Cite this: Green Chem., 2011, 13, 1352

www.rsc.org/greenchem



One-pot preparation of magnetic *N*-heterocyclic carbene-functionalized silica nanoparticles for the Suzuki–Miyaura coupling of aryl chlorides: improved activity and facile catalyst recovery

Hengquan Yang,*^a Yunwei Wang,^a Yong Qin,*^b Yanzhu Chong,^a Qiaozhen Yang,^a Guang Li,^a Li Zhang^a and Wei Li^a

Received 27th December 2010, Accepted 7th March 2011 DOI: 10.1039/c0gc00955e

Based on a reverse micelle strategy, we successfully synthesized new magnetic silica nanoparticles functionalized with a bulky N-heterocyclic carbene (N, N'-bis(2, 6-diisopropylphenyl)imidazol-2-ylidene, denoted as IPr) precursor through the co-condensation of IPr-bridged organosilane and tetraalkoxysilane in a one-pot reaction. TEM and SEM investigations revealed that the particle sizes of the synthesized materials were uniformly distributed in the range 15–30 nm, and could be tuned by varying the amount of siliceous precursors. FT-IR and XPS characterizations showed that the IPr ligand was successfully incorporated onto magnetic silica nanoparticles. Such materials show good coordination capability toward $Pd(acac)_2$ (acac = acetylacetonate), leading to a higher loading in comparison with magnetic silica nanoparticles (without functionalization). This Pd-loaded material is active toward the Suzuki-Miyaura couplings of challenging aryl chlorides under relatively mild conditions (at 80 °C). An 81% yield for biphenyl was achieved in the presence of 0.32 mol% of Pd within 8 h, using iso-propyl alcohol as a solvent and KO'Bu as a base. The activity of the functionalized nanoparticles is much higher than that of mesoporous silica-based catalysts, as well as a commercial Pd/C catalyst. This catalyst can be easily isolated by using a magnetic field and directly used in the next reaction cycle without significant loss of its activity.

Introduction

The Pd-catalyzed Suzuki–Miyaura coupling is currently a fundamental reaction for the construction of C–C bonds and plays an important role in the synthesis of agrochemical and pharmaceutical compounds.¹ The use of aryl chlorides as substrates has proven difficult because of the high bonding energy of C–Cl, but is highly desirable in view of the wide diversity, ready availability and low cost of aryl chlorides, in contrast with aryl bromides and iodides.² It is well-known that Pd–phosphine systems can efficiently promote the coupling reactions of aryl chlorides, but suffer from high toxicity and low stability in air. Recently, the *N*-heterocyclic carbene complex Pd–IPr [IPr = *N*,*N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] has been found not only to have comparable activity with Pd–phosphine complexes in the Suzuki–Miyaura couplings of aryl chlorides but also to be stable in air and have low

Fax: +86-351-7011688; *Tel:* +86-351-7010588

toxicity.³ Moreover, IPr can coordinate other metals such as Au, Ag, Cu, Au, Ni and Ru, yielding many active catalysts for various reactions.⁴ Such advantages make metal-IPr complexes potential catalysts for practical applications, if these complexes can be immobilized in a proper fashion for recovery and reuse.

However, there are few reports on immobilization of the versatile bis(2,6-diisopropylphenyl)-substituted carbene (IPr) ligand and further investigations of its catalytic activity in Suzuki-Miyaura couplings, although the grafting of small methyl-substituted carbene complexes on insoluble supports has been extensively reported, which usually exhibit low activity towards aryl chlorides due to lacking bulky electron-donating substituents on the carbene ligand.5 In our recent work, we have successfully incorporated the IPr ligand into the framework of a cubic mesoporous material and then prepared an active catalyst toward the Suzuki-Miyaura coupling of aryl chlorides.6 However, this solid catalyst required a relatively long time to obtain a high yield (24 h for the Suzuki-Miyaura coupling of chlorobenzene and phenylboronic acid). The limitation of diffusion in nanopores was believed to be one of the reasons for low reaction rate because the activity was lower than its homogeneous counterpart. For this reason, there is still a need

[&]quot;School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, 030006, PR China. E-mail: hqyang@sxu.edu.cn;

^bSchool of Chemistry and Chemical Engineering, Changzhou University, Changzhou, 213164, PR China

to find a method and strategy to prepare a new solid catalyst so as to overcome these limitations.

