and will not result in an advantage of the plasmonic heating. This is also demonstrated by comparing the plasmonic conversion with the thermal contribution for entry 2, 4 and 12, as the plasmonic conversion and the thermal contribution for the three compounds are almost equal. It is observed that for all other substrates, a positive effect on the conversion was observed using plasmonic heating. Furthermore, the aryl boronic acids bearing either electron-donating groups or electron-withdrawing groups can provide the corresponding product (**Error! Reference source not found.**; Entry 14 and 15).

The superiority of heterogeneous catalysts lies in their recyclability. To investigate the potential of the recyclability of the Fe_3O_4/Au/PEG/Pd core-shell nanoparticle catalyst, the used catalyst was recycled by magnetic precipitation, which is performed using an external magnet (**Error! Reference source not found.**). This type of recycling has never been performed using Pd-functionalized Au nanoparticles for the application of plasmonic heating. It results in a faster, easier and more efficient method compared to centrifugation, which is a common used method for the recuperation of Pd functionalized Au nanoparticles and can result in unwanted agglomeration of the valuable nanoparticles.[36]

The catalyst was used for 5 cycles (**Error! Reference source not found.**), and the conditions were kept identical in each cycle. After each run, the core-shell nanoparticle catalyst system was separated by magnetic precipitation and the supernatant was decanted. The nanoparticle

10

catalyst is then subsequently washed with 4 mL of 1,4-dioxane, 4 mL of water, 2 times with 4 mL of ethanol and dried under vacuum. After washing and drying of the catalyst system, it was directly reused without further purification. A correction for the amount of nanoparticles present after the recuperation was taken into account, resulting in a procedure where the amount of starting reagents is adapted to the amount of nanoparticles after the recuperation. Due to this procedure, the loss in activity can only be the result of a change in the composition of the Fe_3O_4/Au/PEG/Pd nanoparticles, and as such the leaching of Pd from the catalyst system. This is examined using ICP-AES (Supplementary Information Table S1). The results show that the catalyst can be reused for at least 5 times, although with a small decrease in conversion.

Knowing that the irradiation of light results in a local increase of the temperature at the catalytic site of the Fe_3O_4/Au/PEG/Pd core-shell nanoparticles, it is interesting to know that temperature. Therefore, the conversion obtained using the light-induced reaction is compared with the conversions obtained using thermal heating at different temperatures (**Error! Reference source not found.**). The light-induced reaction, as well as the thermal reactions, are performed using the model reaction (**Error! Reference source not found.**) under optimized conditions with a reaction time of 2 hours. The difference between both types of reactions is that the light-induced reaction is performed using a pulsed laser beam with a wavelength of 680 nm and an optical power of 500 mW, while the thermal reactions are performed using conventional thermal heating at different temperatures. As can be derived from **Error! Reference source not found.**, the temperature at the catalytic site of the light-induced Suzuki reaction resulting in plasmonic photothermal conversion is between 40 °C and 45 °C.

3.3 Sonogashira cross-coupling reaction
Since good results were obtained for the Suzuki reaction, a second cross-coupling reaction was investigated using Fe_3O_4/Au/PEG/Pd catalyst nanoparticles for the use in plasmonic photothermal conversion of a Sonogashira reaction. In former work a method was developed

using conventional thermal heating, resulting in an aerobic, Cu-free Sonogashira reaction with a reaction time of 3 hours, leading to full conversion at 100 °C.[56]

Therefore, an equal base, solvent, and concentrations are used for the examination of the Sonogashira reaction for plasmonic heating using the Fe_3O_4/Au/PEG/Pd core-shell catalyst nanoparticles. The same model reaction is used as in the previous study, since it resulted in full conversion after a reaction time of 3 hours (**Error! Reference source not found.**). The amount of nanoparticles is varied in order to optimize the catalyst loading, but despite previous success in the light-induced Suzuki reaction, no conversion is obtained in the light-induced Sonogashira reaction (**Error! Reference source not found.**).

