



Synthesis and characterization of recyclable and recoverable MMT-clay exchanged ammonium tagged carbapalladacycle catalyst for Mizoroki–Heck and Sonogashira reactions in ionic liquid media

Vasundhara Singh*, Rajni Ratti, Sukhbir Kaur

Department of Applied Sciences, PEC University of Technology, Chandigarh 160012, India

ARTICLE INFO

Article history:

Received 12 August 2010
Received in revised form 13 October 2010
Accepted 16 October 2010
Available online 5 November 2010

Keywords:

Carbapalladacycle
MMT-clay
Organic–inorganic hybrid materials
Mizoroki–Heck
Sonogashira

ABSTRACT

An efficient synthesis of an ammonium tagged carbapalladacycle **5**, in modest yield, has been achieved. Further, the clay-nanocomposite **6** was prepared by ion exchange of **5** into clay interlayers as a new organic–inorganic hybrid catalytic system. The ionic tag of the ammonium supported carbapalladacycle **5** assists in the pillaring process and enhances the organophilicity of catalyst **6** in the interlayers of clay. The catalytic activity in ammonium based ionic liquid [TMBA] NTf₂ of both the homogeneous and heterogeneous recyclable catalysts **5** and **6** respectively in micromolar concentration of palladium has been tested for Mizoroki–Heck and Sonogashira reactions in good yields with high TON/TOF and negligible metal leaching. Effect of solvent and temperature on the catalytic activity has also been examined.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Development of recoverable and recyclable catalysts for industrial applications has become important from both environmental and economical point of view and has been well reviewed in literature [1]. To achieve this objective several catalysts are anchored or immobilized onto polymeric and inorganic supports [2,3]. Despite the advantages and the progress, homogeneous catalysis has a share of less than 20% in industrial processes because of the issues related to recoverability and recyclability of expensive metal catalysts. In contrast, heterogeneous catalysis exhibits the advantage of easy separation of the catalyst from the products and can be easily adapted to continuous flow processes [4,5]. However, heterogeneous catalysis lacks complete characterization, mechanistic details regarding factors affecting activity and selectivity. Hence, there is a need to synthesize homogeneous–heterogeneous catalysts to overcome the drawbacks of each system and to combine the advantages of both [6]. Successful methods include immobilizing or supporting the active homogeneous catalysts onto various inorganic supports such as zeolites, mesoporous materials, alumina, silica, clays and high surface carbons [7–9] which assists in controlling reactivity, selectivity besides the advantage of easy workability.

Palladium catalyzed C–C and C–heteroatom bond forming reactions are firmly positioned as one of the most important tools in organic synthesis [10]. During the last decade very active systems have been developed in order to improve the stability and efficiency of palladium based catalysts [11]. Carbometallated Pd^{II} complexes, particularly palladacycles have emerged as promising catalysts for various cross-coupling reactions [12]. Of these the potential of oxime derived palladacycles as catalyst precursors for important carbon–carbon coupling reactions has been well explored [13]. The highlighting features of these palladacycles are their extraordinary thermal stability, insensitivity to air or moisture, ready and economic synthetic access and modulation of electronic and steric properties by simple variations in structure. Several dimeric chloro-bridged palladacycles derived from a wide variety of aromatic and aliphatic oximes from benzaldehyde, acetophenone and benzophenone, pinacolone and acetylferrocene have been reported and their catalytic activity checked in different cross-coupling processes [14,15].

Previously, numbers of attempts have been made to immobilize the active oxime carbapalladacycle onto to various supports like silica [16], polystyrene [17], MCM-41, polystyrene–divinylbenzene [18], periodic mesoporous organosilica (PMO) [19], alumina [20] and recently Kaiser resin [21] in an effort to develop supported Pd–ligand complexes thereby enhancing the recyclability of ligand and reducing the metal leaching considerably.

Lately, reports of the use of ionic supported catalysts immobilized in ionic liquids as efficient recyclable catalysts have appeared

* Corresponding author. Tel.: +91 172 2753263.
E-mail address: vasun7@yahoo.co.in (V. Singh).

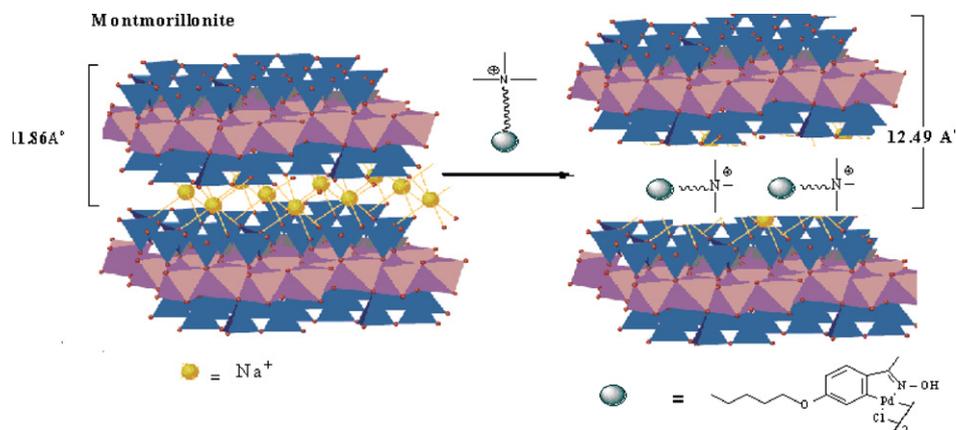


Fig. 1. Preparation of clay nanocomposite catalyst **6**.

in literature [22]. The ionic support enhances the interaction and immobilization of the tagged moiety in the ionic media resulting in high turn over numbers, frequencies with negligible metal leaching and has been recently reviewed in literature [23].

