

Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. K. Rathi, M. B. Gawande, J. Pechousek, J. Tucek, C. Aparicio, M. Petr, O. Tomanec, R. Krikavova, Z. Travnicek, R. S. Varma and R. Zboril, *Green Chem.*, 2015, DOI: 10.1039/C5GC02264A.



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 **Information for Authors**.

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 <u>Ethical guidelines</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.



www.rsc.org/greenchem

Please do not adjust margins Green Chemistry

DOI: 10.1039/C5GC02264A

Green Chemistry



Received 00th July 2015,

Accepted 00th July 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Maghemite decorated with ultra-small palladium nanoparticles (γ -Fe₂O₃-Pd): applications in Heck-Mizoroki olefination, Suzuki reaction and allylic oxidation of alkenes

Anuj K. Rathi,^a Manoj B. Gawande,^a* Jiri Pechousek,^a Jiri Tucek,^a Claudia Aparicio,^a Martin Petr,^a Ondrej Tomanec,^a Radka Krikavova,^b Zdenek Travnicek,^b Rajender S. Varma,^c and Radek Zboril^a*

A nanocatalyst comprising ultra-small Pd/PdO nanoparticles (<5 nm) supported on maghemite was prepared by coprecipitation protocol using inexpensive raw materials and was deployed successfully in various significant synthetic transformations, namely Heck-Mizoroki olefination (upto 95%), Suzuki reaction (60-95%), and allylic oxidation of alkenes under milder conditions. The chemical nature, morphology, size, and loading of palladium nanoparticles over the magnetic support were studied by TEM/EDX, HAADF-STEM chemical mapping, XPS, AAS, and in-field ⁵⁷Fe Mössbauer spectroscopy. The cost-effective catalyst could be easily separated from the reaction mixture by using an external magnet and reused four times without loss of activity; chemical stability and recyclability aspects of the catalyst were investigated.

Introduction

Transition metals and their complexes play a dominant role in catalyzing various common transformations, namely C-C crosscoupling and carbon heteroatom bond formation, oxidation, reduction and reductive amination reactions, thus enabling the synthesis of organic building blocks, natural products,¹ pharmaceuticals, and agrochemicals.^{2,3} Among the various transition-metal catalyzed cross-coupling reactions, Heck-Mizoroki^{4,5} and Suzuki-Miyaura reactions⁶ are the most important and highly effective protocols for the construction of carbon-carbon bonds.⁷⁻¹² However, phosphine-based Pd catalyst such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)^{13}$ and pre-catalysts including Pdcarbene complexes, ¹⁴ palladacycles¹⁵ and also Pd salts are often employed for cross-coupling reactions in the presence of moisture sensitive, expensive and toxic PPh₃,¹⁶ and PCy₃ ligands.¹⁷ In the past few years, numerous effective and selective homogeneous palladium catalytic systems have been developed for such reactions but they have disadvantages such as tedious separation and contamination of the coupled products with Pd species.¹⁸ The applicability of heterogeneous solid-supported catalysts has overcome these limitations with improvements in handling and separation. Recent examples of supported catalysts/nanocatalysts¹⁹ Pd include such

immobilization of Pd(II) on various solid supports such as phosphorylated polyethylene glycols (PPEG),²⁰ carbon,²¹ polymers,²² silica,^{23, 24} zeolites,²⁵ corn starch²⁶ and cellulose.^{27,28} From sustainability viewpoint, high catalytic efficiency, selectivity, convenient separation (isolation) and recyclability are viewed as the main desirable attributes for metal nano-catalysts.^{28b} Nonetheless, chemical endeavours for the development of noble metal nanoparticles to attain the aforementioned features remains a challenging task.

The magnetically separable iron oxides such as magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) provide inert support for the metal nanoparticles, thus enhancing their attractive features by rendering them relatively inexpensive, separable by an external magnet and facilitating recyclability in several reaction cycles for a diverse array of chemical transformations.²⁸⁻³⁹

In recent years, there are various reports on the synthesis of magnetic-decorated metal nanocatalysts (e.g. Pd, Cu etc.,) and their applications in organic transformations.⁴⁰ In most of these reported protocols, various types of linkers and ligands have been used that often require multistep synthesis procedure thus rendering them more expensive. However, the stabilization of metal nanoparticles and/or organoligands over the surface of magnetic support in the absence of linkers or ligands is a significant challenge for organic chemists from the catalytic viewpoint (i.e. leaching). So, it is imperative to design and develop such inexpensive protocols for the catalytic applications. Recently, Moores and co-workers highlighted the importance of bare magnetic nanoparticles, their synthesis, properties and varied applications.⁴¹ Additionally, these magnetic nanoparticles themselves act as catalysts or as a reducer of other metals and their metal leaching is guite comparable to other magnetic decorated catalysts with ligands/linkers, and catalysts prepared by multistep synthesis.⁴¹

^aRegional Centre of Advanced Technologies and Materials, Faculty of Science, Departments of Physical Chemistry and Experimental Physics, Palacky University, Šlechtitelů 27, 783 71, Olomouc, Czech Republic. *Emailmanoj.aawande@upol.cz (Manoj B. Gawande), <u>radek.zboril@upol.cz</u> (Radek

Dorill Zborill ^bRegional Centre of Advanced Technologies and Materials, Faculty of Science,

Department of Inorganic Chemistry, Palacky University, Šlechtitelů 27, 783 71, Olomouc, Czech Republic.

^cSustainable Technology Division, National Risk Management Research Laboratory, US Environmental Protection Agency, 26 West Martin Luther King

ARTICLE

Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39.

In continuation of our ongoing studies on magnetic decorated nanocatalysts without linkers/lingads,⁴² herein, we report an efficient protocol for the preparation of recyclable maghemite-Pd nanoparticles (NPs) and their utility in Suzuki and Heck-Mizoroki reactions of aryl halides and allylic oxidation of alkenes using *tert*-butylhydroperoxide (TBHP) as an oxidant under benign conditions; control experiments with bare maghemite (without Pd) produced no/low yields of the corresponding desired products.

Notably, this catalytic protocol is a simple yet effective approach as it avoids several multistep post synthetic functionalization processes and the use of toxic and complex ligands, which renders the present protocol straightforward and inexpensive.

Results and discussion

In a typical preparation of maghemite-Pd, first maghemite support is prepared from inexpensive iron precursors and Pd nanoparticles are further immobilized by co-precipitation method using PdCl₂ salt. The as-synthesized maghemite-Pd nanocatalyst, characterized by X-ray photoelectron spectroscopy (XPS) Inductively coupled plasma-mass spectrometry (ICP-MS), transmission electron microscopy (TEM), field-emission gun scanning electron microscopy combined with electron dispersive spectrometry (FEG-SEM-EDS), high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Mössbauer spectroscopy.XPS profile of maghemite-Pd is depicted in Fig. 1 where the expected positions of the 3d line for Pd⁰ and PdO,⁴³ respectively, are marked by blue and red colours, respectively. Although the expected Pd line position for Pd(OH)₂ differs by only 0.1 eV with respect to that of PdO, the presence of palladium hydroxide cannot be excluded. It is presumed that PdO and Pd(OH)₂ may have been generated independently during the hydrolysis of PdCl₂ under basic conditions; deposition of palladium^{44a} in the form of Pd(OH)₂ colloids in basic solution are eventually converted into PdO or Pd⁰. The formation of PdO is also deduced from low-intensity broad peak in XRD pattern corresponding to main diffraction line (101) of the PdO phase (see Fig. S1, Supporting Information). These findings are in good agreement with high-resolution Pd3d XPS data, which clearly show the presence of Pd⁰ as indicated by the characteristic peak at 335.50 and 340.76 eV and for PdO at 336.81 and 342.07 $\mathrm{eV}^{\mathrm{44b}}$ (Fig. 1). The relative intensities of the Pd 3d XPS lines show that approx. 84% corresponds to Pd⁰ and 16% to PdO. Thus validating that majority of Pd is efficiently adsorbed onto the surface of maghemite in the Pd⁰ form. The formation of Pd⁰ species is acquired via the reduction of Pd(II) to Pd(0); ethanol acts as a reducing agent during work-up procedure.⁴⁵ The ICP-MS analysis confirmed the presence of 6.3 wt% Pd in the catalyst.

Before decoration with Pd nanoparticles, the chemical nature of the magnetic support was ascertained by ⁵⁷Fe Mössbauer spectroscopy, which is a very sensitive element-selective technique, among others, to the valence state and spin state of iron in the crystal structure. At 5 T, the ⁵⁷Fe Mössbauer spectrum of the magnetic support features two distinct sextets with the values of the Mössbauer hyperfine parameters typically DOI: 10.1039/C5GC02264A Green Chemistry

Green Chemistry Accepted Manuscript



with Pd, the chemical nature of the magnetic support was not changed. The high stoichiometry of maghemite is viewed as a big advantage compared to non-stoichiometric maghemite or magnetite mainly if it is used in redox-systems where the chemical stability of the support is required including applications as magnetically separable catalysts.

observed for y-Fe₂O₃ (see Fig. 2a). The sextet with the lower

isomer shift (δ = 0.34 mm/s) and higher hyperfine magnetic ($B_{\rm hf}$

= 55.6 T) corresponds to the tetrahedral (T) cation sites occupied

by Fe^{3+} in the y-Fe₂O₃ spinel crystal structure while the other

sextet with higher isomer shift (δ = 0.50 mm/s) and lower hyperfine magnetic field (B_{hf} = 47.8 T) belongs to the octahedral

(O) cation sites with Fe^{3+} and vacancies in the γ -Fe₂O₃ spinel

crystal structure. The spectral ratio of the T-to-O sextet is 3:5, a value characteristic of purely stoichiometric γ -Fe₂O₃ phase with



Fig. 1. XPS spectrum of maghemite-Pd; the position of 3d line for metallic Pd⁰ and PdO is denoted by blue and red colour, respectively.



