Structure-Property Relationships of Copper Modified Mesoporous TiO₂ Materials on Alkyne Homocoupling Reactions

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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 to 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 have 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.

Keywords UCT mesoporous TiO₂; Heterogeneous catalysis; Homocoupling; Supported materials

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][5][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][8][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][13][14][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 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 $[\text{Cu}(\text{NO}_3)_2]$ was added to the titanium source simultaneously in the beginning of the synthesis. As a result, copper appears as Cu^+ species in the TiO_2 lattice. For the impregnation and the solvent free methods, the copper source was incorporated into prepared TiO_2 powders with or without solvent (butanol), respectively. As a consequence, copper exists as CuO species on the TiO_2 surface. This study compared the different homocoupling catalytic activities of different copper species with the same mesoporous TiO_2 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 $\text{Cu}(\text{I})$ species.

2. Experimental

2.1 Chemicals

Titanium (IV) isopropoxide ($\geq 97\%$), 1-butanol (anhydrous, 99.8%), Poly(ethylene glycol)-block-Poly(propylene glycol)-block-Poly (ethylene glycol) $\text{PEO}_{20}\text{-PPO}_{70}\text{-PEO}_{20}$ (Pluronic P123), Copper(II) nitrate trihydrate, Phenylacetylene, Toluene ($\geq 99.8\%$) were purchased from Sigma-Aldrich. Concentrated nitric acid (HNO_3 , 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 TiO_2 material was prepared based on the previously developed UCT inverse micelle templated sol-gel approach.[25] The copper source was incorporated into the mesoporous TiO_2 system using three different methods, doping, solvent free, and impregnation methods.

In the doping method, X mol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ($X = 0.0005, 0.001, 0.0015$ 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 HNO_3 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 $M\%\text{Cu-TiO}_2\text{-D}$, where M is the mol% of copper ($M = 5, 10, 15\%$), D is the abbreviation for doping.

In the solvent free method, mesoporous TiO_2 was first prepared without incorporating any copper source. The achieved TiO_2 powder was mixed together with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 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 in air at 450°C for 4 h. The solvent free samples were labeled as M%Cu-TiO₂-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-TiO₂-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, λ =1.5406 Å) 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 (Physical Electronics Industries Inc.), using Al K α radiation (λ =1486.6 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-TiO₂ 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

Figure 1. Cu-TiO₂ samples with various copper loading amounts (0~15 mol%, from bottom to top pattern) prepared by different methods: (a) doping method, (b) solvent free method, and (c) impregnation method.

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. **Figure 1** shows the powdered X-ray diffraction (PXRD) patterns of Cu-TiO₂ samples with different preparation methods, doping (**Figure 1a**), solvent free (**Figure 1b**), and impregnation (**Figure 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 (**Figure 1a-c**). In **Figure 1a**, copper was introduced into the TiO₂ structure as a dopant. With the increasing of 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 lattice without changing the bulk structure. However, by using the solvent free method (**Figure 1b**), the as-synthesized Cu-TiO₂-SF samples possess different crystalline properties. In **Figure 1b**, new diffraction lines were observed in samples with higher copper concentrations (10%Cu-TiO₂ SF, 15%Cu-TiO₂ SF), which can be indexed to (002) planes of CuO species.[26] With higher concentration of copper, the (002) plane displays higher intensity, further manifesting the existence of CuO species. In **Figure 1c**, the Cu-TiO₂ samples prepared by the impregnation methods exhibit similar crystalline properties with SF samples. Diffraction lines belonging to CuO species were observed. Moreover, the CuO species started to appear in the 5%Cu-TiO₂-IMP sample, as the existence of a weak diffraction peak around 35.4° which index to the (002) planes of CuO.[27] In summary, by comparing these three types of Cu-TiO₂ samples,

1 copper oxide (CuO) species can be most easily prepared via the impregnation method. No copper oxide
 2 can be observed in any of the doped samples.

Figure 2. Scanning electron microscopy (SEM) images of 10%Cu-TiO₂-D, 10%Cu-TiO₂-SF, and 10%Cu-TiO₂-IMP samples. Different scales of magnification were used: (a)-(c) 5 μm; (d)-(f) 1 μm.