Montmorillonite clay having a layered 2:1 structure, high cation exchange capacity can be chemically modified by immobilization involving a simple ion exchange of organic and inorganic moieties which can be fine tuned as per industrial requirements and are being considered as potentially cost effective and environmentally benign nano-materials for the future [24,25], especially with amines or quaternary ammonium salts which provides a simple method for the preparation of organic–inorganic hybrid materials. Recently, Kim et al. have reported the preparation of cationic nanoclays by immobilizing ionic liquids as a modifier in the interlayers of clays [26]. A supported ionic-liquid film (SILF) of nanometric thickness containing bis (oxazoline)–copper complexes in clay has been used as recoverable catalysts for enantioselective cyclopropanation reaction [27]. Tao et al. prepared palladium-sepiolite catalysts by immobilizing Pd^{2+} on sepiolite using ionic liquid and used them as efficient catalysts for hydrogenation of alkenes and Heck reaction [28].

Previously, oxime carbapalladacycle with an ionophilic imidazolium tag and its heterogenization with Al/MCM-41 was described by Corma et al. [20] which showed unsatisfactory results for both Mizoroki–Heck and Suzuki couplings due to the specific nature of the imidazolium tag. In continuation to our program involving development of robust recyclable and recoverable catalysts [29–31], we hereby present our work which involves designing the Najera's oxime carbapalladacycle by the introduction of an inert ammonium tag to the main structure, making its immobilization

into the ammonium based ionic liquid-phase facile thus creating a homogeneous supported catalytic system. Further, for the heterogenization of active catalytic species, the ammonium tagged carbapalladacycle **5** has also been supported on to inexpensive and readily available Na^+ -MMT clay by ion-exchange method to create an organic–inorganic hybrid catalytic system **6**. The catalytic activities of both in homogenous and heterogeneous phase have been studied for Mizoroki–Heck and Sonogashira reactions.

2. Experimental

2.1. Synthesis of ammonium tagged carbapalladacycle catalyst **5**

The synthetic route adopted to prepare ammonium tagged carbapalladacycle is as shown in Scheme 1.

4-Hydroxyacetophenone was treated with hydroxylamine hydrochloride to obtain the corresponding oxime **2** as a white solid which on reaction with 1,5-dibromopentane gave compound **3**. Carbapalladation of compound **3** with sodium tetrachloropalladate at room temperature gave **4** as a green solid. The NMR, IR, mass spectroscopic data of compound **4** is in agreement with that reported in literature [20]. The ammonium pendant was then appended to compound **4** using five fold excess of trimethylamine in THF at 50 °C for 36 h, resulting in the formation of compound **5** as a greenish powder (overall yield 20%). IR (KBr, cm^{-1}): 3443.2, 3183.7, 3023.8, 2939.3, 2862.4, 1635.0, 1578.8, 1559.5, 1456.3, 1376.3, 1334.0, 1263.0, 1206.8, 1097.8, 1034.7, 963.0, 907.8, 804.0, 737.9, 638.0, 603.2, 522.8. ^1H NMR (400 MHz, DMSO): δ ppm: 7.19 (m, 1H), 7.07 (d, 1H, $J=7.76$ Hz), 6.55 (d, 1H, $J=6.48$ Hz), 3.95 (t, 2H), 3.34 (s, 2H), 3.05 (s, 9H), 2.15 (s, 3H), 1.75 (4H, s), 1.42 (s, 2H); ^{13}C NMR (400 Mz, DMSO): δ ppm: 162.9, 157.0, 153.6, 137.7, 129.0, 120.3, 109.5, 63.4, 53.5, 31.0, 28.4, 22.9, 22.4, 11.3. MS ESI $^+$: Isotopic distribution for $\text{M}^+-\text{C}_{16}\text{H}_{38}\text{N}_2$ compatible with 2 Pd and 2 Cl (%): m/z 587.2 (0.453), 587.7 (0.997), 588.2 (1.722), 588.7 (3.241), 589.2 (4.827), 589.7 (6.27), 590.2 (7.728), 590.7 (8.612), 591.2 (8.97), 591.7 (7.88), 592.2 (8.27), 592.7 (5.417), 593.2 (5.66), 593.7 (3.059), 594.2 (2.629), 594.7 (1.337), 595.2 (1.110), 595.7 (0.725).

