Applied Catalysis A: General 470 (2014) 232–238

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Clay encapsulated $Cu(OH)_x$ promoted homocoupling of arylboronic acids: An efficient and eco-friendly protocol

Bashir Ahmad Dar [a], Snehil Singh [a], Nalini Pandey [a], A.P. Singh [b], Priti Sharma [b], Anish Lazar [b], Meena Sharma [c], Ram A. Vishwakarma [a,*], Baldev Singh [a,*]

[a] Indian Institute of Integrative Medicine (CSIR), Canal Road, Jammu 180001, India
[b] Catalysis division, National Chemical Laboratory, Pune, MH 411008, India
[c] Department of Chemistry, University of Jammu, Jammu, JK 180004, India

ARTICLE INFO

Article history:
Received 13 July 2013
Received in revised form 24 October 2013
Accepted 26 October 2013
Available online 8 November 2013

Keywords:
Biaryls
Homocoupling
Heterogenous catalyst
Copper
Clay

ABSTRACT

$Cu(OH)_x$ has been encapsulated over montmorillonite-KSF by simple ologomeric deposition strategy. The resulting catalyst has been employed for selective homocoupling of arylboronic acids under ambient conditions without requirement of any ligand or base. This catalyst is easy to recover and shows excellent reusability without losing its activity. Techniques like XRD, SEM, TPR, IR, BET surface area measurement and XPS were used to characterize the catalyst. The present method promises for the simple and clean homocoupling of arylboronic acids.

1. Introduction

The immense scientific and commercial value of symmetrical biaryl motiffs is illustrated by their prevalence as building blocks in natural products, functional molecules, polymers and ligands for catalysts etc. [1]. The structural simplicity of these biaryl compounds contradicts their preparative complexity. Thus search for efficient and convergent syntheses has captivated the attention of synthetic chemists for many decades. Oxidative homocoupling of arylboronic acids has revolutionized our aptitude to generate symmetrical biaryls in a straightforward manner because of their ready availability, nontoxic nature & bench stability. Different catalyst systems like $Ag_2O + CrCl_2$ [2], $PdCl_2$ [3], $Pd(OAc)_2$ [4], $RhCl(PPh_3)_3$ [5], CuCl [6], $Pd(OAc)_2$,/$AgNO_3$ [7], $Pd(PPh_3)_2Cl_2$ [8], $Cu(OAc)_2$ [9], $\{(1,10\text{-phenanthroline})Cu(\mu\text{-}OH)\}2Cl_2]\cdot 3H_2O$ [10], AuCl [11] etc. have been reported to catalyze the homocoupling of aryl boronic acids. Although, excellent yields are obtained from these known catalytic systems, several disadvantages like longer reaction times, high temperature, use of homogeneous transition metal catalyst systems, stoichiometric amounts of ligand/base, could not be avoided in these approaches [12]. Moreover metal contamination, loss of expensive metals due to difficult recovery of homogeneous metal catalysts, chances of undesired product formation due to requirement of ligands and additional reagents for homogeneous catalysts demands for the development of more efficient, economic and environmentally acceptable process.

In continuation to our research work for the development of green chemical protocols, [13–15] we herein report clay encapsulated $Cu(OH)_x$ as heterogeneous catalytic system for oxidative homocoupling of arylboronic acids at room temperature and under atmospheric condition without using base, ligands or any other additives.

Clays are aluminosilicates possessing lamellar structure with interlayer spacing ranging from 10 to 100 Å, thus enabling the intercalation of various ions or neutral species, thus can act as supports for a large variety of reagents. They can be considered as microreactors because of possessing the ability to concentrate high quantities of reactive species between the aluminosilicate layers [13–16]. Clays and clay supported catalysts have many advantages, such as easy handling, easy separation, recycling, environmentally safe disposal, inexpensiveness, improved efficiency due to stable active site and better steric control of a reaction intermediate. Encapsulation of $Cu(OH)_x$ species inside the clay interlayer preserves them in nanosize and restrains their tendency to undergo agglomeration, which otherwise increases the particle size, hence reduces the catalytic activity [17]. Comparatively high stability of a catalyst on solid support sometimes allows the reaction to be less sensitive to

---

* Corresponding author. Tel.: +191 2572002; fax: +191 2548607.
E-mail addresses: ram@iiim.ac.in (R.A. Vishwakarma), drbaldev1@gmail.com (B. Singh).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.10.048

normal ambient conditions. Therefore, clay supported catalyst as a substitute of homogeneous catalyst or an expensive heterogeneous catalyst seems highly desirable [18].