Fig. 2. ⁵⁷Fe Mössbauer spectrum of (a) the magnetic support and (b) the maghemite-Pd catalyst, recorded at a temperature of 5 K with magnetic field of 5 T applied parallel to the γ-rays direction.

In order to monitor the magnetic properties of the γ -Fe₂O₃ nanoparticles and γ -Fe₂O₃ nanoparticles with Pd, hysteresis loops and ZFC/FC magnetization curves were measured for both samples (see Fig. 3). The trends of the hysteresis loops and ZFC/FC magnetization curves for both samples are identical; there is only difference in the magnetization values reflecting the presence of palladium, which behaves in a diamagnetic manner decreasing the magnetic response.

At 5 K, the isothermal magnetization curves of both samples show a hysteresis character implying that γ -Fe₂O₃ nanoparticles are in magnetically blocked regime with their superspins fixed in a particular direction favored by the nanoparticle magnetic anisotropy. The saturation magnetization of the system composed solely of γ -Fe₂O₃ nanoparticles amounts to ~84 Am²/kg, a value very close to that reported for bulk γ -Fe₂O₃ nanoparticles, they still keep their strong magnetic response not affected by finite-size effects. The saturation magnetization of

ARTICLE the assembly of γ -Fe₂O₃ nanoparticles with palladium (~75 Am^2/kg) is decreased by the presence of the catalytic

View Article Online DOI: 10.1039/C5GC02264A

Am²/kg) is decreased by the presence of the catalytic nanoparticles, which show diamagnetic behavior. Moreover, the coercivity and remanence values fall within the range expected for γ-Fe₂O₃ phase. At 300 K, the isothermal magnetization curves of both sample are not hysteretic, indicating a passage of the system to the superparamagnetic state when, due to thermal excitations, nanoparticle superspin fluctuates between directions energetically favored by the nanoparticle magnetic anisotropy. The saturation magnetization of both systems is still very high (~63 Am^2/kg and ~53 Am^2/kg for the γ -Fe₂O₃ nanoparticles without and with palladium, respectively) and is reached at low applied magnetic fields (~1 T), providing successful extraction of the catalyst from the environment by a simple external magnet. The superparamagnetic behavior of both systems is further documented by the profile of the ZFC magnetization curves with a maximum at ~110 K characteristic of the blocking mechanism. From the identical profile of the ZFC/FC magnetization curves, it is evident that the presence of the catalyst nanoparticles does not affect the overall magnetic properties of the system.



DOI: 10.1039/C5GC02264A Green Chemistry

Fig. 3. Hysteresis loops of the γ -Fe₂O₃ nanoparticles and maghemite-Pd sample, recorded at a temperature of (a) 5 K and (b) 300 K. (c) ZFC and FC magnetization curves of the the γ -Fe₂O₃ nanoparticles and maghemite-Pd sample.

TEM analysis of maghemite-Pd (Fig. 4a and 4b) reveals that the size of the as-synthesized spherical maghemite NPs is in the range of 10-20 nm, while Pd nanoparticles covering the maghemite surface are extremely small (<5 nm, see Fig S2). The EDS spectrum shows the presence of Fe, O and Pd species as expected (Fig. 4c).

The element (Pd, Fe, and O) mapping (Fig. 4, e-h) confirms quite homogeneous distribution of ultra-small Pd nanoparticles over the globular maghemite nanoparticle surface. In summary, palladium NPs, dominantly in the form of Pd⁰ (<5 nm), are uniformly distributed onto the surface of highly stoichiometric globular maghemite nanoparticles (10-20 nm) as confirmed by XPS, Mössbauer spectroscopy, XRD, TEM, and HAADF-STEM images. Further, the catalytic performance of maghemite-Pd nanocatalysts was investigated for various organic transformations.

Catalytic applications

Pd-based catalysts are very well-known for cross-coupling reactions and other important organic transformations.^{3,6} In the present work, ultra-fine Pd/PdO nanoparticles on maghemite were tested for Heck-Mizoroki reaction, Suzuki reaction and allylic oxidation reactions.

Green Chemistry

ARTICLE



Fig. 4. (a) TEM image of the maghemite-Pd catalyst; (b) TEM of single maghemite particle showing Pd nanoparticles on the surface of maghemite; (c) EDS spectrum of maghemite-Pd nanocatalyst showing Pd content (yellow highlight); (d) HAADF-STEM of maghemite-Pd at 20 nm; (e-h) HAADF images showing elemental mapping of Pd, Fe, and O atoms at 8 nm.

Heck-Mizoroki reaction.

The catalytic activity was first evaluated for the Heck-Mizoroki reaction between 1-iodo-4-methylbenzene and butyl acrylate in the presence of K_2CO_3 and maghemite-Pd (0.030 mmol of Pd) in various solvents at 110 °C for 12 h (Table 1). The reaction proceeded cleanly in DMF with 99% conversion (95% isolated yield), while other solvents such as tetrahydrofuran (THF) and polyethylene glycol (PEG-200) showed <5%, and 85% conversion, respectively (Table 1, entries 1, 2).

The effect of the catalyst amount and time variation showed that 13 mg (0.0076 mmol of Pd) catalyst provided the optimum results within 2 h (Table 1, entry 6), while 8 mg (0.0045 mmol of Pd) afforded only 85% conversion (Table 1, entry 7). It was noticed that pristine maghemite without palladium did not work for the reaction (Table 1, entry 8).

DOI: 10.1039/C5GC02264A **Green Chemistry**

Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39.

Table 1. Optimization of the Heck-Mizoroki reaction between 1-iodo-4-methylbenzene and butyl acrylate catalyzed by maghemite-Pd.^a

Ĺ) + ~ 0 ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	K ₂ CO _{3 ,} maghe Solvent, 110	mite-Pd °C	° °
Entry	Solvent	Time (h)	Conversion ^f (%)	Isolated yield (%)
1	THF	12	<5	-
2	PEG-200	12	>85	82 ^b
3	DMF	12	>99	95 ^b
4	DMF	2	>99	95 ^b
5	DMF	2	>99	95 [°]
6	DMF	2	>99	95 ^d
7	DMF	2	>85	77 ^e
8	DMF	6		^g

^aReaction conditions: 1-iodo-4-methylbenzene (0.5 mmol), K₂CO₃ (1 mmol), butyl acrylate (1 mmol), solvent (2 mL); 110 °C. ^bMaghemite-Pd (50 mg, 0.030 mmol of Pd), ^cMaghemite-Pd (32 mg, 0.019 mmol of Pd), ^dMaghemite-Pd (13mg, 0.0076 mmol of Pd), ^cMaghemite-Pd (8 mg, 0.0045 mmol of Pd), ^gMaghemite, ^fConversion was determined by GC analysis.

The coupling reaction between aryl halides (I and Br) bearing electron donating and electron withdrawing groups in different positions and various alkenes was carried out under the optimized conditions; corresponding coupled products were obtained in good to excellent yields (Table 2). Notably, the reaction of aryl iodide with electron poor and electron rich substituents proceeded smoothly with 0.0076 mmol of Pd catalyst loading (Table 2, entries 1a-h), while aryl bromide required 0.010 mmol of Pd catalyst to deliver the best yields (Tables 2, entries 1i-m); further increase in the amount of catalyst did not affect the yields.

As expected, sterically hindered o-substituents on the aryl halide affected the reaction progress and slightly lower yield was obtained (Table 2, entries 3h, 3l, 3m). Thus, 1-bromo-2nitrobenzene and 2-bromobenzonitrile needed higher reaction time (Table 2, entries 3I and 3m) than electron donating group and electron withdrawing group on "meta (m)" and "para (p)" position and showed the good to excellent yields (Table 2, entries 3b-3f, 3i-3k). It was noted that *m*-cyano substituted aryl halides showed the moderate yield (Table 2, entry 3g). The reaction of 4-nitro chlorobenzene with butyl acrylate did not work well, giving only 30 % yield after 12 h (Table 2, entry 3 n).

lease do not adjust margins Green Chemistry

Green Chemistry

 Table 2. Maghemite-Pd catalyzed Heck-Mizoroki reaction of aryl halides with different acrylates.^a





R= H, 4-Me, 3-OMe, 2-OMe, 4-NO₂, 3-CN, 3-NO₂, 4-COMe, 2-CN, 2-NO₂ R¹= Butyl acrylate, Methyl acrylate



Please do not adjust margins Green Chemistry

Green Chemistry Accepted Manuscript

DOI: 10.1039/C5GC02264A

Green Chemistry



^a**Reaction conditions:** Aryl iodide (1a-h)/aryl bromide (1i-m)/aryl chloride (1n) (0.5 mmol), K₂CO₃ (1 mmol), alkene (1 mmol), DMF (2 mL), 110 °C, catalyst loading; maghemite-Pd (1a-h; 13 mg, 0.0076 mmol of Pd; and 1i-n; 18 mg, 0.010 mmol of Pd), ^bTime, All yields are isolated yields.