2.2. Preparation of clay nanocomposite catalyst **6**

The complex **5** is intercalated into the clay interlayers to obtain a heterogeneous catalyst as shown in Fig. 1. To the suspension of the complex **5** (100.8 mg, 0.12 mmol) in CH_2Cl_2 (15 ml) was added Na^+ -MMT clay (100 mg) in small portions with vigorous stirring at room temperature and continued for 48 h. The resulting suspension was filtered and the solid was exhaustively soxhlet-extracted with dichloromethane (4×10 ml) to remove excess complex. The result-

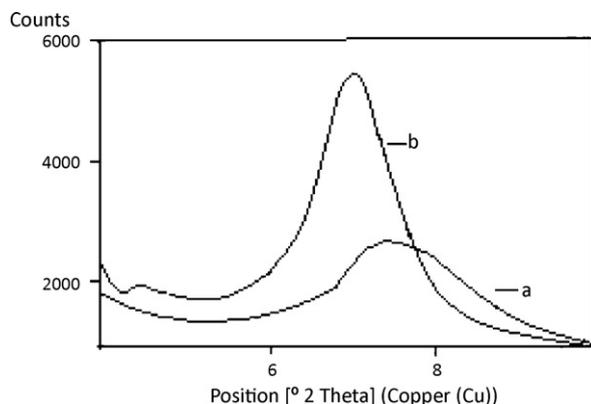
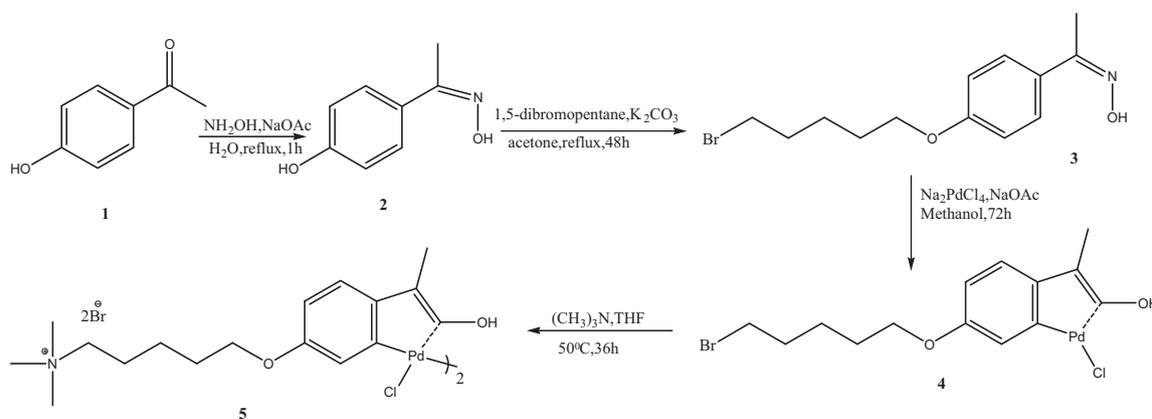


Fig. 2. XRD patterns of (a) Na^+ -MMT clay, (b) catalyst **6**.



Scheme 1. Synthetic route for the preparation of ammonium tagged oxime carbapalladacycle **5**.

ing product was dried under vacuum to get the clay nanocomposite **6**, as a free flowing powder.

2.3. Catalyst characterization

Palladium content of **5** as determined by AAS was found to be 2.39 mmol/g. The carbon, nitrogen and hydrogen content determined by elemental analysis is 32.78, 4.329 and 4.404% respectively. The unmodified Na⁺-MMT clay and catalyst **6** were characterized by using XRD, IR, BET and TGA analysis to determine the structure, surface area and thermal stability respectively. The powder XRD patterns of Na⁺-MMT clay and catalyst **6** are presented in Fig. 2. The characteristic peak at 7.44° corresponds to d_{001} spacing of 11.86 Å in case of Na⁺-MMT clay. Similarly, the peak at 7.07° corresponds to a d_{001} spacing of 12.49 Å in case of catalyst **6** indicating expansion of the interlayers due to exchange of smaller Na⁺ ions with the bulkier carbapalladacycle cation. The IR spectra of oxime **2** shows a characteristic C=N stretching vibration of 1675 cm⁻¹ and the corresponding C=N vibration in **4** was shifted to 1635 cm⁻¹ indicating N-Pd coordination (Fig. 3). Further, the presence of a band at 1636.5 cm⁻¹ in the IR spectrum of catalyst **6**, as shown in Fig. 4, confirms the successful intercalation of catalyst **5** in the clay interlayers. The nitrogen adsorption-desorption isotherms of MMT and catalyst **6** at 77 K were evaluated using an adsorption analyzer. The BET surface area and micropore volume increased from 11.89 to 14.37 m²/g and 0.0253 to 0.0566 cm³/g for MMT clay and catalyst **6** respectively as given in Table 1, which further supports the intercalation process. TGA analysis of catalyst **5** and **6** showed that catalyst **5** was thermally stable up to 450 °C after which it degraded rapidly while catalyst **6** showed thermal stability up to 700 °C which is probably because the ionic liquid is sandwiched in the layers of MMT clay in catalyst **6**. In each case, the specimens were heated from 50 to 750 °C at the rate of 10 °C/min under nitrogen flow.