2. Experimental

2.1. Preparation of the catalyst

Clay encapsulated $Cu(OH)_x$ was prepared by suspending montmorillonite-KSF (10 g) with cation exchange capacity of 120 meq/100 g clay in 200 ml distilled water and the suspension was vigorously stirred at 80 °C for 2 h. Copper oligomer (base hydrolysed cupric chloride with OH/Cu molar ratio of 2.0) was added drop wise to acquire the required wt% loading of copper and the resulting slurry was stirred at 90 °C for 8 h. Heating causes expansion of clay interlayer and makes the intercalation of Cu-oligomer easy. The solid products were filtered, washed several times with distilled water, dried first at room temperature and then at 110 °C for 12 h. To study the effect of calcination on the rate of reaction the catalyst was calcined at different temperatures ranging from 200 to 425 °C. The catalyst was characterised by powder X-ray diffraction using a D-8 ADVANCE (Bruker AXS, Germany) X-ray diffractometer using Ni filter with Cu $K\alpha$ radiation Hitachi (H-7500) in the 2θ range 5°–70° in step scan mode (Step size: 0.02°, Scan speed: 2 s/step). The phases were identified by search match procedure with the help of DIFFRACPLUS software using JCPDS databank. Temperature programmed reduction (TPR) and BET surface area were determined by CHEMBET-3000 TPR/TPD/TPO instrument. SEM of the catalyst was carried out using JEOL.JEM100CXII ELECTRON MICROSCOPE with ASID Accelerating Voltage 40.0 kV. IR spectra were recorded on Perkin-Elmer IR spectrophotometer. The specific surface areas (m^2/g) of the catalyst was estimated with the N_2 adsorption and desorption determined at −196 °C by means of an automated CHEMBET-3000 adsorption apparatus. XPS analysis was performed on a KRATOS-AXIS 165 instrument.

2.2. General experimental procedure for oxidative homocoupling of arylboronic acid

To a solution of arylboronic acid (1 mmol) in methanol (0.5 ml), clay encapsulated $Cu(OH)_x$ (6 mg) was added and this heterogeneous mixture was vigorously stirred at ambient temperature for 30–120 min. After completion of reaction (monitored by TLC), the reaction mixture was filtered to separate the catalyst. Solvent of the filtrate was removed under reduced pressure and then worked up in hexane:water (1:1) system. The aqueous phase was isolated and back extracted with Hexane. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to afford the desired product. The prepared products were characterized NMR and mass spectral analysis. The spectral data and physical properties thus obtained were compared with data reported in literature [references herein]. NMR spectra were recorded on Brucker-Advance DPX FT-NMR 400 MHz instrument. ESI–MS and HRMS spectra were recorded on Agilent 1100 LC and HRMS-6540-UHD machines. Melting points were recorded on digital melting point apparatus. IR spectra were recorded on Perkin-Elmer IR spectrophotometer.

3. Results and discussion

3.1. Characterization of the catalyst

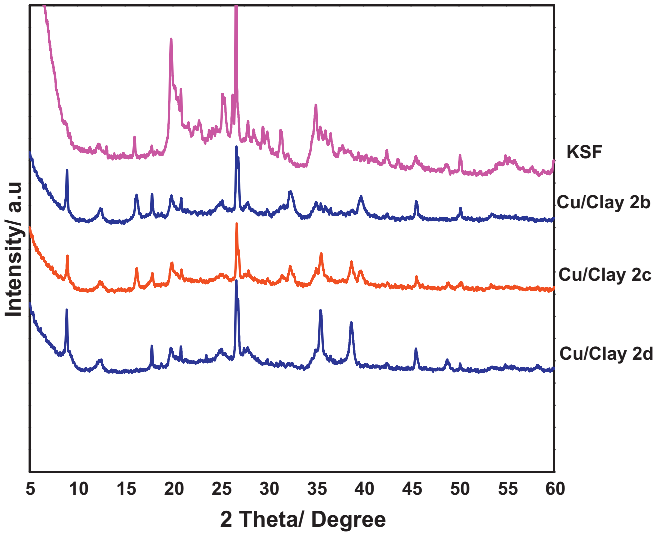


Fig. 1. XRD spectra of (a) Montmorillontie-KSF (b) Cu/clay-2b; (c) Cu/clay-2c; (d) Cu/clay-2d.

The XRD spectra of KSF (montmorillonite-KSF), Cu/clay-2b, Cu/clay-2c and Cu/clay-2d is shown in Fig. 1. Peaks at $2\theta = 21°$, 26.7°, 50.3° and 60° are due to reflection of the quartz [SiO_2] impurities [19–21] and at 12.5°, 19.9° and 27.9° are due to palygorskite [22–24]. Peaks for montmorillonite appear at $2\theta = 8.9°$ (d 0 0 1 reflection), 19.8°, 32.2°, and 62° [25,26]. Presence of kaolinite is implied t° small peaks at 38.8°, and 42.5° [25,26]. The copper loaded on montmorillonite-KSF does not show any characteristic peak of CuO, Cu_2O and metallic Cu but peaks with very low intensity corresponding to mineral atacamite ($Cu_2Cl(OH)_3$) and $Cu(OH)_2$ are observed at $2\theta = 16.1$, 18°, 25.1°, 32.3° and 50.3° [27–29]. Thus, it can be concluded from XRD analysis that copper hydroxide species are deposited with very low crystallinity.

