

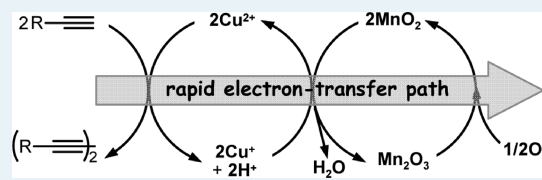
# Conceptual Design of Heterogeneous Oxidation Catalyst: Copper Hydroxide on Manganese Oxide-Based Octahedral Molecular Sieve for Aerobic Oxidative Alkyne Homocoupling

Takamichi Oishi, Kazuya Yamaguchi, and Noritaka Mizuno\*

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Supporting Information

**ABSTRACT:** The supported copper hydroxide catalyst on manganese oxide-based octahedral molecular sieve OMS-2 ( $\text{Cu}(\text{OH})_x/\text{OMS}-2$ ) was designed on the basis of the concept of coupled electron transfer. OMS-2 could act as not only a support for copper hydroxide species but also an electron-transfer mediator (cocatalyst) to generate a rapid electron-transfer path from an alkyne to dioxygen. As a result,  $\text{Cu}(\text{OH})_x/\text{OMS}-2$  showed high catalytic performance (TOF =  $540 \text{ h}^{-1}$ , total TON = 666, and selectivity >99%) and long life (13 times reuse) for aerobic oxidative alkyne homocoupling.



**KEYWORDS:** alkyne homocoupling, copper, electron transfer, heterogeneous catalysis, manganese

Diyne derivatives are a very important class of compounds and have been used as key structural elements for natural product synthesis, polymer chemistry, supramolecular chemistry, and material science.<sup>1–5</sup> Oxidative alkyne homocoupling is one of the most widely utilized procedures for the synthesis of symmetrical diynes. Generally, copper catalysts with appropriate nitrogen bases (as ligands or solvents) and dioxygen as an oxidant have been utilized for homocoupling.<sup>6–21</sup> Quite recently, efficient ligand and base-free homogeneous systems using simple copper salts such as  $\text{CuCl}$  and  $\text{Cu}(\text{OAc})_2$  in DMSO have been reported.<sup>20,21</sup> Most of the reported systems are homogeneous<sup>6–21</sup> and have shortcomings in reuse of catalysts. The development of efficient heterogeneous systems for aerobic alkyne homocoupling without any additives is still a challenging subject (see the Supporting Information and Table S1).<sup>22–28</sup>

Recently, we have reported that supported copper hydroxide on titanium oxide ( $\text{Cu}(\text{OH})_x/\text{TiO}_2$ ) can act as an efficient heterogeneous catalyst for aerobic oxidative alkyne homocoupling.<sup>22</sup> Although various alkynes could be converted into the corresponding diynes, the  $\text{Cu}(\text{OH})_x/\text{TiO}_2$ -catalyzed system possessed a serious problem: inactive copper(I) acetylide species were formed during the homocoupling, probably as a result of the slow reoxidation of copper(I) species (see Figure S1 of the Supporting Information).<sup>29</sup> As a result,  $\text{Cu}(\text{OH})_x/\text{TiO}_2$  was severely deactivated (see the later section), and the turnover frequency (TOF) and turnover number (TON) were still low (TOF =  $36 \text{ h}^{-1}$ , TON = 18; see Table S1 of the Supporting Information).

To overcome the problem, the reoxidation rate of the reduced copper species needs to be increased. Our strategy to design an efficient heterogeneous catalyst for alkyne homocoupling is generation of a rapid electron-transfer path by the combination of thermodynamically favorable electron-transfer reactions.<sup>30–32</sup> The redox potential of the  $\text{MnO}_2/\text{Mn}_2\text{O}_3$  reaction is 1.04 V and lies between those of  $\text{Cu}^{2+}/\text{Cu}^+$  (e.g., 0.67 V for  $\text{CuO}/\text{Cu}_2\text{O}$ , 0.75 V for  $\text{Cu}(\text{OH})_2/\text{Cu}_2\text{O}$ ) and  $\text{O}_2/\text{H}_2\text{O}$  (1.23 V) reactions.<sup>33</sup>