2.4. Methods and materials

¹H NMR was recorded in CDCl₃ on a 400 MHz Bruker instrument using TMS as the internal standard. IR spectra were recorded on a Bio-Rad-Win-IR spectrometer. Na⁺-montmorillonite clay (Na⁺-MMT) with cation exchange capacity of 120 meq/100 g clay, was provided by Kunimine Co. Ltd., Japan. XRD analysis was done using Rigaku D-Max IIIC using Ni-filtered Cu-Kα radiation. BET surface area and pore volume were determined using micromeritics autosorb automated gas sorption system. TGA analysis was carried out using TGA Mettler Toledo system. AAS was determined by GBC Avanta instrument. Elemental analysis was carried out using Analytischer Funktionstest vario EL II. GC-MS had been recorded on a Fisons “GC 8000” with inte-

grated MS “MD 800” [TMBA] NTF₂ [(trimethylbutylammonium bis(trifluoromethylsulfonyl)imide)] was prepared by quaternization of trimethylamine with butyl chloride followed by anion exchange with LiNTf₂ [32].

2.5. Typical experimental procedure for Mizoroki–Heck reaction with catalysts **5** and **6**

Catalyst **5** (0.1 mg, 0.005 mol% Pd)/catalyst **6** (0.2 mg, 0.005 mol% Pd) was dissolved in [TMBA] NTF₂ (0.5 ml) taken in a 25 ml round bottom flask. To this were added iodobenzene (816 mg, 4.0 mmol), *t*-butyl acrylate (512 mg, 4.0 mmol), triethylamine (606 mg, 6.0 mmol). The mixture was magnetically stirred in a pre-heated oil bath at 80 °C for 3 h. The solution was allowed to cool, extracted with diethyl ether (5 × 5 ml) and the ethereal phase was concentrated, purified by column chromatography and analyzed by GC-MS and ¹H NMR. The catalyst was recycled seven times with negligible loss of activity.

2.5.1. (*E*)-*tert*-Butyl-cinnamate

¹H NMR (400 MHz, CDCl₃): δ ppm: 7.56–7.60 (d, 1H, *J* = 15.9 Hz), 7.49–7.52 (m, 2H), 7.36–7.38 (m, 3H), 6.35–6.39 (d, 1H, *J* = 15.9 Hz), 1.55 (s, 9H).

2.6. Typical experimental procedure for Sonogashira reaction with catalyst **5** and **6**

Catalyst **5** (0.1 mg, 0.047 mol% Pd)/catalyst **6** (0.2 mg, 0.047 mol% Pd) was dissolved in [TMBA] NTF₂ (0.5 ml) taken in a 10 ml round bottom flask and 4-iodoacetophenone (123 mg, 0.5 mmol), 3-ethynylbenzene (58 mg, 0.5 mmol), triethylamine (75 mg, 0.742 mmol) were added. The mixture was magnetically stirred in a pre-heated oil bath at 80 °C for 12 h. The solution was allowed to cool, extracted with diethyl ether (5 × 5 ml) and the ethereal phase was dried over Na₂SO₄, filtered, concentrated and purified by chromatography using hexane-ethyl acetate (8:2) to elute the desired coupling product which was analyzed by GC-MS and ¹H NMR. The catalyst was recycled seven times without any loss of activity.

2.6.1. 1,2-Diphenyl ethyne

¹H NMR (400 MHz, CDCl₃): δ ppm: 7.48–7.42 (m, 4H), 7.34–7.27 (m, 6H).

2.7. Leaching tests

Leaching of catalytically active species was tested by allowing the reaction to proceed to less than 50% conversion. The product

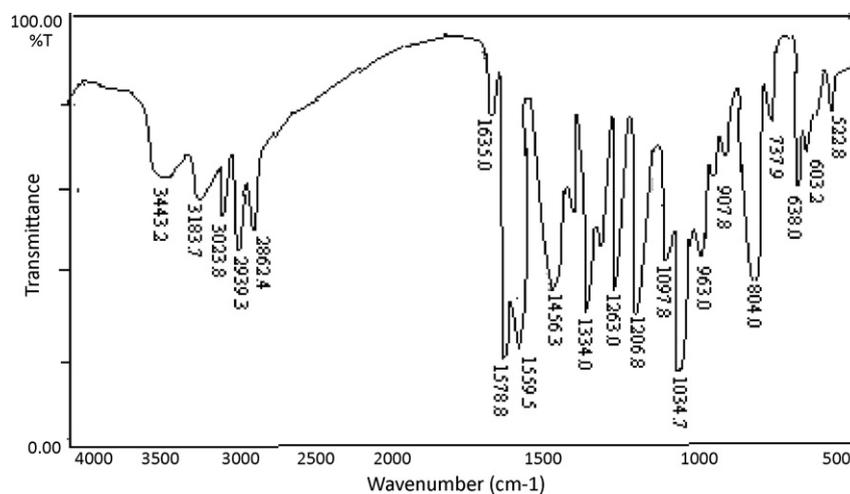


Fig. 3. IR spectrum of catalyst 5.

