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A fascinating Suzuki homo-coupling reaction over anchored gold Schiff base complexes on mesoporous host

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ABSTRACT

We present a study of the use of chloro-functionalized mesoporous silicas as supports for immobilization of Au(III) Schiff base complex, and use of this composite material as heterogeneous catalyst for homocoupling of aryl boronic acid. The catalyst was characterised by XRD, FTIR, UV–vis DRS, TG-DTA, etc. Catalyst was initially tested using the coupling of phenylboronic acid with bromo benzene in the presence of K_2CO_3 and with xylene as solvent. The reaction was also tested in the absence of the aryl halide and K_2CO_3. The results indicate that in our catalytic system base is not needed for the activation of phenylboronic acid, and its only role is to neutralize the boric acid. The optimized catalysts are also active in the coupling of a range of aryl boronic acids, and after four catalytic runs they show virtually no drop in activity.

1. Introduction

Gold was believed to be chemically inert, and with very few exceptions [1–4] the possibilities of homogeneous and heterogeneous gold catalysts for organic reactions were not considered. Recent reports have shown that gold salts, specifically Au(III), can act as a Lewis acid catalyst for a large variety of reactions [5–8]. Gold in homogeneous complexes [2,9] has shown possibilities for several catalytic reactions, including asymmetric aldol condensation, and the asymmetric hydrogenation of alkenes and imines [10,11]. More specifically, it has been recently shown [12] that Au(III) complexes were active and selective catalysts for carrying out the homocoupling of different aryl boronic acids. However, Au(III), unlike Pd complexes, was not able to catalyze cross-coupling reactions. The traditional homogeneous catalysis causes major problems in purification of the product and separation of expensive catalyst that leads to environmental toxic wastes. Immobilized gold catalyst over solid support has been developed in order to overcome these problems facing green chemistry [13–15].

The Suzuki reaction is by far the most versatile synthetic method available for the generation of unsymmetrical biaryl compounds which are important building blocks in natural products and in materials sciences [13,16–22]. Biaryls exhibit a wide variety of physical and chemical properties [23,24] and possess versatile applications in pharmaceuticals, nonlinear optics [25], liquid crystals [26] and optically active ligands [27]. Various metal catalyzed coupling reactions have been recognized as convenient one-step method for assembling complex structures [16,28]. Suzuki coupling has become increasingly popular due to its compatibility with a variety of functional groups, the stability of organoboron precursors, and the ease of working up the reaction mixture. Pd–phosphine complexes [18,29–33] have been the most commonly used catalysts for the Suzuki reaction. However, alternative ligands such as N-heterocyclic carbenes [6,34], imidazol-2-ylidenes [35] and diazabutadienes [36] have been used in Suzuki coupling reactions.

Our interest in this area led us to explore the activity of Au(III) Schiff base complex and anchoring it onto the surface of MCM-41, which can be easily separated from the reaction mixture. MCM-41 is an inorganic support which has some advantageous properties such as excellent stability, good accessibility, and the fact that organic groups can be robustly anchored to the surface [37,38]. Here in we report the synthesis of homogeneous and heterogeneous Au(III) Schiff base complex and its catalytic activity in Suzuki homocoupling reaction. The comparative activity of Pd(II) complexes with same ligands for the same reaction is also studied.

2. Experimental

2.1. Materials and methods

All solvents and reagents were purchased from Aldrich and used without further purification. The arylation products were char-