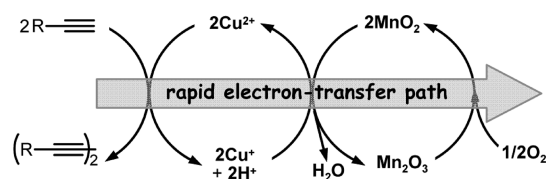
In addition, it is well-known that reduced manganese oxide can readily be reoxidized by dioxygen.<sup>34–38</sup> Therefore, if manganese oxide is used as a support for the copper hydroxide species, it would act as not only a support but also an electron-transfer mediator (cocatalyst) to generate a rapid electron-transfer path (Figure 1).<sup>39</sup> In other words, the large jump in redox potentials from a substrate (or a reduced catalyst) to dioxygen can be avoided, like biological oxidation processes. In this study, we used a manganese oxide-based octahedral molecular sieve ( $\text{KMn}_8\text{O}_{16}$ , OMS-2) because of the following excellent properties; (i) its large (external) surface area ( $\sim 100 \text{ m}^2 \text{ g}^{-1}$ ), (ii) its electron-conducting properties, and (iii) its dioxygen reduction ability.<sup>40–43</sup>

We prepared the supported copper hydroxide catalyst on OMS-2 ( $\text{Cu}(\text{OH})_x/\text{OMS}-2$ ) via the same procedure as that for  $\text{Cu}(\text{OH})_x/\text{TiO}_2$ .<sup>22</sup> As we expected,  $\text{Cu}(\text{OH})_x/\text{OMS}-2$  showed the high catalytic performance for alkyne homocoupling using dioxygen as a sole oxidant. For example, when the homocoupling of phenylacetylene (**1a**) to 1,4-diphenyl-1,3-butadiyne (**2a**) was carried out with  $\text{Cu}(\text{OH})_x/\text{OMS}-2$  (Cu: 1 mol %), 90% yield of **2a** was obtained within only 10 min (Figure 2), and the TOF was  $540 \text{ h}^{-1}$ . In contrast, the homocoupling with  $\text{Cu}(\text{OH})_x/\text{TiO}_2$  gave only 12% yield of **2a** under the same conditions (Figure 2). The catalysis for the  $\text{Cu}(\text{OH})_x/\text{OMS}-2$ -catalyzed homocoupling was truly heterogeneous,<sup>44</sup> and the retrieved catalyst could be reused at least 13 times without an appreciable loss of its high catalytic performance (Figure 3). The total TON for 14 repeated runs reached up to 666.<sup>45</sup> These TOF and TON values were much higher than those of

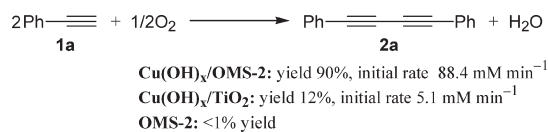
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**Figure 1.** Possible reaction path for the Cu(OH)<sub>x</sub>/OMS-2-catalyzed alkyne homocoupling via coupled electron-transfer reactions.



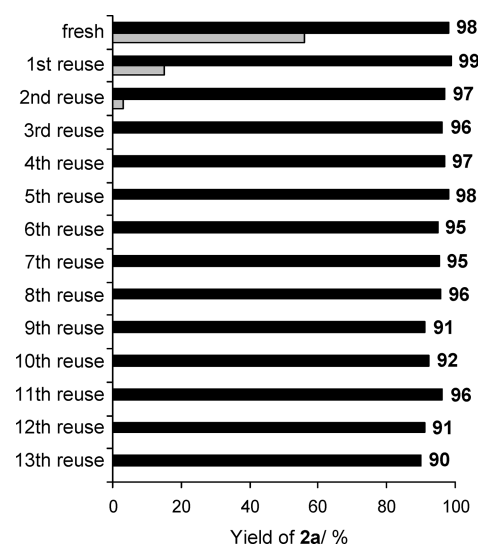
**Figure 2.** Homocoupling of **1a**. Reaction conditions: catalyst (1 mol % for Cu catalysts, 20 mg for OMS-2), **1a** (0.5 mmol), toluene (2 mL), 100 °C, 10 min, under 1 atm of O<sub>2</sub>.

previously reported heterogeneous catalysts for aerobic oxidative alkyne homocoupling (see Table S1).<sup>22–28</sup>