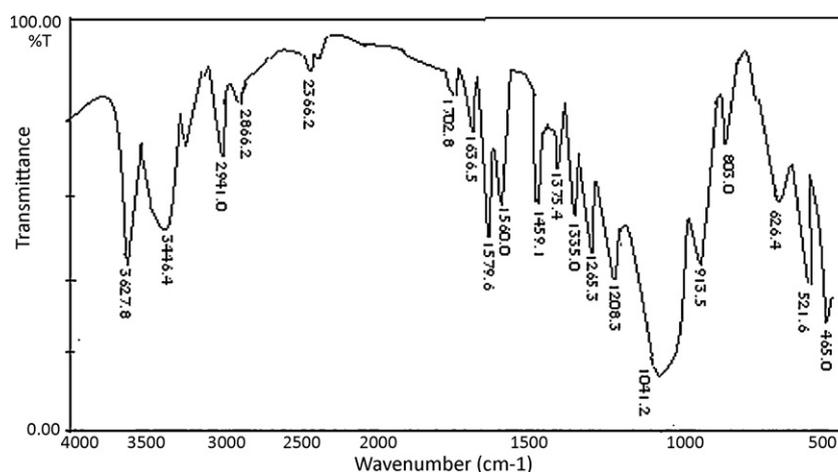


Fig. 4. IR spectrum of catalyst 6.

was extracted with diethyl ether and this extracted product was allowed to react for addition 48 h which was then analyzed by NMR spectroscopy for any further progress of reaction.

2.8. Recovery and reuse of catalyst 6

The recovery and reuse of catalyst was done on running a bigger batch using 4.0–8.0 mmol of the reactants in a typical reaction procedure and vacuum filtered while hot. The remaining solid catalyst 6 was washed with dichloromethane (30 ml per 10 mg of the solid) and was dried for 1 h under reduced pressure. The dry solid was weighed and reused in next run by adding proportional amounts of reactants.

3. Results and discussion

The synthetic route followed as shown in Scheme 1 resulted in moderate yield of the catalyst 5. The formation of palladium–carbon bond in compound 4 has been confirmed by

change in number and pattern of aromatic protons from A_2B_2 to ABM. Moreover, the shift in position of band at 1675 cm^{-1} in case of 3 assigned for C=N stretching to 1635 cm^{-1} further confirmed the formation of the palladacycle. The simplest carbapalladacycle has been reported to be a dimeric species because of the tendency of palladium to form tetra coordinated complexes. In our case also the molecular ion clusters arising from natural isotopic distribution of palladium and chlorine suggests the formation of a dimeric species as inferred from the mass spectrum. On quarternization of trimethylamine with compound 4 gave the ammonium tagged carbapalladacycle 5 wherein the presence of the ammonium tag was confirmed by NMR (δ ppm: 3.05, s, 9H; 3.95, t, 2H) and mass spectral analysis. The mass spectral analysis of 5 showed a molecular ion clusters in consistence with the presence of dimeric species which is contrary to the monomeric oxime carbapalladacycle with an ionophilic imidazolium tag as described by Corma et al. [20].

The intercalation of complex 5 into clay interlayers by ion exchange resulted in the formation of heterogeneous catalyst 6. As expected, on intercalation the d_{001} interlayer spacing showed an

Table 1
Physico-chemical characterization of Na^+ -MMT clay and clay nanocomposite 6.

| Sample | Basal spacing (Å) | Multipoint BET surface area (m^2/g) | Pore volume (cm^3/g) | Elemental analysis (AAS) |
|-------------------------|-------------------|---|--|--------------------------|
| Na^+ -MMT clay | 11.86 | 11.89 | 0.0253 | – |
| Catalyst 6 | 12.49 | 19.83 | 0.0566 | Pd: 1.178 mmol/g |

Table 2

Optimized results of Mizoroki–Heck reaction of variously substituted iodobenzenes with *t*-butyl acrylate at 80 °C using catalyst **5** and **6** in [TMBA] NTf₂.

| S.No. | Haloarene | Catalyst | Time (h) | Yield ^a (%) | TON | TOF (h ⁻¹) |
|-------|-----------------------|----------|----------|------------------------|--------|------------------------|
| 1 | Iodobenzene | 5 | 3 | 94 | 18,800 | 6,266 |
| | | 6 | 3 | 95 | 19,000 | 6,333 |
| 2 | 4-Iodoanisole | 5 | 12 | 92 | 18,400 | 1,533 |
| | | 6 | 12 | 92 | 18,400 | 1,533 |
| 3 | 4-Iodotoluene | 5 | 12 | 87 | 17,400 | 1,450 |
| | | 6 | 12 | 89 | 17,800 | 1,483 |
| 4 | 1-Iodo-3-nitrobenzene | 5 | 3 | 96 | 19,200 | 6,400 |
| | | 6 | 3 | 96 | 19,200 | 6,400 |
| 5 | 4-Iodo-acetophenone | 5 | 3 | 97 | 19,400 | 6,466 |
| | | 6 | 3 | 98 | 19,600 | 6,533 |

^a Isolated yield.

increase from 11.86 Å to 12.49 Å and the BET surface area increased from 11.89 m²/g to 19.83 m²/g as shown in Table 1. The IR spectra of catalyst **6** showed the peaks characteristic of palladacycle thus confirming the exchange of cationic catalyst **5**. The extent of exchange of **5** in clay was determined by the palladium content as determined by AAS and found to be 1.0 meq/1 g of clay. TGA analysis showed the thermal stability of **5** and **6** up to a temperature of 450 °C and 750 °C respectively.

