



# Palladium with spindle-like nitrogen ligand supported on mesoporous silica SBA-15: A tailored catalyst for homocoupling of alkynes and Suzuki coupling

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## ABSTRACT

A mesoporous silica SBA-15-supported palladium with spindle-like nitrogen donor groups, 1,4-diaza-bicyclo[2.2.2]octane, has been successfully prepared and applied for homocoupling of terminal alkynes. The catalyst exhibited very high activity for terminal alkynes carrying various substitution groups, yields ranging from 70% to 94%, with a significant advantage that air acted as the oxidant. It also showed good reusability, could be easily recovered through filtration and washing, and reused at least five times with virtually no evident loss of catalytic performance. Furthermore, it was also proved to be an effective and air-stable heterogeneous catalyst for Suzuki coupling of aryl halides (X = I, Br) with arylboronic acids. The catalyst was systematically characterized by elemental analysis, X-ray photoelectron spectroscopy, high-resolution transmission electron microscope, nitrogen physical adsorption, Brunauer–Emmett–Teller method and X-ray powder diffraction. The analyses indicated that the mesoporous structure of the materials was retained during the immobilization process.

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## 1. Introduction

Homocoupling of alkynes through oxidative dimerisation to form 1,3-diynes has been becoming more and more important because of its potential applications in the construction of linear  $\pi$ -conjugated acetylenic oligomers and polymers for organic conductive materials, natural products with medical significance, and substances used in molecular recognition processes [1–4]. Although the diynes were first synthesized by Glaser in 1869 [5], very limited number of heterogeneous catalysts were developed for homocoupling of alkynes [6–12]. Homogeneous catalysts, which have been widely used for this purpose, are generally thought to have shortcomings such as complicated catalyst separation after the reaction, difficult catalyst recycling and product contamination caused by the residual components of the catalysts [13,14]. Their heterogeneous alternatives can effectively avoid these limitations but those reported catalysts [6–9] still exhibited some drawbacks, such as high pressure of oxygen (>20 atm) was applied [6], substrate was limited to phenylacetylene with a low conversion (less than 60%) [10], and catalyst activity was obviously decreased after recycling [11]. Therefore, developing novel heterogeneous catalysts remains to be necessary.

Because of their advantages such as the easy handling, good recyclability and “green” processes, heterogeneous catalysts are

usually the first choice for constructing a new catalytic system. Normally this was achieved by supporting the active components on prefunctionalized solid materials such as carbon, silicates, alumina, zeolites and organic polymers including xerogel, sol–gel and dendrimers [15–17]. Among them, mesoporous silica materials are apparently at the top of candidate list of the supporting materials, due to their well-defined micro-structure that forms the basis of uniform active sites of the catalyst and well-controlled steric effects [18]. SBA-15 is a representative example for this type of material and has been used as support for palladium catalysts in recent years [19–24]. Chemical, mechanical and thermal stability of the support [25] is usually the first concern during support selection while ease of functionalization of the surface groups required for anchoring the catalyst or its components is a prerequisite also.

Palladium based catalysts with phosphines as the solid carrier prefunctionalization ligands are most frequently used [26], but many phosphines are sensitive to air and moisture, resulting in limitations on their applications. Alternative ligands such as carbenes [27–29], pincer ligands [19,30], palladacycles [31], and thiols [20–22] have also been successfully adopted to overcome these problems, which open up new opportunities in heterogeneous palladium catalysis. Meanwhile, nitrogen-containing ligands can form stable complexes with palladium and thus show a broad arena for developing novel silica supported palladium catalysts due to the huge availability of amine molecules with virtually unlimited possibilities of structures and steric configurations. However, as far as we know,

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the application of the amine-functionalized organic–inorganic hybrid silica materials in palladium-catalyzed carbon–carbon bond formations is rare [32–36], which may imply that selection of proper nitrogen-containing ligands deserves exploring. We have developed several phosphine-free catalytic systems for carbon–carbon bond formation [37–39] and found molecule configurations play a critical role in the performance of the catalysts. Based on these experiences, herein, a spindle-shaped molecule with two nitrogen atoms located at the both tips, 1,4-diaza-bicyclo[2.2.2]octane (DABCO), was used as a ligand to minimize hindrance for reactants approaching the palladium active sites. It is widely believed that during the catalytic cycle, the Pd(II) complexes initially present in the catalyst are reduced to Pd(0) species, and unsaturated Pd(0) complexes can interact strongly with each other to form Pd clusters thus lose its catalytic activity. Shimizu et al. have proposed that mesoporous silica itself could not effectively prevent Pd metal aggregation while ammonium salts could stabilize palladium species [40]. A DABCO functionalized SBA-15 supported palladium catalyst has been synthesized and its catalytic properties in the homocoupling reaction of terminal alkynes to conjugated 1,3-diynes have been examined. Under the selected conditions, the reaction could be carried out smoothly and effectively using air as an oxidant. Furthermore, the catalyst was also proved to be comparatively effective for the Suzuki cross-coupling reaction with the reported polymer-supported DABCO-palladium [41].