Not only are the crystal structures of Cu-TiO₂ samples significantly different, but also the morphologies of each sample are distinct. According to the SEM image (**Figure 2a**), the 10%Cu-TiO₂-D sample displays a relatively smooth surface, without the deposition of copper oxide species (CuO, Cu₂O) on the surface. The copper source (Cu²⁺) may be introduced into the TiO₂ lattice as a dopant. However, both 10%Cu-TiO₂-SF (**Figure 2b**) and 10%Cu-TiO₂-IMP (**Figure 2c**) show rough surfaces, with clusters of particles deposited on the surface, which may be copper oxide species. With higher magnification, a porous structure can be observed in the 10%Cu-TiO₂-D sample (**Figure 2d**). Pores with diameters around 100 nm are well dispersed on the surface of TiO₂. No pores could be detected with the same magnification of 10%Cu-TiO₂-SF (**Figure 2e**) or the 10%Cu-TiO₂-IMP (**Figure 2f**) samples. The surfaces of these two samples were covered with copper oxide species. The SEM results are in agreement with the XRD results. No copper oxide species were detected for the 10%Cu-TiO₂-D sample. Copper oxide (CuO) only appears in 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples.

Figure 3. SEM images with EDX element mapping results of as-prepared (a) 10%Cu-TiO₂-D, (b) 10%Cu-TiO₂-SF, and (c) 10%Cu-TiO₂-IMP samples. Oxygen, titanium, and copper elements were mapped. Scale bars of all images are 5μm.

The EDX elemental mapping technique was further applied to study the dispersion of copper. The elemental mapping of O, Ti, and Cu are shown in **Figure 3**. **Figure 3a** shows that all the elements are distributed uniformly in the whole test area, indicating that Cu existed orderly and uniformly throughout the TiO₂ lattice of the 10%Cu-TiO₂-D sample. The map of O, Ti, and Cu elements fit into the sample morphology, in accordance with XRD (**Figure 1a**) and SEM results (**Figure 2**). No separate CuO species appear on the surface of TiO₂. In 10%Cu-TiO₂-SF (**Figure 3b**) and 10%Cu-TiO₂-IMP (**Figure 3c**) samples, copper is present in the area where there is less titanium. A phenomenon of mutual exclusion was observed between TiO₂ and CuO species. In the elemental mapping of 10%Cu-TiO₂-IMP, especially in the area of CuO gathered, only a very weak Ti signal was detected. Thus, the clusters that deposited on the surface (**Figure 2e, f**) of 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples can be determined for the CuO species that are present separately from the TiO₂ lattice.

Figure 4. N₂ sorption isotherms for (a) bare TiO₂, (b) 10%Cu-TiO₂-D, (c) 10%Cu-TiO₂-SF, and (d) 10%Cu-TiO₂-IMP. The inset figures are the BJH desorption pore-size distribution for each sample (a) 3.4 nm, (b) 4.9 nm, (c) 3.4 nm, and (d) 3.4 nm.

The N₂ adsorption-desorption isotherms and the BJH pore size distribution plots of prepared mesoporous TiO₂ and all Cu-TiO₂ samples are displayed in **Figure 4**. All the isotherms show the typical Type IV isotherm, which is characteristic of mesoporous materials. The bare mesoporous TiO₂ (**Figure 4a**) has a hysteresis loop close to Type H2, which usually refers to an ink-bottle pore with a pore connecting to a smaller pore.[28] With the introduction of Cu into the TiO₂ system, the hysteresis loops of all Cu-TiO₂ samples are different, suggesting a different pore shape, network, and distribution status. The 10%Cu-TiO₂-D sample (**Figure 4b**) has two hysteresis loops, indicating a bimodal pore size distribution in the mesoporous (2-50 nm) and macroporous (> 50 nm) regions. The inset image of **Figure 4b** shows the BJH pore size distribution in the mesoporous region of 10%Cu-TiO₂-D (4.9 nm) is larger than bare TiO₂ (3.4 nm), implying the impact of Cu on the TiO₂ structure. The hysteresis loop of 10%Cu-TiO₂-D in the 0.7-0.9 p/p_0 range suggests another pore size distribution in the macroporous region, which is in accordance with SEM results. The macropore sizes of 10%Cu-TiO₂-D that were measured from SEM image (**Figure 2d**) are around 80 nm. In contrast, the isotherms and the hysteresis loops of 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples (**Figure 4c, d**) are not too different as compared to bare TiO₂. The BJH pore size distributions were preserved (3.4 nm) after Cu incorporation. However, the analysis of pore

