Journal of Catalysis 356 (2017) 255–268

Contents lists available at ScienceDirect

Journal of Catalysis

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

Stabilization of Au NPs on symmetrical tridentate *NNN*-Pincer ligand grafted on magnetic support as water dispersible and recyclable catalyst for coupling reaction of terminal alkyne

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ARTICLE INFO

Article history:
Received 30 August 2017
Accepted 24 October 2017

Keywords:
Supported gold catalysis
Pincer catalysts
Propargylamine
Heterogeneous catalyst

ABSTRACT

A symmetrical tridentate *NNN*-pincer ligand derived from 2-aminopyridine/cyanuric chloride was covalently grafted onto the surface of modified magnetic support to stabilize Au nanoparticles. Spectroscopic evidence (IR, XRD, EDX, TEM, and XRF) and other analyses (TGA, VSM, and H_2-TPR) confirmed successful immobilization and desired catalyst structure. Catalyst loading of 0.07–0.1 mol% was shown to be very effective in the synthesis of propargylamines through addition of terminal alkynes to amine/aldehyde adduct (A^3-coupling). The water-dispersible catalyst allows the use of water as an inexpensive solvent. The high accessibility and robustness of the catalyst enhanced reusability so that no deactivation of catalyst or aggregation of supported Au NPs is observed after seven repeated recycling. Control experiments also showed the true heterogeneous nature of the catalyst in the reaction without significant leaching. All experiments showed that the catalyst is comparable to or even more active than the corresponding species in solution.

1. Introduction

For centuries, gold had been considered a precious, purely decorative inert metal. However, the past two decades have witnessed a tremendous growth in the utilization of gold for numerous catalytic transformations [1–4]. Indeed, high Pauling electronegativity and electron affinity of gold, unique atomic structure, physical stability [5,6], interesting interaction of gold with sulphur [7], quantum size effect of gold [8], the capability of fine-tuning of gold NPs by varying the size, shape, and crystal structure [9], and unique surface properties of gold have made it an attractive transition metal for research rather than the other [10]. In the last 15 years, thousands of chemical transformations, importantly activation of alkynes [11–16], have been effectively catalyzed by gold nanoparticles or homogeneous complexes of Au(I) [11], and Au(III) [11,17–20]. Despite the efficiency of homogeneous gold catalysts [21–24], a literature survey revealed that more than 0.5 mol% of catalyst loading is needed for the reaction [25–27] and only in a few cases, catalysts with high turnover numbers have been reported [21–24]. Notably, gold catalysts are expensive and unrecoverability of homogeneous gold catalysis is a common drawback. Thus, homogeneous gold catalysts would be too expensive to be useful for industrial processes. Accordingly, heterogeneous recyclable gold catalysts have been designed through covalently immobilization of gold complexes or stabilization of gold nanoparticles onto the solid supports [28–33]. Resins [34], micro/mesoporous silica [33,35], polymers [36–38], and Fe_3O_4 [39–41] are among the most preferred supports due to their large surface area. While there are many successes on the use of these heterogeneous gold catalysts, two major obstacles are still considerable: (1) gold leaching and (2) instability of gold NPs due to tending to aggregate during the course of the reaction. Today, the “ligand design” [42,43] come into effect to solve these problems.

In recent years there has been an increasing expansion in the development of pincer compounds, mainly explored by Gerhard van Koten and his co-workers [44–50], so that they have emerged as unique class of ligands in designing of effective metal-based catalysts which is along with the concept of “ligand design” [51–54]. An important characteristic of the pincer platforms is the fact that its three co-planar ligating sites are well organized by the backbone of the ligand led to the formation of five- or six-membered chelate rings with a central bonded metal [55,56]. In most cases, the pincer platform itself acts as a non-innocent ligand or provides,

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https://doi.org/10.1016/j.jcat.2017.10.021

with its pincer-metal manifold, a system that is suitable for executing metal-ligand cooperative (MLC) behavior in catalytic processes [48,57]. Having considered the advantages of heterogeneous catalyst in one hand, and unique and effective properties of pincer ligands on the other hand, recently, a variety of pincer complexes of Ir [58,59], Ru [60], Pd [61,62], Pt [63], Rh [64,65], and Cu [66] metals have been immobilized on different solid supports. According to these reports, most of them have shown heterogeneous catalytic activity comparable to or even more than the corresponding homogeneous species in valuable transformation such as transfer dehydrogenation [67], oxidation [60,63], reduction of CO_2 [59], C—H activation [66], C—C coupling [62,68], photocatalytic H_2 production [69], hydrogenation [58,64], and allylation [65]. However, gold-pincer catalysts have been rarely heterogenized and there are only a few reports on immobilization of *ONN*- and *CNN*-pincer/gold complexes onto the mesoporous silica [70–72].

Here, we have extended a novel heterogeneous magnetic gold catalyst based on stabilization of gold nanoparticles on *NNN*-pincer ligand derived from triazine core [73,74]. More specifically, we have investigated the pincer-Au catalyzed one-pot reaction of terminal alkynes, secondary amines, and aldehydes forsynthesis of propargylamines (A3-coupling reaction).

