Applied Catalysis A: General 466 (2013) 60–67

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

# Clay entrapped $Cu(OH)_x$ as an efficient heterogeneous catalyst for ipso-hydroxylation of arylboronic acids

Bashir Ahmad Dar[a,b], Prince Bhatti[a], A.P. Singh[c], Anish Lazar[c], Parduman R. Sharma[a], Meena Sharma[b], Baldev Singh[a,*]

[a] Indian Institute of Integrative Medicine (CSIR), Canal Road, Jammu 180001, India
[b] Department of Chemistry, University of Jammu, J&K 180004, India
[c] Catalysis Division, National Chemical Laboratory, Pune, Maharastra 411008, India

ARTICLE INFO

*Article history:*
Received 1 February 2013
Received in revised form 15 May 2013
Accepted 29 June 2013
Available online 8 July 2013

*Keywords:*
Phenols
Heterogeneous catalysis
Clay
Copper
Water chemistry

ABSTRACT

A remarkably active, selective and stable montmorilonite-KSF entrapped $Cu(OH)_x$ catalyst, has been prepared for the ipso-hydroxylation of arylboronic acids under ambient conditions without requirement of any ligand or base. This catalyst shows excellent reusability without leaching and any significant loss in catalytic activity. The catalyst was characterized using, XRD, SEM, TPR, IR, XPS and BET surface area measurement techniques.

## 1. Introduction

Many biologically active compounds, ranging from natural products to pharmaceuticals are reported to possess phenols in monomeric or polymeric forms [1,2]. Some of the phenols also serve as important synthetic intermediates for the construction of more complex structures [3,4]. Consequently, the development of methods establishing mild and efficient access to such a structural motif is of immense importance especially in the presence of many functional groups. Hydroxylation of aryl bromides and chlorides into phenols have been reported using palladium-based catalysts in presence of phosphine ligands [5,6]. Hydroxylation of aryl iodides to the corresponding phenols have been achieved using copper catalyst and non-phosphine ligands under thermal conditions [7,8]. However wide range availability of arylboronic acid derivatives, their harmless nature, stability toward heat, air, moisture and their facile conversion to phenols has made them attractive and valuable precursors [9]. Transition metal catalysts such as AuNPs/PVP [PVP = poly(N-vinyl-2-pyrrolidone)] [10], $CuSO_4$-phenanthroline [11], $CuCl_2$-Brij-S-100 [12], $[Ru(bpy)_3Cl_2]{\cdot}6H_2O$ [13], $Pd(COD)Cl_2$(COD = 1,5-cyclooctadiene) [14] have been employed to accomplish hydroxylation of aryl boronic acids. Simple metal salts like potassium peroxymonosulfate [15], and metal free catalytic systems like N,N-dimethyl-4-toluidine N-oxide [16], $NH_2OH$ [17], 3-aminothiophenol [18], $I_2$-$H_2O_2$ [19], $H_2O_2$–poly(N-vinylpyrrolidone) [20], $H_2O_2$ Amberlite IR-120 [21], aqueous $H_2O_2$ [22], etc. have also been developed.

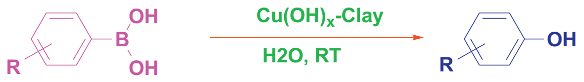
However longer reaction times, use of homogeneous transition metal catalyst systems, organic solvents, stoichiometric amounts of ligand/base, hazardous oxygen sources such as $H_2O_2$ and ozone could not avoided in these approaches [23]. Moreover homogeneous transition metal catalysts despite showing high catalytic activity and selectivity have some serious drawbacks, such as metal contamination, which is highly undesirable from industrial and biological point of view and homogeneous metal catalysts cannot be reused, which results in loss of expensive metals. Increasing demand for the development of more efficient and environmentally acceptable processes in the chemical industry focusing largely on chemical yield, eliminating waste at source and circumventing the use of perilous materials has captivated the interest of researchers in the field of heterogeneous catalysis [24].

Clays and modified 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. The clay-based metal composites have shown their activities in various pioneering works in the field of catalysis [25]. In addition to that clay minerals occur abundantly in nature and their

---

[*] Corresponding author. Tel.: +91 0191 2572002; fax: +91 0191 2548607.
*E-mail address:* 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.2013.06.051



**Scheme 1.** Ipso-hydroxylation of arylboronic acids.

high surface area, sportive and ion-exchange properties have been exploited for catalytic applications through decades. Aluminosilicate layers of Montmorillonite-Clays found in nature are negatively charged due to isomorphous substitution and often these negative charged layers are compensated by the cations between the layers. In aqueous state, the negatively charged aluminosilicate layers attract water molecules to the interlayer for charge balance. This charge balance phenomenon allows swelling and cation exchange to take place. Such properties can be used to intercalate a desired cation into the clay lattice [26].