size distribution based on desorption branch sometimes can be misinterpreted due to a tensile strength effect (TSE). The TSE is common for mesoporous materials in Type VI isotherms and with hysteresis loops of Type H2 or H3. With the TSE, a sudden drop of the desorption curve in the p/p_0 range (0.42-0.45) leads to an incorrect BJH model. [29] In order to figure out whether TSE has a significant effect on our samples, the BJH models were further analyzed for adsorption curves in **Figure S1**. All BJH models analyzed based on adsorption isotherms (black curves) have slightly broader and larger pore size distributions than those obtained from desorption isotherms (blue curves). The 10%Cu-Ti-SF (4.3 nm) and 10%Cu-Ti-IMP (4.0 nm) samples still have similar pore sizes with TiO₂ (4.3 nm). A centered pore size distribution at 6.5 nm can be observed for the 10%Cu-Ti-D sample (**Figure S1b**). No matter which analysis methods (adsorption/desorption) were used, the pore size trend of all samples is the same, TiO₂ $\approx$ 10%Cu-Ti-SF $\approx$ 10%Cu-Ti-IMP < 10%Cu-Ti-D. Above all, the N₂ isotherms and all the pore size distribution analyses indicated that the doped Cu system possesses the largest structural change compared to bare TiO₂.

Figure 5. XPS spectra details for (a) Cu 2p binding energy regions, (b) O 1s level for 10%Cu-TiO₂-D, 10%Cu-TiO₂-SF, and 10%Cu-TiO₂-IMP samples (from top to bottom).

The surface compositions and oxidation states of all Cu-TiO₂ samples were studied by X-ray photoelectron spectroscopy (XPS) analysis. The corresponding experimental results are displayed in **Figure 5**. All the binding energies in the XPS analysis were calibrated using the C 1s peak as an internal standard (**Figure S2**). As shown in **Figure 5a**, the peaks with the highest intensity can be assigned to Cu 2p_{3/2} and the peaks in the region of 952-954 eV are attributed to Cu 2p_{1/2}. [30] The 10%Cu-TiO₂-D sample

exhibits two main peaks at 931.2 and 951.2 eV corresponding to the Cu 2p_{3/2} and Cu 2p_{1/2} levels of the Cu⁺ state, respectively.[31] Compared to the 10%Cu-TiO₂-D sample, clear shifts toward higher binding energy level were achieved for 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples. The Cu 2p_{3/2} and Cu 2p_{1/2} levels of both samples are attributed to the Cu²⁺ state (CuO). Moreover, broad satellite peaks at 943-945 eV can be observed for 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples, both of which prove the presence of the Cu²⁺ state (CuO) on the surface.[32] The binding energies of O 1s results (**Figure 5b**) were analyzed to further study the chemical compositions. With the binding energy of 530.4 eV, the O 1s peak of 10%Cu-TiO₂-D sample was attributed to lattice oxygen.[33] The O 1s binding energy levels of 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples are slightly lower than that for 10%Cu-TiO₂-D, a clear shift towards a lower energy level can be observed in **Figure 5b**. As shown in the literature, the O 1s energy level of 529.2-529.9 eV can be assigned to lattice oxygen of CuO.[34] Therefore, the study of O 1s spectra further indicates 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples have CuO species and Cu⁺ only exists in the 10%Cu-TiO₂-D sample.

Table 1. Homocoupling of phenylacetylene (1a) by various catalysts.^[a]

Entry	Catalyst	Time	Yield 2a (%)	TON ^[b]
1	None	3	nd	-
2	TiO ₂	3	nd	-
3	5%Cu-TiO ₂ -SF	1	11	2.2
4	5%Cu-TiO ₂ -SF	2	20	4.1
5	5%Cu-TiO ₂ -SF	3	45	9.2
6	10%Cu-TiO ₂ -SF	3	16	1.6
7	15%Cu-TiO ₂ -SF	3	20	1.4
8	5%Cu-TiO ₂ -D	3	47	9.6
9	10%Cu-TiO ₂ -D	3	78	8.0
10	15%Cu-TiO ₂ -D	3	94	6.4
11	5%Cu-TiO ₂ -IMP	3	10	2.0
12	10%Cu-TiO ₂ -IMP	3	18	1.8
13	15%Cu-TiO ₂ -IMP	3	12	0.8
14	10%Cu-TiO ₂ -D 350	3	>99	10.2