Decreasing particle sizes down to nanoscale may be an effective way to reduce the diffusion limitations because of the shortened diffusion lengths. However, when the particle sizes are less than 100 nm, to isolate these nanoparticles from a reaction system is relatively difficult and time-consuming when applied in practice. The usual manipulation processes involving a highspeed centrifugation are quite inconvenient for the consecutive processes. Fortunately, magnetically recoverable nanoparticles such as SiO₂-encapuslated Fe₃O₄ nanocomposites are now emerging as new, appealing supports for catalyst recovery.⁷ Fe₃O₄, usually used as a core, confers the catalyst support with a magnetic function. The silica part, as a shell, provides a versatile platform for loading metal catalysts. In the process of catalyst recycling, the catalyst can be magnetically recovered inside the reactor vessel by employing an external magnetic field while draining the liquid products. Because such a magnetic field-assisted separation can minimize energy consumption and catalyst loss, and save the time in achieving catalyst recovery, it is considered a "green" separation approach. Rossi and co-workers have prepared magnetic nanosilica-supported Pd, Rh and Au, which demonstrated their excellent activity and recyclability in alcohol oxidations, as well as hydrogenation.8 Baiker's group synthesized a magnetic Pt/SiO₂/Fe₃O₄ catalyst that showed a high activity and facile recovery in asymmetric hydrogenation.9 The preparation of these magnetically recoverable catalysts often involves two steps: synthesis of the SiO₂-encapuslated Fe₃O₄ nanocomposites and subsequent immobilization of the metal catalyst through a post-modification method (silylation with surface silanols).¹⁰ Compared with the post-modification method, the co-condensation method, that is, condensation of a mixture of complex/ligand-bridged trialkoxysilane and tetraalkoxysilane in a one-pot reaction, is a promising method for preparing solid catalysts because of the ease of controlling the complex/ligand loading and the uniform distribution of the complex/ligand on the solid matrix at a molecular level. This method is currently popular for preparing various hybrid materials and PMO-type (periodic mesoporous organosilica) catalysts.¹¹ However, to our knowledge, so far there has been no report on the preparation and catalytic applications of magnetic organic-inorganic hybrid silica nanoparticles through the cocondensation of bridged organosilane.

Driven by the unique properties of magnetically recoverable nanoparticles and the potential applications of IPr in catalysis, herein, we synthesized new magnetic organic–inorganic hybrid silica nanoparticles functionalized with IPr (denoted as MSN-IPr, as shown in Scheme 1) by co-condensation of IPr-bridged organosilane and tetraalkoxysilane in reverse micelles through a single step. After coordination with Pd(II), these magnetic functionalized silica nanoparticles exhibit a high activity and facile recyclability in the Suzuki–Miyaura coupling of challenging aryl chlorides.

Results and discussion

Synthesis of magnetic silica nanoparticles (MSN-IPr)

In order to incorporate the IPr precursor into silica through a cocondensation process, we needed to synthesise the IPr carbene



Magnetic hybrid silica nanosphere

Scheme 1 A structural description of the magnetic IPr-functionalized silica nanoparticle (MSN-IPr). Note: The $CF_3SO_3^-$ was exchanged by CI^- during the material's synthesis.

precursor with hydrolysable alkoxysilyl groups. We followed a modified route for the introduction of two trialkoxysilyl groups onto the terminals of the IPr precursor. The detailed synthesis of the IPr precursor-bridged organosilica was reported in our recent publication.⁶

As aforementioned, controlling the particle sizes on a nanoscale is an important way to improve the reaction rate. A reverse micelle system was used to synthesize the nanocomposites because the reverse micelle could control the particle sizes through the restrictions of the micelle size.¹² As shown in Scheme 2, the synthesis of magnetic silica nanoparticles functionalized with the IPr precursor began with the construction of a reverse micelle system (water-in-oil). A small amount of water, along with a given amount of Fe(II)/Fe(III), added into a large amount of xylene under vigorous stirring conditions



Scheme 2 A schematic demonstration of the synthesis of magnetic IPrfunctionalized silica nanoparticle (MSN-IPr): (a) reverse micelle (waterin-oil); (b) Fe(II) and Fe(III) are hydrolyzed in the core of the reverse core; (c) TEOS and IPr-bridged organosilane were hydrolyzed under the basic conditions; (d) hydrolyzed silicon moieties are co-condensed around the magnetite core, forming the MSN-IPr.

led to a reverse micelle solution. Due to the thermodynamic driving forces, water and the dissolved ferrous salts formed the cores of the reverse micelles. In the second step, a given amount of aqueous hydrazine (N_2H_4 · H_2O) was added into the system for the hydrolysis of ferrous salts. Iron oxide cores were thus yielded in the reverse micelles under heating conditions. Lastly, a mixture of tetraethyl orthosilicate (TEOS) and IPrbridged silane as siliceous precursors were added into the reverse micelle system. Due to the presence of base and water, siliceous precursors began hydrolyzing at the water/oil interfaces and cocondensation of siliceous precursors around the Fe₃O₄ core then occurred. The isolation and eventual drying gave the magnetic silica nanoparticles (MSN-IPr). By increasing the amounts of tetraethyl orthosilicate (TEOS) and IPr-bridged silane (the molar ratio remained constant), magnetic functionzalized silica nanoparticles with large particle sizes were obtained (denoted as MSNL-IPr).

Characterization

The TEM images of the magnetic silica nanoparticles are displayed in Fig. 1. In Fig. 1A, MSN-IPr materials consist of spherical particles. The particle size distribution is relatively narrow and mainly centered in the range 15-25 nm. Increasing the amounts of TEOS and IPr-bridged silane leads to an increase in particle size. As shown in Fig. 1B, the particles of MSNL-IPr are also broadly spherical in shape, but their sizes undergo an increase. Most of them mainly range from 20-30 nm in size. The results confirm that the particle sizes of magnetic functionalized silica nanoparticles are tunable by variation of the amount of siliceous precursors. The SEM image of MSN-IPr is presented in Fig. 2. In agreement with the TEM results, the SEM image also shows that MSN-IPr consists of densely packed individual spherical nanoparticles. A reverse micelle strategy is believed to be a crucial factor for achieving uniformly spherical nanoparticles.



Fig. 1 TEM images of MSN-IPr (A) and MSNL-IPr (B). The bar is 50 nm.