No reaction proceeded in the presence of just OMS-2 (Figure 2), showing that OMS-2 is not the active site for alkyne homocoupling. In the presence of the catalyst precursor CuCl<sub>2</sub>·2H<sub>2</sub>O, **2a** was not produced at all. In addition, no reaction proceeded with other simple copper(I) and copper(II) salts and complexes, such as CuSO<sub>4</sub>·5H<sub>2</sub>O, Cu(OTf)<sub>2</sub> (OTf = triflate), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (OAc = acetate), CuCl, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>, and copper(I) phenylacetylide ([Cu(I)(C≡CPh)]<sub>n</sub>) in toluene, DMF, and acetonitrile. Although the homocoupling of **1a** with CuCl, CuSO<sub>4</sub>·5H<sub>2</sub>O, and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O in DMSO proceeded to some extent (4–22% yields with 5 mol % catalyst), the performance of Cu(OH)<sub>x</sub>/OMS-2 (90% yield with 1 mol % catalyst) was much higher than those of the copper salts (see Table S2). No homocoupling proceeded with bulk copper oxides and hydroxide such as CuO, Cu<sub>2</sub>O, Cu(OH)<sub>2</sub>, and CuAl-LDH (LDH = layered double hydroxide). In addition, no reaction proceeded with a simple physical mixture of Cu(OH)<sub>2</sub> and OMS-2. All these results show that the highly dispersed copper hydroxide species on OMS-2 is indispensable for the high catalytic performance.

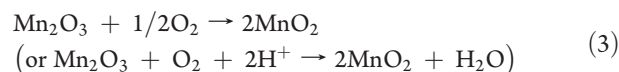
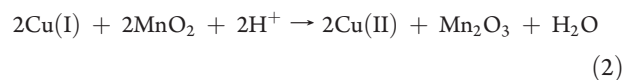
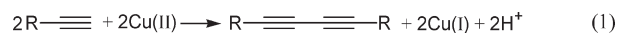
The catalytic reaction rate of Cu(OH)<sub>x</sub>/OMS-2 (under the conditions described in Figure 2) was 88.4 mM min<sup>-1</sup> and 17 times larger than that of Cu(OH)<sub>x</sub>/TiO<sub>2</sub> (5.1 mM min<sup>-1</sup>), suggesting that the reoxidation of copper(I) species is effectively promoted by OMS-2.<sup>46,47</sup> In contrast with the severe deactivation of Cu(OH)<sub>x</sub>/TiO<sub>2</sub> (see gray bars in Figure 3), Cu(OH)<sub>x</sub>/OMS-2 could be reused many times (see black bars in Figure 3), and the oxidation state of copper species in Cu(OH)<sub>x</sub>/OMS-2 was 2+, even after the 13th reuse (confirmed by X-ray photoelectron spectroscopy, Figure S2 of the Supporting Information).<sup>48</sup> Thus, the design of the efficient heterogeneous catalyst for alkyne homocoupling with high performance and long life could be realized by enhancing the reoxidation of reduced copper species.

Next, the role of OMS-2 was investigated. When Cu(OH)<sub>x</sub>/TiO<sub>2</sub> (Cu: 10 μmol) was treated with **1a** under Ar atmosphere, an almost equimolar amount of **1a** (9.3 μmol) with respect to the copper species in Cu(OH)<sub>x</sub>/TiO<sub>2</sub> was converted into **2a** within a few seconds, and then the reaction completely stopped (Figure 4b).<sup>49</sup> In this case, hydrogenated byproducts, for example, styrene and enynes, as well as H<sub>2</sub> were not formed. Thus, the following reaction (eq 1) takes place for Cu(OH)<sub>x</sub>/

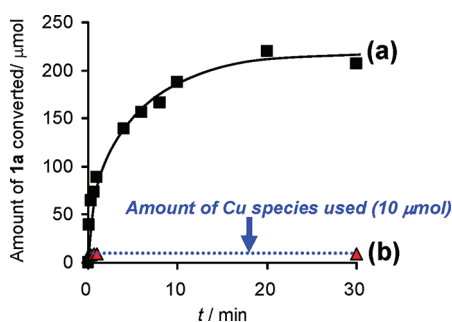


**Figure 3.** Reuse experiments. After the homocoupling, the catalyst was retrieved by filtration. The retrieved catalyst was washed with acetone and water and then dried in vacuo prior to using the next reuse. Black and gray bars indicate the reuse experiments with Cu(OH)<sub>x</sub>/OMS-2 and Cu(OH)<sub>x</sub>/TiO<sub>2</sub>, respectively. Reaction conditions: catalyst (Cu: 2 mol %), **1a** (0.5 mmol), toluene (2 mL), 100 °C, 10 min for Cu(OH)<sub>x</sub>/OMS-2, 60 min for Cu(OH)<sub>x</sub>/TiO<sub>2</sub>, under 1 atm of O<sub>2</sub>.

