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# Palladium containing nanostructured silica functionalized with pyridine sites: a versatile heterogeneous catalyst for Heck, Sonogashira, and cyanation reactions

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**Abstract**—Nanostructured hybrid silica bearing pyridine binding sites was prepared in a template assisted hydrolysis–polycondensation of tetraethylorthosilicate (TEOS) and the ionic precursor *N*,*N*-dimethyl-pyridin-4-yl-(3-triethoxysilyl-propyl)-ammonium iodide using *N*-dodecyl-*N*′-methyl-imidazolium bromide as structure directing agent. After treatment with palladium acetate, the material appeared as a versatile heterogeneous catalyst for Heck, Sonogashira, and cyanation reactions. In Heck and Sonogashira cross-coupling reactions, unchanged catalytic activity was observed in at least five reaction cycles.

## 1. Introduction

The formation of carbon–carbon bonds via palladium-catalyzed cross-coupling reactions plays a crucial role in synthetic organic chemistry. Particular attention has been paid to the coupling reaction of aryl halides with alkenes and alkynes, commonly called Heck[1] and Sonogashira[2] reaction, respectively. These reactions are generally catalyzed by soluble Pd complexes. However, the efficient separation and subsequent recycling of homogeneous transition metal catalysts remains a scientific challenge and an aspect of economical and ecological relevance. Several strategies for catalyst recycling have been explored, including aqueous phase catalysis,[3] fluorous phase catalysis,[4] the use of ionic liquids,[5] and colloidal dispersions,[6] but in particular solid supported catalysts,[7] both on organic[7f] and inorganic support.[7g] Unfortunately, the utility of some of these concepts is often limited by metal leaching or catalyst deterioration.

In the area of heterogeneous catalysts for Heck reactions, Ying et al. recently reported palladium nanoparticles supported on mesoporous silica, which showed good activity for the coupling reaction of various aryl halides with styrene or butylacrylate.[8] Recycling of this catalyst was hampered by significant Pd-metal agglomeration. A modified system reported by Hagiwara et al. consisting of $Pd(OAc)_2$ immobilized in a silica supported ionic liquid phase showed improved properties in terms of metal agglomeration as the ionic liquid acts as a protective shell for the catalyst.[9] However, a small part of the ionic liquid and the metal catalyst may dissolve in the reaction medium during the reaction especially when higher temperatures are required, and may lead to the formation of inactive Pd black.[10] Crudden's mercaptopropyl-modified mesoporous silica containing molecular Pd species elegantly combines high chemical stability, excellent catalytic activity, and negligible metal leaching.[11]

We are currently investigating functionalized silica containing ionic substructures.[12] In an earlier communication,[12b] we showed that the use of various ionic trialkoxysilylated precursor molecules led to modified structural features of the obtained functionalized silica materials obtained by nanocasting, particularly depending on the constitution of the used organic precursor. In continuation of our work on silica based materials for catalysis,[13] we report here nanostructured hybrid silica bearing pyridine binding sites, which can be used as heterogeneous ligands for the immobilization of palladium(II) species through metal–ligand interaction. These functionalized nanostructured silica materials bearing both ammonium substructures and pyridine binding sites may be particularly suitable systems for the immobilization of transition metal catalysts, as the stability of the immobilized metallic species can be enhanced by synergetic effects involving (i) metal–ligand interactions and (ii) ionic

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*Keywords*: Nanostructured hybrid silica; Heck reaction; Sonogashira reaction; Cyanation; Imidazolium salts.

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interactions involving the ionic species covalently grafted on the surface of the silica support and the ionic metal species. In our study, we used the Pd-containing silica based material as catalyst in Heck and Sonogashira reaction as well as in cyanation of aryl iodides.