Complex **5** in homogenous phase and **6** in homogenous–heterogeneous phase were checked for their catalytic activity in Heck and Sonogashira couplings using [TMBA] NTf₂ as solvent. The immobilization of catalyst **5** and **6** in [TMBA] NTf₂ ionic liquid was confirmed by repeated extraction using diethyl ether with negligible presence of both the catalysts in the ethereal phase.

Mizoroki–Heck and Sonogashira reaction, as shown in Schemes 2 and 3, were carried out under optimized conditions in ionic liquid media resulting in excellent yield and conversion with high TON and TOF of the desired products as confirmed by NMR and GC–MS analysis. The optimization of reaction conditions was done by varying the reaction temperature and catalyst loading. The reaction proceeds at micromolar concentration of palladium at lower temperature of 80 °C. Significantly, the Sonogashira reaction gave good results without the use of copper (I) salts as co-catalyst as compared to previous reports [33]. Alonso et al. carried out Sonogashira reaction catalyzed by untagged oxime carbapalladacycle using 0.1–0.5 mol% of catalyst at a higher temperature of 110 °C with no recyclability reports of catalyst [34]. Contrary to this, the ammonium tagged carbapalladacycle **5** and **6** are recyclable and required in a comparatively smaller amount of 0.047 mol% giving good conversions at 80 °C. GC–MS analysis indicated the absence of Glaser type homocoupling products. Further both reactions were studied on various substrates containing electron releasing and electron withdrawing groups to examine the versatility of the catalyst **5** and **6**. The results are summarized in Tables 2 and 3. The analysis of the results in Tables 2 and 3 showed that the coupling of deactivated electron-rich haloarenes took longer hours while the reactions with activated electron poor iodoarenes were accomplished in lesser time duration. High yields and excellent TONs and TOFs were achieved in all the cases.

For recycling studies, the typical reactions as discussed in Sections 2.5 and 2.6, were carried out under optimized conditions. After every cycle the catalytic system remains as a clear solution though there is an increase in viscosity due to the formation of a quaternary ammonium salt by reaction of triethylamine and the haloarene. Negligible loss of activity of catalysts **5** and **6** was noticed even after seven cycles for both Mizoroki–Heck and Sonogashira reaction. The results for the recycling studies are as shown in Figs. 5 and 6. No precipitation of palladium black was observed

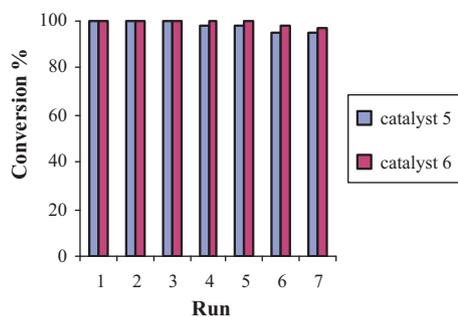


Fig. 5. Recycling studies for Mizoroki–Heck reaction of iodobenzene and *t*-butyl acrylate.

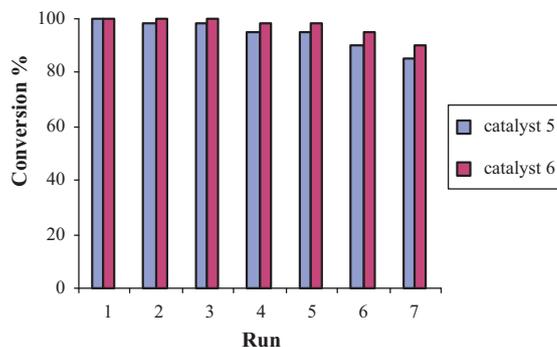


Fig. 6. Recycling studies for Sonogashira reaction of 4-iodoacetophenone and 3-ethynylbenzene.

in both reactions indicating the stability of the catalyst **5** in ionic liquid media and catalyst **6** due to immobilization in the interlayers of clays and in ionic liquid media. Recoverability of the heterogeneous catalytic system **6** has been measured by the “Quantitative” catalyst recovered after each cycle.

Kinetics of both the reactions was also studied using catalyst **5** and **6** under optimized conditions. The results are as shown in Figs. 7 and 8.

The hot filtration test performed to ensure that the activity is actually because of the heterogenized palladacycle or due to the soluble palladium leached out from the supported catalyst suggested that there is negligible leaching of catalytically active species which indicates a heterogeneous catalysis operational in case of catalyst **6** as the filtered solution did not exhibit any further reactivity.