The N_2 adsorption–desorption isotherm and pore size distribution of $Cu(OH)_x$-clay calcined at 250 °C (Cu/clay-2b) are shown in Fig. 2. The sample displayed type-IV isotherms with H1 hysteresis related to capillary condensation steps. Textural properties such as BET surface area, pore volume (BJH) and the pore radius (BJH) of $Cu(OH)_x$-clay(Cu/clay-2b) are summarized in Table 1. The

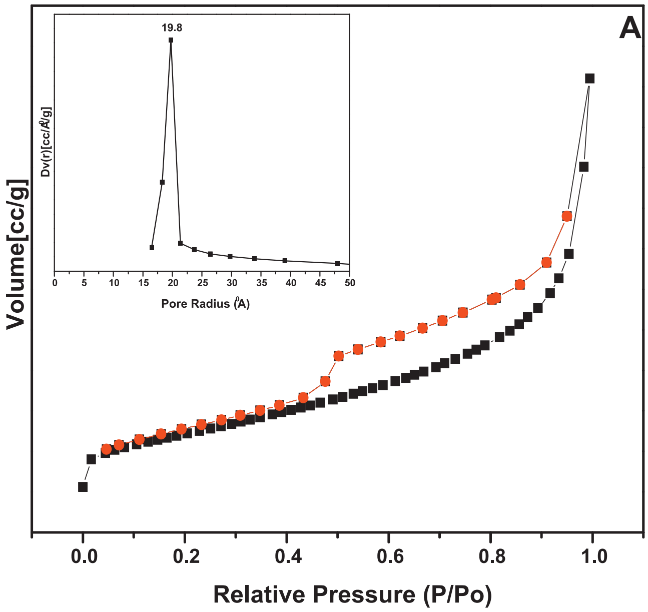
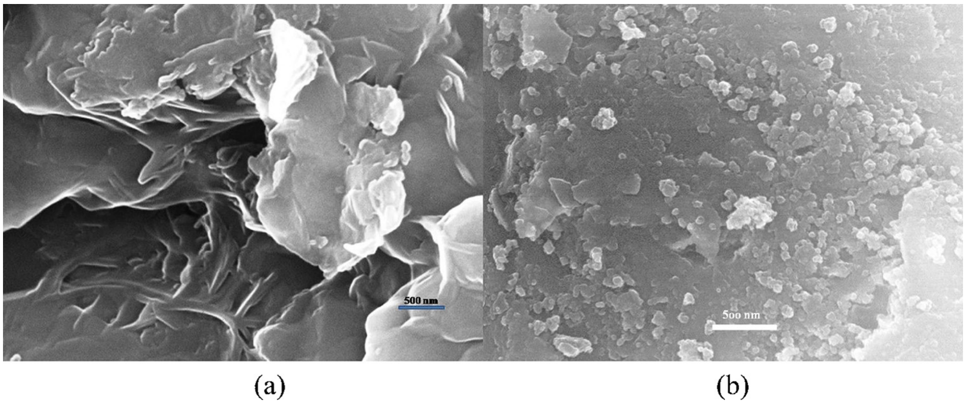


Fig. 2. N_2 adsorption–desorption isotherm and pore size distribution curve (inset) of Cu/clay-2b



(a) (b)

Fig. 3. SEM images of (a) Montmorillonite-KSF (b) Cu/clay-2b.

Table 1
Textural properties of Cu/KSF.

Entry	Sample	Surface area [m^2/g]	Pore volume [cm^3/g]	Pore radius [Å]
1	Cu/KSF	54.42	0.156	19.75

$Cu(OH)_x$-clay shows BET surface area, 54.42 m^2/g; pore volume, 0.156 cm^3/g; and pore radius, 19.75 Å. The increased sharpness in the N_2 condensation step points to the uniformity of the mesopore structure. The SEM images of (A) KSF and (B) the $Cu(OH)_x$-clay(Cu/clay-2b) catalyst are depicted in Fig. 3 and showed the presence of coarse surface (thus elevated surface area). Thus, the $Cu(OH)_x$-clay catalyst is able to adsorb substrate and/or reagent to a great extent.

To understand the reduction behavior and thermal stability of the active metal species, temperature programmed (TPR) was done. The reduction profile provides information about the dispersion of the metal species on the support and interaction of these metal species with the support. The H_2-TPR spectra of (a) KSF (b) Cu/clay-2b are depicted in Fig. 4. The Montmorillonite-KSF support (Fig. 4a) showed a broad peak at a higher reduction temperature, 524 °C, which can probably be attributed to the reduction of some iron species in the montmorillonite-KSF material [30,31]. The first peak in Fig. 4d, centered at 255 °C, was assigned to the reduction of Cu^{2+} nanoparticles located on the surface probably at the entrance of pores of the Montmorillonite-KSF. Moreover, the reduction peaks, centered at 300 °C and 318 °C, were assigned to the reduction of clay intercalated Cu^{2+} species to Cu^+ and CuO cluster to Cu^0, respectively. Further, the reduction peak, centered at 440 °C is very less pronounced, was assigned to the reduction of Cu^+ to Cu^0 [31,32]. The results indicate that the Cu^{2+} ions are mostly encapsulated in the interlamellar space of Montmorillonite-KSF.