## 2. Results and discussion

### 2.1. Precursor synthesis

The trialkoxysilylated precursor *N*,*N*-dimethyl-pyridin-4-yl-(3-triethoxysilyl-propyl)-ammonium iodide was easily synthesized by heating 4-(*N*,*N*-dimethylamino)pyridine (DMAP) and 3-iodopropyltriethoxysilane in acetonitrile in a Schenk tube under inert atmosphere. The $^{1}H$ NMR spectrum of the resulting product shows a singlet at $\delta$=3.24 ppm characteristic for methyl groups linked to quaternary nitrogen atoms. This result indicates that the reaction exclusively yields the ammonium salt and keeps the pyridine site intact, which was essential for subsequent complexation with $Pd(OAc)_2$ (Scheme 1).

### 2.2. Materials' synthesis

The functionalized nanostructured silica was prepared by nanocasting[14] using *N*,*N*′-dodecyl-methyl-imidazolium bromide as structure directing agent. Imidazolium based ionic liquids recently appeared as efficient templates for nanocasting techniques.[15] We chose an imidazolium salt as structure directing agent as the interaction between the ammonium precursor bearing pyridine substructures and imidazolium salts may be more favorable than that between the ionic precursor and surfactants based on ammonium substructures such as CTAB.[16] Hydrolysis–polycondensation of the precursor with tetraethylorthosilicate (TEOS) led to the formation of nanostructured silica **I** functionalized with ionic pyridine binding sites. After removal of the template by washing, the heterogeneous catalyst was obtained by subsequent treatment with $Pd(OAc)_2$. The schematic illustration of the synthesis of the catalytic material **I-Pd** is given in Scheme 2.

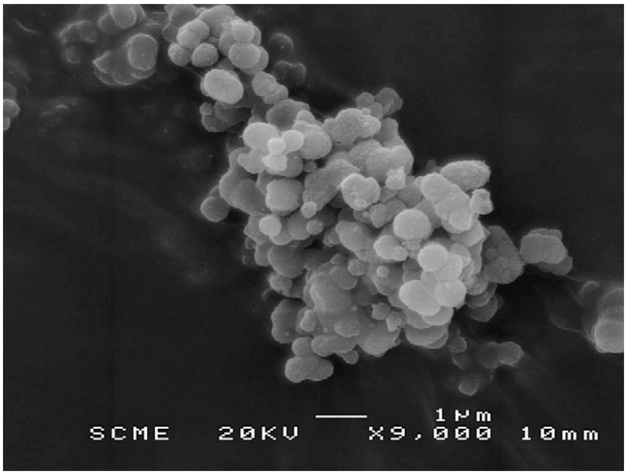
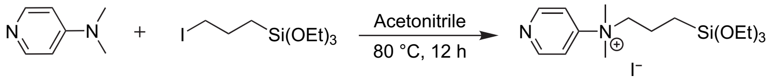


**Figure 1**. SEM image of hybrid silica catalyst **I-Pd**.

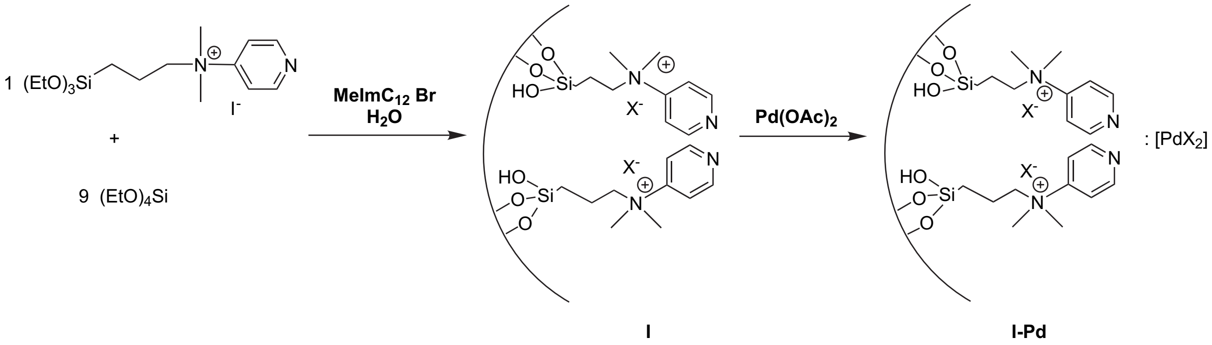
Electronic microscopy gave information about the morphology of the synthesized Pd containing nanostructured hybrid silica **I-Pd**. The SEM image shows agglomerates of particles with diameters in the range of several hundreds of nanometer up to a micrometer (Fig. 1). X-ray fluorescence experiment with the material gave a Si/Pd molar ratio of 95.2:4.8. As the materials were synthesized using a 9:1 ratio of TEOS and the ionic precursor, this result indicates a 2:1 ratio of the immobilized pyridine substructures and supported Pd species. The complete incorporation of the organic substructure in the material was also confirmed by elemental analysis.