It should be mentioned that the amount of catalyst loading is not the reason for the failure of the Sonogashira reaction, since the catalyst loading, expressed in mol% Pd, of the working Sonogashira reaction in the previous study, giving rise to full conversion at a temperature of 100 °C, was approximately 3 times lower compared with the highest tested amount of nanoparticles in this study. Therefore, the reason can be assigned to the temperature created around the nanoparticle. Knowing that for similar type of nanoparticles the Sonogashira-reaction only resulted in conversion at a temperature higher than 55 °C and that no conversion was obtained at 30 °C, there can be concluded that no sufficiently high temperature was created at the catalytic site. This can also be depicted in **Error! Reference source not found.**, where the temperature at the catalytic site is studied for the Suzuki reaction. From these results there can be concluded that the plasmonic photothermal conversion only gives rise to a temperature between 40 °C and 45 °C at the catalytic site, which is not high enough to result in conversion for the Sonogashira reaction, resulting in a limitation of reactions depending on their required reaction temperature.

4 Conclusion

It can be concluded that Fe_3O_4/Au/PEG/Pd core-shell nanoparticle catalyst can be used for plasmonic heating during a Suzuki cross-coupling reaction. Optimal results were obtained using 0.2 mg of Fe_3O_4/Au/PEG/Pd core-shell nanoparticles, resulting in a Pd amount of 0.82 10^{-3} mol%. Furthermore, due to the presence of the magnetite core in the catalyst system, it is possible to remove and reuse the catalyst using a magnet. In this way, it is possible to incorporate a straightforward and easy recuperation method for the use of light-induced Suzuki reactions. It is found that the catalyst can be reused for at least 5 cycles with a relatively small decrease of conversion. The advantage of using plasmonic heating is only possible using compounds without a negative charge in presence of the used reaction conditions, and not all substrates give rise to high conversions. It should be mentioned that the irradiation of light results in a temperature between 40 °C and 45 °C at the catalytic site using Fe_3O_4/Au/PEG/Pd core-shell nanoparticles. Although good results were obtained for the Suzuki reaction, it can be concluded that no conversion is possible for the Sonogashira reaction using light, since no desired product was obtained. This is due to the fact that Sonogashira reactions are only possible at high temperatures using our catalyst system.

Acknowledgments

Notes and references

[1]   N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.

13

[2]   A. Molnár, *Chem. Rev.* **2011**, *111*, 2251–2320.

[3]   B. W. Glasspoole, C. M. Crudden, *Nat. Chem.* **2011**, *3*, 912–913.

[4]   A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, *Chem. Soc. Rev.* **2011**, *40*, 5181.

[5]   G. Chacón, C. Pradel, N. Saffon-Merceron, D. Madec, M. Gomez, M. Gomez, *French-Ukrainian J. Chem.* **2016**, *4*, 37–50.

[6]   F. Fernández, B. Cordero, J. Durand, G. Muller, F. Malbosc, Y. Kihn, E. Teuma, M. Gómez, *Dalt. Trans.* **2007**, 5572.

[7]   F. Chahdoura, C. Pradel, M. Gómez, *Adv. Synth. Catal.* **2013**, *355*, 3648–3660.

[8]   H. Veisi, A. Amini Manesh, N. Eivazi, A. R. Faraji, *RSC Adv.* **2015**, *5*, 20098–20107.

[9]   V. Polshettiwar, C. Len, A. Fihri, *Coord. Chem. Rev.* **2009**, *253*, 2599–2626.

[10]   Z. Zheng, H. Li, T. Liu, R. Cao, *J. Catal.* **2010**, *270*, 268–274.

[11]   P. Han, X. Wang, X. Qiu, X. Ji, L. Gao, *J. Mol. Catal. A Chem.* **2007**, *272*, 136–141.