Good results were obtained for Sonogashira at room temperature also though longer reaction time of 24 h is required for complete conversion. Typical Mizoroki–Heck and Sonogashira

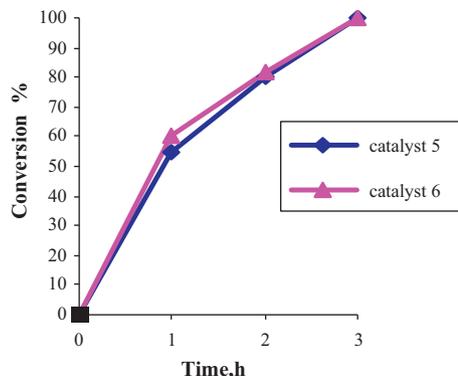
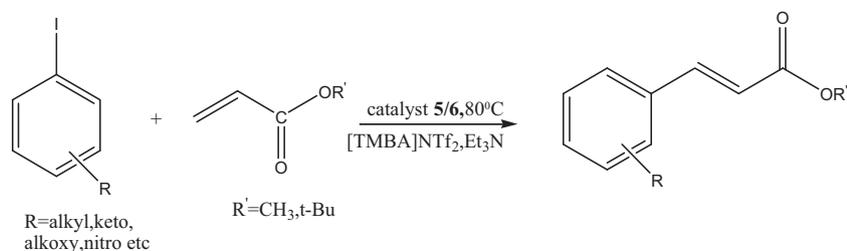
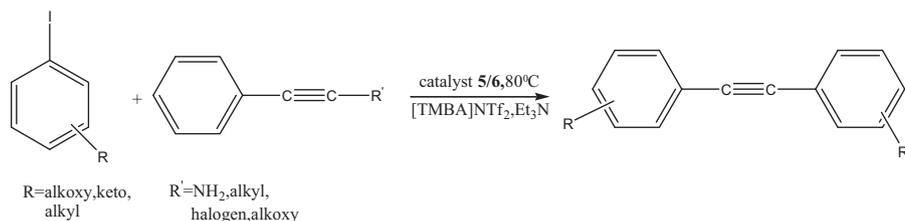


Fig. 7. Kinetic curves of Mizoroki–Heck reaction of iodobenzene and *t*-butyl acrylate.



Scheme 2. Mizoroki–Heck reaction using catalysts **5** and **6**.



Scheme 3. Sonogashira reaction using catalysts **5** and **6**.

Table 3
Optimized results for Sonogashira of various haloarenes with aryl acetylenes at 80 °C using catalyst **5** and **6** in [TMBA] NTf₂.

| S.No. | Haloarene | Substituted acetylenes | Catalyst | Time (h) | Yield ^a (%) | TON | TOF (h ⁻¹) |
|-------|------------------------|---------------------------|----------|----------|------------------------|------|------------------------|
| 1 | Iodobenzene | 1-Phenylacetylene | 5 | 12 | 90 | 1914 | 159 |
| | | | 6 | 12 | 92 | 1957 | 163 |
| 2 | Iodobenzene | 3-Ethynylaniline | 5 | 12 | 94 | 2000 | 166 |
| | | | 6 | 12 | 95 | 2021 | 168 |
| 3 | 4-Iodo-acetophenone | 1-Phenylacetylene | 5 | 12 | 94 | 2000 | 166 |
| | | | 6 | 12 | 94 | 2000 | 166 |
| 4 | 4-Iodo-acetophenone | 3-Ethynylaniline | 5 | 12 | 96 | 2042 | 170 |
| | | | 6 | 12 | 97 | 2063 | 171 |
| 5 | 4-Iodotoluene | 3-Ethynylaniline | 5 | 15 | 88 | 1872 | 124 |
| | | | 6 | 15 | 90 | 1914 | 127 |
| 6 | 4-Iodoanisole | 3-Ethynylaniline | 5 | 15 | 90 | 1914 | 127 |
| | | | 6 | 15 | 90 | 1914 | 127 |
| 7 | 1-Iodo-3-nitrobenzene | 3-Ethynylaniline | 5 | 12 | 97 | 2063 | 171 |
| | | | 6 | 12 | 99 | 2106 | 175 |
| 8 | 1-Iodo-3-nitrobenzene | 3-Chloro-1-ethynylbenzene | 5 | 12 | 90 | 1914 | 159 |
| | | | 6 | 12 | 93 | 1978 | 164 |
| 9 | 1-Bromo-4-nitrobenzene | 3-Ethynylaniline | 5 | 24 | 80 | 1702 | 70 |
| | | | 6 | 24 | 82 | 1744 | 72 |

^a Isolated yield.

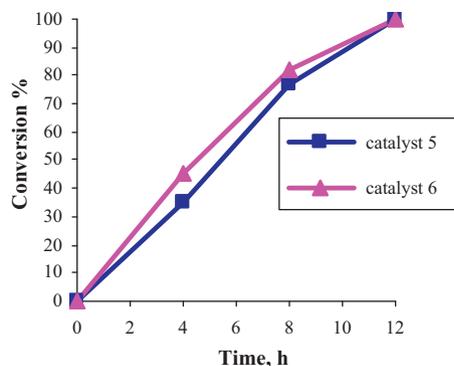


Fig. 8. Kinetic curves of Sonogashira reaction of 4-iodoacetophenone and 3-ethynylbenzene.

reaction were also carried in toluene and water as reaction media which gave products in satisfactory yield, however, there were problems related to recoverability and formation of palladium black in toluene.