The TEM micrograph of some smaller particles of the functionalized silica catalyst **I-Pd** (Fig. 2) clearly indicates nanostructured morphology of the material. This material appears of high regularity, as all of the observed particles show high degree of structuration.

Nitrogen adsorption–desorption experiment with the palladium containing material **I-Pd** resulted in a typical type IV isotherm. Nitrogen sorption experiments of the catalyst showed a BET surface area of 154 $m^2/g$ and



**Scheme 1**. Synthesis of *N*,*N*-dimethyl-pyridin-4-yl-(3-triethoxysilyl-propyl)-ammonium iodide.



**Scheme 2**. Synthesis of the catalytic material **I-Pd** by nanocasting using *N*,*N*-dodecyl-methyl-imidazolium bromide.

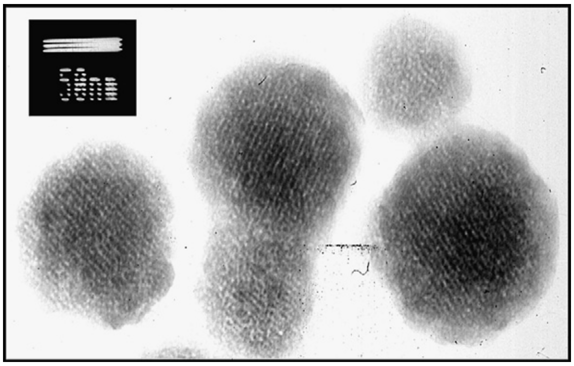


**Figure 2**. TEM image of hybrid silica catalyst **I-Pd**.

a pore volume of 0.366 $cm^3/g$. The average pore size can be estimated to be 3.5 nm.

The material was also characterized by solid state MAS NMR spectroscopy. The $^{29}Si$ CP-MAS spectra (Fig. 4) show two characteristic signals. The signal at $-100$ and $-109$ ppm can be assigned to $Q^3$ and $Q^4$ sites corresponding to $SiO_4$ substructures of different condensation degree. The signal at $-66$ ppm can be assigned to major $T^3$ sites for $RSiO_3$ units possessing three siloxane bridges. In order to identify organic functionalities attached to the silica support, a $^{13}C$ CP-MAS experiment was performed. The spectrum shows signals at 24, 40, 60, 108, 142 and 157 ppm, similar to the chemical shifts found in the liquid $^{13}C$ NMR spectrum of the silylated organic precursor molecule (Fig. 3).

In consequence, the synthesized material incorporating palladium species is a mesoporous silica with nanostructured morphology functionalized with pyridine binding sites covalently linked to the silica support. The material appears of high textural homogeneity, which is an important feature in the view of the elaboration of materials showing high stability and long-lasting catalytic activity.