Suzuki Reaction.

ARTICLE

The catalytic activity of the maghemite-Pd nanocatalyst was explored for the Suzuki reaction between 1-iodo-4-methylbenzene and 4-methoxyphenylboronic acid as model substrates in the presence of K_2CO_3 as base and DMF:H₂O solvent system at 110 °C (Table 3). After optimizing the reaction conditions, the scope of the catalytic activity was investigated for a variety of substituted aryl halides (-Br and -I) and boronic acids; the reaction was completed within 1 h for aryl iodide

(Table 3, 4a and b), while aryl bromide required 2-2.5 h to afford excellent yields with 0.010 mmol of Pd catalyst loading (Table 3, 4c-i). All substrates bearing an electron donating and withdrawing group in different position (o and p) afforded excellent yields (Table 3) with the exception of *p*-cyano phenyl boronic acid which gave slightly moderate yield (Table 3, entry 6h). Sterically hindered aryl bromide reacted smoothly with *p*-tolylboronic acid, providing good yield of the desired product (Table 3, entry 6i).

Green Chemistry

Table 3. Maghemite-Pd catalyzed Suzuki reaction of aryl halides with boronic acid.^a



X= I, Br R¹= 4-Me, 4-NO₂, 4-t-Butyl, 4-COMe, 3-NO₂, 2-CN R²= H, 4- OMe, 4-Me, 4- Ph, 4-CN

Entry	Aryl iodide	Boronic acid	Time (h)	Product	Yield ^b (%)
1	4a	B(OH) ₂	1	6a	90
2	4b	B(OH) ₂	1	6b	94 (92) ^c
3	Br 4c	B(OH) ₂	2	6c	90
4	O ₂ N 4d	B(OH) ₂	1.5	O ₂ N 6d	95
5	Br 4e	B(OH) ₂	2	6e	80
6	O 4f	B(OH) ₂	2	O 6f	90

Please do not adjust margins Green Chemistry







Allylic Oxidation of Alkenes.

Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39.

Allylic oxidation is an important reaction in organic synthesis and, generally, the reaction is conducted using a variety of reagents and conditions. $^{\rm 48,49}$

Table 4. Optimization of allylic oxidation of cyclohexene.^a



			Time	Conversions ^b (%)		ıs ^b
Entry	try Solvent Catalysts		(h)	а	b	SM
1	DCM	maghemite-Pd	16	63	9	27
2	Toluene	maghemite-Pd	16	0.7	0.2	92
3	ACN -		16	<1	-	>99
4 ^c	ACN	maghemite-Pd	16	81	7	11
5 ^d	ACN	maghemite-Pd	14	93	7	-
6 ^e	ACN +H ₂ O ₂	maghemite-Pd	16	2.7	10.5	19

^aReaction conditions: Alkene (0.5 mmol), K_2CO_3 (0.6 mmol), ACN (3 mL), TBHP (2.5 mmol), Temp 85 °C, ^bConversion calculated on the basis of GC

analysis; ^cMaghemite-Pd (80 mg, 0.047 mmol of Pd) ^dMaghemite-Pd (100mg, 0.059 mmol of Pd), ^eH₂O₂ (2.5 mmol), SM–starting material.

However, allylic oxidation with metal complexes frequently encounters typical problems such as poor functional group tolerance, low regioselectivity, higher costs, and difficult catalyst preparation.⁵⁰ The versatility of maghemite-Pd was further established by conducting allylic oxidation of simple alkenes using tert-butyl hydroperoxide (TBHP) solution as an oxidant. First, the optimization of the reaction was performed using cyclohexene as substrate to identify the ideal solvent, temperature, and catalyst quantity (Table 4). It was noticed that increasing the amount of catalyst from 0.047 mmol of Pd to 0.059 mmol of Pd enhanced the conversion and selectivity towards the cyclohex-2-enone with decreased reaction time (Table 2, entries 4 and 5); in the absence of maghemite-Pd, the reaction did not proceed (Table 2, entry 3). In terms of the solvent, the best results were obtained in acetonitrile (ACN) with upto 93% selectivity of cyclohex-2-enone (Table 4, entry 5), while dichloromethane (DCM) showed the 63% conversion of cyclohex-2-enone (Table 4, entry 1); toluene gave less conversion (Table 4 entry 2). Additionally, when the reaction was performed in ACN in the presence of H₂O₂ (30%), cyclohex-2-enol 10.5% and cyclohex-2-enone 2.7% were formed respectively with other impurities (Table 4, entry 6).

Green Chemistry

ARTICLE

Under the optimized reaction conditions, the reaction of 4methyl substituted cyclic alkene (1-methylcyclohex-1-ene) showed selectivity (88%) for 3-methylcyclohex-2-enol, presumably due to steric effects (Scheme 1).

Scheme 1. Maghemite-Pd catalyzed allylic oxidation of olefins.^a



^a**Reaction conditions**: Alkene (0.5 mmol), K_2CO_3 (0.6 mmol), maghemite-Pd (100 mg, 0.059 mmol of Pd), ACN (3 mL), TBHP (2.5 mmol), temp. 85 °C. ^bConversion calculated on the basis of GC analysis.

Evidently, the developed magnetic-Pd nanocomposites were found to be high-performance catalysts for Heck-Mizoroki reaction of aryl halides with different acrylates and Suzuki reaction of aryl halides with boronic acids; protocols are quite comparable, when matched with the reported procedures. Often, reported processes took several hours (1-48 h) to complete the reaction, while present method gets completed within 1-2h (Table S1 and S2, Supporting Information). The Turn Over Frequency (TOF) for both reactions are calculated and compared with some selected reported protocols; TOF is comparable with reported protocols (Table S3 and S4, Supporting Information). Additionally, the catalysts worked well for allylic oxidation of cyclohexene and 1-methylcyclohex-1-ene with excellent selectivity.

Recycling ability of the maghemite-Pd nanocatalyst.

The reusability of the catalytic system has to be taken into account to develop a practical catalyst material with cost effective and sound environmental attributes. The reusability of the catalyst for the Suzuki reaction was examined under optimized condition with 1-iodo-4-methylbenzene and 4-methoxyphenylboronic acid as model reactants. After completion of the reaction the catalyst was recovered with the help of an external magnet and washed with ethyl acetate, water and finally ethanol, dried at 80 °C in an oven and then reused for the next cycles. Importantly, the reusability tests for

four consecutive cycles did not show any indication of catalyst deactivation (Fig. 5); the conversion and yield after several reaction cycles are still over 97 and 92%, respectively (Table S6, Supporting Information).



Fig. 5. Reusability study of maghemite-Pd nanocatalyst. Blue column - conversion of the reactant; Red column–yield.

The ICP-MS analysis confirmed the presence of 6.3 wt%, 6.2 wt%, 6.0 wt% and 5.7wt% of Pd content from first to fourth cycle, respectively. From these results, it is clear that the catalyst is stable up to 3^{rd} catalytic cycle and after fourth cycle, some drop of Pd leaching was observed, but importantly it does not affect the yield of the corresponding product (Table S5, 94% after first cycle and 92% after fourth cycle). In addition, the TEM image also showed that the size of the nanoparticles remained unchanged even after 4^{th} cycle, thus confirming the strong grafting of Pd-NPs onto the maghemite surface and avoiding the aggregation of the nanoparticles under the reaction conditions (Please see Figure S2c).

Interestingly, XPS analysis of the catalyst after the first cycle shows the exclusive presence of Pd⁰ while the lines typical for PdO are drastically diminished (see Fig. S3, Supporting Information). The combination of DMF and water in presence of K₂CO₃ plays an important role in the reaction, as it serves the dual function of a solvent and a reducing agent (PdO to Pd⁰) under heating conditions.^{51,52} To prove this, maghemite-Pd catalyst was stirred at 110 °C in DMF-water in presence of K₂CO₃; PdO was completely converted to Pd⁰ as confirmed by XPS. Importantly, the reduction of Pd(II) during the catalyst recycling does not affect its efficiency in terms of conversion and yield.

DOI: 10.1039/C5GC02264A Green Chemistry

CONCLUSIONS

In summary, we have developed retrievable maghemitesupported ultra-small Pd/PdO nanoparticles (~5 nm) useful for a variety of organic transformations namely Heck-Mizoroki olefination of aryl halides and Suzuki reaction in excellent yields under milder conditions and at low maghemite-Pd catalyst loading. In addition, the catalyst was effective for allylic oxidation of olefins. The developed system shows several superior features compared to other reported catalysts including very short reaction time for completion of the reaction (1-2 hr), high yield and excellent selectivity, and reusability that keeps the catalyst efficient after four cycles. Most importantly, the use of catalyst circumvents the traditional filtration/isolation processes via a simple magnetic decantation enabling more than 95% of the catalysts recovery.

EXPERIMENTAL SECTION

Materials and Methods

Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39

Palladium chloride (99.9%), potassium chloride (99.9%), ammonium hydroxide, sodium hydroxide, sodium sulfate (99%), boronic acids, aryl halides, *tert*-Butylhydroperoxide (TBHP), potassium carbonate and other solvents were purchased from Sigma-Aldrich and were used without any further purification.

General procedure for the synthesis of maghemite $(\gamma\text{-}\mathsf{Fe}_2\mathsf{O}_3)$ NPs.

