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Short communication

Heterogeneous selective synthesis of 1,2-dihydro-1,3,5-triazines from alcohols and amidines *via* Cu/OMS-2-catalyzed multistep oxidation

Xu Meng [a], Xiuru Bi [a], Yanmin Wang [a], Gexin Chen [a], Baohua Chen [b], Zhenqiang Jing [c], Peiqing Zhao [a],*

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, China*
[b] *State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China*
[c] *Suzhou Institute of Nano-Tech and Nano-Bionic (SINANO), Chinese Academy of Sciences, Suzhou 215123, China*

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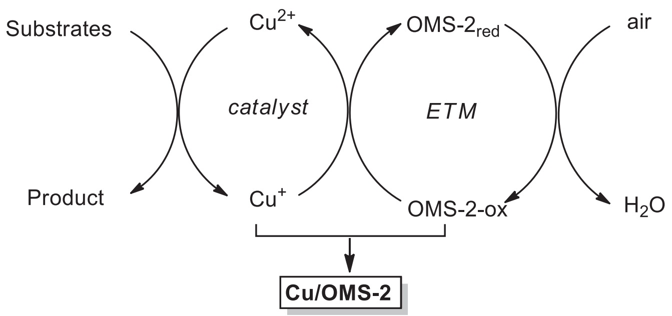
ABSTRACT

Copper supported on octahedral manganese oxide molecular sieve (OMS-2) which was obtained *via* reducing $KMnO_4$ by TBHP was prepared and found to be an efficient catalyst for the synthesis of 1,2-dihydro-1,3,5-triazines directly from alcohols and amidines in one-pot *via* multistep oxidation. The recyclable heterogeneous catalyst was characterized by BET, XRD, FTIR, TEM and SEM, and the catalytic system can tolerate a wide range of substrates under air with low catalyst loading of supported copper (0.25 mol%), employing OMS-2 as the electron-transfer mediator (ETM) and support.

1. Introduction

In recent years, multistep catalytic oxidation using green oxidants, such as O_2 and H_2O_2, has gained importance in organic synthesis and catalysis compared with direct oxidation using stoichiometric amounts of metallic oxidants because of environmental and economic factors [1]. In particular, Backväll's group developed a series of Pd/BQ/Fe(Pc)/O_2 system which can improve electron-transfer *via* decreasing the redox barriers between catalytic metals and oxidants by the use of electron-transfer mediator (ETM) [2–7]. More recently, Sundén's group reported a multistep electron transfer NHC catalytic system which was able to selectively synthesize α,β-unsaturated esters *via* the introduction of quinone and Fe(Pc) as ETMs [8]. In 2015, Largeron's group used copper as ETM to discover an *o*-iminoquinone-catalyzed multistep oxidation for the synthesis of benzimidazoles initiated by transamination process [9,10]. However, heterogeneous multistep catalytic oxidation is a more acceptable pathway compared with the aforementioned homogeneous counterparts, due to the ease in separation, recovery and recycling. Consequently, there is an incentive to develop a heterogeneous system able to catalyze the organic transformations by multistep oxidation with green oxidants by the use of recyclable catalysts.

As a part of our continuing efforts on heterogeneous synthesis, we have developed several systems for the heterocycles synthesis by employing a series of manganese oxide-supported copper (Cu/OMS-2) as catalysts and air as green oxidant [11–13]. In terms of catalytic mechanism, we envisaged the catalytic system combines two redox couples: supported Cu acts as catalytic component and is reoxidized by mixed valent OMS-2 [14–20], whereas support OMS-2 acts as ETM and is reoxidized by O_2 (Scheme 1). In this way, the electrons in an oxidation transfer quickly from substrates to green oxidant *via* multistep oxida-



Scheme 1. Aerobic multistep oxidation using Cu as catalytic metal and OMS-2 as ETM and support.

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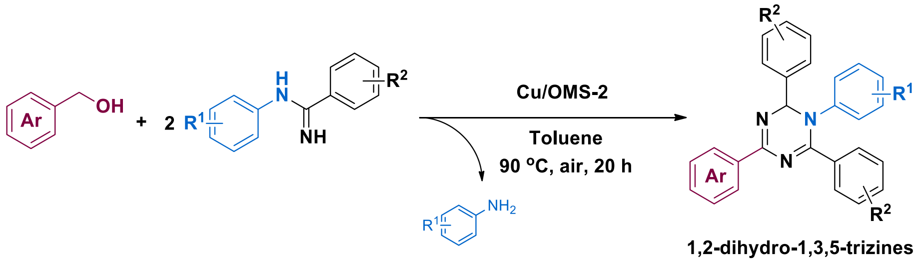
* Corresponding author.
E-mail address: zhaopq@licp.cas.cn (P. Zhao).



Scheme 2. Access to 1,2-dihydro-1,3,5-triazines catalyzed by Cu/OMS-2.