[12]   S. Rohani, G. Mohammadi Ziarani, A. Badiei, A. Ziarati, R. Luque, *Catal. Letters.* **2019**, *149*, 2984–2993.

[13]   S. Moussa, A. R. Siamaki, B. F. Gupton, M. S. El-Shall, *ACS Catal.* **2012**, *2*, 145–154.

[14]   A. R. Siamaki, A. E. R. S. Khder, V. Abdelsayed, M. S. El-Shall, B. F. Gupton, *J. Catal.* **2011**, *279*, 1–11.

[15]   A. Leyva, H. García, A. Corma, *Tetrahedron.* **2007**, *63*, 7097–7111.

[16]   Y. Zheng, P. D. Stevens, Y. Gao, *J. Org. Chem.* **2006**, *71*, 537–542.

[17]   N. Yılmaz Baran, T. Baran, A. Menteş, M. Karakışla, M. Saçak, *J. Organomet. Chem.* **2018**, *866*, 87–94.

[18]   S. Ogasawara, S. Kato, *J. Am. Chem. Soc.* **2010**, *132*, 4608–4613.

[19]   I. Beletskaya, A. Kashin, I. Khotina, A. Khokhlov, *Synlett.* **2008**, *10*, 1547–1552.

[20]   R. Najman, J. K. Cho, A. F. Coffey, J. W. Davies, M. Bradley, *Chem. Commun.* **2007**, *47*, 5031–5033.

[21]   A. R. Siamaki, Y. Lin, K. Woodberry, J. W. Connell, B. F. Gupton, *J. Mater. Chem. A.* **2013**, *1*, 12909.

[22]   V. I. Sokolov, E. G. Rakov, N. A. Bumagin, M. G. Vinogradov, *Fullerenes, Nanotub. Carbon Nanostructures.* **2010**, *18*, 558–563.

[23]   C. Deraedt, D. Wang, L. Salmon, L. Etienne, C. Labrugère, J. Ruiz, D. Astruc, *ChemCatChem.* **2015**, *7*, 303–308.

[24]   C. Deraedt, L. Salmon, D. Astruc, *Adv. Synth. Catal.* **2014**, *356*, 2525–2538.

[25]   L. Wu, B.-L. Li, Y.-Y. Huang, H.-F. Zhou, Y.-M. He, Q.-H. Fan, *Org. Lett.* **2006**, *8*, 3605–3608.

[26]   K. R. Gopidas, J. K. Whitesell, M. A. Fox, *Nano Lett.* **2003**, *3*, 1757–1760.

[27] F. X. Llabrés i Xamena, A. Abad, A. Corma, H. Garcia, *J. Catal.* **2007**, *250*, 294–298.

[28] J. A. Bobb, A. A. Ibrahim, M. S. El-Shall, *ACS Appl. Nano Mater.* **2018**, *1*, 4852–4862.

[29] A. Gniewek, J. J. Ziółkowski, A. M. Trzeciak, M. Zawadzki, H. Grabowska, J. Wrzyszcz, *J. Catal.* **2008**, *254*, 121–130.

[30] M. Lakshmi Kantam, S. Roy, M. Roy, B. Sreedhar, B. M. Choudary, *Adv. Synth. Catal.* **2005**, *347*, 2002–2008.

[31] P. D. Stevens, G. Li, J. Fan, M. Yen, Y. Gao, *Chem. Commun.* **2005**, *35*, 4435.

[32] H. A. Elazab, A. R. Siamaki, S. Moussa, B. F. Gupton, M. S. El-Shall, *Appl. Catal. A Gen.* **2015**, *491*, 58–69.

[33] H. Veisi, P. Sarachegol, S. Hemmati, *Polyhedron.* **2018**, *156*, 64–71.

[34] H. Veisi, J. Gholami, H. Ueda, P. Mohammadi, M. Noroozi, *J. Mol. Catal. A Chem.* **2015**, *396*, 216–223.