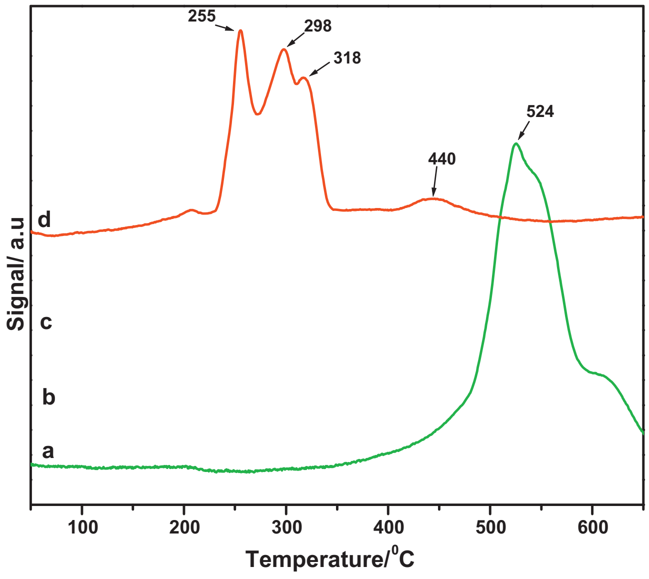


Fig. 4. H_2-TPR spectra of (a) Montmorillonite-KSF (b) Cu/clay-2b.

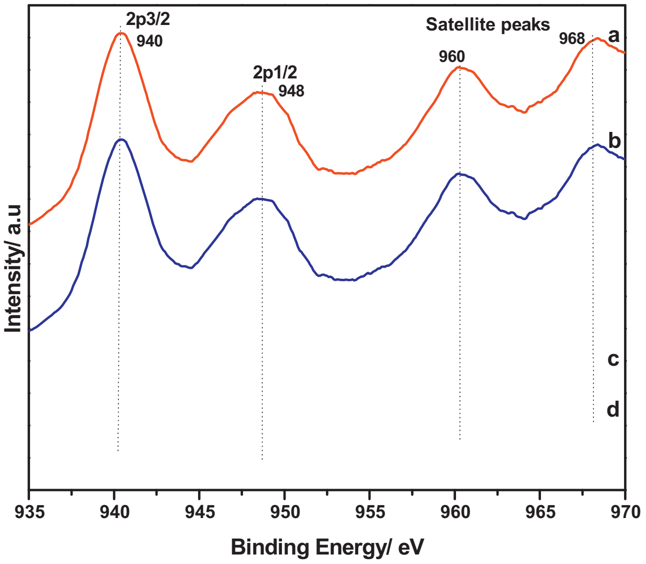


Fig. 5. XPS spectra of (a) Cu/clay-2b (b) Cu/clay-2b after 10th cycle of reaction.

XPS is a surface technique which provides valuable information about the oxidation state and chemical environment of atoms due to the shift in binding energies. The XPS spectra of (a) fresh (Cu/clay-2b) (b) Cu/clay-2b after 10th cycle of reaction are represented in Fig. 5. Two main peaks having binding energies of about 940 eV due to Cu $2p_{3/2}$ and 948 eV due to Cu $2p_{1/2}$ and four satellite peaks around 960 and 968 eV are shown in XPS spectra with a variety of intensities, which are corresponding to Cu (II) species [33].

3.2. *Homocoupling of arylboronic acids*

Previously we studied the copper catalyzed reactions of arylboronic acids and during these studies it was observed that homo-coupling of arylboronic acids occur exclusively [34]. At the onset of this methodology phenylboronic acid was chosen as model substrate to optimize the reaction conditions and all the reactions were conducted at room temperature. Cu-clay catalysts with

Table 2
Effect of various catalytic conditions for homocoupling of arylboronic acids[a].

Entry	Catalyst	Metal loading (wt%)[b]	Amount of catalyst (mg)	Time	Yield (%)[c]
1	Cu/clay-1	10	20	6 h	32
2	Cu/clay-2d	15	20	6 h	48
3	Cu/clay-3	20	20	6 h	47
4	Cu/clay-2a	15	20	10 min	69[d]
5	Cu/clay-2a1	15	20	20 min	87[d]
6	Cu/clay-2b	15	20	20 min	98
7	Cu/clay-2b	15	15	20 min	98
8	Cu/clay-2b	15	10	20 min	98
9	Cu/clay-2b	15	5	20 min	96
10	Cu/clay-2b	15	6	20 min	98
11	Cu/clay-2c	15	15	100 min	51
12	CuO	–	15	6 h	31
13	Cu_2O	–	15	6 h	27
14	$Cu(OH)_2$	–	15	45 min	62[d]
15	$CuSO_4{\cdot}5H_2O$	–	15	45 min	Traces
16	$Cu(NO_3)_2{\cdot}3H_2O$	–	15	45 min	41
17	$Cu(Ac)_2{\cdot}H_2O$	–	15	45 min	34
18	CuCl	–	15	45 min	56
19	$CuCl_2{\cdot}2H_2O$	–	15	45 min	Traces
20	CuI	–	15	45 min	12
21	CuCN	–	15	45 min	7
22	Ni/clay	–	15	3 h	Traces
23	Cu-Ni/clay[e]	–	15	3 h	19