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (50 mg), toluene (3 mL), 110 °C, under ambient atmosphere. Yields were determined by GC. nd = not detected (below 1 % yield). [b] Turnover number (TON) = [moles of converted substrate (phenylacetylene)] × (moles of Cu)⁻¹.

Figure 6. (a) Results of yield as a function of reaction time (0-3 h) by using solvent free method prepared catalyst (10%Cu-TiO₂-SF). Results of yield as a function of copper loading amounts (0-15 mol %) of samples prepared by different methods: (b) doping, (c) solvent free, and (d) impregnation methods.

The catalytic activities of all prepared catalysts were tested by the homocoupling reaction of phenylacetylene (**1a**) to 1,4-diphenyl-1,3-butadiyne (**1b**). All catalysts were compared in toluene under ambient atmosphere at 110 °C (**Table 1**). The focus of this study was to study how the copper concentration and the chemical status of copper affect the catalytic activity. Thus, catalysts with different concentrations of copper and with various preparation methods were tested. First, a control experiment without any catalysts was conducted. No significant amount of **1b** product can be obtained (under GC limitation, **Table 1**, entry 1). No reaction proceeded in the presence of bare mesoporous TiO₂, suggesting that TiO₂ does not have any active sites for alkyne homocoupling (**Table 1**, entry 2). However, after the introduction of copper into the TiO₂ system, the yields were significantly improved. In order to determine whether the homocoupling reaction is a time-dependent reaction, different reaction times were used (1-3 h). In **Figure 6a**, the **1b** product yield is linearly increasing with time. The effects of copper concentration were then investigated. As shown in **Figure 6b**, with higher concentration of copper, the Cu-TiO₂-D catalysts show better catalytic activity. In contrast, for Cu-TiO₂-SF catalysts, higher copper concentrations give lower yields (**Figure 6c**). Moreover, the copper concentration is also not a key factor for the Cu-TiO₂-IMP sample either (**Figure 6d**). With higher amounts of copper, no obvious increase or decrease in catalytic activity can be observed. Above all, copper is a critical factor for the

homocoupling reaction, but the increasing concentration of copper does not consequently give a higher yield.

4. Discussion

Through the studies of Cu-TiO₂ samples prepared via different methods, factors that affect the homocoupling catalytic activity can be summarized as follows:

4.1 Cu (I) and Cu (II) active sites

Copper is regarded as the active site since bare TiO₂ shows no catalytic activity during the alkyne homocoupling process. Both Cu (I) and Cu (II) species have been reported as active sites on the alkyne homocoupling reaction. Supported Cu (II) salts such as Cu(OH)₂, Cu(OAc)₂ · H₂O, and CuCl₂ serve as homocoupling catalysts that have been reported previously.[35] [36] Oishi et al. proposed a rapid electron-transfer path that use MnO₂ supported Cu (II) species as the homocoupling catalyst.[37] Cu (II) will be reduced to Cu (I) during the coupling process. The support (MnO₂) would not only act as a support but also an electron acceptor that oxidizes Cu (I) back to Cu (II). Subsequently the reduced Mn₂O₃ species are further oxidized to MnO₂ by O₂. In this study, in terms of XPS results (**Figure 5a**), Cu (II) exists in 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples. The electron-transfer path should also occur in these two samples. However, the reaction rates of these two samples are much slower than that reported for the Cu (II)/MnO₂ sample. Despite the different experimental conditions, the main difference is the support. Compared to manganese, titanium has lower electronegativity, which means Ti⁴⁺ is more difficult to attract an electron to form Ti³⁺. During the homocoupling reaction, Cu (II) was reduced to Cu (I), forming a free electron. If the free electron cannot be rapidly accepted by Ti⁴⁺ to form Ti³⁺, the entire reaction rate will be significantly decreased. This is the reason why 10%Cu-TiO₂-SF (yield = 16%) and 10%Cu-TiO₂-IMP (yield = 18%) show very low yields in coupling reactions.