[35] F. Wang, C. Li, H. Chen, R. Jiang, L.-D. Sun, Q. Li, J. Wang, J. C. Yu, C.-H. Yan, *J. Am. Chem. Soc.* **2013**, *135*, 5588–5601.

[36] Q. Xiao, S. Sarina, E. Jaatinen, J. Jia, D. P. Arnold, H. Liu, H. Zhu, *Green Chem.* **2014**, *16*, 4272.

[37] E. Kang, H. Shin, D.-K. Lim, *Catalysts.* **2018**, *8*, 463.

[38] A. De Cattelle, A. Billen, W. Brullot, T. Verbiest, G. Koeckelberghs, *J. Organomet. Chem.* **2019**, *899*, 120905.

[39] K. Watanabe, D. Menzel, N. Nilius, H.-J. Freund, *Chem. Rev.* **2006**, *106*, 4301–4320.

[40] H. H. Richardson, Z. N. Hickman, A. O. Govorov, A. C. Thomas, W. Zhang, M. E. Kordesch, *Nano Lett.* **2006**, *6*, 783–788.

[41] P. K. Jain, X. Huang, I. H. El-Sayed, M. A. El-Sayed, *Acc. Chem. Res.* **2008**, *41*, 1578–1586.

[42] S. Lal, S. E. Clare, N. J. Halas, *Acc. Chem. Res.* **2008**, *41*, 1842–1851.

[43] M. Rycenga, Z. Wang, E. Gordon, C. M. Cobley, A. G. Schwartz, P. C. S. Lo, P. Y. Xia, *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 9924.

[44] W. Hasan, C. L. Stender, M. H. Lee, C. L. Nehl, J. Lee, T. W. Odom, *Nano Lett.* **2009**, *9*, 1555–1558.

[45] X. Chen, H. Zhu, J. Zhao, Z. Zheng, X. Gao, *Angew. Chemie Int. Ed.* **2008**, *47*, 5353–5356.

[46] H. Zhu, X. Ke, X. Yang, S. Sarina, H. Liu, *Angew. Chemie Int. Ed.* **2010**, *49*, 9657–9661.

[47] W. H. Hung, M. Aykol, D. Valley, W. Hou, S. B. Cronin, *Nano Lett.* **2010**, *10*, 1314–1318.

[48] P. Christopher, H. Xin, S. Linic, *Nat. Chem.* **2011**, *3*, 467–472.

[49] A. Billen, A. de Cattelle, J. K. Jochum, M. J. Van Bael, J. Billen, J. W. Seo, W. Brullot, G. Koeckelberghs, T. Verbiest, *Phys. B Condens. Matter*. **2019**, *560*, 85–90.

[50] S. Zhou, M. Johnson, J. G. C. Veinot, *Chem. Commun.* **2010**, *46*, 2411.

[51] S. Shabbir, S. Lee, M. Lim, H. Lee, H. Ko, Y. Lee, H. Rhee, *J. Organomet. Chem.* **2017**, *846*, 296–304.

[52] S. Li, Y. Lin, J. Cao, S. Zhang, *J. Org. Chem.* **2007**, *72*, 4067–4072.

[53] L. Li, S. Zhao, A. Joshi-Pangu, M. Diane, M. R. Biscoe, *J. Am. Chem. Soc.* **2014**, *136*, 14027–14030.

[54] W. Chen, P. Li, L. Wang, *Tetrahedron*. **2011**, *67*, 318–325.

[55] Q. Xiao, S. Sarina, E. Jaatinen, J. Jia, D. P. Arnold, H. Liu, H. Zhu, *Green Chem.* **2014**, *16*, 4272.

[56] A. De Cattelle, A. Billen, G. O'Rourke, W. Brullot, T. Verbiest, G. Koeckelberghs, *J. Organomet. Chem.* **2019**, *904*, 121005.