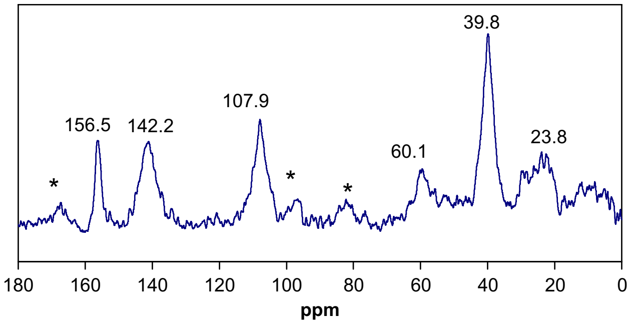


**Figure 3**. $^{13}C$ CP-MAS NMR spectrum of material **I-Pd** (spinning side bands are marked with asterisks).

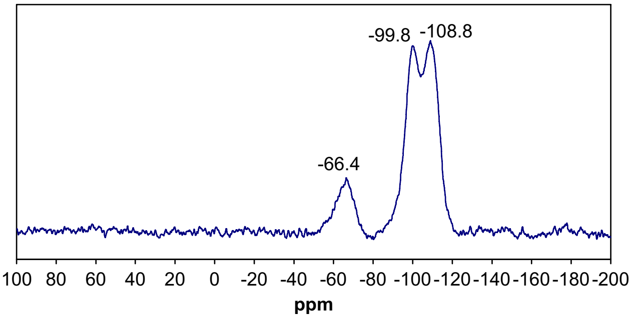
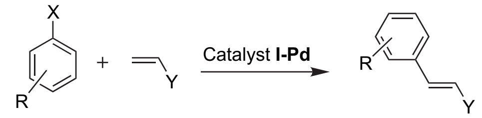


**Figure 4**. $^{29}Si$ CP-MAS NMR spectrum of material **I-Pd**.

### 2.3. Catalytic tests

In order to explore the catalytic properties of this nanostructured silica **I-Pd**, we studied the utilization of this material as heterogeneous catalyst in Heck, Sonogashira, and cyanation reactions.

**2.3.1. Heck reactions.** The Heck coupling reaction (Scheme 3) was performed using a variety of substrates. Firstly, the reaction conditions were optimized using iodobenzene and methyl acrylate as a substrate. After screening a range of usual inorganic and organic bases and exploring the scope of various solvents, we found that the catalyst is most efficient for Heck reaction using triethylamine as a base and acetonitrile as a solvent. The efficiency of this catalyst was studied in the Heck reaction of various aryl halides and alkenes under optimized reaction conditions. The results are summarized in Table 1.



R - H, alkyl, aryl
X - Halide
Y - $CO_2CH_3$, $C_6H_5$

**Scheme 3**. Heck coupling reaction using nanostructured hybrid silica catalyst **I-Pd**.

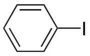
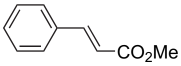
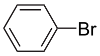
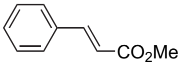
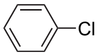
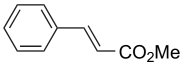
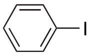
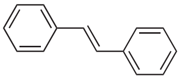
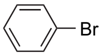
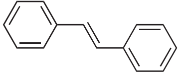
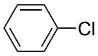
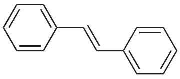
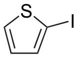
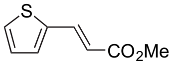
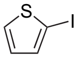
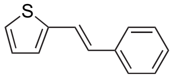
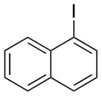
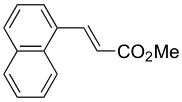
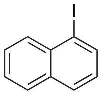
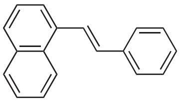
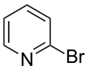
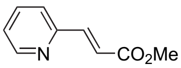
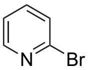
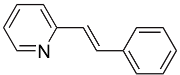
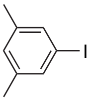
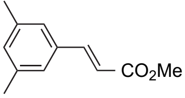
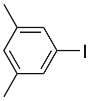
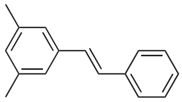
We found that aryl iodides and -bromides were efficiently coupled with methyl acrylate and styrene to give the corresponding 1,2 substituted alkenes in good to excellent yields. Unfortunately, reactivity toward chloroarenes, which was observed by others,[17] was not achieved with our catalyst system (entries 3 and 6). The reactions with 2-iodothiophene were successfully achieved (entries 7 and 8), providing a useful way for introduction of unsaturated group on the thiophene ring. Our efforts for employing 2-bromopyridine (entries 11 and 12) produced low product yields.