Supported Cu (I) salts were also reported as efficient catalysts for coupling reactions. For example, copper (I)-modified zeolites were reported as efficient catalysts for the coupling reactions by behaving as an acidic Glaser-type catalyst.[38] The terminal alkyne will be dehydrogenated by a Cu ion and forms a Cu (I) phenylacetylide intermediate.[4] [39] With further exposure to oxygen, oxidative dimerization to diphenyldiacetylene can be obtained. In this study, based on XPS results (**Figure 5a**), Cu (I) exists in the 10%Cu-TiO₂-D sample and catalyzes the coupling reaction by following the Glaser mechanism. The proposed mechanism in the 10%Cu-TiO₂-D system will be as follows. First the phenylacetylene particle dehydrogenates on the surface of the catalyst and binds with Cu (I) sites. With further exposure to air, two adjacent Cu (I) phenylacetylide intermediates dimerize with each other and leave the surface of the

catalyst. Without the redox reactions between Cu species ($\text{Cu}^+/\text{Cu}^{2+}$) and Ti species ($\text{Ti}^{4+}/\text{Ti}^{3+}$), the reaction rate in the 10%Cu-TiO₂-D system is much higher than in the 10%Cu-TiO₂-SF or 10%Cu-TiO₂-IMP systems, which result in much higher yield (94 %). Above all, in terms of different forms of copper species, different homocoupling mechanisms were followed.

4.2 Materials properties, the decisive role of structure

Material (catalyst) properties, such as surface area, pore structure and morphologies significantly influence the catalytic activity in heterogeneous catalytic systems.[40] Generally, higher surface area brings more active sites, leading to higher catalytic activity. The surface areas of all samples have been determined by the Brunauer–Emmett–Teller (BET) theory (**Table S1**). Compared to other samples, the 10%Cu-TiO₂-D has the largest surface area (96 m²/g). In other words, with the same amount of catalysts in the homocoupling reactions, there will be more active sites on the surface of 10%Cu-TiO₂-D than on the surface of 10%Cu-TiO₂-SF or 10%Cu-TiO₂-IMP samples. Therefore, 10%Cu-TiO₂-D exhibits higher catalytic activity.

Another key element is the porous structure of all samples. In the study of zeolite supported Cu materials, the larger the pore size, the higher the yield. This occurs because the pores are able to accommodate rod-shaped diynes.[41] In this study, all the prepared materials possess a mesoporous structure, with different pore size distributions summarized in **Table S1**. Both the 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples have a pore size distribution of 3.4 nm. The pore size distribution is relatively small compared to that in the 10%Cu-TiO₂-D sample (4.9 nm). Mesopores are able to facilitate mass transport. The rod-shaped diynes can not only bind with the surface active sites, but also can be transported into the porous structure and can further interact with more active sites without blocking the pores. More importantly, according to SEM images (**Figure 2a**), 10%Cu-TiO₂-D also has macropores with a pore size of around 80 nm. With the combination of mesopores and macropores, the reagent molecules can be better diffused and transported. The catalytic activity was therefore improved.

Moreover, the effect of morphology of the material is also a critical factor for catalytic performance.[42] The differences of morphologies of all the prepared catalysts can be clearly seen from the SEM images (**Figure 2**). These differences are attributed to the different preparation methods and the differently formed copper species. The sample prepared via the doping method (10%Cu-TiO₂-D) has a relatively smooth surface. Copper exists as Cu⁺ species in the TiO₂ lattice. In contrast, samples prepared via the solvent free (10%Cu-TiO₂-SF) and the impregnation (10%Cu-TiO₂-IMP) methods have large CuO clusters on the surface. The large sizes (3 – 10 μm) of these agglomerated CuO clusters impede the close contact

between the active sites and TiO_2 support, which further depresses the catalytic activity, especially for samples prepared via solvent free methods ($\text{Cu-TiO}_2\text{-SF}$). This is shown in **Figure 6c**, with higher loading of copper, the catalytic activity is lower since high metal loadings favor particle agglomeration.[43] The surface agglomeration of CuO species gives rise to a series of negative consequences, such as reduced surface area, blocked pores, and undesirable phase transformation, which cause significant decrease in catalytic performance.[44]

Figure 7. Characterization of 10%Cu-TiO₂-D/350 sample by using (a) N₂ sorption (onset image: BJH pore size distribution at 3.4 nm); (b) SEM images with different scale bars (1, 5 μm); (c) EDX elemental mapping of oxygen, titanium, and copper elements.