[a] Reaction conditions: phenylboronic acid (1 mmol), Methanol (0.5 ml), Reaction temperature: r.t, air.
[b] Calculated metal loading.
[c] Isolated yield.
[d] conversion > 99%, mixture of ipso-hydroxylation and homocoupling products.
[e] catalyst contains Cu = 8 wt% and Cu = 2 wt% and is calcined at 425 °C.

different copper loadings and each calcined at 425 °C for 3 h were screened to get optimum metal loading. Cu loading was found to have significant effect on the reaction efficiency and 15 wt% of copper on montmorillonite-KSF (Cu/clay-2d) was found to be the optimum loading (Table 2, entry 2). Decreasing the metal loading to 10 wt% (Cu/clay-1) decreases the reaction rate (Table 2, entry 1), whereas no improvement in the conversion or yield was perceived upon increasing the copper loading to 20 wt% (Cu/clay-3) (Table 2, entry 3). Thus a fresh lot of Cu/clay catalysts with 15 wt% copper loading on montmorillonite-KSF was prepared and calcined at different temperatures to study the effect of calcinations temperature on the activity of the catalyst. We observed that the uncalcined form of the catalyst (Cu/clay-2a) provides excellent conversion but with decreased selectivity and ipso-hydroxylation occurs as a significant side reaction. Moreover bulk leaching of copper and massive loss of catalytic activity renders this catalyst as non-heterogeneous (Table 2, entry 4). The catalyst calcined at 200 °C (Cu/clay-2a1) was found to furnish the desired product with increased selectivity and the copper leaching in this catalyst was stopped to a great extent (Table 2, entry 5). Using the catalyst calcined at 300 °C (Cu/clay-2c) the leaching of copper metal from the catalyst was almost completely stopped, but the activity of the catalyst was dropped to a great extent (Table 2, entry 11). The catalyst calcined at 250 °C (Cu/clay-2b) exhibits excellent catalytic activity without copper leaching (Table 2, entry 6) and copper species like $Cu(OH)_2$ and $Cu_2Cl(OH)_3$ are reported to remain stable at this temperature [35]. Optimization of the catalyst amount revealed that 6 mg is sufficient to catalyze model reaction expeditiously (Table 2, entry 10). When Cu/clay-2b was replaced by commercially available CuO (Table 2, entry 12), and Cu_2O (Table 2, entry 13) for the model reaction under the standard conditions, it was observed that Cu/clay-2b is much more active as well as selective than these commercially available copper oxides. Various copper salts like $CuSO_4{\cdot}5H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(Ac)_2{\cdot}H_2O$, CuCl, $CuCl_2{\cdot}2H_2O$, CuI and CuCN were also compared with Cu/clay-2b for phenylboronic acid homocoupling under the optimized conditions but only $Cu(NO_3)_2{\cdot}3H_2O$ (Table 2, entry 16), CuCl (Table 2, entry 18) and $Cu(Ac)_2{\cdot}H_2O$ were found to catalyze the reaction to some extent, all other salts were very sluggish.

Table 3
Effect of solvents for ipso-hydroxylation of arylboronic acid[a].

Entry	Solvent	Time	Yield[b](%)
1	Methanol	30 min	98
2	Ethanol	100 min	41
3	Acetonitrile	3 h	Traces
4	Ethylacetate	3 h	3
5	DMF	3 h	Traces
6	THF	3 h	Traces
7	DMSO	3 h	11
8	CH_2Cl_2	3 h	8
9	$CHCl_3$	3 h	7
10	Hexane	3 h	12
11	Toluene	3 h	13
12	Water	30 min	Traces

Mixture of biphenyl, phenol and toluene and the reactant conversion = 31%.
[a] Reaction conditions: phenylboronic acid (1 mmol), Solvent (0.5 ml), Reaction temperature: r.t, air.
[b] Isolated yields after purification.

Screening of various solvents for Cu/clay-2b catalyzed homocoupling of phenylboronic acid reveal that the desired product is formed excellently (98% yield within 30 min) in methanol solvent under atmospheric conditions, but the reaction conducted in solvents like acetonitrile, dimethylformamide (DMF), THF and water failed to produce the expected product under these conditions and only traces were obtained even after for 6 h (Table 3, entries 3, 5, 6, 12). Small conversions were obtained in solvents like ethyl acetate, dimethylsulfoxide (DMSO), CH_2Cl_2, $CHCl_3$, hexane and Toluene (Table 3, entries 4, 7–11), when methanol was replaced with ethanol the product yield was decreased to a great extent and only 41% of the desired product was obtained in a reaction time of 100 min, but the major compounds formed in water was corresponding phenol (Table 3, entry 12). Using acetonitrile as solvent furnished very low conversions containing a mixture phenol, biphenyl and toluene (Table 3, entry 3).