Comparatively high stability of a catalyst on solid support sometimes allows the reaction to be less sensitive to normal ambient conditions. Therefore, clay supported catalyst as a substitute of homogeneous catalyst or an expensive heterogeneous catalyst seems highly desirable [27]. In continuation of our research interest for organic transformations through eco-friendly routes [28–30], we herein report a highly efficient synthesis of phenols by ipso-hydroxylation of arylboronic acids using inexpensive, air-stable and efficient Clay entrapped $Cu(OH)_x$ as a recyclable heterogeneous catalyst under base free and ligand-free conditions (Scheme 1). The solvent used for this catalytic system is water and the reactions proceeds smoothly at room temperature. Using water as solvent is highly advantageous from the viewpoint of cost, safety, availability and environment friendliness [31].

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Synthesis of clay entrapped $Cu(OH)_x$ [Cu/KSF]

Clay entrapped $Cu(OH)_x$ [Cu/KSF] was prepared by suspending montmorillonite-KSF (10 g) with cation exchange capacity of 120 mequiv./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 prepare the required wt% loading of copper and the resulting slurry was stirred at 90 °C for 8 h. 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 (250–425 °C).

#### 2.1.2. Synthesis of Cu/Cs KSF [basic clay]

Cu/Cs KSF [basic clay] was synthesized by dropwise addition of 7.5 g of $CsCO_3$ in 200 ml water solution into a suspension of montmorilonite-KSF (10 g) in distilled water (200 ml) with vigorous stirring. The resulting slurry was stirred for 15 h, and then the water was evaporated. The powder thus formed was kept overnight at 110 °C in an air oven and then calcined at 550 °C for 3 h and labeled as basic clay. The basic clay was suspended in 200 ml distilled water, and to this, copper oligomer (base hydrolysed cupric chloride with OH/Cu molar ratio of 2.0) was added drop wise to prepare the required wt.% loading of copper, and the resulting slurry was stirred at room temperature for 8 h. The solid products were filtered, washed several times with distilled water, dried first at room temperature and then at 110 °C for 12 h and then calcined at 425 °C.

#### 2.1.3. Synthesis of Cu/acidic KSF [acidic clay]

In typical synthesis procedure, 300 ml (1 M) aqueous solution of $NH_4Cl$ was added drop wise to a suspension of montmorilonite-KSF (10 g) in distilled water (200 ml) with vigorous stirring. The resulting slurry was stirred for 15 h, and then the water was evaporated. The powder thus formed was kept overnight at 110 °C in an air oven and then calcined at 550 °C for 3 h and labeled as acidic clay. The acidic clay was suspended in 200 ml distilled water, and to this copper oligomer (base hydrolysed cupric chloride with OH/Cu molar ratio of 2.0) was added drop wise to prepare the required wt.% loading of copper, and the resulting slurry was stirred at room temperature for 8 h. The solid products were filtered, washed several times with distilled water, dried first at room temperature and then at 110 °C for 12 h and then calcined at 425 °C.

All synthesized catalysts were characterized 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 where 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 ($m^2/g^{-1}$) of the catalyst was estimated with the $N_2$ adsorption and desorption was 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. Procedure for ipso-hydroxylation of arylboronic acid

To a solution of arylboronic acid (1 mmol) in deionized water (1.5 ml), clay entrapped $Cu(OH)_x$ (13 mg) was added and this heterogeneous mixture was vigorously stirred at ambient temperature for 20–100 min. The reaction progress was monitored by TLC. Ethyl acetate was added and the aqueous phase was isolated and back extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by $SiO_2$ column chromatography to afford the desired product. The prepared phenols were characterized by comparing the observed spectral data and physical properties with those of authentic samples. Most of the products formed were primarily identified by comparing their TLC with the standard samples. NMR spectra were recorded on Brucker-Avance 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. The catalyst was washed several times with ethanol followed by distilled water and used for next reaction cycle.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

The XRD spectra of (a) Cu/KSF [15 wt% Cu on as such clay (calcined at 250 °C Cu/Clay-2a2)] (b) Cu/KSF after 10th cycle of reaction (c) Cu/Cs KSF [Cu/Clay-3] (d) Cu/acidic KSF [Cu/Clay-1] are 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 [32–34] and at 12.5°, 19.9° and 27.9° are due to palygorskite [35–37]. Peaks for montomorillonite appear at $2\theta = 8.9°$ ($d$ 0 0 1 reflection), 19.8°, 32.2°, and 62° [38,39]. Presence of Kaolinite is implied to small peaks at 38.8°, and 42.5° [38,39]. The copper loaded on montmorilonite-KSF does not show