**2.3.2. Sonogashira reactions.** Similarly, the nanostructured material **I-Pd** was used as catalyst in the Sonogashira coupling reaction (Scheme 4). Here, the reaction conditions were optimized for the cross-coupling of iodobenzene with phenyl acetylene as the model reaction. Using acetonitrile as a solvent and triethylamine as a base, the material showed good catalytic activity and led to various disubstituted alkynes in 65–80% yield (Table 2).

R - H, aryl
Z - $C_6H_5$, 4-Me-$C_6H_5$

**Scheme 4**. Sonogashira coupling reaction using nanostructured hybrid silica catalyst **I-Pd**.

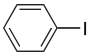
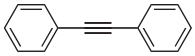
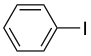
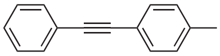
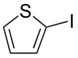
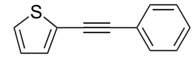
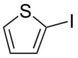
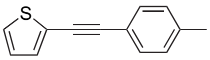
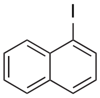
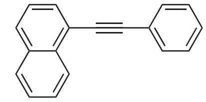
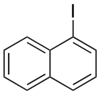
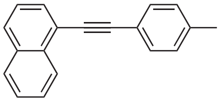
**Table 1**. Heck reaction of aryl halides and alkenes using catalyst **I-Pd**[a]

| Entry | Aryl halide | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 90 |
| 2 |  |  | 82 |
| 3 |  |  | No reactivity detected |
| 4 |  |  | 77 |
| 5 |  |  | 70 |
| 6 |  |  | No reactivity detected |
| 7 |  |  | 93 |
| 8 |  |  | 84 |
| 9 |  |  | 80 |
| 10 |  |  | 79 |
| 11 |  |  | 12 |
| 12 |  |  | 10 |
| 13 |  |  | 87 |
| 14 |  |  | 87 |

[a] Reaction was carried out using 1 mmol of aryl halide, 1.5 mmol of alkene, 2 mmol of triethylamine, and 500 mg (0.1 mmol as $Pd(OAc)_2$) catalyst in refluxed acetonitrile.

[b] Yield was determined by GC with dodecane as internal standard with respect to aryl halide, and was confirmed by $^1H$ NMR spectroscopy.

**Table 2**. Sonogashira reaction using catalyst **I-Pd**[a]

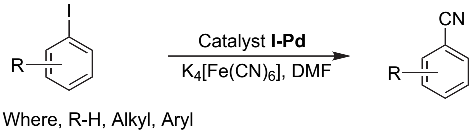
| Entry | Aryl halide | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 80 |
| 2 |  |  | 82 |
| 3 |  |  | 65 |
| 4 |  |  | 70 |
| 5 |  |  | 70 |
| 6 |  |  | 71 |

[a] Reaction was carried out using 1 mmol of aryl halide, 1.5 mmol of alkene, 2 mmol of triethylamine, and 500 mg (0.1 mmol as $Pd(OAc)_2$) catalyst in refluxed acetonitrile.

[b] Yield was determined by GC with dodecane as internal standard with respect to aryl halide, and was confirmed by $^1H$ NMR spectroscopy.

