

Formation and catalytic activity of Pd nanoparticles on silica in supercritical CO₂

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Metal complexes of polydimethylsiloxane-derived ligands can be adsorbed onto silica and subsequently reduced *in-situ* in supercritical CO₂ (scCO₂) to generate metal nanoparticles. Pd nanoparticles on silica, generated during C–C coupling reactions in scCO₂, can be recycled several times without any loss in activity. Focusing on Heck and Suzuki coupling reactions, the products showed no contamination of the organic products with Pd using quantitative ICP emission spectroscopy. The use of scCO₂ prevents the desorption of the Pd nanoparticles from their support. Build-up of ammonium salts as by-products in these coupling reactions leads to reduced activity for these heterogeneous catalysts after four runs.

Introduction

Palladium catalysed coupling reactions have been the subject of intensive research over the last twenty years.^{1–3} The main use of these reactions is to create biaryls. The Suzuki reaction, reaction of aryl or vinyl halides or triflates with boronic acids, is of particular importance to the pharmaceutical and agrochemical industries. For example, it is used in the industrial production of Losartan, a Merck antihypertensive drug.⁴ The Heck reaction, which results in C–C bond formation between alkenes and aromatic rings, is used in at least five commercial processes on a scale in excess of 1 ton per year.⁵ Attempts to perform these reactions more cleanly can be divided into two areas, the use of supported/recyclable catalysts and the use of environmentally benign media.

Recent reports on palladium based heterogeneous catalysts for these reactions include Suzuki couplings using Pd/C in DMF/water,⁶ continuous Heck and Suzuki reactions using Pd(0) within ion-exchange resins using *N*-methylpyrrolidinone or DMF/water as the solvent, biomaterial supported Pd in xylene for Suzuki and Heck reactions,^{7,8} and nanosized Pd particles in silica or carbon aerogels for Heck reactions in acetonitrile.⁹

A number of groups have performed ‘ligand-free’ Pd catalysed Suzuki reactions in water.^{10,11} Suzuki reactions have also been performed in PEG-400 and ionic liquids/water.^{12,13} Since the first reported Pd catalysed C–C bond forming reactions in scCO₂,^{14,15} a wide range of substrates and substances have been transformed in this medium using Pd.^{16,17} Recent examples include cyclotrimerization reactions and C–N bond formations.^{18,19}

More recently researchers have combined these areas of green chemistry and have performed reactions using heterogeneous catalysts in benign media. For example, “solventless” Suzuki coupling reactions have been conducted using palladium-doped potassium fluoride alumina,²⁰ Pd/C has been used as a recyclable catalyst in Suzuki cross-coupling reactions in water,²¹ and polyurea-encapsulated Pd has been used in Heck, Stille and Suzuki reactions in scCO₂.^{22,23}

In this paper, we describe the *in situ* preparation of Pd nanoparticles on silica in scCO₂ and the use of this material as a recyclable catalyst for C–C bond forming reactions in scCO₂.

Experimental

Reagents were purchased from Aldrich or Lancaster. Palladium salts were purchased from Precious Metals Online Ltd (Australia). Polydimethylsiloxane monocarbinol and phenyl(tri-*n*-butyl)tin were purchased from ABCR Gelest. Liquid reagents were deoxygenated by three freeze–pump–thaw cycles prior to use. PDMS-PPh₂, Fig. 1, Pd(PDMS-PPh₂)₂Cl₂ and Pd(PDMS-PPh₂)₂Cl₂ on silica (supported pre-catalyst), Fig. 2, were prepared according to literature procedures.²⁴

Toluene was dried over sodium-benzophenone, distilled under argon and subsequently stored in ampoules under nitrogen. Deuterated chloroform was dried over CaH₂, distilled and then stored under nitrogen in the presence of molecular sieves.