To further prove that the above-discussed factors are critical for the homocoupling reaction, a sample with higher surface area, appropriate pore size, and smooth surface morphology was prepared and tested by homocoupling reactions. Based on the above catalytic results (**Table 1**), we chose the doping method as the preparation procedure, due to its highest catalytic activity. A lower calcination temperature (350 °C) was used to achieve enhanced properties. As shown in **Figure 7a**, 10%Cu-TiO₂-D/350 sample exhibits a Type IV isotherm and the pore size distribution is in the mesopore range (2-50 nm), but with much higher surface area (128 m²/g) than all other samples (**Table S1**). The morphological properties (**Figure 7a**) are similar to that for the 10%Cu-TiO₂-D sample, a relatively smooth surface and well dispersed macropores. Most importantly, copper is well dispersed in the TiO₂ lattice in terms of EDX

elemental mapping results (**Figure 7c**). The catalytic activity of the 10%Cu-TiO₂-D/350 sample was tested under identical conditions with all other samples and the results show the highest activity (> 99% yield, **Table 1**, entry 14). All the properties of the 10%Cu-TiO₂-D/350 sample are in accordance with the above discussed prerequisites for high catalytic activity, further suggesting the definite role of the structure of materials during the catalytic reaction.

4.3 The stability and recyclability

Figure 8. (a) PXRD patterns of all samples collected after homocoupling reaction. (b) The recyclability tests of 10%Cu-TiO₂-D/350 material (reaction temperature: 110 °C, reaction time: 3h, 50 mg of catalyst).

Stability is one of the most important properties of the catalysts. Thus, after being tested by the homocoupling reaction, all the catalysts were collected, dried and characterized by PXRD and EDX elemental mapping. All the PXRD patterns are shown in **Figure 8a**. Compared to XRD patterns of as-synthesized samples (**Figure 1**), no new or missing diffraction lines can be observed, indicating all the samples preserved their crystallinity and crystal structure. The diffraction lines of CuO species in 10%Cu-TiO₂-SF and 10%Cu-TiO₂-IMP samples were also preserved after homocoupling reactions, manifesting the stability of CuO species during the catalytic reaction. The stability of copper (Cu⁺ and CuO species) was further proven by elemental mapping (**Figure S3**). The high dispersion of copper was preserved in all samples after reaction in comparison to as-prepared samples (**Figure 3**) and no obvious agglomeration occurred. The recyclability tests were carried out by reusing the recycled catalyst from a previous run. The 10%Cu-TiO₂-D/350 sample was retrieved by filtration and dried in ambient air with no washing or reactivation processes (**Figure 8b**). After the three cycles of the reaction, most of the catalytic activity was preserved (yield = 74%). The small loss of catalytic activity may be due to the loss of copper active sites. In **Figure S3**, the copper elemental mapping result of 10%Cu-TiO₂-D/350 exhibits agglomeration in

a small area. This small area of agglomeration leads to slight loss of active sites, and further decreases the catalytic activity.

5. Conclusions

In this article, a series of copper modified TiO_2 materials were prepared via three methods: doping ($\text{Cu-TiO}_2\text{-D}$), solvent free ($\text{Cu-TiO}_2\text{-SF}$), and impregnation ($\text{Cu-TiO}_2\text{-IMP}$) methods. Copper appears as Cu^+ species in the TiO_2 lattice of $\text{Cu-TiO}_2\text{-D}$ samples. Copper is present as CuO species on the TiO_2 surface in $\text{Cu-TiO}_2\text{-SF}$ and $\text{Cu-TiO}_2\text{-IMP}$ samples. Through the catalytic tests on the homocoupling of terminal alkynes reactions, copper doped TiO_2 samples ($\text{Cu-TiO}_2\text{-D}$) show much higher activity (yield= 94%) than the other samples ($\text{Cu-TiO}_2\text{-SF}$ or $\text{Cu-TiO}_2\text{-IMP}$). The 1,4-diphenyl-1,3-butadiyne yield increases with higher loading amount (0-15%) of copper only in the doped samples. In solvent free and impregnation samples, the increasing concentration of copper does not consequently bring higher yields. Based on all the experimental results and discussion, large surface area, combination of mesopores (≈ 4 nm) and macropores (≈ 80 nm), and Cu(I) species as active sites, are the key factors for high catalytic activity. The 10% $\text{Cu-TiO}_2\text{-D/350}$ sample, which has the highest surface area ($128 \text{ m}^2/\text{g}$) and two pore size distributions shows the highest yield ($> 99\%$) compared to all other samples with identical reaction conditions. The majority of the high yield (74%) was preserved even after three cycles of reaction.