Fig. 3 shows the N₂ sorption isotherms and pore size distribution plots of MSN-IPr and MSNL-IPr. The two materials both show type III isotherms with a capillary condensation/evaporation step at high relative pressure ($P/P_0 = 0.9$ –1.0), indicating the presence of large pores on the magnetic silica nanoparticles. These large pores probably arise from the apertures between nanoparticles. These findings are in agreement with the SEM observations that honeycomb networks are present throughout the materials, as shown Fig. 2. The determined specific surface area (BET) of MSNL-IPr is 206 m² g⁻¹. The decrease in the surface area probably suggests that the



Fig. 2 A SEM image of MSN-IPr. The bar is 100 nm.



Fig. 3 N₂ adsorption/desorption isotherms of MSN-IPr and MSNL-IPr. MSN-IPr, offset vertically by 100.

particle sizes increase, which is in good agreement with the TEM observations.

Fig. 4 shows the wide angle XPD pattern of MSN-IPr. A broad peak at *ca*. $2\theta = 23^{\circ}$ is observed, which is assigned to the amorphous silica. A series of characteristic peaks including (200), (331), (440), (511) and (533) reflections of Fe₃O₄ are also clearly identified. As expected, MSN-IPr has magnetic properties that can be inferred from the magnetic field dependence of the magnetization displayed in Fig. 5A. The magnetization curve of MSN-IPr measured at room temperature exhibits moderate magnetism with a saturation magnetization of *ca*. 14 emu g⁻¹. Such a magnetization is sufficient for performing a magnetic separation. As shown in Fig. 5B, the catalyst was easily isolated magnetically by placing a magnet beside the reactor wall. MSN-IPr could re-disperse into the reaction medium when the external magnet was removed (a negligible magnetic hysteresis loop at room temperature).

The FT-IR spectrum of MSN-IPr is shown in Fig. 6. The spectrum exhibits peaks at 2970, 1540, 1465 and 1095 cm⁻¹. The peaks at 2970 and 1465 cm⁻¹ correspond to C–H stretching and C–H bending vibrations, respectively. The peak at 1540 cm⁻¹ is related to the characteristic vibrations of the imidazole ring



Fig. 4 The wide angle XRD pattern of MSN-IPr.



Fig. 5 A hysteresis loop for MSN-IPr at 298 K (A) and an image showing isolation of the magnetic solid by employing an external field (B).



Fig. 6 The FT-IR spectrum of MSN-IPr.

of the IPr precursor. The presence of the characteristic peak indicates that the IPr precursor was successfully introduced onto the solid materials. The strong peak at 1095 cm⁻¹ is attributable to the stretching vibrations of Si–O–Si, which were formed through the hydrolysis–condensation of the siliceous precursors. The quantitative determination of the IPr incorporated onto the magnetic silica nanoparticles was made with elemental analysis. The C and N contents of MSN-IPr are 0.96 wt% and 19.73 wt%, respectively. Based on the results of the N contents, it is estimated that the IPr loading on MSN-IPr is

Table 1 The change of Pd loadings on MSN-IPr with the amount of $Pd(acac)_2$ added

Materials	MS MSN-IPr				
Pd(acac) ₂ wt [%] Theoretical Pd contents (wt [%]) ^b Determined Pd contents ([%]) ^c The molar ratio of IPr/Pd ^d	2% 0.68 0.40	2% 0.68 0.63 5.7	3% 1.01 0.78 4.6	4% 1.34 0.86 4.1	5% 2.58 0.90 3.6

^{*a*} The weight of added Pd(acac)₂ with respect to MSN-IPr. ^{*b*} Theoretical Pd contents on the assumption that all Pd(acac)₂ molecules were completely introduced onto MSN-IPr. ^{*c*} The determined Pd contents on MSN-IPr by ICP-AES. ^{*d*} The actual molar ratio of IPr/Pd on the Pd(χ)/MSN-IPr.

 0.34 mmol g^{-1} . The determined C content is higher with respect to the theoretical value, which is calculated according to the determined N contents. These results can be explained by the fact that a certain amount of sodium dodecylbenzenesulfonate is present on the surface of MSN-IPr (an inorganic oxide surface usually has a high adsorption capacity toward anionic surfactants).

To probe the coordination capacity of IPr carbene incorporated on MSN-IPr, we chose $Pd(acac)_2$ (acac = acetylacetonate) to coordinate with the hybrid materials because the Pd-IPr complex formed was reported to be stable in air and catalytically active in the Suzuki-Miyaura reaction of aryl chlorides. The amount of Pd(acac)₂ was tuned from 2 wt% to 5 wt% (with respect to the weight of MSN-IPr). Magnetic silica nanoparticles (MSN) without incorporation of the IPr ligand were also synthesized for comparison. The coordination was conducted in a 1,4-dioxane solution under the refluxing conditions. ICP-AES was employed to determine the Pd loadings on the solid materials. These results are summarized in Table 1. In the cases of using 2 wt% Pd(acac)₂, the Pd loading on MSN (without incorporation of IPr) was determined to be 0.40 wt%. This value is lower than the theoretical value (0.68 wt%), indicating that a portion of the $Pd(acac)_2$ molecules were not captured by MSN. While for MSN-IPr (with the incorporation of IPr), the Pd loading was determined to increase up to 0.63 wt%, which was nearly equal to the theoretical value (0.68 wt%) and much higher than the case of MSN. The significantly improved Pd loading demonstrates the role of the IPr ligand in the coordination of Pd. Increasing the amount of $Pd(acac)_2$ led to an increase in the determined Pd loading on MSN-IPr. When 4 wt% of Pd(acac)₂ was added, the determined Pd loading on the solid materials was 0.86 wt%. However, further increasing the Pd(acac)₂ amount up to 5 wt%, did not result in an apparent increase in the determined Pd loading. The results suggest that 4 wt% of Pd(acac)₂ is the most suitable for obtaining high Pd loading. On this occasion, the ratio of IPr/Pd was estimated to be ca. 4. The loading lower than the theoretical values was explained by the fact that a portion of the IPr ligands incorporated on MSN-IPr were inaccessible to the relatively bulky Pd complex.