Reaction mixtures and products were analysed on a Jeol EX 270 or a Bruker AMX-500 NMR spectrometer. ¹H NMR spectra were referenced to residual protons in the deuterated solvent. DRIFT spectra were obtained on a IR Bruker Equinox 55 equipped with a Specac Diffuse Reflectance accessory. TEM was performed on a Tecnai 12 BIO TWIN operating at 120 kV in the Biology Department at the University of York. Simultaneous TGA, differential TGA (DTGA) and DSC were conducted using a Stanton Redcroft STA 625 GTA under a nitrogen atmosphere. ICP analyses was performed on a UNICAM 701 Series Emission Spectrometer by the Advanced Chemical and Materials Analysis service of

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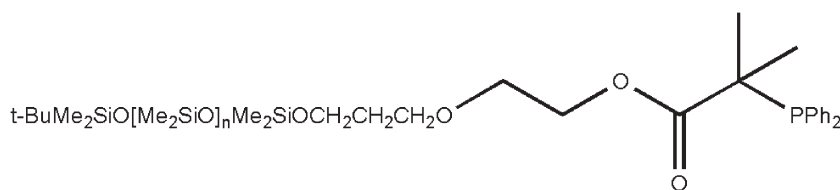


Fig. 1 Poly(dimethylsiloxane)-derived phosphine ligand, PDMS-PPh₂.

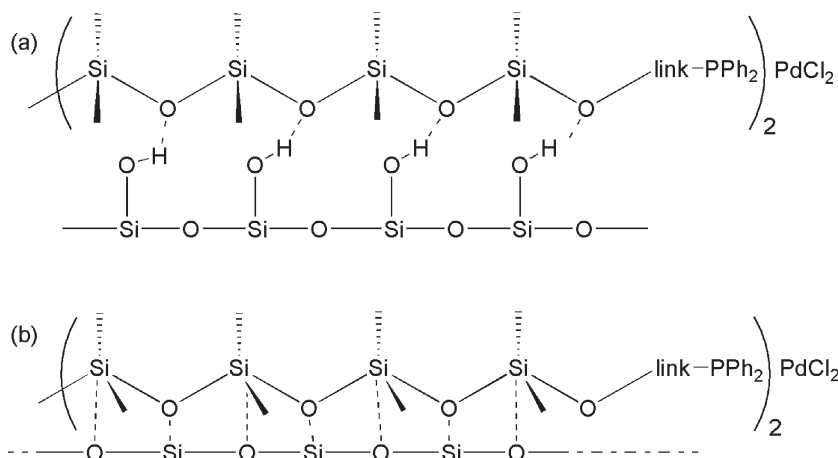


Fig. 2 Proposed adsorption mechanism of PDMS-PPh₂ complexes on silica through (a) hydrogen-bonding and (b) van der Waals interactions.

the University of Newcastle. Elemental analyses were performed by Elemental Microanalysis Ltd, Devon.

In order to check the reproducibility of the catalytic reactions and the recyclability of the catalyst, they were performed at least twice. The average conversions from the experiments are reported, Table 1.

Heck reaction using supported catalyst in toluene

A Schlenk tube was charged with the supported pre-catalyst (0.80 g, 2 mol% Pd), toluene (18 mL), 4-iodotoluene (0.26 g, 1.2 mmol), methyl acrylate (0.50 g, 5 mmol), and *N,N*-diisopropylethylamine (0.23 g, 1.78 mmol). The reaction mixture was stirred for 3 h at 75 °C. Once cooled to room temperature, the mixture was filtered under nitrogen, the siliceous material retained for reuse and the solvent removed under vacuum. The product-containing mixture was analyzed by ¹H NMR spectroscopy. The isolated orange-brown silica was reused under the same conditions. Conversions were 96% in run 1, 85% in run 2, 65% in run 3 and 10% in run 4.

Heck reaction using supported catalyst in scCO₂

Using a glovebox or a Schlenk line, the supported pre-catalyst (0.80 g, 2 mol% Pd), 4-iodotoluene (0.27 g, 1.2 mmol), methyl acrylate (0.50 g, 5 mmol), *N,N*-diisopropylethylamine (0.23 g, 1.78 mmol) and a stir bar were placed in a 25 mL stainless steel pressure vessel (Thar technologies). The vessel was sealed and heated to 75 °C and stirred for 10 minutes. It was then pressurised to 100 bar with carbon dioxide.† This temperature

† As with all processes under high pressure, appropriate safety precautions must be taken.

and pressure were maintained for 18 h. The vessel was allowed to cool and was then vented into toluene (10 mL) under nitrogen, washed with dry toluene and the contents filtered inside the glovebox. The catalyst was dried under vacuum and reused whilst avoiding contact with the air. Conversions were 98% in run 1 (or 55% if the reaction time was reduced to 3 h), 96% in run 2, 92% in run 3, 92% in run 4 and 48% in run 5. If the reactions were worked-up in air, the conversion in run 2 was reduced to 41%.