**2.3.3. Cyanation reactions.** We finally explored the utility of this nanostructured silica **I-Pd** for cyanation of aryl iodides. For many years, the only method for cyanation of an aryl halide required stoichiometric CuCN and harsh reaction conditions.[18] Since the discovery of Pd-catalyzed cyanation reactions allows the conversion of aryl halides to nitriles,[19] more selective methods have been reported. Palladium-catalyzed cyanation reactions are particularly attractive due to their functional group tolerance, air stability, and high catalytic activity. $K_4[Fe(CN)_6]$, recently reported as a cyanide source by Beller et al., is particularly intriguing because it is inexpensive, easily handled, and nontoxic. Furthermore, all cyano groups of the complex are available for the cyanation reaction under homogeneous condition.[20] However, homogeneous catalysts suffer from the problems associated with the difficulty of catalyst recovery, separation, and deactivation via the formation of Pd aggregates in situ. In this field, the use of heterogeneous catalyst systems can be advantageous.

The cyanation reaction (Scheme 5) was performed using a variety of substrates. Firstly, the reaction conditions were optimized using iodobenzene as a substrate. We found that the heterogeneous Pd-catalyst is most efficient for cyanation reaction in presence of triethylamine as a base and DMF as a solvent. Using optimized reaction conditions, the efficiency of this catalyst was studied for cyanation reaction of various aryl halides. The results are summarized in Table 3.

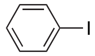
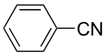
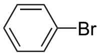
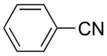
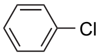
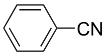
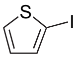
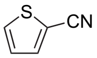
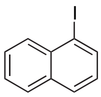
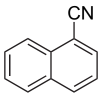
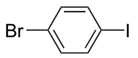
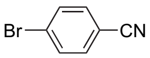
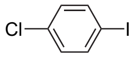
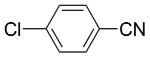
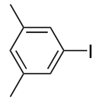
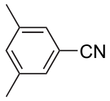


**Scheme 5**. Cyanation reaction using nanostructured hybrid silica catalyst **I-Pd**.

It appeared that aromatic iodo compounds were efficiently reacted to give cyanated products in good yields (entries 1, 5, and 8). Reactions with 2-iodothiophene were also successfully achieved (entry 4), providing a useful way for introduction of cyanide groups on thiophene ring. However, the catalyst shows no activity toward aryl bromides or chlorides (entries 2 and 3), which can be used for selective cyanation of iodo groups keeping bromo or chloro functionalities intact (entries 6 and 7).

**2.3.4. Recycling experiments.** For practical applications of heterogeneous systems, the lifetime of the catalyst and its

**Table 3**. Cyanation reaction of aryl iodides using catalyst **I-Pd**[a]

| Entry | Aryl halide | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 78 |
| 2 |  |  | No reaction |
| 3 |  |  | No reaction |
| 4 |  |  | 76 |
| 5 |  |  | 78 |
| 6 |  |  | 76 |
| 7 |  |  | 76 |
| 8 |  |  | 77 |

[a] Reaction was carried out using 1 mmol of aryl iodide, 0.7 mmol of $K_4[Fe(CN)_6]$, 2 mmol of triethylamine, and 500 mg nanostructured hybrid silica catalyst in refluxed DMF.

[b] Yield was determined by GC with dodecane as internal standard with respect to aryl iodide.

level of reusability are very important features. To clarify this issue, we performed set of experiments using the recycled catalyst. We found that the catalyst showed excellent recyclability in the Heck coupling reaction of iodobenzene with methyl acrylate (Table 4). All runs were carried out under similar conditions in refluxing acetonitrile. After the first reaction giving methyl cinnamate in 90% yield, the catalyst was recovered by filtration, washed with dichloromethane and acetone, and finally dried at 100 °C for 1 h. A new reaction was then performed with fresh solvent and reactants under similar conditions. The nanostructured hybrid silica catalyst **I-Pd** shows unchanged catalytic activity after simple washing and drying in at least five reaction cycles. No catalyst deterioration was observed, confirming the high stability of the heterogeneous catalyst under the reaction conditions.