XPS spectroscopy was employed to investigate the elemental compositions and coordination states of Pd species on the MSN-IPr surface. In Fig. 7, an XPS elemental survey scan of surface elementals of MSN-IPr derived with $Pd(acac)_2$ reveals that Si, O, Fe, C, N, Cl and Pd elements are present in the solid material. The S element (CF₃SO₃⁻ of the IPr precursor) was not found



Fig. 7 The XPS spectrum of MSN-IPr (elemental scan).

while Cl was detected. These findings may be explained by the fact that the $CF_3SO_3^-$ of the IPr precursor was displaced with CI^- , which derived from the excess Fe salts. Fig. 8 displays the Pd XPS spectra for Pd(acac)₂ and Pd/MSN-IPr. Pd(acac)₂ exhibits two peaks centered at 338.2 and 343.5 eV, which are assigned to Pd(II) $3d_{5/2}$, and Pd $3d_{3/2}$, respectively. Compared with this pure complex, the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks for Pd/MSN-IP) slightly shift down to 337.9 and 343.1 eV, respectively. Such changes may imply that new Pd(II) species were formed on the solid surface of MSN-IPr.



Fig. 8 The XPS spectra for Pd on Pd/MSN-IPr (a) and pure Pd(acac)₂ compound (b).

Suzuki-Miyaura reaction

We chose Pd/MSN-IPr [MSN-IPr derived with 4 wt% Pd(acac)₂] to investigate its catalytic performance in view of the above findings that 4 wt% Pd(acac)₂ led to the maximum loading of Pd. Aryl chlorides were used as the major substrates under investigation because they were very challenging, especially for heterogeneous catalysts. 1,4-Dioxane/KO'Bu were used as the solvent/base because this system was found to be very

efficient for the Suzuki-Miyaura reactions of aryl chlorides in homogeneous catalysis.^{3a,3e} As shown in Fig. 9, using 0.5 mol Pd% with respect to chlorobenzene, Pd/MSN-IPr gave a 73% conversion within 5 h at 80 °C. In order to further evaluate the performance of this catalyst, we compared the activities of our previous catalyst Pd/SBA-IPr (IPr incorporated on mesoporous materials through the hydrolysis-condensation method, the molar ratio of IPr-bridged organosilane to TEOS was the same as MSN-IPr).6 Under the same conditions, Pd/SBA-IPr gave a 42% conversion (Fig. 9). Obviously, the catalytic activity of MSN-IPr is much higher than that of Pd/SBA-IPr. The higher activity may be due to the shortened diffusion pathway on Pd/MSN-IPr with a small particle size. To examine the hypothesis, we also tested the activity of Pd/MSNL-IPr under the same conditions. Pd/MSNL-IPr gave a 62% conversion, which is lower than that for Pd/MSN-IPr. The comparative results further demonstrate the role of the catalyst particle size in improving the catalytic activity.



Fig. 9 The catalytic activity comparison of the different solid catalysts.

Under identical reactions conditions, the commercial Pd/C (with a Pd loading of 1 wt%) gave a conversion of only 12%, which was much lower than that for Pd/MSN-IPr (73%). These comparative results further highlight the performances of Pd/MSN-IPr. Several types of heterogeneous catalysts for Suzuki-Miyaura couplings were reported, such as Pd/C, mesoporous silica-supported palladium, polymer-incarcerated palladium, polyurea-encapsulated palladium and dendrimersupported palladium catalysts (in reference 5d). These heterogeneous systems successfully catalyzed the Suzuki-Miyaura couplings of aryl bromides but failed in the couplings of aryl chlorides (especially deactivated aryl chlorides) except in limited examples.^{5d,5h,6,13} In this context, our catalyst Pd/MSN-IPr could represent one of the most efficient heterogeneous catalysts for the Suzuki-Miyaura coupling of aryl chlorides in view of the relatively mild conditions plus a low loading of Pd.

To evaluate the catalytic performances of Pd/MSN-IPr, the Suzuki–Miyaura couplings of various aryl halides and phenylboronic acid were conducted (shown in Table 2). At a Pd loading of 0.32%, the solid catalyst gave biphenyl in an isolated yield of

$\mathbb{R} \xrightarrow{\hspace{1cm}} \mathbb{A} + \mathbb{A} \xrightarrow{\hspace{1cm}} \mathbb{B}(OH)_2 \xrightarrow$							
Entry	Substrate	Product	Pd (mol%)	Time (h)	Yield ^a (%)		
1	CI	$\bigcirc - \bigcirc$	0.32	8	81		
2	° CI	$\rightarrow \frown \rightarrow \frown$	0.32	5	87		
3	Н3С-СІ		0.32	10	74		
4	н₃со-		0.32	10	86		
5	СК СКАЗ		0.32	12	82		
6			0.32	16	59		
7	Br	$\bigcirc - \bigcirc$	0.16	2	90		
8	H ₃ CO-Br		0.16	2	91		
9	° Br	$\rightarrow \frown \rightarrow \frown$	0.16	1	92		
10	CH ₃ CH ₃		0.16	4	75		
" The isolat	ed yield.						