Maghemite was prepared by the co-precipitation method. Typically, FeSO₄.7H₂O (6.06 g, 21.79 mmol) and FeCl₃.6H₂O (11.75 g, 45.08 mmol) were dissolved in 120 mL of deionized water. The resulting mixture was stirred for 15 min and heated at 60 $^{\circ}$ C under vigorous stirring. After attaining the desired temperature at 60 $^{\circ}$ C, aqueous NH₄OH (30 mL, 25-28% NH₃ in water) was added dropwise; a black precipitate ensued immediately and heating was continued for 2h under N₂ atmosphere. The precipitate was magnetically separated and washed thoroughly with deionised water until the supernatant liquor reached neutrality. The resulting material was dried in an oven at 100 $^{\circ}$ C for 12 h; 75% yield of maghemite was observed.

General procedure for the preparation of maghemite-Pd NPs.

A solution of palladium chloride (349 mg) in water (80 mL) and potassium chloride (1 g) was stirred together for 5 min and maghemite (3g) was added to it. The resulting mixture was stirred at room temperature for 1 h and the suspension was adjusted to pH 12~13 by the slow addition of sodium hydroxide (1.0 M) and further stirred for 24 h. The aqueous layer was decanted with the help of an external magnet and the ensuing material was washed with deionised water (5 × 50 mL) under sonication at 45 °C followed by ethanol washing and drying under vacuum at 60 °C for 12 h to afford maghemite-Pd.

General procedure for the Heck-Mizoroki reaction of aryl halide and acrylate.

A stirred mixture of aryl halide (0.5 mmol), potassium carbonate (1 mmol), maghemite-Pd (0.0076 to 0.010 mmol of Pd) in N,Ndimethylformamide (DMF, 2 mL) was degassed for 5 minute under N₂ and alkene (1 mmol) was added to it. The resulting mixture was stirred at 110 °C under N₂ for appropriate reaction time (Scheme 2) and progress of the reaction was monitored by thin layer chromatography (silica gel; n-hexane/ethyl acetate). After completion of the reaction, the catalyst was separated with external magnet and volatiles were removed under reduced pressure and the obtained crude material was diluted with water and extracted with ethyl acetate (3 × 30 mL). The combined ethyl acetate fractions were washed with brine, dried, and concentrated under reduced pressure using a rotary evaporator. The crude product was purified by column chromatography (silica 230-400; n-hexane/ethyl acetate mixture) to afford the desired product. All compounds were characterized by ¹H and ¹³C NMR spectroscopy.

General procedure for the Suzuki reaction of aryl halide and boronic acid.

To a stirred degassed mixture of aryl halide (0.5 mmol), potassium carbonate (1 mmol), boronic acid (0.6 mmol) in DMF:H₂O (3 mL, 3:1,v/v), under N₂, maghemite-Pd (0.01 mmol of Pd) was added. The resulting mixture was stirred at 110 °C for appropriate reaction time (Scheme 3) and the progress of the reaction was monitored by TLC (silica gel; n-hexane/ethyl acetate). After completion of the reaction, the volatiles were removed under reduced pressure and the residual material was diluted with water and extracted with ethyl acetate (3 × 30 mL). The combined ethyl acetate fractions were washed with brine, dried, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica 230–400; n-hexane/ethyl acetate mixture) to afford the desired product. All compounds were characterized by ¹H and ¹³C NMR spectroscopy.

General procedure for the allylic oxidation of alkenes.

To a stirred mixture of olefin (0.5 mmol), K_2CO_3 (0.6 mmol), and maghemite-Pd (0.059 mmol of Pd) in acetonitrile (3 mL), TBHP (2.5 mmol), was added *via* a syringe. The resulting mixture was stirred at 85 °C for an appropriate time (Table 4 and Scheme 4). The progress and conversion of the reaction was monitored by GC (gas chromatography) and compared with standard samples.

Acknowledgements

The authors thank Ms. J. Stránská for TEM, David milde and Radka Kralova for elemental analysis, and Dr. V. Ranc for GC analysis. The authors acknowledge support from the Ministry of Education, Youth and Sports of the Czech Republic (LO1305), by Technology Agency of the Czech Republic "Competence Centres" (project TE01020218), by the Operational Program Education for Competitiveness - European Social Fund (project

Please do not adjust margins Green Chemistry

Green Chemistry

CZ.1.07/2.3.00/30.0041 and CZ.1.07/2.4.00/31.0189) of the Ministry of Education, Youth and Sports of the Czech Republic. The work is also funded by the Palacky University Institutional support and IGA grant (Project No. IGA-PrF-2015-017).

Disclaimer: The U.S. Environmental Protection Agency, through its Office of Research and Development, funded and managed, or partially funded and collaborated in, the research described herein. It has been subjected to the Agency's administrative review and has been approved for external publication. Any opinions expressed in this paper are those of the author(s) and do not necessarily reflect the views of the Agency, therefore, no official endorsement should be inferred. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

+Electronic supplementary information (ESI) available.

Mössbauer analysis, catalyst recycling studies, comparison with earlier heterogeneous reactions, XPS data for reused catalyst and 1 H and 13 C NMR data for products are included.

Notes

Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39

The authors declare no competing financial interest.

References

- 1 K. C Nicolaou, P. G. Bulger and D. Sarlah, Angew. Chem. Int. Ed., 2005, 44, 4442.
- 2 J. A. Baur, and D. A. Sinclair, Nat. Rev. Drug Discov., 2006, 5, 493.
- 3 C. Torborg and M. Beller, Adv. Synth. Catal., 2009, 351, 3027.
- 4 A. Biffis, M. Zecca and M. Basato, J. Mol. Catal. A: Chem., 2001, 173, 249.
- 5 N. J. Whitcombe, K. K. Hii and S. E. Gibson, *Tetrahedron*, 2001, **57**, 7449.
- 6 F. -S. Han, Chem. Soc. Rev., 2013, **42**, 5270.
- 7 C. C. C. J. Seechurn, M. O. Kitching, T. J. Colacot and V. Snieckus, Angew. Chem. Int. Ed., 2012, **51**, 5062.
- 8 Y. Zhong and W. Han, Chem. Commun., 2014, 50, 3874.

9 M. Tobisu, T. Xu, T. Shimasaki and N. Chatani, J. Am .Chem. Soc., 2011, 133, 19505.

- 10 R. Zhang, C. Miao, S. Wang, C. Xia and W. Sun, ChemCatChem, 2013, 5, 142.
- 11 I. P. Beletskaya and A. V. Cheprakov, Coord. Chem. Rev., 2004, 248, 2337.
- 12 J. Mao, J. Guo, F. Fang and S.-J. Ji, Tetrahedron, 2008, 64, 3905.
- 13 M. J. Mphahlele and M. M. Mphahlele, Molecules, 2010, 15, 7423.
- 14 M. Yigit, Molecules, 2009, 14, 2032.

15 I. P. Beletskaya and A. V. Cheprakov, J. Organomet. Chem., 2004, 689, 4055.

16 M. Blangetti, H. Rosso, C. Prandi, A. Deagostino and P. Venturello, *Molecules*, 2013, **18**, 1188.

17 C. Liu, Q. Ni, P. Hu and J. Qiu, Org. Biomol. Chem., 2011, 9, 1054.

18 M. Butters, D. Catterick, A. Craig, A. Curzons, D. Dale, A. Gillmore, S. P Green, I. Marziano, J.-P. Sherlock and W. White, *Chem. Rev.*, 2006, **106**, 3002.

19 Q. M. Kainz, R. Linhardt, R. N. Grass, G. Vile, J.Perez-Ramirez, W. J. Stark and O. Reiser, *Adv. Funct. Mater.*, 2014, **24**, 2020.

20 N. Iranpoor, H. Firouzabadi, A. Riazi, and A. Shakerpoor, *Appl. Organomet. Chem.*, 2013, **27**, 451.

21 Y. Lim, S. K. Kim, S.-C. Lee, J. Choi, K. S.Nahm, S. J. Yoo and P. Kim, *Nanoscale*, 2014, *6*, 4038.

22 N. Kann, Molecules, 2010, 15, 6306.

23 V. Polshettiwar, C. Len, and A. Fihri, Coord. Chem. Rev., 2009, 253, 2599.

24 R. B. N. Baig and R. S. Varma, RSC Adv., 2014, 4, 6568.

25 L. Djakovitch, and K. Koehler, J. Am . Chem. Soc., 2001, 123, 5990.

26 M. J. Gronnow, R. Luque, D. J. Macquarrie and J. H. Clark, *Green Chem.*, 2005, 7, 552.

27 K. R. Reddy, N. S. Kumar, P. S. Reddy, B. Sreedhar and M. L. Kantam, J. Mol. Catal. A: Chem., 2006, 252, 12.

28 (a) Q. Du and Y. Li, *Beilstein J. Org. Chem.*, 2011, **7**, 378.; (b) S. Zhou, M. Johnsona, and J. G. C. Veinot, *Chem. Commun.*, 2010, **46**, 2411-2413

29 L. Yin and J. Liebscher, Chem. Rev. 2007, 107, 133.

30 M. B. Gawande, P. S. Branco and R. S. Varma, Chem. Soc. Rev., 2013, 42, 3371.

31 R. B. N. Baig and R. S. Varma, Chem. Commun., 2013, 49, 752.

32 D. Wang and D. Astruc, Chem. Rev., 2014, 114, 6949.

33 M. B. Gawande, R. Luque and R. Zboril, *ChemCatChem*, 2014, 6, 3312.
34 S. N. Shelke, S. R. Bankar, G. R. Mhaske, S. S. Kadam, D. K. Murade, S. B. Bhorkade, A. K. Rathi, N. Bundaleski, O. M. N. D. Teodoro, R. Zboril, R. S. Varma and M. B. Gawande, *ACS Sustainable Chem. Eng.*, 2014, 2, 1699.