Table 4
The homocoupling of various arylboronic acids using $Cu(OH)_x$-clay catalyst[a].

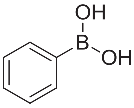
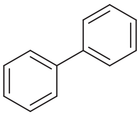
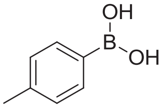
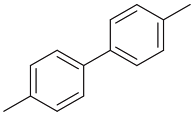
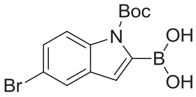
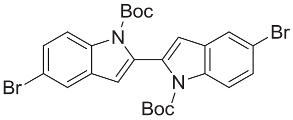
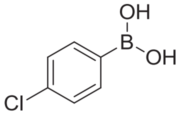
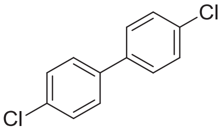
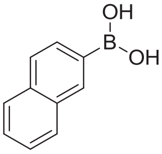
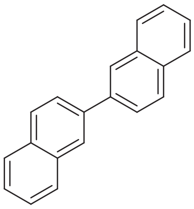
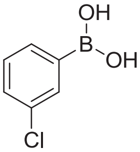
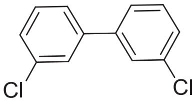
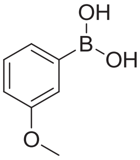
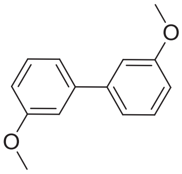
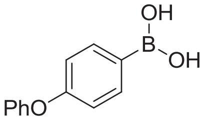
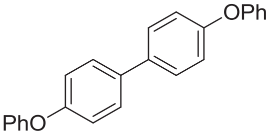
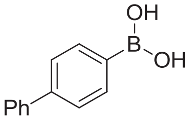
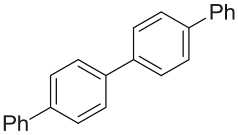
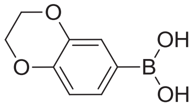
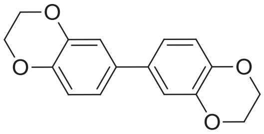
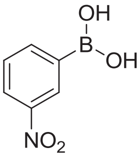
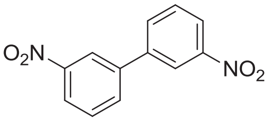
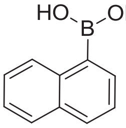
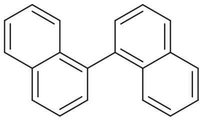
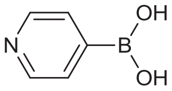
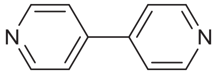
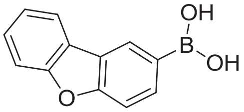
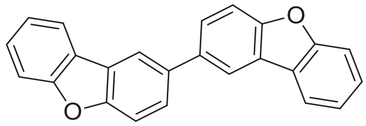
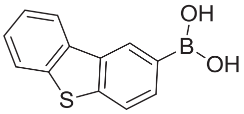
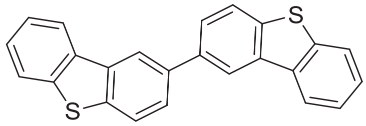
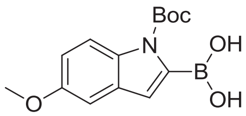
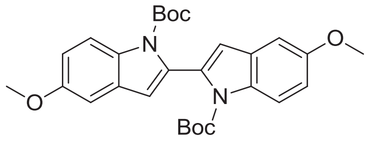
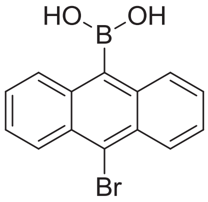
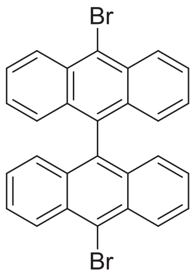
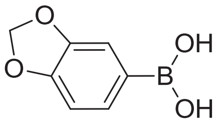
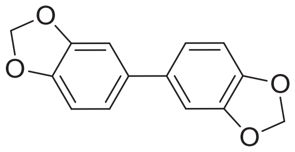
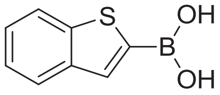
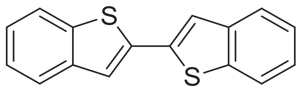
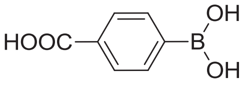
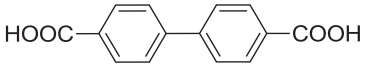
Entry	Substrate	Product	Time (min)	Yield[b] (%)
1			30	98
2			30	98
3			35	93
4			35	92
5			30	95
6			30	90
7			30	94
8			35	90
9			30	88
10			100	61
11			60	77

Table 4 (*Continued*)

Entry	Substrate	Product	Time (min)	Yield[b] (%)
12			30	96
13			40	81
14			80	92
15			100	63
16			100	77
17			60	41
18			60	67
19			60	89
20			60	Traces

[a] Reaction conditions: arylboronic acid (1 mmol), catalyst (6 mg%) solvent (0.5 ml) at room temperature, under aerobic conditions.