Table 2 The Suzuki-Miyaura couplings of various aryl halides and phenylboronic acid over Pd/MSN-IPr

81% at 80 °C within 8 h (Table 2, entry 1). For an aryl chloride bearing an electron-withdrawing group, a yield up to 87% was obtained in a shorter time (5 h, Table 2, entry 2). To our delight, for deactivated aryl chlorides with electron-donating groups such as $-CH_3$ and $-OCH_3$, good yields (74% and 86%) were achieved (Table 2, entries 3 and 4) within 10 h. The deactivated chlorobenzene bearing an *o*-substituted electron-donating group was also smoothly converted, and an 82% yield was obtained (Table 2, entry 5). Remarkably, in the case of sterically hindered, deactivated aryl chlorides (2,6-dimethylchlorobenzene), a 59% yield was afforded within 16 h (Table 2, entry 6). These results further demonstrated the good performance of our catalyst. The

good performance may be contributable to another factor that the bulky NHC (*N*-heterocyclic carbene) ligand incorporated on the magnetic silica provided a strong electron-donor to the Pd centre.

The solid catalyst developed also has high activity toward various aryl bromides. With the Pd loading down to 0.16 mol%, both bromobenzene and deactivated bromobenzene were completely converted to the corresponding products in 90–91% yields within 2 h (Table 2, entries 7 and 8). For an activated aryl bromide, the reaction proceeded more easily, affording a high yield within only 1 h (Table 2, entry 9). For the highly sterically hindered, deactivated aryl bromide 2,6-dimethylbromobenzene,



Table 3 The Suzuki-Miyaura couplings of various phenylboronic acids and chlorobenzene over Pd/MSN-IPr

^a Isolated yields; ^b Bromobenzene as the substrate, 2 h, other reaction conditions are the same as the case of chlorobenzene.

a satisfactory yield could be obtained within 4 h (75%, Table 2, entry 10).

We further tested the catalytic performances for the couplings of various arylboronic acids with chlorobenzene (Table 3). For arylboronic acids bearing electron-withdrawing groups such as -F and $-CF_3$, Pd/MSN-IPr gave 76–84% yields within 8 h (Table 3, entries 1 and 2). 73–84% yields were achieved in the cases of arylboronic acids bearing electron-donating groups such as methyl, methoxy and *tert*-butyl groups (Table 3, entries 3–5). The moderately sterically demanding arylboronic acids were also smoothly converted to the corresponding products in 70–86% yields (Table 3, entries 6 and 7). For the coupling of naphthylboronic acid and bromomide, an 86% yield was achieved within 2 h (Table 3, entry 8).

The recyclability of Pd/MSN-IPr was investigated with consecutive Suzuki–Miyaura couplings of 4'-chloroacetophenone with phenylboronic acid. Due to the unavoidable loss of solid catalyst during the course of recovery and washing, the reaction scale was amplified 7 times to ensure that catalyst of good quality was available for us to perform several recycling reactions. The recycling results of Pd/MSN-IPr are reflected in Fig. 10. Under the scale-up conditions, the fresh solid catalyst Pd/MSN-IPr gave the product in a 91% yield within 10 h. After the first reaction cycle, the catalyst could be separated from the reaction liquid by using an external magnetic field. The magnetic separation was easy, fast and clean, avoiding the centrifugation and filtration that required extra energy. After the reaction liquid was removed, diethyl ether and acetone in sequence were added to wash the recovered solid catalyst. After washing and drying, the recovered catalyst was directly used for the next reaction cycle. For the second and third reaction cycles, 90% yields were achieved within the same time as the first run. From the fourth reaction cycles, the activity of the reused catalyst was observed to slightly decrease. An 88% yield was obtained within 12 h. The high yield could be obtained by slightly prolonging the reaction time. For the fifth reaction cycle, a reaction time of 14 h led to



Fig. 10 The recyclability test of Pd/MSN-IPr with the Suzuki-Miyaura coupling reaction.

a yield of up to 92%. In the sixth run of the solid catalyst, an 84% yield was still obtained. Although the activity of the solid catalyst decreased during the consecutive recycling reactions, it represents an efficient heterogeneous catalyst for the Suzuki–Miyaura coupling of the aryl chlorides in view of the relatively low Pd loading (0.32 mol%). We determined the Pd content in the filtrate after the first reaction cycle. The Pd content in the filtrate was *ca.* 1.2 ppm. The low Pd content in the filtrate the most of Pd species are still on the solid catalyst at the end of the reaction.

Additionally, this solid catalyst exhibited high stability in air. It was found that there was no decrease in activity after the catalyst was exposed to air for several days. In this aspect, the developed catalyst is also superior to the immobilized phosphine catalysts.