TiO<sub>2</sub>. In contrast, when the same reaction was carried out with Cu(OH)<sub>x</sub>/OMS-2 (Cu: 10 μmol), the amount of **1a** converted to **2a** (220 μmol for 20 min) much exceeded that of the copper species in Cu(OH)<sub>x</sub>/OMS-2 (Figure 4a). This result clearly indicates that the reoxidation of reduced copper species takes place even under Ar atmosphere, in addition to the reaction in eq 1.<sup>39</sup> It is thermodynamically possible that the reoxidation (electron-transfer from reduced copper species to OMS-2) proceeds according to eq 2. Under catalytic turnover conditions, the reduced manganese species can be reoxidized by dioxygen (eq 3).<sup>34–38</sup> The larger (catalytic) reoxidation rate of copper species in Cu(OH)<sub>x</sub>/OMS-2 is likely attributed to the reactions in eqs 2 and 3.<sup>47</sup>

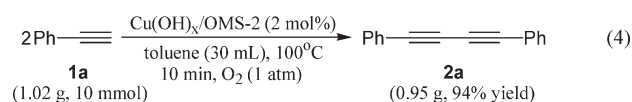


Finally, we turned our attention to the synthetic scope of the Cu(OH)<sub>x</sub>/OMS-2-catalyzed alkyne homocoupling (Table 1). In all cases, selectivities to the desired diynes were >99%. The products (diynes) could easily be isolated by simple column chromatography on silica gel, and the isolated yields for some diynes are reported in Table 1 (see values in the parentheses). The oxidative homocoupling of phenylacetylene derivatives (**1a–1j**) with electron-donating as well as -withdrawing substituents at various positions efficiently proceeded to give the corresponding 1,4-diphenyl-1,3-diyne derivatives. Although a longer reaction time (40 min) was required under an air atmosphere, the homocoupling of **1a** efficiently proceeded to give a quantitative yield of **2a** (see entry 2). No dehalogenation proceeded in the case of



**Figure 4.** Reaction profiles for the homocoupling of **1a** with (a)  $\text{Cu}(\text{OH})_x/\text{OMS-2}$  and (b)  $\text{Cu}(\text{OH})_x/\text{TiO}_2$  under Ar atmosphere. Reaction conditions: catalyst (Cu: 2 mol %, **1a** (0.5 mmol), toluene (2 mL), 100 °C, under 1 atm of Ar.

halogen-substituted phenylacetylene derivatives (**1f–1h**). A hetero-aromatic alkyne (**1k**) was also converted into the corresponding diyne. Interestingly, with regard to less reactive aliphatic alkynes (**1l–1o**), the reactions also smoothly proceeded to give the corresponding aliphatic diynes. An enyne (**1p**) gave the corresponding diyne in high yield. Furthermore, the present system could be applied to the homocoupling of a silylacetylene derivative (**1q**). The homocoupling of a propargylic alcohol (**1r**) and a propargylic amine (**1s**) also efficiently proceeded. Even in the case of the gram-scale transformation of **1a** (1.02 g, 20-fold scale-up), the reaction efficiently proceeded to afford 0.95 g of **2a** (94% yield) without any decrease in the performance in comparison with the small-scale transformation in Table 1 (eq 4).



In summary, we successfully designed an efficient heterogeneous oxidation catalyst through the combination of thermodynamically favorable electron-transfer reactions: The designed catalyst ( $\text{Cu}(\text{OH})_x/\text{OMS-2}$ ) showed high catalytic performance (TOF =  $540 \text{ h}^{-1}$ , total TON = 666, and selectivity >99%) and long life (13 times reuse) for aerobic oxidative alkyne homocoupling, and the synthetic scope was very wide.

## EXPERIMENTAL SECTION

The  $\text{Cu}(\text{OH})_x/\text{OMS-2}$  catalyst (Cu content: 1.5 wt %) was prepared via the same procedure as that for  $\text{Cu}(\text{OH})_x/\text{TiO}_2$  (see the Supporting Information for preparation and characterization).<sup>22</sup> A typical procedure for alkyne homocoupling is as follows: Into a Pyrex screw cap vial were successively placed  $\text{Cu}(\text{OH})_x/\text{OMS-2}$  (typically 2 mol %), alkyne (0.5 mmol), and toluene (2 mL). A Teflon-coated magnetic stir bar was added, and the reaction mixture was vigorously stirred (800 rpm) at 100 °C under 1 atm of  $\text{O}_2$  for 10 min. Conversion and product yields were determined by GC. After the reaction was completed, the spent  $\text{Cu}(\text{OH})_x/\text{OMS-2}$  catalyst was retrieved by filtration, washed with acetone and deionized water, and then dried in vacuo prior to being recycled. The product was isolated by silica gel column chromatography (*n*-hexane or a mixed solvent of *n*-hexane and diethylether was used as an eluent). Data of diynes are summarized in the Supporting Information.