35 J. Liu, X. Peng, W. Sun, Y. Zhao and C. Xia, Org. Lett., 2008, 10, 3933.

36 (a) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J.-M. Basset, *Chem. Rev.* 2011, **111**, 3036 –3075; (b) M. Ojeda, A. M. Balu, V. Barrón, A. Pineda, Á. G. Coleto, A. Á. Romero and R. Luque, *J. Mater. Chem., A.*, 2014,**2**, 387-393; (c) M. Ojeda, A. Pineda, A. A. Romero, V. Barrón and R. Luque, *ChemSusChem*, 2014, **7**, 1876–1880.; (d) Polshettiwar and R. S. Varma, *Org. Biomol. Chem.* 2009, **7**, 37.

37 M. B. Gawande, A. K. Rathi, J. Tucek, K. Safarova, N. Bundaleski, O. M. N. D. Teodoro, L. Kvitek, R. S. Varma and R. Zboril, *Green Chem.*, 2014, **16**, 4137.

38 J. V. Coelho, M. S. Guedes, R. G. Prado, J. Tronto, J. D. Ardisson, M. C. Pereira, and L. C. A. Oliyeira, *Appl. Catal.*, *B*. 2014, **144**, 792.

39 (a) F. Nador, M. Alicia Volpe, F. Alonso and G. Radivoy, *Tetrahedron*, 2014, 70, 6082; (b)
 D. Horvath, L. Toth and L. Guczi, *Catal. Lett.* 2000, 67, 117.

40. (a) M.-J. Jin, and D.-H. Lee, *Angew. Chem. Int. Ed.*, 2010, **49**, 1119; (b) X. Sun, Y. Zheng, L. Sun, H. Su, and C. Qi, *Catal. Lett.*, 2015, **145**, 1047; (c) M. Demirelli, E. Karaog'iu, A. Baykal, H. Sözeri , E. Uysal, and O. Duygulu, *J. Inorg. Organomet. Polym.*, 2013, **23**, 937; (d) L. Zhang, P. Li, J. Yang, M. Wang, and L. Wang, *ChemPlusChem* 2014, **79**, 217; (e) R. Abu-Reziq, H. Alper, D. Wang, and M. L. Post, *J. Am. Chem. Soc.*, 2006, **128**, 5279; (f) T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores, and C. J. Li, *Org. Lett.*, 2011, **13**, 442.

41 R. Hudson, Y. Feng, R. S. Varma and A. Moores, *Green Chem.*, 2014, **16**, 4493-4505.

42 (a) M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. A. Ghumman, N. Bundaleski, and O. M. N. D. Teodoro, *Chem. Eur. J.*, 2012, **18**, 12628 ; (b) M. B. Gawande, A. K. Rathi, I. D Nogueira, R. S. Varma and P. S. Branco, *Green Chem.*, 2013, **15**, 1895.

43 H. Gabasch, W. Unterberger, K. Hayek, B. Kloetzer, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Haevecker, A. Knop-Gericke, R. Schloegl, J. Han, F. H. Ribeiro, B. Aszalos-Kiss, T. Curtin and D. Zemlyanov, *Surf. Sci.*, 2006, **600**, 2980.

44 (a) T. Schalow, B. Brandt, D. E. Starr, M. Laurin, S. K. Shaikhutdinov, S. Schauermann, J. Libuda and H. J. Freund, *Angew. Chem. Int. Ed.*, 2006, **45**, 3693; (b) M. Brun, A. Berthet and J. C. Bertolini, *J. Electron. Spectrosc. Relat. Phenom.*, 1999, **104**, 55.

45 (a) M. Beygzadeh, A. Alizadeh, M.M. Khodaei, and D. Kordestani, *Catal. Commun.*, 2013, **32**, 86–91; (b) A. Beck, A. Horvath, A. Szucs, Z. Schay, Z.E. Horvath, Z. Zsoldos, I. Dekany, and L. Guczi, *Catal. Lett.*, 2000, **65**, 33.

46 J. Tuček, L. Machala, J. Frydrych, J. Pechoušek and R. Zbořil, Mössbauer Spectroscopy: Applications in Chemistry, Biology, and Nanotechnology. John Wiley and Sons, 2013, 351.

47 J. Tucek, R. Zboril and D. Petridis, *J. Nanosci. Nanotechnol.*, 2006, **6**, 926. 48 A. Nakamura and M. Nakada, *Synthesis*, 2013, **45**, 1421.

49 (a) A. J. Catino, R. E. Forslund and M. P. Doyle, J. Am .Chem. Soc., 2004, **126**, 13622. (b) I.I. Moiseev and M.N. Vargaftik, *Coordination Chem. Rev.*, 2004, **248**, 2381; (c) T. K. M. Shing, Y. Yeung, and P. L. Su, *Org. Lett.*, 2006, **8**, 3149; (d) A. L. García-Cabeza, R. Marín-Barrios, F. J. Moreno-Dorado, M. J. Ortega, G. M. Massanet, and F. M. Guerra *Org. Lett.*, 2014, **16**, 1598.

50 T. K. M. Shing, Y.-Y. Yeung and P. L. Su, Org. Lett., 2006, 8, 3149.

51 I. Pastoriza-Santos and L. M. Liz-Marzan, Pure Appl. Chem., 2000, 72, 83.

52 G.-Q. Gao and A.-W. Xu, New J. Chem., 2014, 38, 4661.

Please do not adjust margins Green Chemistry

View Article Online DOI: 10.1039/C5GC02264A Green Chemistry

ARTICLE

Table of Content



Maghemite decorated with ultra-small palladium nanoparticles (γ-Fe₂O₃-Pd): applications in Heck-Mizoroki olefination, Suzuki reaction and allylic oxidation of alkenes

Anuj K. Rathi,^a Manoj B. Gawande,^a* Jiri Pechousek,^a Claudia Aparicio,^a Martin Petr,^a Ondrej Tomanec,^a Radka Krikavova,^b Zdenek Travnicek,^b Rajender S. Varma,^c and Radek Zboril^a*

Abstract

Ultra-small palladium nanoparticles (<5 nm) supported on maghemite promoted Heck-Mizoroki olefination, Suzuki reaction and allylic oxidation of alkenes under milder conditions.



SUPPORTING INFORMATION

Maghemite decorated with ultra-small palladium nanoparticles (γ-Fe₂O₃-Pd): applications in Heck-Mizoroki olefination, Suzuki reaction and allylic oxidation of alkenes

Anuj K. Rathi,^a Manoj B. Gawande,^a* Jiri Pechousek,^a Jiri Tucek, ^a Claudia Aparicio,^a Martin Petr,^a Ondrej Tomanec,^a Radka Krikavova,^b Zdenek Travnicek,^b Rajender S. Varma,^c and Radek Zboril^a*

 ^aRegional Centre of Advanced Technologies and Materials, Faculty of Science, Department of Physical Chemistry, Palacky University, Šlechtitelů 27, 783 71, Olomouc, Czech Republic.
 ^bRegional Centre of Advanced Technologies and Materials, Faculty of Science, Department of Inorganic Chemistry, Palacky University, Šlechtitelů 27, 783 71, Olomouc, Czech Republic.
 ^cSustainable Technology Division, National Risk Management Research Laboratory, US Environmental Protection Agency, 26 West Martin Luther King Drive, MS 443, Cincinnati, Ohio, 45268, USA.

Contents

General information	2
Characterization techniques	2-3
Experimental analysis	4
TEM and HRTEM images showing size and morphology of reused catalyst	4-5
Comparison with earlier heterogeneous Catalyst used	5-9
Reusability study	9
XPS spectrum of reused catalyst	9
Characterization data of compounds	10-16
NMR spectra of compounds	17-35
References	36

General information. All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 pre-coated were used, respectively. The spots were visualized with iodine, and UV light.

Characterization techniques

X-ray powder diffraction (XRD) patterns for maghemite and maghemite-Pd samples were recorded at room temperature using a X'Pert PRO MPD diffractometer (PANalytical) in Bragg–Brentano geometry with iron-filtered, Co-K α radiation (40 kV, 30 mA, $\lambda = 0.1789$ nm) equipped with an X'Celerator detector and programmable divergence and diffracted beam antiscatter-slits. The angular range of measurement was set as $2\theta = 10-105^{\circ}$, with a step size of 0.017°. The identification of the crystalline phases in the experimental XRD pattern was obtained using the X'Pert High Score Plus software that includes a PDF-4+ and ICSD databases. Scanning Electron Microscope (SEM) was performed on Hitachi SU6600 with accelerating voltage15 kV. Energy Dispersive Spectrometry (EDS) was acquired in SEM by Thermo Noran System 7 with Si(Li) Detector. Accelerating voltage was 15 kV and acquisition time was 300 s.