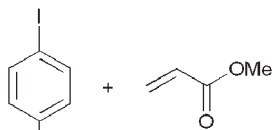
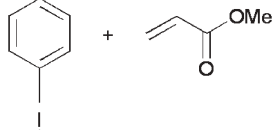
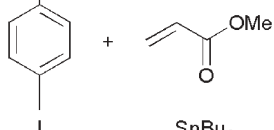
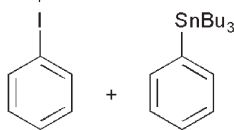
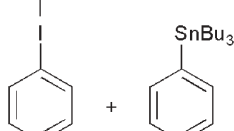
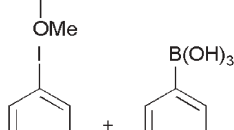
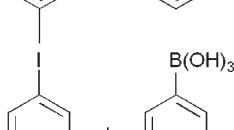
Stille reaction using supported catalyst in toluene

A Schlenk tube was charged with the supported pre-catalyst (0.40 g, 2 mol% Pd), toluene (18 mL), 4-aryl iodide (0.6 mmol), phenyl(*tri-n*-butyl)tin (0.25 g, 0.6 mmol). The reaction mixture was stirred for 3 h at 75 °C. Upon cooling to room temperature, the mixture was filtered under nitrogen, the siliceous material retained for reuse and the solvent was removed under vacuum. The product-containing mixture was analyzed by ¹H NMR spectroscopy. The isolated orange-brown silica was reused under the same conditions. Conversions were 100% in run 1 and 96.5% in run 2 with iodotoluene, and 100% in run 1 and 100% in run 2 for iodoanisole.

Suzuki reaction using supported catalyst in toluene

A Schlenk tube was charged with the supported pre-catalyst (0.80 g, 2 mol% Pd), toluene (18 mL), 4-iodotoluene (0.26 g, 1.2 mmol), phenylboronic acid (0.24 g, 2.5 mmol) and *N,N*-diisopropylethylamine (0.23 g, 1.78 mmol). The reaction mixture was stirred for 18 h at 75 °C. Upon cooling to room temperature, the mixture was filtered and the solvent was removed under vacuum. The product-containing mixture was

Table 1 Coupling reactions and effect of catalyst recycling on conversions

Entry	Substrates	Reaction conditions	Conversion
1		Toluene, 75 °C, 3 h, recycled under N ₂	Run 1–96% Run 2–85% Run 3–65% Run 4–10%
2		CO ₂ , 75 °C, 100 bar, 18 h, recycled under N ₂	Run 1–98% Run 2–96% Run 3–92% Run 4–92% Run 5–48%
3		CO ₂ , 75 °C, 100 bar, 18 h, recycled in air	Run 1–98% Run 2–41%
4		Toluene, 75 °C, 3 h, recycled under N ₂	Run 1–100% Run 2–97%
5		Toluene, 75 °C, 3 h, recycled under N ₂	Run 1–100% Run 2–100%
6		Toluene, 75 °C, 3 h, recycled under N ₂	Run 1–95% Run 2–63%
7		CO ₂ , 75 °C, 100 bar, 18 h, recycled under N ₂	Run 1–96% Run 2–93% Run 3–93% Run 4–91% Run 5–52% Run 6–38% Run 7–12%

analyzed by ¹H NMR spectroscopy. The isolated orange-brown silica was reused under the same conditions. Conversions were 95% in run 1 and 62.5% in run 2.

Suzuki reaction using supported catalyst in scCO₂

The reactions were performed under similar conditions to the Heck reaction using the supported catalyst in scCO₂. However, phenylboronic acid (0.24 g, 2.5 mmol) was used instead of methyl acrylate. Conversions were 96% in run 1, 93% in run 2, 93% in run 3, 91% in run 4, 52% in run 5, 38% in run 6 and 12% in run 7.