Conclusions

We adopted a reverse micelle strategy to synthesize new magnetic silica nanoparticles functionalized with a bulky N-heterocyclic carbene precursor by co-condensation of IPr-bridged organosilane and tetraalkoxysilane. Their particle sizes are uniformly distributed in the range 10-30 nm, and could be tuned by varying the amount of siliceous precursors. The IPr ligand was successfully incorporated in magnetic silica nanoparticles. Such hybrid nanoparticles were able to coordinate Pd(acac)₂, leading to an active solid catalyst for the Suzuki-Miyaura couplings of challenging aryl chlorides, even with steric hindrances. Its activity depended on the particle size, but was generally higher than for the mesoporous silica-based catalyst, as well as a commercial Pd/C catalyst. The improved activity is attributable to the decreased particle sizes. This catalyst can be easily isolated by using a magnetic field and directly used in the next reaction cycle without a significant loss of its activity. This study not only demonstrates a new method to synthesize organic-inorganic hybrid magnetic silica nanoparticles, but also supplies a new, efficient solid catalyst for the Suzuki-Miyaura couplings of challenging aryl chlorides.

Experimental

Reagents and materials

Sodium dodecylbenzenesulfonic acid, xylene, hydrazine, FeCl₂·4H₂O, Fe(NO₃)₃·9H₂O and most aryl halides were purchased from Aladdin Company. Pd(acac)₂ (acac = acetylacetonate) was obtained from Kaida Metal Catalyst & Compounds Co. Ltd (China). Various arylboronic acids were obtained from Beijing Pure Chemical Co. Ltd. 2,6-Diisopropylaniline, ICl and other reagents were obtained from Shanghai Chemical Reagent Company of Chinese Medicine Group. All solvents were of analytical quality.

Synthesis of magnetic IPr-functionalized silica nanoparticle (MSN-IPr)

A microemulsion was prepared by dissolving 1.75 g of sodium dodecylbenzenesulfonate in 15 mL of xylene by sonication and stirring. 1 mmol of FeCl₂·4H₂O and 2 mmol of Fe(NO₃)₃·9H₂O were dissolved in 0.9 mL of deionized water. The aqueous solution was added into the above microemulsion under vigorous stirring. After the system was kept at room temperature for 12 h, it was slowly heated to 90 °C under a N₂ atmosphere for another 1 h. 1 mL of hydrazine (34 wt% aqueous solution) was injected into the system. Afterwards, the mixture was maintained at 90 °C for a further 3 h and then cooled down to 40 °C. After the temperature was stabilized at 0 °C, a methanolic solution consisting of 0.355 mmol of IPr-bridged silane, 6.390 mmol of TEOS and 1.42 g of ethanol) was added into the above mixed system under vigorous stirring. After further stirring for 12 h at this temperature, the resultant solid was isolated using an external field. After washing with diethyl ether and methanol and drying, the magnetic IPr-functionalized silica nanoparticles were eventually obtained, denoted at MSN-IPr. The amount of siliceous precursor added at the final stage determined the particle sizes of MSN-IPr. Under the same conditions, addition of 0.533 mmol IPr-bridged silane and 9.585 mmol of TEOS led to the magnetic IPr-functionalized silica with larger sizes, denoted as MSNL-IPr.

Coordination of MSN-IPr with Pd(acac)₂

0.5 g of MSN-IPr (dried at 120 °C for 4 h) was dispersed in 12 mL of dry 1,4-dioxane containing a given amount of Pd(acac)₂ (acac = acetylacetonate). After the mixed system was stirred at 100 °C for 40 h under a N₂ atmosphere, the magnetic solid was collected by employing a magnetic field. The solid was repeatedly washed with dry 1,4-dioxane and dried under vacuum. The eventually achieved solid was designated as Pd(χ)/MSN-IPr (χ means added amount of Pd(acac)₂). By variation of the amount of Pd(acac)₂, we obtained a series of solid catalyst Pd(χ)/MSN-IPr, where $\chi = 2$ wt%, 3 wt%, 4 wt% and 5 wt%

General procedure for the Suzuki–Miyaura coupling of aryl chlorides and arylboronic acids

A mixture of aryl chloride (2 mmol), phenylboronic acid (2.2 mmol), potassium *tert*-butoxide (3 mmol), *iso*-propyl alcohol (6 mL), and the solid catalyst were stirred at 80 °C under a N_2 atmosphere for a given time. At the end of reaction, the mixture was cooled down to room temperature and the liquid was isolated with the aid of an external field. The solid catalyst was repeatedly washed with diethyl ether. The combined organic layers were concentrated and the resulting product was purified by column chromatography on silica gel. The products were confirmed by ¹H NMR and its purity was confirmed by GC.

The recycling test for the Suzuki–Miyaura coupling was conducted as follows. For the first run, a mixture of 12 mmol of 4'chloroacetophenone, 13.2 mmol of phenylboronic acid, 18 mmol of potassium *tert*-butoxide, Pd(4%)/MSN-IPr (0.32 mol% Pd with respect to aryl chloride) and 36 mL of *iso*-propyl alcohol were stirred at 80 °C under a N₂ atmosphere. At the end of the reaction, the mixture was cooled down to room temperature and the liquid was isolated with the aid of an external field. The recovered catalyst was washed with diethyl ether, water, methanol and acetone in sequence and then dried under vacuum. The recovered catalyst was weighed again. The fresh solvent and substrates were added, but the molar ratio of substrate to Pd remained the same as that in the first run.