Microscopic images were obtained by HRTEM TITAN 60-300 with X-FEG type emission gun, operating at 80 kV. This microscope is equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution is 0.06 nm in TEM mode. The elemental mappings were obtained by STEM-Energy Dispersive X-ray Spectroscopy (EDS) with acquisition time 20 min. For HRTEM analysis, the powder samples were dispersed in ethanol and 5 min ultrasonicated. One drop of this solution was placed on a copper grid with holey carbon film. The sample was dried at room temperature.

XPS surface investigation has been performed on the PHI 5000 VersaProbe II XPS system (Physical Electronics) with monochromatic Al-K α source (15 kV, 50 W) and photon energy

Green Chemistry

of 1486.7 eV was employed. Dual beam charge compensation was used for all measurements. All the spectra were measured in the vacuum of 1.3 x 10-7 Pa and at the room temperature of 21 °C. The analyzed area on each sample was spot of 200 μ m in diameter. The survey spectra was measured with pass energy of 187.850 eV and electronvolt step of 0.8 eV while for the high resolution spectra was used pass energy of 23.500 eV and electronvolt step of 0.2 eV. The spectra were evaluated with the MultiPak (Ulvac - PHI, Inc.) software. All binding energy (BE) values were referenced to the carbon peak C1s at 284.80 eV.

The transmission ⁵⁷Fe Mössbauer spectra were recorded on homemade Mössbauer spectrometer operating at a constant acceleration mode and equipped with 50 mCi ⁵⁷Co(Rh) source. For low-temperature (5 K) and in-field (5 T) measurements, the sample was placed inside the chamber of the Spectromagoryomagnetic system (Oxford Instruments); with the Mössbauer spectrometer attached to the system, the setup works in a parallel geometry when the external magnetic field is applied in a parallel direction with respect to the propagation of γ -rays. For fitting the Mössbauer spectra, the MossWinn software program was used. The isomer shift values are referred to α -Fe at room temperature. NMR spectra were measured in JNM-ECA600II NMR spectrometer (JEOL, 298 Japan) at Κ. DMSO- d_6 on a Tetramethylsilane (TMS) was used as the internal reference standard for ¹H and ¹³C NMR experiments. The conversion and selectivity of the reactions were analyzed by GC employing chromatograph Agilent 6820 (Agilent, United States), equipped with flame ionisation detector (FID) and chromatographic column DB5 (30x0.250x0.25). Following experimental parameters were applied: initial temperature 100 °C, increased to 250 °C with a rate of 10 °C/min.

Experimental analysis



Fig. S1. Miller indices, corresponding to maghemite and PdO are shown in black and red numbers, respectively.





Fig. S2. (a-b) HRTEM images of maghemite-Pd showing ultrasmall Pd nanoparticles (<5 nm) covering globular (maghemite nanoparticles (ca. 10-20) nm. (c) TEM image of maghemite-Pd nanoparticles in Suzuki reaction after four cycles.

Entry	Catalyst	Conditions	Yield (%) ^a	Ref.
1	Pd(0)/C	TBAB, 2 M Na ₂ CO ₃ , DME, 80 °C, O/N	21-95%	1
2	Pd/MgLa mixed oxide	80 °C, Ethanol, K ₂ CO ₃ , 1-6h	37-98	2
3	Pd ⁺² -sepiolite	100-130 °C, K ₂ CO ₃ , DMF, 20- 24h	23-94 ^b	3
4	Pd HAP-1 (2 X 10 ⁻³)	120 °C, K ₂ CO ₃ , o-Xylene, 4-24 h	80-98 ^b	4
5	Pd (II)-SBA-16	Pd (II)-SBA-16, K ₂ CO ₃ , 80 °C, EtOH : H ₂ O, 2.5-12 h	28-99	5
6	PANI-Pd	95 °C, K ₂ CO ₃ , Dioxane: H ₂ O, 4h	75-95	6
7	SBA-15-XH-Pd	100 °C, DMF: H ₂ O, NaOAc, 15h	67-98	7
8	Maghemite-Pd	100°C, K ₂ CO ₃ , DMF: H ₂ O, 2h	60-95	Present work

Table S1. Comparison of selected heterogeneous catalysts used for Suzuki reaction.

^a Isolated yield, ^bGC yield

Entry	Catalyst	Conditions	Yield ^a (%)	Ref.
1	SBA-15-XH-Pd	100 °C, DMF, K ₂ CO ₃ , 15h	93-97	7
2	Pd-MCM-41	150 °C, Na ₂ CO ₃ , Bu ₄ NCl, NMP, 3-22h	54-100°	8
3	PANI-Pd	140 °C, K ₂ CO ₃ , DMA, 40 h	41-98	6
4	$\{[Pd(NH_3)_4]/NaY\}$	140 °C, NaOAc, NMP, 6-24 h	23-79	9
5	C-(KTB-Pd)	120 °C, K ₃ PO ₄ ·3H ₂ O, DMF, 2- 12h	72-99	10
6	Maghemite-Pd	110°C, K ₂ CO ₃ , DMF, 1h	60-95	Present work

Table S2. Comparison of selected heterogeneous catalyst used for Heck reaction.

^a Isolated yield, ^bGC yield, ^cConversion

Table S3. TOF comparison of various supported Pd catalysts for the reaction of 1-bromo-4methylbenzene with phenyl boronic acid.

	Br +	B(OH) ₂ catalyst base, solvent		
Entry	Pd Catalyst (mol %)	Conditions	$TOF(h^{-1})$	Ref.
1	Fe ₃ O ₄ -Bpy-Pd(OAc) ₂	K ₂ CO ₃ , toluene, 12h, 80 °C	4	11
2	Pd- Fe ₃ O ₄ @C	K ₂ CO ₃ , EtOH, 2h, 60 °C	37	12
3	Pd-Fe ₃ O ₄ heterodimer NCs	K ₃ PO ₄ , 1,4-dioxane, 24h, reflux	29	13
4	Pd-SBA-16	K ₂ CO ₃ , EtOH: H ₂ O, 8h, 80 °C	10	14
5	SBA-15-SH-Pd	K ₂ CO ₃ , DMF: H ₂ O, 15h	54	15

Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39.

TOF(L-1).	Yield 100	mmol of reactant	
101 (11)	Time (h)	^ mmol of Pd	

100°C, K₂CO₃, DMF: H₂O, 2h

43

Present

work

Maghemite-Pd

6

Table S4. TOF comparison of various supported Pd catalysts for the reaction of iodobenzene with butyl acrylate.



Entry	Catalyst	Conditions	$TOF(h^{-1})$	Ref.
1	Fe ₃ O ₄ -NH ₂ -Pd	K ₂ CO ₃ , NMP,130 °C, 10h	10	16
2	Pd-PVP@laponite	Et ₃ N,100 °C, 4h	70 ^a	17
3	MNP@NHC-Pd	NaHCO ₃ , DMF, reflux, 3h	2	18
4	Maghemite-Pd	100°C, K ₂ CO ₃ , DMF: H ₂ O, 2h	31	Present work
^a GC y	yield,			•





^a**Reaction conditions:** 1-iodo-4-methylbenzene (0.5 mmol), K_2CO_3 (1 mmol), 4-methoxyphenylboronic acid (0.7 mmol), maghemite-Pd (18 mg, 0. 0.010 mmol of Pd), DMF: H₂O (3 mL), 110°C, ^bConversion was measured by GC analysis, ^cIsolated yield.



Fig. S3. XPS spectrum of reused maghemite-Pd sample after first cycle. The position of the metallic Pd^0 is denoted by blue color.

Characterization data of compounds

(E)-Butyl cinnamate (3a)¹⁹



Transparent oil, 94%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 7.72 (2H, dd, *J*=6.6 Hz, *J*=2.8 Hz), 7.65 (1H, d, *J*=15.9 Hz), 7.42 (3H, m), 6.64 (1H, d, *J*=16.5 Hz), 4.15 (2H, t, *J*=6.6 Hz), 1.62 (2H, qui, *J*= 7.7 Hz), 1.38 (2H, sext, *J*=7.7 Hz), 0.91 (3H, t, *J*=7.4 Hz) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 166.28, 144.40, 134.01, 130.45, 128.91, 128.36, 118.12, 63.73, 30.28, 18.67, 13.59 ppm.

(E)-Butyl 3-p-tolylacrylate (3b)¹⁹



Transparent oil, 95%. ¹H NMR (600 MHz, DMSO- d_6): δ = 7.61 (3H, m), 7.23 (2H, d, *J*=8.2 Hz), 6.57 (1H, d, *J*=15.9 Hz), 4.14 (2H, t, *J*=6.6 Hz), 2.32 (3H, s), 1.61(2H, qui, *J*= 7.7 Hz), 1.37 (2H, sext, *J*=7.7 Hz), 0.91 (3H, t, *J*=7.4 Hz) ppm. ¹³C NMR (600 MHz, DMSO- d_6): δ = 166.39, 144.38, 140.43, 131.30, 129.52, 128.35, 117.00, 63.63, 30.30, 21.01, 18.67, 13.58 ppm.

(E)-Methyl 3-p-tolylacrylate (3c)²⁰



White solid, 93%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 7.61 (3H, m), 7.23 (2H, d, *J*= 7.7 Hz), 6.57 (1H, d, *J*=15.9 Hz), 3.71 (3H, s), 2.33 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 166.79, 144.54, 140.48, 131.27, 129.52, 128.35, 116.67, 51.39, 21.01 ppm.





