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Cerium-containing MCM-41 catalyst for selective oxidative arene cross-dehydrogenative coupling reactions

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ABSTRACT

Cerium (IV)-mediated intermolecular direct biaryl coupling of aromatic tertiary amines and naphthol via dual C—H bond activation has been reported. The new C—C bond is formed regioselectively *ortho* to the amino and hydroxyl substituents under oxidative conditions to give substituted bifunctional amino naphthols. We report here the use of Ce-MCM-41 catalyst for the synthesis of these unsymmetrical biaryls via oxidative cross coupling under mild conditions. The catalyst was recovered by simple filtration and reused for several cycles with consistent activity.

1. Introduction

The constructions of C—C bonds, especially aryl–aryl linkages, are among the most important reactions in organic synthesis [1]. Biaryl structures are a ubiquitous motif in biological, pharmaceutical, and material sciences [2]. Numerous economically important pharmaceuticals and agrochemicals such as valsartan, boscalid, and liquid-crystalline NCB 807 have biaryl units as indispensable substructures [3]. A vast majority of biaryl linkages are constructed via metal-mediated cross coupling of two pre-functionalized arene building blocks [4]. However, the required organometallic nucleophilic reagents are relatively expensive and rarely commercially available. With the emergence of the concepts of atom economy and green chemistry, metal-catalyzed C—H bond activation as well as direct use of unactivated C—H bonds for C—C bond formation has attracted much interest in recent years [5]. Moreover, it has been reported that biaryls containing amino naphthols functionalities act as organo catalysts and ligand precursors in asymmetric catalysis [6]. Although several reports have been published on homo-coupling of either naphthols or aniline derivatives, the regioselective cross-coupling of unactivated moieties is often challenging [7]. An efficient approach for the formation of new C—C bonds involves the direct oxidative coupling of two arene C—H substrates under mild conditions [8].

In recent years, several groups have reported cross dehydrogenative coupling reactions [9]. In particular, the C—H activation of aromatic tertiary amines and subsequent C—C bond formation with nucleophiles has gained much attraction [10]. These oxidative coupling reactions require the presence of metal ions together with a one-electron oxidant [11]. A majority of these coupling reactions are catalyzed by salts of transition metals (such as copper, iron, nickel palladium, ruthenium and rhodium), under appropriate conditions [12]. There is a growing demand for the development of new catalyst systems based on readily available and relatively cheap non-noble metals. In this regard, cerium salts are particularly appealing, since they have low toxicity, reasonable solubility in many organic media, air stable, easily handled, and are inexpensive [13].

The propensity of Ce(IV) to efficiently participate in one-electron transfer reactions while existing in stable oxidation states +3 and +4, and its high reduction potential (1.61 V vs. normal hydrogen electrode), makes it a very efficient oxidizing agent compared to many other metal cations. Its salts, such as the commercially available cerium ammonium nitrate (CAN), have found wide spread use as one-electron oxidants [14]. The dual role of CAN as an oxidant and a Lewis acid facilitates its catalytic role in cross-dehydrogenative coupling (CDC) reactions [15]. Various oxidative reactions involving CAN in homogeneous media have

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been reported by several groups [16]; however, they suffer from serious limitations such as high catalyst loading, difficulty in recovery and reusability of the catalyst and tedious work-up procedures. The development of highly active and reusable heterogeneous catalysts for C—C cross dehydrogenative coupling reactions is an open challenge [17].

In the last few decades, mesoporous materials have received much attention in the field of catalysis, especially for their use as solid supports [18]. These porous supports have uniform pore size and large surface area and are ideal materials for heterogenization of various metal salts. The most widely used mesoporous silica, MCM-41, exhibits a highly ordered hexagonal array of one dimensional mesopores with diameters varying from 15 to 100 Å [19]. In Ce-MCM-41, cerium (IV) ions are covalently anchored to silica. It is well known that cerium, coordinated with tetrahedral silicon via oxygen bridges, acts as a Lewis acid catalyst for selective oxidations in the presence of peroxides [20]. Therefore, it was conceptualized that the use of Ce-MCM-41 as catalyst should result in good yields of biaryls under mild conditions as compared to homogenous system. Herein, we report a facile and reusable heterogeneous catalyst, namely Ce-MCM-41 for the synthesis of unsymmetrical biaryls through C—H activation [21].

2. Experimental

2.1. Chemicals and reagents

Sodium silicate ($NaSiO_3 \cdot 9H_2O$), cetyl trimethyl ammonium bromide (CTAB), ceric ammonium nitrate (CAN), tertiary butyl hydrogen peroxide (TBHP, 70 wt% in water), ditertiary butyl peroxide (DTBP), H_2O_2 (30 wt% in water), and all other starting materials and reagents were purchased from Sigma–Aldrich and are used as received. All the solvents used are of analytical grade and were purchased from Merck India Ltd. Deionized water was used to prepare the aqueous solutions. Sulfuric acid and sodium hydroxide were used to control the pH of the aqueous solutions.