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References

- [1] A.L.K. Shi Shun, R.R. Tykwinski, *Angew. Chem. Int. Ed. Engl.* 45 (2006) 1034–1057.
- [2] R. Gleiter, D.B. Werz, *Chem. Rev.* 110 (2010) 4447–4488.
- [3] J. Liu, J.W.Y. Lam, B.Z. Tang, *Chem. Rev.* 109 (2009) 5799–5867.
- [4] C. Glaser, *Berichte Der Dtsch. Chem. Gesellschaft* 2 (1869) 422–424.
- [5] K. Kamata, S. Yamaguchi, M. Kotani, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed. Engl.* 47 (2008) 2407–2410.
- [6] D. Wang, J. Li, N. Li, T. Gao, S. Hou, B. Chen, *Green Chem.* 12 (2010) 45–48.
- [7] A. Lei, M. Srivastava, X. Zhang, *J. Org. Chem.* 67 (2002) 1969–1971.
- [8] I.J.S. Fairlamb, P.S. Bäuerlein, L.R. Marrison, J.M. Dickinson, *Chem. Commun.* (2003) 632–633.
- [9] A.S. Batsanov, J.C. Collings, I.J.S. Fairlamb, J.P. Holland, J.A.K. Howard, Z. Lin, T.B. Marder, A.C. Parsons, R.M. Ward, J. Zhu, *J. Org. Chem.* 70 (2005) 703–706.
- [10] W.A. Herrmann, V.P. Böhm, C.W. Gstötmayr, M. Grosche, C.-P. Reisinger, T. Weskamp, *J. Organomet. Chem.* 617–618 (2001) 616–628.
- [11] S.M. Auer, M. Schneider, A. Baiker, *J. Chem. Soc. Chem. Commun.* (1995) 2057–2058.
- [12] P. Siemsen, R. Livingston, F. Diederich, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 2632–2657.
- [13] S.E. Allen, R.R. Walvoord, R. Padilla-Salinas, M.C. Kozlowski, *Chem. Rev.* 113 (2013) 6234–6458.
- [14] A.E. Wendlandt, A.M. Suess, S.S. Stahl, *Angew. Chem. Int. Ed. Engl.* 50 (2011) 11062–11087.
- [15] C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* 111 (2011) 1780–1824.
- [16] C. Gonzalez-Arellano, A.M. Balu, R. Luque, D.J. Macquarrie, *Green Chem.* 12 (2010) 1995–2002.
- [17] F. Alonso, T. Melkonian, Y. Moglie, M. Yus, *European J. Org. Chem.* 2011 (2011) 2524–2530.
- [18] K. Yamaguchi, Y. Wang, T. Oishi, Y. Kuroda, N. Mizuno, *Angew. Chem. Int. Ed. Engl.* 52 (2013) 5627–5630.
- [19] T. Oishi, T. Katayama, K. Yamaguchi, N. Mizuno, *Chemistry* 15 (2009) 7539–7542.
- [20] Y. Shiraishi, H. Sakamoto, Y. Sugano, S. Ichikawa, T. Hirai, *ACS Nano* 7 (2013) 9287–9297.