Transparent oil, 95%. ¹H NMR (600 MHz, DMSO- d_6): δ = 7.62 (1H, d, *J*=15.9 Hz), 7.32 (2H, m), 7.28 (1H, m), 6.99 (1H, dd, *J*=7.7 Hz, *J*=2.2 Hz), 6.67 (1H, d, *J*=15.9 Hz), 4.15 (2H, t, *J*=6.6 Hz), 3.79 (3H, s), 1.62 (2H, m), 1.38 (2H, sext, *J*=7.7 Hz), 0.91 (3H, t, *J*=7.4 Hz) ppm.¹³C NMR (600 MHz, DMSO- d_6): δ = 166.29, 159.60, 144.36, 135.44, 129.91, 121.00, 118.46, 116.63, 112.86, 63.72, 55.23, 30.28, 18.67, 13.58 ppm.

(E)-Butyl 3-(3-nitrophenyl)acrylate (3e, 3k)²⁰



Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39

Light yellow solid, 90% and 88%. ¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.55 (1H, s), 8.22 (2H, m), 7.76 (1H, d, *J*=15.9 Hz), 7.70 (1H, t, *J*=7.8 Hz), 6.85 (1H, d, *J*=16.5 Hz), 4.16 (2H, t, *J*=6.6 Hz), 1.63 (2H, m), 1.38 (2H, sext, *J*=7.5 Hz), 0.91 (3H, t, *J*=7.4 Hz) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ = 165.85, 148.28, 141.96, 135.92, 134.11, 130.32, 124.55, 123.02, 121.13, 63.94, 30.23, 18.64, 13.55 ppm.

(E)-Butyl 3-(4-nitrophenyl)acrylate (3f, 3i, 3n)²⁰



Yellow solid, 85%, 83%, and 30%. ¹H NMR (600 MHz, DMSO- d_6): δ = 8.23 (2H, m), 8.01 (2H, m), 7.75 (1H, d, *J*=16.5 Hz), 6.85 (1H, d, *J*=15.9 Hz), 4.17 (2H, t, *J*=6.6 Hz), 1.63 (2H, qui, *J*=7.7 Hz), 1.38 (2H, sext, *J*=7.7 Hz), 0.92 (3H, t, *J*=7.4 Hz) ppm. ¹³C NMR (600 MHz,

DMSO- d_6): δ = 165.73, 148.04, 141.80, 140.47, 129.45, 123.89, 122.43, 64.07, 30.20, 18.63,

13.55 ppm.

(E)-Butyl 3-(3-cyanophenyl)acrylate (3g)²¹



Transparent oil, 62%. ¹H NMR (600 MHz, DMSO- d_6): δ = 8.27 (1H, s), 8.07 (1H, d, J=7.7 Hz), 7.87 (1H, d, J=7.8 Hz), 7.67 (1H, d, J=15.9 Hz), 7.62 (1H, t, J=7.8 Hz), 6.82 (1H, d, J=15.9 Hz), 4.16 (2H, t, J=6.6 Hz), 1.63 (2H, m), 1.38 (2H, sext, J=7.7 Hz), 0.91 (3H, t, J=7.4 Hz) ppm. ¹³C NMR (600 MHz, DMSO- d_6): δ = 165.94, 142.10, 135.35, 133.48, 132.79, 131.89, 130.06, 120.66, 118.36, 112.11, 63.93, 30.23, 18.64, 13.56 ppm.

(E)-Butyl 3-(2-methoxyphenyl)acrylate (3h)²²



Transparent oil, 82%. ¹H NMR (600 MHz, DMSO- d_6): δ = 7.88 (1H, d, *J*=15.9 Hz), 7.71 (1H, dd, *J*=7.7 Hz, *J*=1.1 Hz), 7.42 (1H, t, *J*=7.8 Hz), 7.09 (1H, d, *J*=8.2 Hz), 6.98 (1H, t, *J*=7.4 Hz), 6.60 (1H, d, *J*=15.9 Hz), 4.14 (2H, t, *J*=6.6 Hz), 3.87 (3H, s), 1.62 (2H, qui, *J*=7.7 Hz), 1.36 (2H, sext, *J*=7.7 Hz), 0.91 (3H, t, *J*=7.4 Hz) ppm. ¹³C NMR (600 MHz, DMSO- d_6): δ = 166.58, 157.83, 139.13, 132.03, 128.65, 122.20, 120.71, 118.15, 111.73, 63.64, 55.65, 30.29, 18.67, 13.57 ppm.

(E)-Butyl 3-(4-acetylphenyl)acrylate (3j)²²



Transparent oil, 84%. ¹H NMR (600 MHz, DMSO- d_6): δ = 7.97 (2H, d, *J*=8.3 Hz), 7.87 (2H, d, *J*=8.3 Hz), 7.70 (1H, d, *J*=15.9 Hz), 6.78 (1H, d, *J*=15.9 Hz), 4.16 (2H, t, *J*=6.6 Hz), 2.60 (3H, s), 1.63 (2H, m), 1.38 (2H, m), 0.92 (3H, t, *J*=7.4 Hz) ppm. ¹³C NMR (600 MHz, DMSO- d_6): δ = 197.43, 165.98, 143.01, 138.31, 137.69, 128.63, 128.54, 120.63, 63.92, 30.24, 26.81, 18.65, 13.56 ppm.

(E)-Methyl 3-(2-nitrophenyl)acrylate (3l)²²



Yellow solid, 82%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 8.08 (1H, d, *J*=8.2 Hz), 7.93 (2H, m), 7.78 (1H, t, *J*=7.4 Hz), 7.68 (1H, t, *J*=7.6 Hz), 6.64 (1H, d, *J*=15.9 Hz), 3.75 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 165.96, 148.27, 139.65, 133.91, 131.03, 129.33, 129.20, 124.71, 122.27, 51.80 ppm.

(E)-methyl-3-(2-cyanophenyl)acrylate (3m)²³



White solid, 67%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 8.11 (1H, d, *J*= 7.7 Hz), 7.92 (1H, d, *J*=7.7 Hz), 7.80 (1H, d, *J*=15.9 Hz), 7.77 (1H, t, J= 7.7 Hz), 7.62 (1H, t, *J*=7.7 Hz), 6.90 (1H, d, *J*=15.9 Hz), 3.77 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 165.97, 138.94, 136.31, 133.64, 133.50, 130.85, 127.44, 122.58, 117.18, 111.70, 51.89 ppm.

4-methylbiphenyl (6a, 6c)²⁴



White solid, 90%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 7.63 (2H, d, *J*=7.6 Hz), 7.55 (2H, d, *J*=7.6 Hz), 7.45 (2H, t, *J*=7.6 Hz), 7.34 (1H, d, *J*=7.3 Hz), 7.27 (2H, d, *J*=7.6 Hz), 2.34 (3H,

Green Chemistry

s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 140.08, 137.29, 136.69, 129.51, 128.87, 127.10, 126.50, 126.41, 20.65 ppm.

4-methoxy-4'-methylbiphenyl (6b)²⁵



White solid, 94%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 7.55 (2H, m), 7.49 (2H, d, *J*=7.7 Hz), 7.22 (2H, d, *J*=8.2 Hz), 6.99 (2H, m), 3.78 (3H, s), 2.32 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 158.66, 136.96, 135.84, 132.48, 129.43, 127.44, 125.97, 114.28, 55.10, 20.59 ppm.

4-methoxy-4'-nitrobiphenyl (6d)²⁶



Yellow solid, 95%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 8.26 (2H, d, *J*=8.8 Hz), 7.91 (2H, d, *J*=8.8 Hz), 7.76 (2H, d, *J*=8.8 Hz), 7.09 (2H, d, *J*=8.8 Hz), 3.82 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 160.18, 146.28, 145.99, 129.91, 128.56, 126.99, 124.08, 114.68, 55.31 ppm.

4-tert-butylbiphenyl (6e)²⁷



White solid, 80%. ¹H NMR (600 MHz, DMSO-*d*₆): δ=7.64 (2H, m), 7.58 (2H, m), 7.48 (2H, m), 7.45 (2H, m), 7.34 (1H, m), 1.31 (9H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 149.82, 140.08, 137.34, 128.86, 127.13, 126.50, 126.35, 125.68, 34.22, 31.09 ppm.





White solid, 90%. ¹H NMR (600 MHz, DMSO-*d*₆): δ=8.01 (2H, d, *J*=7.5 Hz), 7.79 (2H, d, *J*=7.4 Hz), 7.64 (2H, d, *J*=8.3 Hz), 7.31 (2H, d, *J*=8.3 Hz), 2.60 (3H, s), 2.36 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 197.43, 144.43, 137.90, 135.97, 135.36, 129.68, 128.88, 126.80, 126.51, 26.72, 20.71 ppm.

1-(1,1':4',1''-terphenyl-4-yl)ethanone (6g)²⁸



White solid, 88%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 8.06 (2H, d, *J*=7.9 Hz), 7.89 (2H, m), 7.87 (2H, m), 7.82 (2H, m), 7.74 (2H, m), 7.50 (2H, t, *J*=7.5 Hz), 7.41 (1H, t, *J* = 7.4 Hz), 2.63 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ = 197.52, 143.94, 140.08, 139.40, 137.82, 135.69, 129.05, 128.98, 127.76, 127.55, 127.35, 126.74, 126.67, 26.81 ppm.