Results and discussion

We have previously reported the synthesis of a range of polydimethylsiloxane derived phosphine and phosphinite

ligands.²⁴ These ligands are soluble in scCO₂ and can be used to catalyse C–C bond forming reactions in this medium. During the course of this research, we discovered that these ligands and their complexes adsorbed onto silica to afford free-flowing powders and this provided an easy way to store and manipulate these oily materials. The ligands adsorb onto silica through the mechanisms previously reported for siloxane based polymers, Fig. 2.^{25–28} Upon addition of oven-dried silica to an orange hexane solution of complex Pd(PDMS-PPh₂)₂Cl₂, the solvent becomes colourless and the silica turns yellow. Typically, 0.200 g of complex are adsorbed onto 2.00 g of silica. No free ligand or complex are present in the supernatant solvent when analysed by ¹H NMR, ³¹P NMR and FT-IR spectroscopies. Upon changing the solvents, the complex remains adsorbed in non-polar solvents such as hydrocarbons, whereas it quantitatively desorbs in ethers, alcohols and acetonitrile.

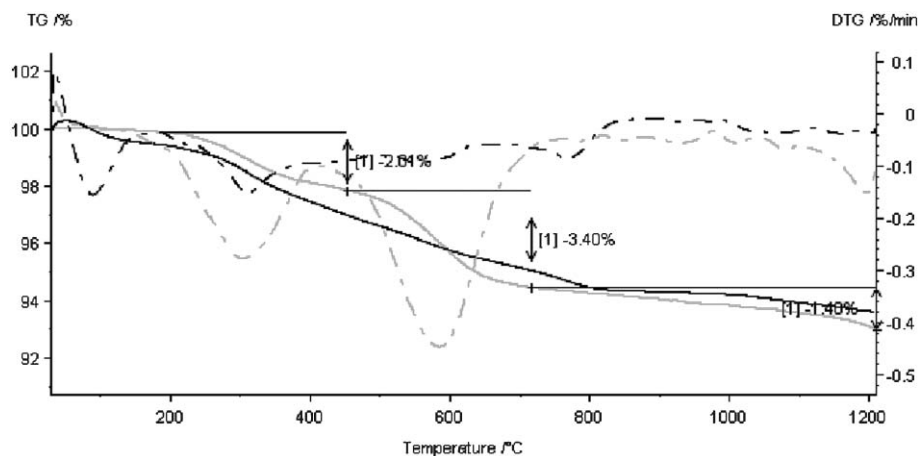


Fig. 3 TGA, DTGA (light grey graphs) and DSC thermographs (black graphs) of supported pre-catalyst.

Herein, we report on the thermal stability of the adsorbed complex. Fig. 3 displays the TGA and differential TGA (DTGA) (light grey solid and dotted curves respectively) for the Pd supported pre-catalyst. The solid line is a mass loss curve and the dotted line is the derivative of the mass loss curve with respect to time. The derivative curve indicates that there are two main mass loss events. The first is centred at about 305 °C and the second at about 600 °C with weight losses of 2.01 and 3.40% respectively. These peaks correspond to the exothermic decomposition of the organic components in the supported pre-catalyst. Since the catalyst loading on silica, in this case, was 100 mg g⁻¹, this result shows that the pre-catalyst degrades thermally to give Pd and silica. The thermal weight loss corresponds to all the phosphorus, carbon, hydrogen and chlorine degrading by this point. This correlates with the results obtained from the elemental analysis of Pd(PDMS-PPh₂)₂Cl₂ (C, 39.91; H, 7.92; Cl, 1.87; O, 17.72; P, 1.63; Pd, 2.81; Si, 28.14). This curve also indicates that the supported pre-catalyst is thermally stable at temperatures lower than 300 °C.