NMR data for the coupling products

Biphenyl (CDCl₃, 300 MHz, ppm): δ 7.57 (d, 4 H, J = 9 Hz); 7.41–7.46 (m, 4 H); 7.34 (t, 2 H, J = 7.5 Hz). 4-Acetylbiphenyl (CDCl₃, 300 MHz, ppm): 8.03 (d, 2 H, J = 6 Hz); 7.36–7.69 (m, 7 H); 2.67(s, 3 H). 4-Methylbiphenyl (CDCl₃, 300 MHz, ppm): 7.59 (d, 2 H, J = 6 Hz), 7.24–7.57 (m, 7 H), 2.40 (s, 3 H). 4-Methoxybiphenyl (CDCl₃, 300 MHz, ppm): 7.55–7.60 (m, 4 H); 7.45 (t, 2 H, J = 7.5 Hz); 7.33 (m, 1 H); 7.00 (d, 2H, J = 9 Hz); 3.88 (s, 3H). 2-Methylphenyl (CDCl₃, 300 MHz, ppm): 7.11-7.26 (m, 9 H); 2.15 (s, 3 H). 2,6-Dimethylphenyl (CDCl₃, 300 MHz, ppm): 7.07-7.35 (m, 8 H), 2.19 (s, 6 H). 4-Trifluoromethylbiphenyl (CDCl₃, 300 MHz, ppm): 7.62 (s, 4 H), 7.51-7.54 (d, J = 6.9 Hz, 2 H), 7.30-7.42 (m, 3 H). 4-Fluorobiphenyl (CDCl₃, 300 MHz, ppm): 7.50–7.53 (m, 4 H); 7.40-7.420 (m, 2 H); 7.32-7.33 (m, 1 H), 7.08-7.12 (m, 2 H). 4-'Butylbiphenyl (CDCl₃, 300 MHz, ppm): 7.16-7.46 (m, 9 H), 1.19 (s, 9 H). 1-Phenylnaphthalene (CDCl₃, 300 MHz, ppm): 7.28-7.38 (m, 8 H); 7.68-7.47 (m, 4 H).

Characterization and analysis

Wide-angle powder X-ray powder diffraction was performed on a Rigaku D/Max 3400 powder diffraction system. N₂ physical adsorption was carried out on a micrometritics. ASAP2020 volumetric adsorption analyzer (before measurements, samples were out gassed at 125 °C for 6 h). The Brunauer-Emmett-Teller (BET) surface area was evaluated from data in the relative pressure range of 0.05 to 0.15. The total pore volume of each sample was estimated from the amount adsorbed at the highest P/P_0 (above 0.99). Pore diameters were determined from the adsorption branch using the Barrett-Joyner-Halenda (BJH) method. Magnetization measurements M(T, H) were performed by using a superconducting quantum interference device magnetometer (LakeShore 7410). FT-IR spectra were collected on a Thermo-Nicolet-Nexus 470 infrared spectrometer. Pd content was analyzed with inductively coupled plasmaatomic emission spectrometry (ICP-AES, AtomScan16, TJA Co.). X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Ultra DLD, and the C_{1s} line at 284.8 eV was used as a reference. TEM micrographs were taken with a JEM-2000EX transmission electron microscope. SEM micrographs were taken with a SUPRA-5S scan electron microscope (ZEISS). GC analysis was conducted on a SP-GC6800A.

Acknowledgements

We acknowledge Specialized Research Fund for the Doctoral Program of Higher Education (200801081035), Shanxi Natural Science Foundation for Youths (2009021009), Jiangsu Natural Science Foundation (BK2009554), the Natural Science Foundation of China (20903064), Shanxi University Innovative Experimental Project for Undergraduates and Jiangsu Key Lab. of Fine Petrochemistry for financial supports (KF0802).