Heterogeneity and Pd leaching of this catalyst were examined by the 'hot filtration' test for the Heck reaction of iodobenzene and methyl acrylate. We examined the leaching of Pd at two different points in the reaction. Filtration using Whatman filter paper after 1 h (7% conversion) followed by an additional 24 h of reaction gave a final conversion of 90% for the catalyst-containing portion, and 8% conversion for the filtered portion. In another test, after 3 h, the reaction was split at a conversion of 17%. After an additional 24 h, the portion containing the suspended catalyst had proceeded to 90% conversion, while the catalyst free portion reacted only up to 20%. Pd leaching was also studied by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, indicating that the liquid part of Heck reaction mixture contained 0.9 ppm of palladium accounting for 0.08% of the initially added amount of Pd.

**Table 4**. Recyclability of catalyst **I-Pd** in the Heck coupling reaction of iodobenzene with methyl acrylate

| Run | Reaction condition | Selectivity (%) | Conversion (%) |
|---|---|---|---|
| 1 | 80 °C/12 h | 100 | 90 |
| 2 | 80 °C/12 h | 100 | 88 |
| 3 | 80 °C/14 h | 100 | 89 |
| 4 | 80 °C/14 h | 100 | 90 |
| 5 | 80 °C/15 h | 100 | 89 |

**Table 5**. Recyclability of catalyst **I-Pd** in the cyanation reaction

| Run | Reaction condition | Conversion (%) |
|---|---|---|
| 1 | 130 °C/24 h | 81 |
| 2 | 130 °C/24 h | 76 |
| 3 | 130 °C/24 h | 74 |
| 4 | 130 °C/24 h | 52 |
| 5 | 130 °C/24 h | 32 |

However, the catalyst showed reduced recyclability in the cyanation of iodobenzene (Table 5). Once again, all runs were carried out under similar conditions in refluxing DMF. We found that the catalyst showed good catalytic performance in three reaction cycles, but decreased activity starting from the fourth run. This result may be due to catalyst deterioration under the harsh conditions of the cyanation reaction.

We believe that the low Pd leaching observed in Heck and Sonogashira coupling reactions is due to immobilized pyridine binding site located on the surface of the nanostructured silica, which acts as a ligand through metal–ligand interaction. The anchoring of Pd species by pyridine sites supported on nanostructured silica minimizes catalyst deterioration and metal leaching and therefore allows efficient catalyst recycling.

## 3. Conclusion

In summary, we report a palladium containing nanostructured silica bearing trialkyl-(4-pyridyl)-ammonium binding sites, which was efficiently used as heterogeneous catalyst for Heck and Sonogashira coupling reactions as well as in cyanation reactions involving various iodo- and bromoarenes. The reported material system shows interesting features in heterogeneous catalysis: (i) low Pd leaching due to (1) non-covalent anchoring and (2) Coulombic interactions between pyridine binding site and the immobilized Pd species; (ii) nanostructured morphology of the heterogeneous catalyst, which ensures strong interaction between substrates and the solid, allowing high catalytic activity, and (iii) high efficiency and economy gain by simple reaction processing and easy recovery and re-use of the catalyst.

## 4. Experimental section

### 4.1. Synthesis of *N*,*N*-dimethyl-pyridin-4-yl-(3-triethoxysilyl-propyl)-ammonium iodide

4-(*N*,*N*-Dimethyl)aminopyridine 1.22 g (0.01 mol) and (3-iodopropyl)triethoxysilane 3.98 g (0.012 mol) were dissolved in 10 mL of acetonitrile in a Schlenk tube. The reaction mixture was stirred under inert atmosphere at 80 °C for 24 h. After completion of reaction, solvent was evaporated and product was washed with ether to remove excess of (3-iodopropyl)triethoxysilane, to yield 4.2 g (92%) of pure product. FTIR (KBr): 3157, 2975, 2930, 1650, 1564, 1077, 959 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 0.55 (t, 2H), 1.16 (t, 9H), 1.94 (m, 2H), 3.24 (s, 6H), 3.71 (q, 6H), 4.26 (t, 2H), 6.97 (d, 2H), 8.27 (d, 2H) ppm; $^{13}C$ NMR ($CDCl_3$): $\delta$ 6.87, 18.35, 25.06, 40.80, 58.69, 59.90, 108.52, 142.29, 156.24 ppm; $^{29}Si$ NMR ($CDCl_3$): $\delta$ −46.19 ppm; HRMS ($FAB^+$): calculated for $C_{16}H_{31}O_2N_2Si$ ($M^+$) 227.2104, found 227.2108.

