



Structure–property relationships of copper modified mesoporous TiO₂ materials on alkyne homocoupling reactions



Zhu Luo^a, Shaylin A. Cetegen^b, Ran Miao^c, Ting Jiang^b, Sheng-Yu Chen^c, Tahereh Jafari^a, Yashan Zhang^c, Steven L. Suib^{a,b,c,*}

^a Institute of Materials Science, U-3136, University of Connecticut, Storrs, CT 06269, United States

^b Department of Chemical and Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States

^c Department of Chemistry, U-3060, University of Connecticut, Storrs, CT 06269-3060, United States

ARTICLE INFO

Article history:

Received 22 January 2016

Revised 6 March 2016

Accepted 7 March 2016

Available online 16 March 2016

Keywords:

UCT mesoporous TiO₂

Heterogeneous catalysis

Homocoupling

Supported materials

ABSTRACT

Three different modification (doping, solvent free, and impregnation) methods were used to obtain a series of mesoporous Cu–TiO₂ materials with various copper loading amounts (0–15 mol%). The influence of the modification procedure on the physico-chemical properties was characterized by PXRD, N₂ sorption, SEM, EDX elemental mapping, and XPS techniques. The presence of copper species has been detected either in the TiO₂ lattice as Cu⁺ (via doping methods) or on the surface of TiO₂ as CuO species (via solvent free and impregnation methods). With the modification of Cu, the surface area of mesoporous Cu–TiO₂ materials can be increased up to 128 m²/g. The catalytic activities of Cu–TiO₂ materials were investigated using the alkyne–alkyne homocoupling reaction with air as the sole oxidant under mild reaction conditions without any additives. The doped Cu–TiO₂ materials show the highest catalytic activity (1,4-diphenyl-1,3-butadiyne yields > 99%). The different catalytic mechanisms, active sites, and structure–property relationships of all the catalysts are discussed. Definitive features affecting the catalytic performance of the obtained Cu–TiO₂ materials are the loading amounts and the states of Cu, surface area, and pore size distributions. Reusability tests were conducted on the collected sample without washing, and 74% yield was achieved even after three cycles.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Carbon–carbon triple bond compounds occur widely in nature. Among them, diyne derivatives are a very important class of compounds with significant antibacterial, anti-HIV, anticancer, and anti-inflammatory biological activities [1]. In particular, 1,3-Diynes have a rod-like molecular shape and high rigidity, which play important roles in the construction of molecular complexes and serve as connectors to build up conjugated polymers, liquid crystals, and nonlinear optic materials, etc. [2,3].

Given their significance, synthesis of 1,3-Diynes has attracted a great deal of attention. The most widely used procedure for preparing symmetrical diynes is the oxidative alkyne homocoupling reaction [4–6]. Generally, the metal catalyzed homocoupling of terminal alkynes is the most efficient route. Due to the efficiency and mildness, the combination of palladium (Pd) and copper salts is the most straightforward process for homocoupling reactions

[7–9]. However, the high cost of Pd and the air-sensitive experimental conditions limit their wider applicability. Another concern is the most of the reported systems are homogeneous and have shortcomings such as the difficulty of catalyst/product separation and reusability [10,11]. Among the heterogeneous systems, copper based catalysts [CuI, CuCl, Cu(OH)₂, Cu(OAc)₂] with appropriate additives and oxygen as an oxidizing agent have been applied for homocoupling [12–15]. Although the copper catalyzed homocoupling system has been studied for decades, the development of efficient heterogeneous systems for homocoupling reactions without any additives still poses a challenge from economical and environmental viewpoints [16,17]. Moreover, it is not efficient to use copper materials without any supports based on previous studies [18].

No homocoupling reactions proceeded with only bulk copper oxide such as CuO and Cu₂O [19]. Highly dispersed copper species are indispensable for high catalytic homocoupling activity. Therefore, an appropriate support that facilitates the dispersion of copper species is necessary for the homocoupling catalytic system. Titanium dioxide (TiO₂) is one of the most studied metal oxide supports for heterogeneous catalytic systems [20,21]. TiO₂ is cheap, environmentally friendly, and can be easily incorporated with

* Corresponding author at: Institute of Materials Science, U-3136, University of Connecticut, Storrs, CT 06269, United States.

E-mail address: steven.suib@uconn.edu (S.L. Suib).

other elements [22]. Mesoporous TiO₂ has a high specific surface area, uniform pore-size distribution in the targeted range and chemical stability. These attributes make mesoporous TiO₂ a promising candidate to serve as a support in the homocoupling catalytic system. Moreover, the strong interactions between TiO₂ and the incorporated elements (such as C, Au, Cu, and Pt), prevent surface agglomeration and enhance the dispersion of incorporated species [23,24].

Herein, we prepared the copper modified TiO₂ materials via three different methods to achieve different Cu species. The mesoporous TiO₂ support was prepared using previously developed UCT methods [25]. The incorporation of copper is mainly done through three ways, doping, solvent free, and impregnation methods. In the doping method, a copper source [Cu(NO₃)₂] was added to the titanium source simultaneously in the beginning of the synthesis. As a result, copper appears as Cu⁺ species in the TiO₂ lattice. For the impregnation and the solvent free methods, the copper source was incorporated into prepared TiO₂ powders with or without solvent (butanol), respectively. As a consequence, copper exists as CuO species on the TiO₂ surface. This study compared the different homocoupling catalytic activities of different copper species with the same mesoporous TiO₂ support. Special attention was paid to study the structure–property relationships on the catalytic activity. The highest homocoupling catalytic activity is attributed to the large surface area, appropriate pore size, and the existence of Cu (I) species.