References

- (a) N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, 1981, 11, 513; (b) L. Yin and J. Liebscher, *Chem. Rev.*, 2007, 107, 133; (c) J. S. Carey, D. Laffan, C. Thomson and M. T. Williams, *Org. Biomol. Chem.*, 2006, 4, 2337.
- E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, Angew. Chem., Int. Ed., 2007, 46, 2768; (b) O. Diebolt, P. Braunstein, S. P. Nolan and C. S. J. Cazin, Chem. Commun., 2008, 3190; (c) H. Q. Yang, G. Y. Zhang, X. L. Hong and Y. Y. Zhu, J. Mol. Catal. A: Chem., 2004, 210, 143; (d) H. Q. Yang, X. J. Han, Z. C. Ma, R. Q. Wang, J. Liu and X. F. Ji, Green Chem., 2010, 12, 441; (e) X. J. Feng, M. Yan, T. Zhang, Y. Liu and M. Bao, Green Chem., 2010, 12, 1758; (f) M. Z. Cai, G. M. Zheng, L. F. Zha and J. Peng, Eur. J. Org. Chem., 2009, (10), 1585.
- 3 (a) M. G. Organ, M. Abdel-Hadi, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. Sayah and C. Valente, *Chem.– Eur. J.*, 2008, 14, 2443; (b) N. Marion, E. C. Ecarnot, O. Navarro, D. Amoroso, A. Bell and S. P. Nolan, *J. Org. Chem.*, 2006, 71, 3816; (c) N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott and S. P. Nolan, *J. Am. Chem. Soc.*, 2006, 128, 4101; (d) H. Q. Yang, G. Li, Z. C. Ma and J. B. Chao, *J. Phys. Chem. C*, 2010, 114, 22221; (e) N. Marion, P. D. Frémont, I. M. Puijk and E. C. Ecarnot, *Adv. Synth. Catal.*, 2007, 349, 2380.
- 4 (a) S. Díez-González, N. Marion and S. P. Nolan, Chem. Rev., 2009, 109, 3612.
- 5 (a) P. Han, H. M. Zhang, X. P. Qiu, X. L. Ji and L. X. Gao, J. Mol. Catal. A: Chem., 2008, 295, 57; (b) V. Polshettiwar, P. Hesemann and J. J. E. Moreau, Tetrahedron Lett., 2007, 48, 5363; (c) J. H. Kim, J. W. Kim, M. Shokouhimehr and Y. S. Lee, J. Org. Chem., 2005, 70, 6714; (d) D. H. Lee, J. H. Kim, B. H. Jun, H. Kang, J. Park and Y. S. Lee, Org. Lett., 2008, 10, 1609; (e) H. Hagiwara, K. H. Ko, T. Hoshi and T. Suzuki, Chem. Commun., 2007, 2838; (f) H. Q. Yang, X. J. Han, G. Li and Y. W. Wang, Green Chem., 2009, 11, 1184; (g) J. W. Byun and Y. S. Lee, Tetrahedron Lett., 2004, 45, 1837; (h) B. Karimi, D. Elhamifar, J. H. Clark and A. J. Hunt, Chem.–Eur. J., 2010, 16, 8047.
- 6 H. Q. Yang, G. Li, Z. C. Ma, J. B. Chao and Z. Q. Guo, J. Catal., 2010, 276, 123.
- 7 (a) S. Shylesh, V. Schünemann and W. R. Thiel, Angew. Chem., Int. Ed., 2010, 49, 3428; (b) J. P. Ge, T. Huynh, Y. X. Hu and Y. D. Yin, Nano Lett., 2008, 8, 931; (c) C. O. Dálaigh, S. A. Corr, Y. Guńko and S. J. Connon, Angew. Chem., Int. Ed., 2007, 46, 4329; (d) S. Shylesh, L. Wang, S. Demeshko and W. R. Thiel, ChemCatChem, 2010, 2, 1543; (e) P. D. Stevens, G. Li, J. Fan, M. Yen and Y. Gao, Chem. Commun., 2005, 4435; (f) M. Shokouhimehr, Y. Piao, J. Kim, Y. Jang and T. Hyeon, Angew. Chem., Int. Ed., 2007, 46, 7039; (g) V. Polshettiwar, B. Baruwati and R. S. Varma, Chem. Commun., 2009, 1837; (h) S. Shylesh, V. Schünemann and W. R. Thiel, Angew. Chem., Int. Ed., 2010, 49, 3428; (i) R. Abu-Reziq, H. Alper, D. Wang and M. L. Post, J. Am. Chem. Soc., 2006, 128, 5279; (j) M. Kawamura and K. Sato, Chem. Commun., 2007, 3404.
- 8 (a) R. L. Oliveira, P. K. Kiyohara and L. M. Rossi, *Green Chem.*, 2010, **12**, 144; (b) M. J. Jacinto, O. H. C. F. Santos, R. F. Jardim, R. Landers and L. M. Rossi, *Appl. Catal.*, A, 2009, **360**, 177.
- 9 B. Panella, A. Vargas and A. Baiker, J. Catal., 2009, 261, 88.

- 10 (a) C. Che, W. Z. Li, S. Y. Lin, J. W. Chen, J. Zheng, J. C. Wu, Q. X. Zheng, G. Q. Zhang, Z. Yang and B. W. Jiang, *Chem. Commun.*, 2009, 5990; (b) H. J. Yoon, J. W. Cho, H. Kang, T. Kang, S. M. Lee, B. H. Jun and Y. S. Lee, *Synlett*, 2010, 16, 2518; (c) I. J. Bruce and T. Sen, *Langmuir*, 2005, 21, 7029; (d) S. Z. Luo, X. X. Zheng, H. Xu, X. L. Mi, L. Zhang and J. P. Cheng, *Adv. Synth. Catal.*, 2007, 349, 2431; (e) S. Shylesh, L. Wang and W. R. Thiel, *Adv. Synth. Catal.*, 2010, 352, 425.
- 11 (a) V. Dufaud, F. Beauchesne and L. Bonneviot, Angew. Chem., Int. Ed., 2005, 44, 3475; (b) C. Baleizão, B. Gigante, D. Das, M. Vlvaro,

H. García and A. Corma, *J. Catal.*, 2004, **223**, 106; (*c*) A. Corma, D. Das, H. García and A. Leyva, *J. Catal.*, 2005, **229**, 322; (*d*) H. Q. Yang, Z. C. Ma, Y. Qin, G. Y. Xie, J. Gao, L. Zhang, J. H. Gao and L. Du, *Appl. Catal.*, *A*, 2010, **382**, 312; (*e*) Q. H. Yang, J. Liu, L. Zhang and C. Li, *J. Mater. Chem.*, 2009, **19**, 1945.

- 12 J. Lee, Y. Lee, J. K. Youn, H. B. Na, T. Yu, H. Kim, S. M. Lee, Y. M. Koo, J. H. Kwak, H. G. Park, H. N. Chang, M. Hwang, J. G. Park, J. Kim and T. Hyeon, *Small*, 2008, 4, 143 and references therein.
- 13 M. J. Jin and D. H. Lee, Angew. Chem., Int. Ed., 2010, 49, 1119.