



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



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## ABSTRACT

$\text{Cu}(\text{OH})_x$  has been encapsulated over montmorillonite-KSF by simple oligomeric 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.

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## 1. Introduction

The immense scientific and commercial value of symmetrical biaryl motifs 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  $\text{Ag}_2\text{O} + \text{CrCl}_2$  [2],  $\text{PdCl}_2$  [3],  $\text{Pd}(\text{OAc})_2$  [4],  $\text{RhCl}(\text{PPh}_3)_3$  [5],  $\text{CuCl}$  [6],  $\text{Pd}(\text{OAc})_2/\text{AgNO}_3$  [7],  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  [8],  $\text{Cu}(\text{OAc})_2$  [9],  $\{(1,10\text{-phenanthroline})\text{Cu}(\mu\text{-OH})\}_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  [10],  $\text{AuCl}$  [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  $\text{Cu}(\text{OH})_x$  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  $\text{Cu}(\text{OH})_x$  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

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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  $\text{Cu}(\text{OH})_x$  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  $2\theta$  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 ( $\text{m}^2/\text{g}$ ) of the catalyst was estimated with the  $\text{N}_2$  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  $\text{Cu}(\text{OH})_x$  (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  $\text{MgSO}_4$ . 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 Bruker-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

The XRD spectra of KSF (montmorillonite-KSF), Cu/clay-2b, Cu/clay-2c and Cu/clay-2d is shown in Fig. 1. Peaks at  $2\theta = 21^\circ$ ,

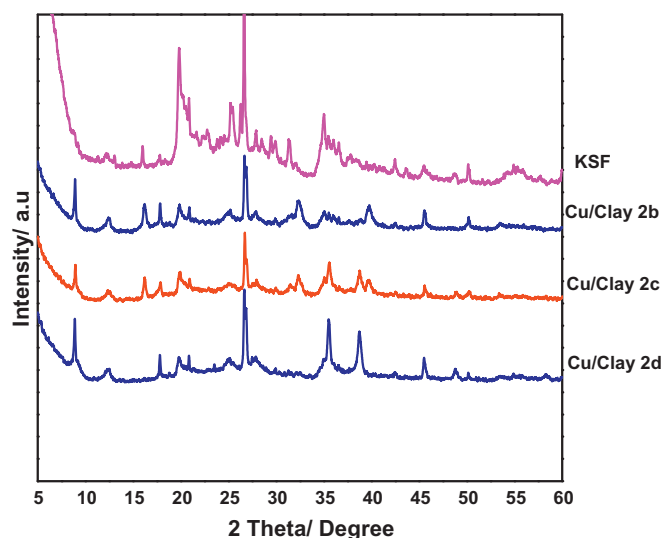


Fig. 1. XRD spectra of (a) Montmorillonite-KSF (b) Cu/clay-2b; (c) Cu/clay-2c; (d) Cu/clay-2d.

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

The  $\text{N}_2$  adsorption–desorption isotherm and pore size distribution of  $\text{Cu}(\text{OH})_x$ -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  $\text{Cu}(\text{OH})_x$ -clay (Cu/clay-2b) are summarized in Table 1. The

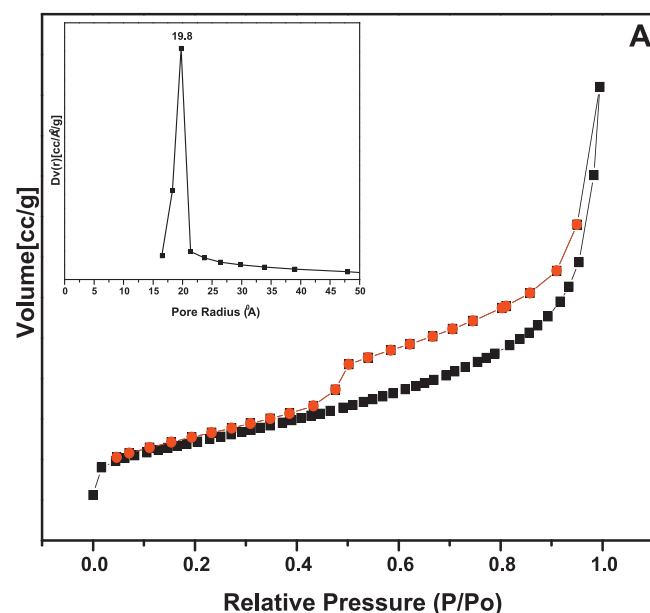


Fig. 2.  $\text{N}_2$  adsorption–desorption isotherm and pore size distribution curve (inset) of Cu/clay-2b

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