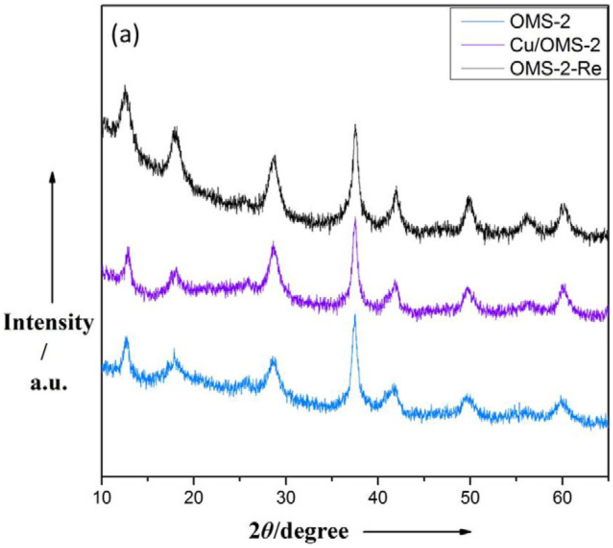


Fig. 1. The XRD patterns of OMS-2, Cu/OMS-2 and OMS-2-Re.

tion generated by Cu/OMS-2, which can avoid unselective reactions. With this in mind, we envisioned the possibility of employing recyclable Cu/OMS-2-based materials to selectively synthesize important heterocycles, like polyfunctional 1,2-dihydro-1,3,5-triazines, starting from readily available substrates through multistep oxidation.

Polyfunctional dihydro-1,3,5-triazine is one of the most important nitrogen-containing heterocycles because of their various biological activities, such as antibacterial, antimalarial, antitumor and anti-inflammatory properties [21]. Furthermore, dihydrotriazine derivatives are applied in commercialized herbicides, corrosion inhibitors and insecticides [22]. However, the synthetic methods for polyfunctional 1,2-dihydro-1,3,5-triazines are limited [23,24]. Herein, we would like to disclose that OMS-2 was prepared for the first time through the reduction of $KMnO_4$ by the low loading of TBHP and employed as support and ETM in supported catalyst Cu/OMS-2. In the presence of Cu/OMS-2, polyfunctional 1,2-dihydro-1,3,5-triazines were synthesized in a highly selective pathway directly from alcohols and N-arylamidines in one-pot *via* multistep oxidation (Scheme 2).

2. Experimental

2.1. Catalyst preparation

1 mL of TBHP (70% water solution) was added to a buffer solution consisting of 2.5 mL of acetic acid and 5 g of KOAc in 20 mL of deionized water. A solution of 3.25 g of $KMnO_4$ in 75 mL of deionized water was then added dropwise to the above mixture while stirring. The resulting solution was refluxed at 100 °C for 10 h, and the product OMS-2 was filtered, washed, dried in air at 80 °C overnight to remove water and dried at 120 °C for 2 h. Next, Support OMS-2 (2 g) was added to a 50 mL round-bottom flask. A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.05 g) in deionized water (20 mL) was added to OMS-2, and additional deionized water (6 mL) was added to wash down the sides of the flask. Then the flask was submerged into an ultrasound bath for 3 h at room temperature and stirred for further 20 h at room temperature. After that, the water was distilled under reduced pressure on a rotary evaporator at 80 °C for more than 2 h. Finally, the black powder was dried into an oven at 110 °C for 4 h followed by calcination at 350 °C for 2 h.

2.2. Typical procedure for the synthesis of dihydrotriazines

Cu/OMS-2 (10 mg, 0.25 mol%), benzyl alcohol (2 mmol), N-arylamidine (0.5 mmol), toluene (2 mL) were added to a flask with a bar. The flask was stirred at 90 °C for 20 h under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 40/1–50/1 as eluent) to yield corresponding product. The identity and purity of the products were confirmed by ^1H, ^{13}C NMR spectroscopic and HRMS analysis.

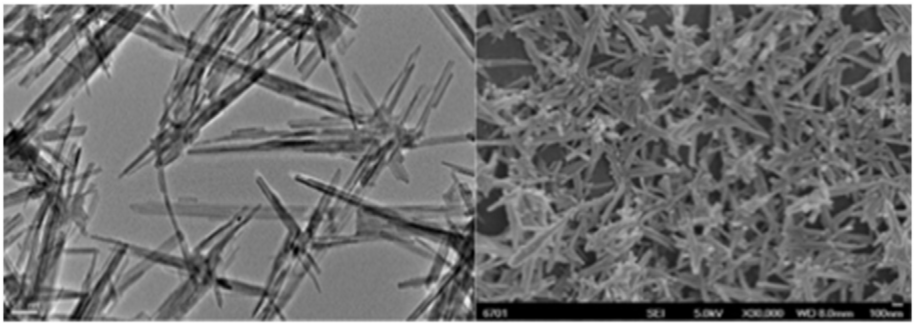


Fig. 2. The TEM and SEM images of OMS-2.