4. Conclusion

In summary, catalyst **5** with enhanced ionophilicity has been synthesized by anchoring it to a catalytically inert ammonium tag which assists in improving the solubility of carbapalladacycle in ionic liquid media and reduces the palladium leaching. The ammonium tag facilitates the heterogenisation of catalyst **5** into the layers of montmorillonite clay resulting in the formation of an organic-inorganic hybrid catalyst **6**. Micromolar concentrations of recyclable **5** and recyclable and recoverable catalyst **6** efficiently promote the Mizoroki–Heck and Sonogashira couplings both in

homogeneous as well as heterogeneous forms. In particular, Sonogashira reaction was performed under copper free condition with no cross coupling side products.

Acknowledgements

The authors (RR and SK) are thankful to IFCPAR (3405-2), New Delhi for fellowship and financial support, RIL (R&D), Vadodara and RSIC, Chandigarh for the analytical data.

References

- [1] J.A. Gladysz, *Pure Appl. Chem.* 73 (2001) 1319–1324.
- [2] C.E. Song, S.G. Lee, *Chem. Rev.* 102 (2002) 3495–3524.
- [3] T.J. Dickerson, N.N. Reed, K.D. Janda, *Chem. Rev.* 102 (2002) 3325–3344.
- [4] C. Wiles, P. Watts, *Eur. J. Org. Chem.* (2008) 1655–1671.
- [5] G.J. Hutchings, *J. Mater. Chem.* 19 (2009) 1222–1235.
- [6] A. Corma, H. Garcia, *Top. Catal.* 48 (2008) 8–31.
- [7] V. Polshettiwar, A. Molnar, *Tetrahedron* 63 (2007) 6949–6976.
- [8] A.P. Wight, M.E. Davis, *Chem. Rev.* 102 (2002) 3589–3614.
- [9] B. Desai, C.O. Kappe, *Top. Curr. Chem.* 241 (2004) 177–208.
- [10] X. Chen, K.M. Engle, D-Hui Wang, J-Quan Yu, *Angew. Chemie. Int. Ed.* 48 (2009) 5094–5115.
- [11] J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, 2004.
- [12] J. Dupont, C.S. Consorti, J. Spencer, *Chem. Rev.* 105 (2005) 2527–2572.
- [13] E. Alacid, D.A. Alonso, L. Botella, C. Najera, M.C. Pacheco, *Chem. Rec.* 6 (2006) 117–132.
- [14] E. Alacid, C. Nájera, *J. Org. Chem.* 73 (2008) 2315–2322.
- [15] E. Alacid, C. Nájera, *Eur. J. Org. Chem.* (2008) 3102–3106.
- [16] C. Baleizao, A. Corma, H. Garcia, A. Leyva, *Chem. Commun.* (2003) 606–607.
- [17] F.T. Luo, C. Xue, S.L. Ko, Y.D. Shao, C.J. Wu, Y.M. Kuo, *Tetrahedron* 61 (2005) 6040–6045.
- [18] C. Baleizao, A. Corma, H. Garcia, A. Leyva, *J. Org. Chem.* 69 (2004) 439–446.
- [19] A. Corma, D. Das, H. Garcia, A. Leyva, *J. Catal.* 229 (2005) 322–331.
- [20] A. Corma, H. Garcia, A. Leyva, *Tetrahedron* 60 (2004) 8553–8560.
- [21] E. Alacid, C. Najera, *J. Organomet. Chem.* 694 (2009) 1658–1665.
- [22] N. Audic, H. Clavier, M. Maudit, J.C. Guillemin, *J. Am. Chem. Soc.* 125 (2003) 9248–9249.
- [23] R. Šebesta, I. Kmentova, S. Toma, *Green Chem.* 10 (2008) 484–496.
- [24] R.S. Varma, *Tetrahedron* 58 (2002) 1235–1255.
- [25] R.A. Schoonheydt, *Clay Clay Miner.* 50 (2002) 411–420.
- [26] N.H. Kim, S.V. Malhotra, M. Xanthos, *Micropor. Mesopor. Mat.* 96 (2006) 29–35.
- [27] M.R. Castillo, L. Fousse, J.M. Fraile, J.I. García, J.A. Mayoral, *Chem. Eur. J.* 13 (2007) 287–291.
- [28] R. Tao, S. Miao, Z. Liu, Y. Xie, B. Han, G. An, K. Ding, *Green Chem.* 11 (2009) 96–101.
- [29] V. Singh, V. Sapehiya, G.L. Kad, *J. Mol. Catal. A: Chem.* 210 (2004) 119–124.
- [30] V. Singh, S. Kaur, V. Sapehiya, J. Singh, G.L. Kad, *Catal. Commun.* 6 (2005) 57–60.
- [31] R. Ratti, S. Kaur, M. Vaultier, V. Singh, *Catal. Commun.* 11 (2010) 503–507.
- [32] C. Tiyapiboonchaiya, D.R. Mac Farlane, D.R. Sung, M. Foreyth, *Macromol. Chem. Phys.* 203 (2002) 1906–1911.
- [33] E.M. Marza, A.M. Segarra, C. Claver, E. Peris, E. Fernandez, *Tetrahedron Lett.* 44 (2003) 6595–6599.
- [34] D.A. Alonso, C. Najera, M.C. Pacheco, *Adv. Synth. Catal.* 345 (2003) 1146–1158.