[b] Isolated yields.

In order to explore the generality and scope of the present protocol, homocoupling of various arylboronic acids was studied in the presence of $Cu(OH)_x$-clay catalyst. The method proved to be compatible with a wide range of substrates and the desired products were obtained in good to excellent yields (41–98%) in very short reaction times. Phenylboronic acid was converted into corresponding biphenyl in 98% yield within 30 min. (Table 4, entry 1). Electron–rich arylboronic acids were found to react slightly faster than the electron-deficient ones, thus electron-rich bipenyls can be easily generated using this heterogeneous catalytic system. Arylboronic acid derivatives bearing electron-neutral, electron-donating, and electron-withdrawing substituents, which seem difficult to remain intact under previously reported basic conditions, were successfully converted to the corresponding biphenyls and these functional groups are well tolerated. To be honest, the substrates containing –COOH groups did not show homocoupling reaction properly; instead some unknown byproducts were formed (Table 4, entry 20). The reaction was also compatible with naphthylboronic acids (Table 4, entry 12) as well as heteroarylboronic acids (Table 4, entries 3, 13–16, 19). Thus the tolerance of different functional groups to these reaction conditions illustrates the flexibility and generality of clay-encapsulated $Cu(OH)_x$ catalyst. All the compounds so prepared were stable and were characterized by NMR and MS analysis and compared with reported data.

Clay encapsulated $Cu(OH)_x$ being a solid heterogeneous catalyst could be easily recovered by simple filtration; thus the recyclability

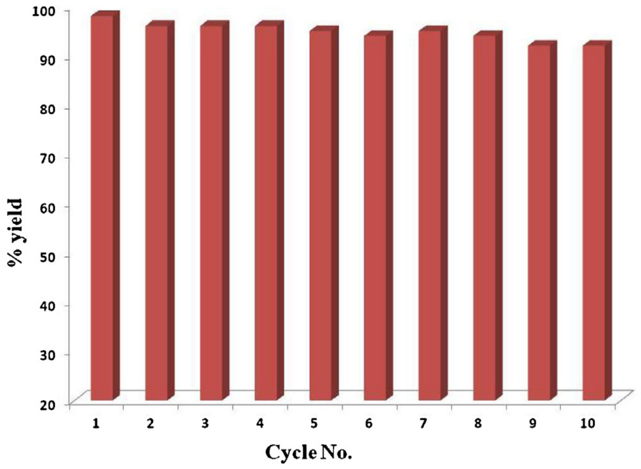
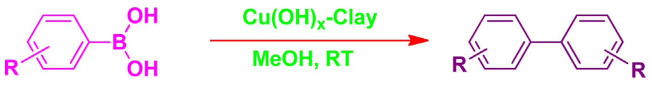


Fig. 6. Recyclability of Cu(OH)$_x$ clay catalyst in homocoupling of arylboronic acid.



Scheme 1. Homocoupling of arylboronic acids.

of the catalyst was investigated for model reaction. The catalyst was washed several times with methanol before using for every next cycle. This experiment proved that the catalyst has excellent recycling capability as no significant loss of activity was observed even after 10 consecutive cycles (Fig. 6). The ICP–AES analysis of the used catalyst after 10th consecutive cycle showed negligible loss of active metal from the catalyst (<0.2 from 14.07 wt%), which attributes to the stability of the catalysts even after recycling. To evaluate the heterogeneity of catalyst, we performed filtration test on model reaction. After 15 min (almost 50% conversion (GC) the catalyst was filtered off and the filtrate was allowed to react further, but no further reaction was observed even after 6 h (GC) suggesting that the copper catalyst remains on the support during the reaction (Scheme 1).

4. Conclusions

In conclusion, we have developed a very active, selective and stable heterogeneous and inexpensive Cu(OH)$_x$-clay catalyst for the homocoupling of arylboronic acids. The catalyst is easy to prepare and provides high yields of desired products under ligand free, base free and mild reaction conditions in very short reaction time. The catalyst is leaching-free, environmentally friendly and recyclable several times without significant loss of activity. This catalyst was found to be much more efficient than other commercially available catalysts based on copper. Overall the present protocol is fast, practical, interesting and inexpensive for arylboronic acids homocoupling. These features make this methodology economical and attractive for use in industrial preparation.

Acknowledgment

We are grateful to the Director of Indian Institute of Integrated Medicine (IIIM), Canal Road, Jammu for providing necessary facilities and good environment to carry out the research work. We are also thankful to CSIR-Delhi for the financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.10.048.