The differential scanning calorimetric (DSC) results for the supported pre-catalyst are also shown in Fig. 3 (black graphs). There are two endotherms observed for the hybrid catalyst in the 100 to 300 °C regions. There are a few smaller ones after this temperature. The first endotherm at about 100 °C is due to evaporation of trace water. The second endotherm at 300 °C in the DSC correlates with the first large weight loss in the TGA. However, the DSC and TGA events do not seem to tie in at around 600 °C, where the major weight loss (3.4%) is seen. For this weight loss, no corresponding endotherm on the differential DSC trace is observed. We propose that ligand degradation is occurring at the lower temperature (around 300 °C). However, the gaseous products remain physisorbed onto the surface of the metal and silica and then desorb (endothermic event) at the higher temperature. At the same time, the crystallization of the Pd into microdomains/nanoparticles (exothermic event) is taking place and therefore, these two processes cancel each other out in the DSC trace.

Pd(PDMS-PPh₂)₂Cl₂ is an air-stable species; no change in its spectroscopic data, particularly its ³¹P NMR spectrum, was observed over a six month period when exposed to the air.

Therefore, the adsorbed species on silica can also be considered air-stable prior to reaction. Pd(PDMS-PPh₂)₂Cl₂ on silica (supported pre-catalyst) was screened in Heck, Suzuki and Stille reactions in toluene and scCO₂, as described in the Experimental section.

When mixtures from Heck reactions performed in toluene were filtered in air, the catalyst gave negligible conversions when reused under the same conditions. The conversions were 45% in run 1, 3% in run 2, and 2% in run 3. ¹H NMR spectra of the crude product showed that some ligand leaching occurred. Also, the low conversions using the recycled catalyst indicated that the active species formed *in situ* was air-sensitive. Therefore, the Heck reaction experiments in toluene were repeated under a nitrogen atmosphere. The conversions were improved; 96% in run 1, 85% in run 2, 65% in run 3 and 10% in run 4. However, ligand leaching was still evident, indicating that the active catalyst does not have the PDMS-derived phosphine bound. Although the conversions decreased significantly during catalyst recycling, no palladium black precipitate was seen in the products or in the silica.

For reactions in scCO₂, the pressure vessel was loaded with the silica supported pre-catalyst and reagents in a glovebox or using a Schlenk line. The vessel was sealed, pressurised and heated to the required temperature, Table 1. Upon cooling, the vessel was vented into toluene under nitrogen using a Schlenk line. Then, the vessel and its contents were washed with dry toluene. The silica-based material was dried and reused. In the Heck reaction, the conversions were 98% in run 1, 96% in run 2, 92% in run 3, 92% in run 4 and 48% in run 5. The diisopropylethylammonium iodide salt is not soluble in toluene; therefore, it gradually built up on the supported catalyst after each run and the weight of the recovered silica increased. The colour of the catalyst changed from yellow to grey during the third run and by the fifth run, it was white. The dramatic drop in conversion for the fifth run can be attributed to the covering of active sites on the Pd/silica catalyst with diisopropylethylammonium iodide. The Pd particles became inaccessible to the reagents and led to a considerable loss of activity. DRIFT spectra, Fig. 5, confirmed the build up of the ammonium salt. Attempts to remove this salt build up by washing the catalyst with degassed and dried polar solvents

such as ethanol or acetone led to leaching of the Pd out of the silica. After washing the catalyst with these solvents, Pd black particles immediately started to precipitate from the mixture and the resulting colourless silica did not show any catalytic activity.

ICP analysis of the products was used to assess the extent of any Pd leaching. The crude products from each run were stirred with 10% HCl and were analysed using ICP for Pd content. No Pd was detected. In previously reported examples of supported Pd catalysts, preconditioning washing steps were essential to remove loosely bound Pd and avoid Pd leaching during the course of reaction.^{7,29,30} Therefore, it is particularly noteworthy that no Pd leaching occurred in this study. We propose that this is a result of using scCO_2 as the solvent, as it will have minimal interactions with the silica surface and therefore, will not displace the Pd. However, the stabilization of the nanoparticles on the silica by ammonium salts, as has been reported for phosphine-free Pd catalysts,³¹ cannot be ruled out.