### 4.2. Typical preparation of catalyst I-Pd

TEOS/*N*,*N*-dimethyl-pyridin-4-yl-(3-triethoxysilyl-propyl)-ammonium iodide/$H_2O$/$NH_4OH$/*N*-methyl dodecyl imidazolium bromide were mixed in the ratio of 0.9:0.1:114:8:0.12.[12a] In typical experimental procedure, template *N*-methyl-*N*′-dodecyl-imidazolium bromide (0.32 g) was dissolved in water (14 g) and ammonium hydroxide (7 g). To this stirred solution, an organic sol–gel precursor *N*,*N*-dimethyl-pyridin-4-yl-(3-triethoxysilyl-propyl)-ammonium iodide (0.36 g) was added and stirred for 15 min, in which an inorganic sol–gel precursor TEOS (1.6 mL) was added and the mixture is stirred at 80 °C for 2 days. The removal of template was carried out by Soxhlet extraction of material using ethanol (with 10% HCl) for 24 h. After template removal, material was washed with ethanol and acetone, and then dried. Two grams of this material was then stirred with $Pd(OAc)_2$ (0.14 g) in ethanol overnight. $Pd(OAc)_2$ encapsulated catalyst was filtered and washed with ethanol, acetone, and finally refluxed with acetonitrile to remove traces of physically adsorbed $Pd(OAc)_2$. Found elemental analysis/%: C: 12.19, H: 2.12; N: 2.72; Si: 33.61; Pd: 3.62. Si/Pd ratio found by scanning electron microscopy: 95.2:4.8. The amount of $Pd(OAc)_2$ encapsulated was 0.34 mmol $g^{-1}$ based on elemental analysis.

### 4.3. General experimental procedure for Heck reactions

To a suspension of heterogeneous catalyst **I-Pd** (300 mg) in acetonitrile (10 mL), aryl halide (1 mmol), alkene (1.5 mmol), triethylamine (2 mmol), and dodecane as internal standard were added. The mixture was refluxed for 24 h and was monitored by GLC. After completion, the reaction mixture was filtered using Whatman filter paper and the solvent was evaporated. The crude product was dissolved in diethyl ether. The organic phase was washed with 10% HCl and dried over sodium sulfate. Evaporation of ether gives crude product, which was confirmed by GC–MS and liquid NMR. All the prepared compounds are known and compared with authentic sample.

### 4.4. General experimental procedure for Sonogashira reactions

The reactions were carried out in similar way as for Heck reaction, by using catalyst **I-Pd** (300 mg, 0.1 mmol as $Pd(OAc)_2$), aryl iodide (1 mmol), alkynes (1.5 mmol), triethylamine (2 mmol), and dodecane as internal standard. The mixture was refluxed for 24 h in acetonitrile at 80 °C. All the prepared compounds are known and compared with authentic sample.

### 4.5. General experimental procedure for cyanation reactions

To a suspension of nanostructured hybrid silica catalyst **I-Pd** (300 mg) in DMF (5 mL), aryl halide (1 mmol), dry $K_4[Fe(CN)_6]$ (0.7 mmol), triethylamine (2 mmol), and dodecane as internal standard were added. The mixture was refluxed for 24 h and was monitored by GLC. After completion, the reaction mixture was filtered using Whatman filter paper. The crude product was dissolved in ethyl acetate. The organic phase was washed with 10% HCl and dried over sodium sulfate. Evaporation of solvent gives crude product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

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## Supplementary data

Full characterization of the organic precursor molecule and the nanostructured heterogeneous catalyst are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.073.

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