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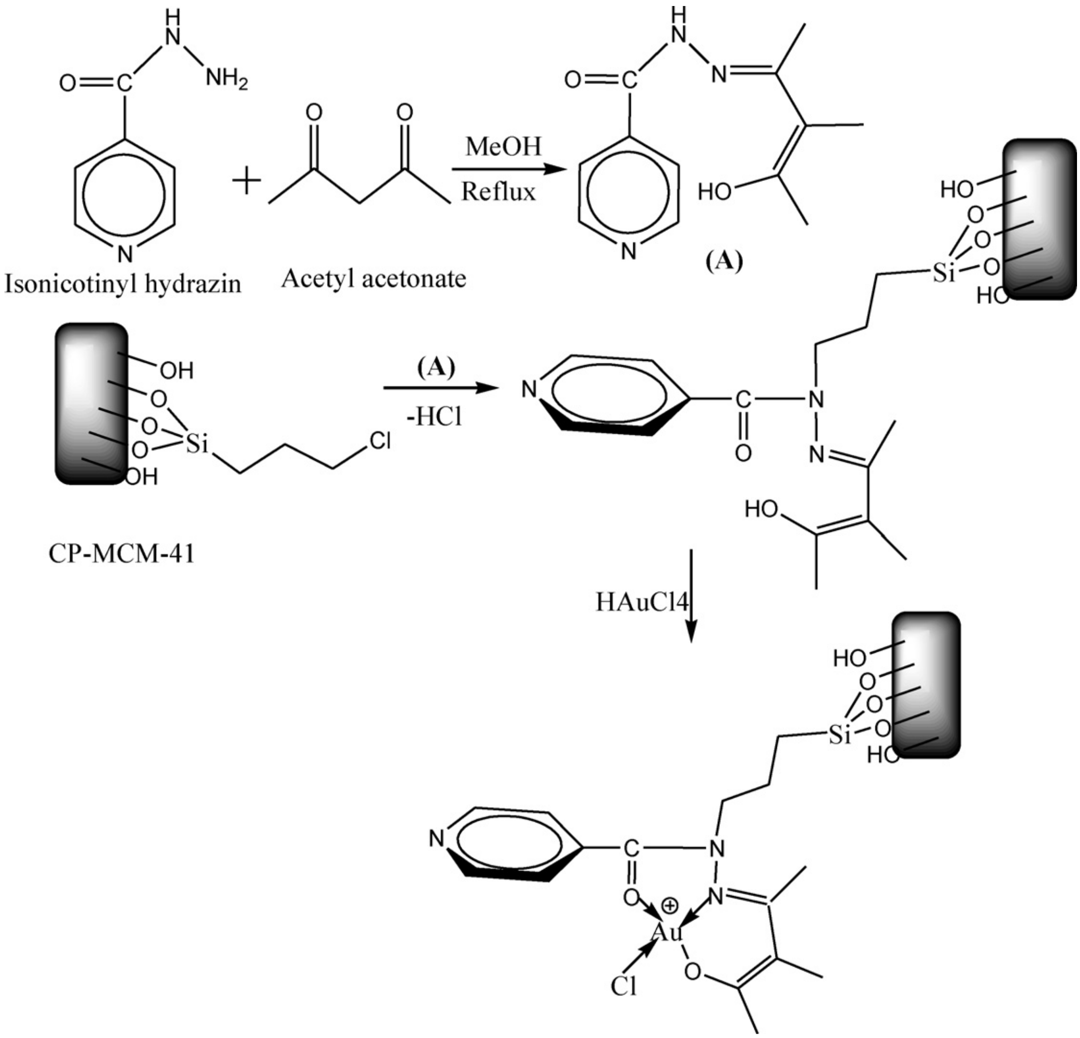

Scheme 1. Schematic representation of the formation of Au(III) Schiff-base complex within the pore channels of MCM-41.

acterised by comparison of their spectra and physical data with authentic samples.

Powder X-ray diffraction (XRD) patterns of the heterogeneous samples were obtained on Rigaku D/Max III VC diffractometer with Cu Kα radiation at 40 kV and 40 mA in the range of $2\theta = 0–10^{\circ}$. The FTIR spectra of the samples were recorded using Varian 800-FTIR in KBr matrix in the range of 4000–400 cm^{-1}. The co-ordination environments of the samples were examined by diffuse reflectance UV–vis spectroscopy. The spectra were recorded in Varian-100 spectrophotometer in the wavelength range of 200–800 nm in $BaSO_4$ phase. The thermal stability of the material is also characterised by TG-DTA using Toledo-Mettler TG/DTA/851^{e}. The metal loading and leaching of the reaction solution were determined by atomic absorption spectroscopy (AAS) with a Perkin-Elmer Analysis 300 using acetylene (C_2H_2) flame. Transmission electron microscopy (TEM) analyses were performed on Philips TECHNAI G^2 operated at 200 kV.

2.2. Preparation of MCM-41-Cl

MCM-41-Cl was prepared by co-condensation method [39] using $C_{16}H_{33}N(CH_3)_3Br$ (CTAB) as template, tetraethyl orthosilicate (TEOS) as silica precursor and chloropropyltriethoxysilane (CPTES) as organo alkoxysilane precursor.

2.3. Preparation of Schiff base ligand

The reactions were performed under inert atmosphere of dry nitrogen using distilled dried solvents. Schiff base ligand (A) was synthesized by co-condensation method taking isoniazid and acetyl acetone in 1:1 molar ratio. In a typical experiment, 10 mmol of isoniazid (1.37 g) was dissolved in 20 ml methanol. To this acetyl acetone (10 mmol) was added and refluxed for 6 h. Then the reacting mixture was cooled and allowed to crystallize. Finally the ligand was recrystallized from methanol.

2.4. Preparation of immobilized ligand on MCM-41

MCM-41-Cl (1 g) was added to a solution of Schiff base ligand (0.123 g, 0.562 mmol) in dry toluene and the resulting suspension was refluxed for 48 h under inert atmosphere. The ligand was thought to be heterogenized by the elimination of HCl. This can be observed as the appearance of pale yellow colour in the reaction mixture. The heterogenized ligand was filtered, washed thoroughly with dry toluene and finally dried at 80 °C.

2.5. Preparation of MCM-41 immobilized metal complexes

Immobilized complex catalyst was prepared under dinitrogen by conventional Schlenk-tube technique, the solvents were care-