- [21] R. Si, J. Tao, J. Evans, J.B. Park, L. Barrio, J.C. Hanson, Y. Zhu, J. Hrbek, J.A. Rodriguez, *J. Phys. Chem. C* 116 (2012) 23547–23555.
- [22] N. Khakpash, A. Simchi, T. Jafari, *J. Mater. Sci. Mater. Electron.* 23 (2011) 659–667.
- [23] F. Benaskar, V. Engels, E. V Rebrov, N.G. Patil, J. Meuldijk, P.C. Thüne, P.C.M.M. Magusin, B. Mezari, V. Hessel, L.A. Hulshof, E.J.M. Hensen, A.E.H. Wheatley, J.C. Schouten, *Chemistry* 18 (2012) 1800–1810.
- [24] R. Miao, Z. Luo, W. Zhong, S.-Y. Chen, T. Jiang, B. Dutta, Y. Nasr, Y. Zhang, S.L. Suib, *Appl. Catal. B Environ.* 189 (2016) 26–38.
- [25] Z. Luo, A.S. Poyraz, C.-H. Kuo, R. Miao, Y. Meng, S.-Y. Chen, T. Jiang, C. Wenos, S.L. Suib, *Chem. Mater.* 27 (2015) 6–17.
- [26] M.S.P. Francisco, V.R. Mastelaro, *Chem. Mater.* 14 (2002) 2514–2518.
- [27] W. Wang, Y. Zhan, G. Wang, *Chem. Commun.* (2001) 727–728.
- [28] Z. Chen, D. Cummins, B.N. Reinecke, E. Clark, M.K. Sunkara, T.F. Jaramillo, *Nano Lett.* 11 (2011) 4168–4175.
- [29] J.C. Groen, L.A. Pfeffer, J. Pérez-Ramírez, *Microporous Mesoporous Mater.* 60 (2003) 1–17.
- [30] Z. Wang, Y. Liu, D.J. Martin, W. Wang, J. Tang, W. Huang, *Phys. Chem. Chem. Phys.* 15 (2013) 14956–14960.
- [31] J. Ghijsen, L.H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G.A. Sawatzky, M.T. Czyzyk, *Phys. Rev. B* 38 (1988) 11322–11330.
- [32] Y.S. Lee, D. Chua, R.E. Brandt, S.C. Siah, J. V Li, J.P. Mailoa, S.W. Lee, R.G. Gordon, T. Buonassisi, *Adv. Mater.* 26 (2014) 4704–4710.
- [33] P.E. Laibinis, G.M. Whitesides, *J. Am. Chem. Soc.* 114 (1992) 9022–9028.
- [34] A. Amri, X. Duan, C.-Y. Yin, Z.-T. Jiang, M.M. Rahman, T. Pryor, *Appl. Surf. Sci.* 275 (2013) 127–135.
- [35] F. Alonso, M. Yus, *ACS Catal.* 2 (2012) 1441–1451.
- [36] X. Jia, K. Yin, C. Li, J. Li, H. Bian, *Green Chem.* 13 (2011) 2175.
- [37] T. Oishi, K. Yamaguchi, N. Mizuno, *ACS Catal.* 1 (2011) 1351–1354.
- [38] P. Kuhn, A. Alix, M. Kumarraja, B. Louis, P. Pale, J. Sommer, *European J. Org. Chem.* 2009 (2009) 423–429.

- [39] J. Björk, Y.-Q. Zhang, F. Klappenberger, J. V. Barth, S. Stafström, J. Phys. Chem. C 118 (2014) 3181–3187.
- [40] T. Jiang, S. Du, T. Jafari, W. Zhong, Y. Sun, W. Song, Z. Luo, W.A. Hines, S.L. Suib, Appl. Catal. A Gen. 502 (2015) 105–113.
- [41] P. Kuhn, P. Pale, J. Sommer, B. Louis, J. Phys. Chem. C 113 (2009) 2903–2910.
- [42] T. Jiang, A.S. Poyraz, A. Iyer, Y. Zhang, Z. Luo, W. Zhong, R. Miao, A.M. El-Sawy, C.J. Guild, Y. Sun, D.A. Kriz, S.L. Suib, J. Phys. Chem. C 119 (2015) 10454–10468.
- [43] F. Maillard, S. Schreier, M. Hanzlik, E.R. Savinova, S. Weinkauf, U. Stimming, Phys. Chem. Chem. Phys. 7 (2005) 385–393.
- [44] G. Tian, H. Fu, L. Jing, B. Xin, K. Pan, J. Phys. Chem. C 112 (2008) 3083–3089.

Graphical Abstract