**Table 1.** Scope of the  $\text{Cu}(\text{OH})_x/\text{OMS-2}$ -Catalyzed Homocoupling<sup>a</sup>

entry	alkyne	product	yield (%)
1			<b>2a</b> 98(91)
2 <sup>b</sup>			>99
3			<b>2a</b> 94
4			<b>2b</b> 98(94)
5 <sup>c</sup>			<b>2c</b> 99(87)
6			<b>2d</b> 98
7			<b>2e</b> 99
8			<b>2f</b> 93(90)
9			<b>2g</b> 98
10			<b>2h</b> 99(83)
11 <sup>d</sup>			<b>2i</b> 88(73)
12 <sup>c</sup>			<b>2j</b> 99(92)
13			<b>2k</b> 92(80)
14 <sup>c</sup>			<b>2l</b> 83
15 <sup>c</sup>			<b>2m</b> 85(75)
16 <sup>c</sup>			<b>2n</b> 74
17 <sup>e</sup>			<b>2o</b> 99(83)
18 <sup>e</sup>			<b>2p</b> 99(91)
19 <sup>d</sup>			<b>2q</b> 97(90)
20 <sup>c</sup>			<b>2r</b> 78
21 <sup>c</sup>			<b>2s</b> 84

<sup>a</sup> Reaction conditions:  $\text{Cu}(\text{OH})_x/\text{OMS-2}$  (Cu: 2 mol %), alkyne (0.5 mmol), toluene (2 mL), 100 °C, 10 min, under 1 atm of  $\text{O}_2$ . Yields were determined by GC. Values in the parentheses are isolated yields. <sup>b</sup> 40 min, under 1 atm of air. <sup>c</sup> Cu: 5 mol %. <sup>d</sup> Cu: 3 mol %. <sup>e</sup> Cu: 10 mol %.

## ASSOCIATED CONTENT

**S Supporting Information.** Full experimental section, data of diynes, Tables S1 and S2, Figure S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone: +81-3-5841-7272. Fax: +81-3-5841-7220. E-mail: [tmi-zuno@mail.ecc.u-tokyo.ac.jp](mailto:tmi-zuno@mail.ecc.u-tokyo.ac.jp).

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- (45) The total TON based on manganese species was 16, showing that the reaction is also catalytic from the standpoint of the amount of manganese species utilized.
- (46) In the case of Cu(OH)<sub>x</sub>/TiO<sub>2</sub>, the catalytic reaction rate (5.1 mM min<sup>-1</sup>) corresponds to that of eq 5. In the case of Cu(OH)<sub>x</sub>/OMS-2, the reoxidation rate of reduced copper species (eqs 2 and 3, at least 88.4 mM min<sup>-1</sup>) was much larger than that of eq 5.



(47) The initial rate (based on the consumption of **1a**) for the Cu(OH)<sub>x</sub>/OMS-2-catalyzed homocoupling of **1a** showed the first-order dependence on the amount of Cu(OH)<sub>x</sub>/OMS-2 (Cu: ~0.8 mol%) and the partial pressure of dioxygen (0.2–1.0 atm) and was almost independent of the concentration of **1a** (0.23–0.88 M). In addition, a kinetic isotope effect was hardly observed for the homocoupling of **1a** and **1a'** (D content: 98%) ( $k_{\text{H}}/k_{\text{D}} = 1.1 \pm 0.1$ ). All these results suggest that the reoxidation of copper(I) species (by eqs 2 and 3) is included in the rate-determining step.

(48) The average oxidation state of manganese species in the catalyst (Figure S2) as well as the structure of OMS-2 (Figure S3) were preserved, even after the 13th reuse.

(49) The redox potential of the TiO<sub>2</sub>/Ti<sub>2</sub>O<sub>3</sub> reaction is -0.56 V.<sup>33</sup> Thus, the electron transfer from reduced copper species to TiO<sub>2</sub> is thermodynamically unfavorable.