2. Experimental

2.1. Chemicals

Titanium (IV) isopropoxide (≥97%), 1-butanol (anhydrous, 99.8%), Poly(ethylene glycol)-block-Poly(propylene glycol)-block-Poly(ethylene glycol) PEO₂₀-PPO₇₀-PEO₂₀ (Pluronic P123), Copper (II) nitrate trihydrate, Phenylacetylene, Toluene (≥99.8%) were purchased from Sigma–Aldrich. Concentrated nitric acid (HNO₃, 68–70%) was purchased from J.T. Baker. All chemicals were used as received and used without further purification.

2.2. Catalyst preparation

The mesoporous TiO₂ material was prepared based on the previously developed UCT inverse micelle templated sol–gel approach [25]. The copper source was incorporated into the mesoporous TiO₂ system using three different methods, doping, solvent free, and impregnation methods.

In the doping method, X mol Cu(NO₃)₂·3H₂O ($X = 0.0005, 0.001, 0.0015$ mol) was added to titanium precursor solution [0.01 mol (2.84 g) of titanium isopropoxide was dissolved in a solution containing 0.094 mol (7 g) of 1-butanol, 0.016 mol (1 g) of HNO₃ and 1.72×10^{-4} mol of P123 surfactant in a 150 mL beaker at room temperature (RT)]. A clear bright blue gel was obtained after 30 min of magnetic stirring and was then placed in an oven at 120 °C for 4 h. For all doped samples, the obtained dark green, transparent (rigid) films were calcined in a furnace under air at 450 °C for 4 h. The doped samples were labeled as $M\%Cu-TiO_2-D$, where M is the mol% of copper ($M = 5\%, 10\%, 15\%$), D is the abbreviation for doping.

In the solvent free method, mesoporous TiO₂ was first prepared without incorporating any copper source. The achieved TiO₂ powder was mixed together with Cu(NO₃)₂·3H₂O in an agate mortar, with a different molar ratios (Cu/Ti = 5, 10, 15 mol%) for 30 min. The obtained mixture was then calcined in a furnace under air at 450 °C for 4 h. The solvent free samples were labeled as $M\%Cu-TiO_2-SF$, where M is the mol% of copper ($M = 5\%, 10\%, 15\%$).

In the impregnation method, mesoporous TiO₂ was first prepared without incorporating any copper source. The achieved TiO₂ powder was introduced into a beaker containing 3 mL aqueous solution of Cu(NO₃)₂·3H₂O. The Cu/Ti ratios were kept at 5%, 10%, and 15%. After stirring for 3 h, the mixture solution was dried overnight in an 80 °C oven. The obtained light blue powder was then calcined in a furnace under air at 450 °C for 4 h. The impregnation samples were labeled as $M\%Cu-TiO_2-IMP$, where M is the mol% of copper ($M = 5\%, 10\%, 15\%$).

2.3. Characterization

Powder X-ray diffraction (PXRD) analyses were performed on a Rigaku Ultima IV diffractometer (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$) with an operating voltage of 40 kV and a current of 44 mA. Nitrogen (N₂) sorption experiments were conducted on a Quantachrome Autosorb-1-1C automated sorption system. The powders were degassed at 150 °C for 3 h prior to the measurements. The surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and the pore size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method from the desorption isotherm. Morphological characterization was done using an FEI Nova NanoSEM 450 with an accelerating voltage of 2.0 kV. Energy dispersive X-ray spectroscopy (EDX) was performed on an Oxford Aztec Energy microanalysis system with an X-Max 80 silicon drift detector. X-ray photoelectron spectroscopy (XPS) measurements were performed in a PHI model 590 spectrometer with multiprobes (Φ Physical Electronics Industries Inc.), using Al K α radiation ($\lambda = 1486.6 \text{ eV}$) operated at 250 W. The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard.

2.4. Catalytic activity measurements

A typical procedure for the alkyne homocoupling reaction is as follows. A mixture of phenylacetylene (0.5 mmol), $M\%Cu-TiO_2$ catalysts (50 mg), and toluene (3 mL) was added in a 25 mL round-bottom flask equipped with a condenser. The reaction mixture was heated to reflux under vigorous stirring (600 rpm) for the required time (1–3 h). After reaction, the catalyst was removed by filtration. The liquid product was collected and analyzed by GC/MS (gas chromatography/mass spectrometry).

3. Results

To prepare copper based catalysts, previously reported UCT mesoporous TiO₂ was chosen as the support [25]. Copper nitrate [Cu(NO₃)₂] was used as the copper precursor. The copper source was introduced into the mesoporous TiO₂ systems via three different preparation methods (doping, solvent free, and impregnation). Different forms of copper (either present in the TiO₂ lattice, or as copper oxide on the TiO₂ surface) are expected. Besides the introduction methods of copper, all the other preparation processes are the same. Fig. 1 shows the powdered X-ray diffraction (PXRD) patterns of Cu–TiO₂ samples with different preparation methods, doping (Fig. 1a), solvent free (Fig. 1b), and impregnation (Fig. 1c) methods. For each of the methods, samples with different concentrations (5–15%) of copper were synthesized. As a comparison, the PXRD pattern of bare TiO₂ is plotted in each figure (Fig. 1a–c). In Fig. 1a, copper was introduced into the TiO₂ structure as a dopant. With the increase in copper content (0–15%), the crystallinity of each sample did not significantly change. Compared to bare TiO₂ (black pattern), doped samples show no new diffraction lines that correspond to copper oxide species (CuO or Cu₂O), indicating the copper precursor (Cu²⁺) was successfully doped into the TiO₂

Download English Version:

<https://daneshyari.com/en/article/60621>

Download Persian Version:

<https://daneshyari.com/article/60621>

[Daneshyari.com](https://daneshyari.com)