References

[1] R. Luque, B. Baruwati, R.S. Varma, Green Chem. 12 (2010) 1540–1543.
[2] J.R. Falck, S. Mohapatra, M. Bondlela, S.K. Venkataraman, Tetrahedron Lett. 43 (2002) 8149–8151.
[3] G.W. Kabalka, L. Wang, Tetrahedron Lett. 43 (2002) 3067–3068.
[4] K. Cheng, B. Xin, Y. Zhang, J. Mol. Catal. A: Chem. 273 (2007) 240–243.
[5] T. Voglera, A. Studer, Adv. Synth. Catal. 350 (2008) 1963–1967.
[6] G. Cheng, M. Luo, Eur. J. Org. Chem. (2011) 2519–2523.
[7] L.M. Klingensmith, N.E. Leadbeater, Tetrahedron Lett. 44 (2003) 765–768.
[8] S. Punna, D.D. Díaz, M.G. Finn, Synlett 13 (2004) 2351–2354.
[9] A.S. Demir, O. Reis, M. Emrullahoglu, J. Org. Chem. 68 (2003) 10130–10134.
[10] N. Kirai, Y. Yamamoto, Eur. J. Org. Chem. 12 (2009) 1864–1867.
[11] T. Matsuda, T. Asai, S. Shiose, K. Kato, Tetrahedron Lett. 52 (2011) 4779–4781.
[12] K. Wilson, J.H. Clark, Pure Appl. Chem. 72 (2000) 1313–1319.
[13] B.A. Dar, A.K. Sahu, P. Patidar, P.R. Sharma, D. Vyas, S. Maity, M. Sharma, B. Singh, J. Ind. Eng. Chem. 19 (2013) 412–417.
[14] B.A. Dar, A. Singh, A.K. Sahu, P. Patidar, A. Chakraborty, M. Sharma, B. Singh, Tetrahedron Lett. 53 (2012) 5497–5502.
[15] B.A. Dar, M. Sharma, B. Singh, Bull. Chem. Reac. Eng. Catal. 7 (2012) 79–84.
[16] A.C.P. Yip, F.L.Y. Lamb, X. Hu, Chem. Commun. (2005) 3218–3220.
[17] D. Amarajothi, V. Pitchai, T. Vairaperumal, P. Kasi, Catal. Commun. 16 (2011) 15–19.
[18] D.F. Bishop, G. Stern, M. Fleischman, L.S. Marshall, Ind. Eng. Chem. Proc. Des. Dev. 7 (1968) 110–117.
[19] K.V.R. Chary, G.V. Sagar, C.S. Srikanth, V.V. Rao, J. Phys. Chem. B 111 (2007) 543–550.
[20] R.A. Alvarez-Puebla, C. Aisa, J. Blasco, J.C. Echeverría, B. Mosquera, J. Garrido, J. Appl. Clay Sci. 25 (2004) 103–110.
[21] C. Deng, H. Hu, X. Ge, C. Han, D. Zhao, G. Shao, Ultrason. Sonochem. 18 (2011) 932–937.
[22] N. Wongpisutpaisan, P. Charoonsuk, N. Vittayakorn, W. Pecharapa, Energy Proc. 9 (2011) 404–413.
[23] J. Barrault, C. Bouchoule, K. Echachoni, N. Frini, S.M. Trabelsi, F. Bergaya, Appl. Catal., B 15 (1998) 269–274.
[24] J.D. Jeffers, R.C. Reynolds, Clays Clay Miner. 35 (1987) 473–476.
[25] M. Eloussaief, I. Jarraya, M. Benzina, Appl. Clay Sci. 46 (2009) 409–413.
[26] R.A. Alvarez-Puebla, C. Aisa, J. Blascob, J.C. Echeverria, B. Mosquer, J.J. Garrido, Appl. Clay Sci. 25 (2004) 103–110.
[27] T. Theodoros, C. Jean-FranAois, M. Enrico, J. Lubos, R. Petra, G. Dimitrios, Chem. Eur. J. 18 (2012) 9305–9311.
[28] E.N. Muhamad, R. Irmawati, A.H. Abdullah1, Y.H. Taufiq-Yap 1, S.B. Abdul Hamid, Malar. J. Anal. Sci. 11 (2007) 294–301.
[29] R. Ben Achma, A. Ghorbel, A. Dafinov, F. Medina, Appl. Catal., A 349 (2008) 20–28.
[30] J.U.K. Oubagaranadin, Z.V.P. Murthy, Appl. Clay Sci. 50 (2010) 409–413.
[31] T. Mishra, P. Mohapatra, K.M. Parida, Appl. Catal., B 79 (2008) 279–285.
[32] R. Ben Achma, A. Ghorbel, S. Sayadi, A. Dafinov, F. Medina, J. Phys. Chem. Solids 69 (2008) 1116–1120.
[33] M. Fujiwara, T. Matsushita, S. Ikeda, Anal. Sci. 9 (1993) 289–291.
[34] B.A. Dar, P. Bhatti, A.P. Singh, Anish Lazar, P.R. Sharma, M. Sharma, B. Singh, Appl. Catal., A 466 (2013) (2013) 60–67.
[35] C.N. Sisik, L.J. Hope-Weeks, J. Mater. Chem. 18 (2008) 2607–2610.