The Suzuki reaction was also performed under similar conditions to the Heck reaction above, but with phenylboronic acid instead of methyl acrylate. The conversions were 96% in run 1, 93% in run 2, 93% in run 3, 91% in run 4, 52% in run 5, 38% in run 6 and 12% in run 7. Similarly to the Heck reaction, a considerable drop in yield was observed after the 4th run, which can be attributed to the blocking of active sites. Again, quantitative ICP analysis did not show any Pd in the products. Stille couplings were also performed but only in toluene to further demonstrate the utility of this system. Interestingly, conversions remained high upon reuse, thus providing further evidence for ammonium salts blocking active sites, as no ancillary base is used in these catalytic reactions. However, as the tin reagents used in these reactions are toxic, and therefore not green, Stille couplings were not performed in scCO_2 .

As there was evidence for leached ligand in the crude products, Si–Me environments in the ^1H NMR spectra, and no leached palladium, it was likely that Pd nanoparticles had formed and were catalysing the reactions. The leached ligand can be adsorbed onto fresh silica when purifying the organic products and can be reused if kept under a nitrogen atmosphere. PDMS-PPH₂ is air-sensitive and will oxidize to the corresponding phosphine-oxide if exposed to air.

Recently, there have been significant advances in the use of scCO_2 in materials preparation and processing, particularly in the production of metal nanoparticles.^{32–39} Practically, CO_2 -soluble metal precursors are generally sprayed into a CO_2 receiving solution containing a reducing agent such as $\text{NaBH}(\text{OAc})_3$ or H_2 and fluorocarbon stabilizing ligands to produce metallic nanoparticles with sizes ranging from 1 to 15 nm, and TEM has been used widely to determine the range and variation in particle size.³⁶ TEM has also been used in analyzing reaction mixtures for Pd nanoparticles in other catalysed reactions.^{8,9,31,35,40–42} As it appeared that during the course of the catalytic reactions, Pd nanoparticles were produced and were stabilised on the silica support, TEM analysis was performed on the recovered catalyst, Fig. 4. Unfortunately, the particles overlap with each other and it is therefore difficult to measure the size of the particles, but by a

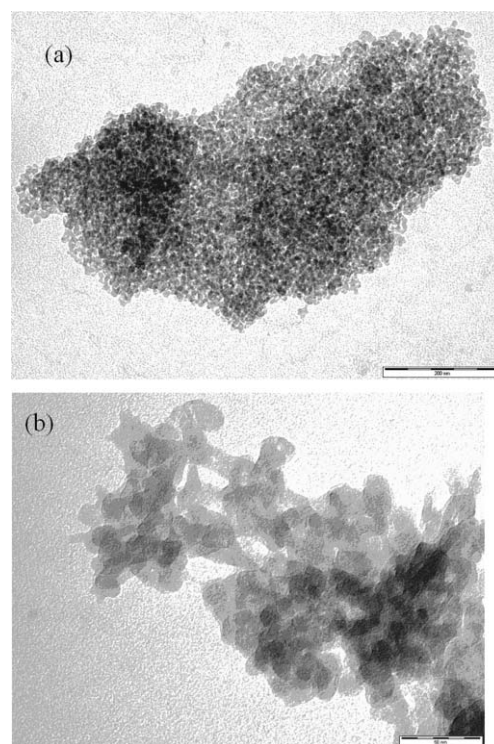


Fig. 4 Representative TEM microphotographs of recovered catalyst, scale (a) 200 nm (b) 50 nm.

careful inspection of particles near the edges of the image, an approximate diameter of 10 nm can be assigned. Despite the overlapping nature of the particles, Fig. 4 clearly illustrates the homogeneous dispersion of the particles throughout the silica. TEM analysis of the supported pre-catalyst before reaction at high and low magnifications showed no Pd particles. On a stereomicroscope, the silica particles in the pre-catalyst are visible with a homogeneous smooth yellow layer on their surface.