2.2. Instrumentation

The Thin Layer Chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates using ethyl acetate and hexane as eluting agents. Thin layer chromatography plates were visualized by exposure to UV-light/iodine and/or by immersion in an acidic staining solution of phosphomolybdic acid followed by heating on a hot plate. Purification of products was carried out by column chromatography using silica gel (100–200 mesh) and a mixture of ethyl acetate and hexane as eluting agent. All the products were characterized by Mass, ^1H and ^{13}C NMR spectroscopy. The NMR spectra of samples were acquired on a Varian Unity Inova 500 MHz, Inova 400 MHz, and Bruker Avance 300 MHz spectrometer using TMS as an internal standard in $CDCl_3$. Mass spectra were acquired on a Thermo LCQ fleet ion trap mass spectrometer. High-resolution mass spectra were acquired on a Q STAR XL Hybrid LC/MS/MS system, Applied Biosystems, USA. FT-IR data were acquired on a Thermo Nicolet Nexus 670 FT-IR spectrometer with DTGS KBr detector. XPS spectra were recorded on a Kratos AXIS 165 with a dual anode apparatus using the Mg Kα anode. X-ray powder diffraction data were collected on a Siemens/D-5000 diffractometer using Cu Kα radiation. The particle size and external morphology of the samples were observed on a Philips TECNAI F12 FEI transmission electron microscopy (TEM). SEM-EDX was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300 instrument. Diffuse reflectance UV/vis spectra for samples as KBr pellets were recorded on a GBC Cintra 10e UV–vis spectrometer in the range 200–800 nm with a scan speed 400 nm/min.

2.3. Synthesis of catalyst (Ce-MCM-41)

MCM-41 was prepared by the direct hydrothermal method described in the literature [22] and dried at 80 °C for 10 h prior to use. The cerium-loaded MCM-41 mesoporous material was prepared by a wet impregnation method using 10% and 15% ceric ammonium nitrate solution respectively [23]. All the characterization studies were carried out with Ce-MCM-41 loaded with 15 wt% of cerium. The calcined template-free MCM-41 (0.21 g) was added to 10 mL of an aqueous solution of ceric ammonium nitrate (0.12 g, 0.02 M) and stirred vigorously for 24 h at room temperature. The solid was isolated by evaporation of the solvent, dried overnight at 100 °C and then calcined at 500 °C in air for 5 h to obtain Ce-MCM-41 containing 15 wt% of cerium.

2.4. Experimental procedure for the synthesis of N,N-dialkyl aniline derivatives

To a solution of aniline (1 mmol) in glacial acetic acid (7 mL) under argon was added paraformaldehyde (10 mmol) and sodium cyanoborohydride (5 mmol). After stirring overnight, the reaction mixture was poured into ice cooled water (~100 mL) containing NaOH (7 g). This mixture (pH 14) was extracted thrice with CH_2Cl_2 (3×350 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain the crude product. Flash chromatographic purification of the crude product using silica gel and a mixture of hexane and ethyl acetate as the eluent provided the pure product.

2.5. General procedure for the synthesis of 1-(5-R-2-(piperidin-1-yl)phenyl)naphthalen-2-ol (R = alkyl, alkoxy, halide)

A suspension of phenyl boronic acid (2.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (10 mol%) and powdered 4 Å molecular sieves (0.75 g) in dichloromethane (8 mL) was stirred for 5 min at room temperature. To this mixture was added the amine (1.0 mmol). The reaction vessel was sealed with a rubber septum and stirred at 40 °C under oxygen for 24 h. The reaction mixture was then filtered through a plug of Celite and the product was purified by column chromatography using silica gel and a mixture of hexane and ethyl acetate as the eluent.

2.6. General procedure for the synthesis of unsymmetrical biaryls

A 25 mL round bottomed flask was charged with N,N-dialkylaniline (0.5 mmol), 2-naphthol (0.5 mmol) and acetonitrile (3 mL), followed by 10 mg of Ce-MCM-41 and TBHP (2 equiv.) via syringe. The mixture was heated to 60 °C and stirred for 3 h in open air. After completion of the reaction, as judged by TLC, the solution was cooled and the catalyst was removed by filtration. The resulting crude mixture was gently evaporated under reduced pressure and purified by column chromatography using silica gel and a mixture of hexane and ethyl acetate as the eluent.

3. Results and discussion

The optimization studies for cross-dehydrogenative coupling reaction were performed in a 0.5 mmol scale using *N,N*,4-trimethylaniline and 2-naphthol as the model substrates in acetonitrile at 60 °C. Employing 2 equiv. of TBHP as the oxidant, various cerium salts such as $CeCl_3$, $Ce(SO_4)_2$, CAN, 5% Ce-MCM-41,10% Ce-MCM-41,15% Ce-MCM-1and 20% Ce-MCM-41, were examined for their catalytic activity. Among cerium salts screened, CAN was found superior to other salts such as $CeCl_3$ and $Ce(SO_4)_2$, and furnished the corresponding cross coupled product in moderate to