## 2. Experimental

### 2.1. Reagents and materials

Mesoporous silica SBA-15 was purchased from Fudan University. Pd(OAc)<sub>2</sub> (99%) was obtained from Strem. (3-chloropropyl) trimethoxysilane (97%), 4-iodoanisole (98%), 1-iodo-4-nitrobenzene (98%), 4-bromoanisole (98%), 4-bromotoluene (98%), 4'-chloroacetophenone (98%), but-3-yn-2-ol (98%), phenylacetylene (98%), CuI (99.999%) were obtained from Alfa Aesar. DABCO (97%), 1-bromo-4-nitrobenzene (99%), 4-chloronitrobenzene (98%), 4'-bromoacetophenone (98%), phenylboronic acid (98%), 4-ethynyltoluene (97%), 4-fluorophenylacetylene (98%), but-3-yn-1-ol (97%), 3,3-dimethylbut-1-yne (98%), hex-1-yne (98%) were obtained from Acros. Iodobenzene (CP) and biphenyl (CP) were obtained from Sinopharm Chemical Reagent Co., Ltd. 4-methoxyphenylboronic acid (98%), 2-methylbut-3-yn-2-ol (98%), hex-5-yn-1-ol (98%) were purchased from Lancaster. Bromobenzene (98%, Shanghai Qingpu Chemical Reagent Company), dec-1-yne (98%, International Laboratory, USA), K<sub>2</sub>CO<sub>3</sub> (99%, Shanghai Chemical Reagent Company of Chinese Medical Group) were used as received without any further pretreatment. Toluene (Tianjin Chemical Reagent Co., Ltd.) and dichloromethane (Tianjin Chemical Reagent Co., Ltd.) were analytical grade and dried over CaH<sub>2</sub> and distilled before use. All other solvents were analytical grade and used without further purification.

### 2.2. Characterization

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/Max 2400 using CuK $\alpha$  radiation with the following operating parameters: 60 mA, 40 kV, 2 $\theta$  scanning from 0.5° to 6° for low-angle XRD. Nitrogen physical adsorption was carried out on a Micrometrics ASAP2010 volumetric adsorption analyzer. The Brunauer–Emmett–Teller (BET) surface area was evaluated from data in the relative pressure range from 0.05 to 0.20. The total pore volume of each sample was estimated from the amount adsorbed at the highest  $P/P^0$  (at 0.99). Pore diameters were determined from the adsorption branch using Barrett–Joyner–Halenda (BJH) method. Palladium content was analyzed by an IRIS Advantage

ICP/AES, Thermo Jarrel Ash, Franklin, MA, USA). X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALAB 210 X-ray photoelectron spectrometer, using Monochrome MgK $\alpha$  as the excitation source. Th. C and N content analyses were conducted on a Vario EL (Elementar). High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM2010 (JEM2010, JEOL) microscope operated at 200 kV. The conversion was determined by gas chromatography (GC7890II, Techcomp) analysis equipped with a SE-54 column (30 m  $\times$  0.32 mm  $\times$  0.50  $\mu$ m film thickness) and a flame ionization detector (FID) using biphenyl as an internal standard. The injection temperature, column temperature and detection temperature were set to 280, 240 and 300 °C, respectively.

### 2.3. Preparation of SBA-15@DABCO-Pd

#### 2.3.1. Synthesis of SBA-15@Cl

In the typical procedure, parent silica based SBA-15 (1 g) was firstly dispersed in boiling toluene (25 mL) and then (3-chloropropyl) trimethoxysilane (1.5 mL) was added dropwise. The mixture was refluxed for 24 h. The resultant solid contents was recovered by filtration and extracted thoroughly in a Soxhlet extractor with dichloromethane before dried in vacuum at 70 °C for 5 h. This solid powder was designated as SBA-15@Cl.

#### 2.3.2. Preparation of SBA-15@DABCO

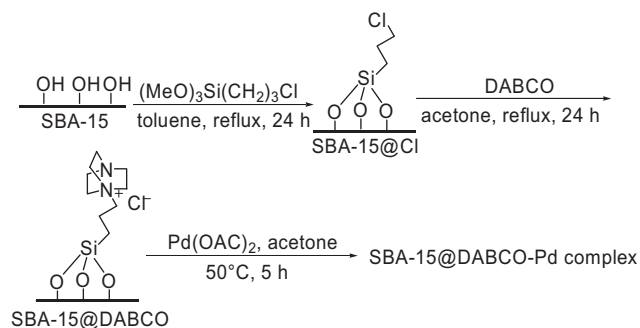
SBA-15@Cl (1 g) was refluxed with DABCO (73 mg) in acetone (60 mL) for 24 h under argon atmosphere. The resulting solid powder was recovered by filtration and extracted with dichloromethane in a Soxhlet extractor overnight and then dried in vacuum at 50 °C for 4 h. The white powder, designated as SBA-15@DABCO, was collected.

#### 2.3.3. Immobilization of palladium salt in the pore channels of DABCO-functionalized mesoporous silica SBA-15 (SBA-15@DABCO-Pd)

Typically, SBA-15@DABCO (1 g) was refluxed with Pd(OAc)<sub>2</sub> (117.6 mg) in acetone (30 mL) at 50 °C for 5 h. After filtration, the resulting solid powder was washed three times with ethyl ether (10 mL) and methanol (10 mL), respectively, and then dried under air. Finally, the yellow powder was collected. We designated it as SBA-15@DABCO-Pd complex. The whole process is illustrated in Scheme 1 [21].

### 2.4. Typical procedure for the SBA-15@DABCO-Pd catalyzed homocoupling reactions of terminal alkynes

A mixture of alkyne (0.8 mmol), SBA-15@DABCO-Pd (0.23 mol%), CuI (1.0 mol%), DABCO (0.8 mmol, 1 equiv.), and CH<sub>3</sub>CN (4 mL) was stirred at room temperature for the desired time until complete



Scheme 1. Preparation of SBA-15@DABCO-Pd complex.

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