2. Experimental

2.1. Materials and methods

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), ammonia (25%), tetraethyl orthosilicate (TEOS), (3-aminopropyl)triethoxysilane (APTS), cyanuric chloride (2,4,6-trichloro-1,3,5-triazine), and $HAuCl_4$ (gold(III) chloride hydrate, 50% Au basis) were obtained from Sigma-Aldrich and used without further purification. *N*,*N*-Diisopropylethylamine (DIEA) was purchased from Merck and distilled before use. 2-aminopyridine (GC, >98%) was purchased from Merck and used without further purification. Various commonly used organic solvents (Merck) were dried with several different drying agents. FT-IR spectra of samples were taken using an ABB Bomen MB-100 FT-IR spectrometer. Thermogravimetric analysis (TGA) was acquired under an argon atmosphere with a TGA Q 50 thermogravimetric analyzer. High Resolution Transmission Electron Microscopy (HR-TEM) was performed on a JEOL JEM-2100F electron microscope with an accelerating voltage of 200 kV. Magnetization of catalyst was measured by vibrating sample magnetometer (Meghnatis Daghigh Kavir Co., Kashan, Iran). Powder X-ray Diffraction analysis was performed using a Rigaku MiniFlex-600 diffractometer with Cu Kα radiation (λ = 1.5406 Å) at room temperature. X-ray fluorescence (XRF) was taken using Phillips 1404 XRF instrument. Atomic absorption spectrometry (AAS, Shimadzu 680 A) or inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Perkin-Elmer DV 4300) were used for elemental measurements. Temperature programmed analysis was conducted on a Micromeritics AutoChem II 2920 and H_2-TPR measurements were performed with a heating ramp rate of 10 $°C{\cdot}min^{-1}$ and a 10% H_2/Ar was used at a flow rate of 50 $ml{\cdot}min^{-1}$. ^1H and ^{13}C NMR spectra were recorded on a Bruker NMR 500 MHz instrument.

2.2. Preparation of amine functionalized magnetic nanoparticles (MNP@APTS)

Fe_3O_4 nanoparticles were synthesized and coated by SiO_2 layer based on our previously reported method (MNP) [75]. MNPs (1.0 g) were ultrasonically dispersed in 50 mL toluene. Then, APTS (10 mmol, 2.3 mL) was added and the mixture was stirred at 80 °C for 24 h. The APTS coated magnetic nanoparticles (MNP@APTS) were magnetically separated and washed several times with methanol (4 × 30 mL) and dried under vacuum at 50 °C.

2.3. Functionalization of MNP@APTS with trichlorotriazine (MNP@TADC, route 1)

In a round bottom flask, MNP@APTS (0.95 g) was ultrasonically dispersed in dry THF (30 mL). Then, trichlorotriazine (5 mmol, 0.92 g) and DIEA (7 mmol, 1.2 mL) were added and the flask was put in an ice bath. The mixture was stirred for 3 h under N_2 atmosphere. The product was magnetically separated and washed with MeOH (5 × 10 mL) and dried under vacuum at room temperature (MNP@ TADC, 0.9 g).

2.4. Preparation of tridentate NNN-pincer ligand grafted MNP (MNP@NNN-pincer)

In a three-necked flask, MNP@TADC (0.9 g) was ultrasonically dispersed in dry MeCN (20 mL). A solution of 2-aminopyridine (8 mmol, 0.76 g) and DIEA (10 mmol, 1.7 mL) in dry MeCN (5 mL) was added to flask. The flask was equipped with a condenser and the mixture was refluxed for 12 h to produce MNP@NNN-pincer ligand. The magnetic pincer ligand was separated using an external magnet and washed with methanol (5 × 10 mL) and dried under vacuum at 50 °C (0.8 g).

2.5. Synthesis of catalyst MNP@Au/NNN-pincer

For stabilization of Au nanoparticles on heterogeneous pincer ligand, MNP@*NNN*-pincer (0.50 g) was dispersed in H_2O (10 mL) and $HAuCl_4$ (0.02 M, 5 mL) was added to the mixture. The solution *p*H was adjusted to 6 by dropwise addition of NaOH (0.01 M) and the mixture was allowed to stir for 5 h at room temperature. Nanoparticles then collect using an external magnet and the solution was decanted. The nanoparticles were redispersed in 10 mL H_2O and a solution of $NaBH_4$ (1 mmol in 10 mL H_2O) was added to the mixture and allowed to stir for another 12 h. The final catalyst (MNP@Au/*NNN*-pincer) was magnetically separated and washed with H_2O (excess) and MeOH (2 × 10 mL) and dried under vacuum at 50 °C (0.45 g).

2.6. General procedure for the synthesis of propargylamines using MNP@Au/NNN-pincer

Aldehyde (2 mmol), amine (2.4 mmol), alkyne (2 mmol) and catalyst (0.07 and 0.1 mol% for aromatic and aliphatic alkynes, respectively) were loaded in a 25 mL round bottom flask containing H_2O (6 mL). Then the mixture was stirred at 85 °C until completion of the reaction (monitoring by TLC). After completion of the reaction, catalyst was magnetically separated, washed with methanol (3 × 10 mL) and dried for another run. The product mixtures were extracted with EtOAc and concentrated to give the crude product. The crude product was then purified through a silica gel column chromatography (20 and 5 cm in length and diameter) using mixtures of different ratio of hexane/ethyl acetate as eluent.

2.7. General procedure for the recycling and reusing test

Experiments were carried out following the procedure above detailed for the model reaction. After completion of the reaction, the solid catalyst was magnetically collected at the bottom of the flask and aqueous solution was decanted in another flask for further work up. The catalyst was washed three times with methanol and used for the next run without further treatment. In the recycling test by this way, the catalyst was not separate from the