3'-nitrobiphenyl-4-carbonitrile (6h)²⁹



Light yellow solid, 60%. ¹H NMR (600 MHz, DMSO-*d*₆): δ =8.51 (1H, t), 8.29 (1H, d, *J*=8.2 Hz), 8.22 (1H, d, *J*=7.8 Hz), 8.00 (4H, m), 7.81 (1H, t, *J*=7.9 Hz) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ = 148.47, 142.24, 139.84, 133.68, 133.04, 130.72, 128.06, 123.34, 121.70, 118.60, 111.18 ppm.

4'-methylbiphenyl-2-carbonitrile (6i)³⁰



White solid, 82%. ¹H NMR (600 MHz, DMSO-*d*₆): δ= 7.92 (1H, dd, *J*=7.7 Hz, *J*=1.1 Hz), 7.76 (1H, td, *J*=7.7 Hz, *J*=1.1 Hz), 7.59 (1H, d, *J*=7.7 Hz), 7.55 (1H, td, *J*=7.7 Hz, *J*=1.1 Hz), 7.46 (2H, d, *J*=8.3 Hz), 7.33 (2H, d, *J*=8.3 Hz), 2.38 (3H, s) ppm. ¹³C NMR (600 MHz, DMSO-*d*₆): δ= 144.54, 138.26, 134.97, 133.81, 133.46, 129.98, 129.29, 128.55, 127.93, 118.64, 110.08, 20.75 ppm.

¹H and ¹³C NMR spectra of compounds

(E)-Butyl cinnamate (3a)





¹HNMR 3b_Proton.jdf M04(m) Normalized Intensity 2.33 M01(m*) 0 0.91 0.90 o 0.85 0.80 0.75 0.70 0.65 0.60 M07(m) 0.55 4.13 0.50 0.90 0.45 M11(m) ~7.61 _7.60 = 0.40 M10(d) M08(d) 0.35 7.23 6.55 6.55 7.59 0.30 4.15 7.62 0.25 M02(m) 0.20 M03(m) 0.15 0.10 0.05 0 2.90 1.98 1.00 2.04 2.94 ⊔ 2.01 2.02 3.00 7.5 8.0 7.0 6.5 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 Chemical Shift (ppm) 6.0 ¹³CNMR Normalized Intensity 3b_Carbon.jdf o ∐ 129.52 128.35 0 0.20 0.15 30.30 63,63 117.00 144.38 13.58 0.10 66.39 131.30 140.43 0.05 0 176 160 152 112 80 64 56 48 40 32 24 Chemical Shift (ppm) 168 144 136 128 120 104 96 88 72

(E)-Butyl 3-p-tolylacrylate (3b)



18

Green Chemistry Accepted Manuscript

(E)-Methyl 3-p-tolylacrylate (3c)

Published on 02 December 2015. Downloaded by UNIVERSITY OF NEBRASKA on 08/12/2015 16:29:39.



Chemical Shift (ppm)



(E)-Butyl 3-(3-nitrophenyl)acrylate (3e)





(E)-Butyl 3-(4-nitrophenyl)acrylate (3f)







(E)-Butyl 3-(3-cyanophenyl)acrylate (3g)









80

64 56 48

72

32

24

40

122.20

157.83

152

144 136 128 120 112 104 96 88

0.05

0

176

168 160

Chemical Shift (ppm)

(E)-Butyl 3-(4-acetylphenyl)acrylate (3j)



(E)-Methyl 3-(2-nitrophenyl)acrylate (31) ¹HNMR 3I_Proton.jdf Normalized Intensity M03(m*) NO_2 o 3.75 **O** 1.0 0.9 0.8 0.7 0.6 0.5 0.4 M08(m) M04(d) M09(d) M07(t) 0.3 6.65 6.62 7.94 0.2 8.09 7.67 7.80 0.1 0 0.96 1.96 1.01 0.99 1.00 2.95 8.0 7.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 7.5 6.5 6.0 1.5 Chemical Shift (ppm) ¹³CNMR Normalized Intensity 3I_Carbon.jdf **NO**₂ o ∬ `0^{_} 0.40 0.35 0.30 51.80 0.25 122.27 133.91 131.03 129.33 139.65 124.71 0.20 0.15 165.96 129.20

148.27

136 128 120

112

104 96 88

80

64 56 48 40 32

72

0.10

0.05

0

176

160 152 144

168

(E)-methyl-3-(2-cyanophenyl)acrylate (3m)





4-methylbiphenyl (6a)







4-methoxy-4'-methylbiphenyl (6b)





125.97

_136.96 _135.84 132.48

136

128 120 112 88 80 72 64 56 48 40 32 24

104 96

58.66

160 152 144 Chemical Shift (ppm)

20.59

Chemical Shift (ppm)

55.10

0.90 0.85

0.80 0.75 0.70 0.65 0.60

0.55

0.50 0.45 0.40 0.35 0.30

0.25 0.20 0.15 0.10 0.05 0

176

168



¹HNMR



Green Chemistry Accepted Manuscript

4-tert-butylbiphenyl (6e)













1-(1,1':4',1''-terphenyl-4-yl)ethanone (6g)







4'-methylbiphenyl-2-carbonitrile (6i)





Green Chemistry

References

- 1. T. Tagata and M. Nishida, J. Org. Chem. 2003, 68, 9412.
- 2. A. Cwik, Z. Hell and F. Figueras, Org. Biomol. Chem. 2005, 3, 4307.
- 3. K. Shimizu, T. Kan-no, T. Kodama, H. Hagiwara and Y. Kitayama, Tetrahedron Lett., 2002, 43, 5653.
- 4. K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, J. Am. Chem. Soc., 2002,

124, 11572.

- 5. S. Wei, Z. Ma, P. Wang, Z. Dong and J. Ma, J. Mol. Catal. A: Chem., 2013, 370, 175.
- 6. H. A. Patel, A. L. Patel and A. V. Bedekar, Appl. Organomet. Chem. 2015, 29, 1.
- 7. C. M. Crudden, M. Sateesh and R. Lewis, J. Am. Chem. Soc., 2005, 127, 10045.
- 8. A. Papp, G. Galbacs and R. Molnar, Tetrahedron Lett., 2005, 46, 7725.
- 9. S. Noel, C. Luo, C. Pinel and L. Djakovitch, Adv. Synth. Catal., 2007, 349, 1128.
- 10. K. Song, P. Liu, J. Wang, L. Pang, J. Chen, I. Hussain, B. Tan and T. Li, *Dalton Trans.*, 2015,44, 13906-13913
- 11. Y.Q. Zhang, X.W.Wei and R. Yu, Catal Lett., 2010, 135, 256.
- 12. R. Li, P. Zhang, Y. Huang, P. Zhang, H. Zhong and Q. Chen, J. Mater. Chem., 2012, 22, 22750.
- 13. Y. Jang, J. Chung, S. Kim, S. W. Jun, B. H. Kim, D. W. Lee, B. M. Kim and T. Hyeon, *Phys. Chem.*

Chem. Phys., 2011, 13, 2512.

- 14. S. Wei, Z. Ma, P. Wang, Z. Dong and J. Ma, J.Mol. Catal. A: Chem. 2013, 370, 175.
- 15. C. M. Crudden, M. Sateesh and R. Lewis, J. Am. Chem. Soc., 2005, 127, 10045.
- 16. F. Zhang, J. Jin, X. Zhong, S. Li, J. Niu, R. Li and J. Ma, Green Chem., 2011,13, 1238.
- 17. <u>A.</u> V. Martínez, A. Leal-Duaso, José I. García, J. A. Mayoral, RSC Adv., 2015, 5, 59983.
- 18. A. Z. Wilczewska and I. Misztalewska, Organometallics, 2014, 33, 5203.
- 19. C.-H. Ying, S.-B.Yan, and W.-L. Duan, Org. Lett., 2014, 16, 500.
- 20. Y.-Q. Yuan, and S.-R. Guo, Synth. Commun., 2012, 42, 1059.
- 21. X. Cui, Z. Li, C.-Z. Tao, Y. Xu, J. Li, L. Liu, and Q.-X. Guo, Org. Lett., 2006, 8, 2467.
- 22. Y. Peng, J. Chen, J. Ding, M. Liu, W. Gao, and H.Wu, Synthesis, 2011, 2, 2136.
- 23. B. V. Rokade, and K. R. Prabhu, J. Org. Chem., 2012, 77, 5364.
- 24. T. Kawamoto, A. Sato, and I. Ryu, Org. Lett., 2014, 16, 2111.
- 25. X. Chen, H. Ke, and G. Zou, ACS Catal., 2014, 4, 379.
- 26. E. Yamamoto, K. Izumi, Y. Horita, and H. Ito, J. Am. Chem. Soc., 2012, 134, 19997.
- 27. C. Zhou, Q. Liu, Y. Li, R. Zhang, X. Fu, and C. Duan, J. Org. Chem., 2012, 77, 10468.
- J. M. Antelo Miguez, L. A. Adrio, A. Sousa-Pedrares, J. M. Vila, and K. K. Hii, J. Org. Chem., 2007, 72, 7771.
- J. M. Antelo Miguez, L. A. Adrio, A. Sousa-Pedrares, J. M. Vila, and K. K. Hii, *J. Org. Chem.*, 2007, 72, 7771.
- 30. B.Tao, and D. W. Boykin, J. Org. Chem., 2004, 69, 4330.
- G. A. Edwards, M. A. Trafford, A. E. Hamilton, A. M. Buxton, M. C. Bardeaux, and J. M. Chalker, J. Org. Chem., 2014, 79, 2094.