DRIFT spectroscopy was conducted on the supported pre-catalyst and recovered catalyst after the first through to third runs of the Heck reaction in scCO_2 . The DRIFT spectrum, Fig. 5, of the pre-catalyst shows a strong O–H stretching vibration at 3656 cm^{-1} assigned to free silanol residues, hydrogen bonded OH groups between $3600\text{--}3100\text{ cm}^{-1}$, aromatic C–H stretching bands (attributed to Ph groups of the ligand) at 2985 cm^{-1} , C=O stretching band (also within the ligand, Fig. 1) at 1640 cm^{-1} and Si–O stretching band centered at 1049 cm^{-1} . A decrease in the number of strongly and weakly hydrogen-bonded groups on the silica surface during the course of the reaction was clearly observed in the region $3600\text{--}3100\text{ cm}^{-1}$ in the DRIFT spectrum of the recovered silica samples. The same observation has been made during the heat treatment of silica supported catalysts.⁴³ The intensity of the C=O band at 1640 cm^{-1} decreased after the first run and disappeared after the third run. This provides additional confirmation of ligand leaching during the different runs, in addition to ^1H NMR data. The appearance of a C–N stretching band for aliphatic ammonium salts at 1380 cm^{-1} after the first run indicates the build up of diisopropylethylammonium iodide and its intensity increases considerably

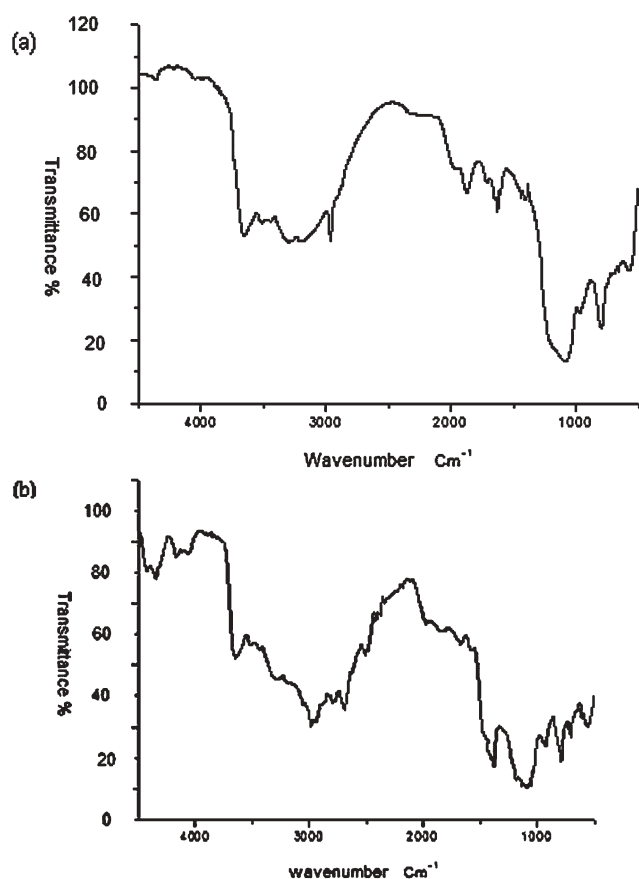


Fig. 5 (a) DRIFT spectrum of the silica supported pre-catalyst (b) DRIFT spectrum of recovered catalyst from run 3 (Heck reaction in $scCO_2$).

with each run. Elemental analysis of the used catalysts also indicated an increase in N levels consistent with the deposition of ammonium salts.

Conclusions

$Pd(PDMS-PPh_2)_2Cl_2$ on silica as a pre-catalyst to dispersed palladium nanoparticles on silica gave reproducible results during the course of Heck and Suzuki reactions and could be recovered and re-used for four times without substantial activity drops. TEM analysis shows the presence of Pd nanoparticles. These are probably responsible for the catalysis and the considerable drop in conversions after four runs is likely a result of quaternary ammonium salts depositing on the catalyst surface thereby blocking the active catalytic sites. The presence of these salts was proved using elemental analysis and DRIFT experiments. Additional experiments, such as XPS, would prove the presence of Pd(0) nanoparticles. Although the activity of these materials is not very high, this research provides further evidence for active Pd nanoparticles in C–C bond forming catalysis and indicates that, in this case, the use of $scCO_2$ in batch reactions for recycling such species is superior to conventional solvents. Future work will involve the use of a continuous flow-reactor to produce catalytic metal nanoparticles and performing other catalytic reactions.

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