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Mesoporous Copper/Manganese Oxide-Catalyzed Coupling of Alkynes: Evidence for Synergistic Cooperative Catalysis

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Abstract

Copper oxide supported on mesoporous manganese oxide (meso Cu/MnO_x) was synthesized by an inverse micelle templated evaporation induced self-assembly procedure. Controlled aggregation of nanoparticles and a monomodal size distribution of mesopores with tunable structural properties were observed. The material possessed superior catalytic activity in aerobic oxidative coupling of terminal alkynes. Excellent conversion (>99% in most cases) and selectivity were observed in both homo and cross-coupling of alkynes using the optimized reaction conditions. Use of air as the sole oxidant, avoidance of any kind of additives, ease of product separation, great functional group tolerability, wide synthetic scope, and superior reusability (up to 8th cycle) are the notable features of our catalytic protocol. While elucidating the reaction mechanism, a synergistic cooperative effect between the copper and manganese has been established, which is responsible for superior catalytic activity. The labile lattice oxygen of the meso Cu/MnO_x played a vital role in deprotonation of the alkyne proton as supported from the TPD and TGA studies. Moreover, for the first time, we designed model complexes for the active sites of the catalyst by DFT calculations and provided a qualitative description of the coupling mechanism, which supports the experimental findings.

Keywords: Alkyne, coupling, Copper, Manganese oxide, Density functional theory

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1. Introduction

1,3-diyne moieties are a common feature in compounds with interesting medicinal, electronic, and optical properties^{1,2}. Pioneered by Glaser in 1869, by using stoichiometric amounts of copper salt, oxidative homo-coupling of terminal alkynes was considered the most straightforward route for synthesizing diyne molecules³. Since then, many ligand/metal salt combinations have been reported for alkyne coupling under homogeneous and mild reaction conditions⁴⁻¹⁰. From the viewpoint of a green and environmental perspective, heterogeneous catalysts are more advantageous over the homogeneous systems due to their easy separation, recyclability, and high stability¹¹⁻¹³. In this context, palladium based immobilized heterogeneous systems have been successfully used¹⁴⁻¹⁶. However, the high price of palladium, tedious synthesis methodology, and the use of copper as co-catalyst in some cases hinder their practical application.

Copper based heterogeneous catalysts, in particular supported copper catalysts, are specifically attractive, as they provide similar or higher performance compared to palladium ¹⁷⁻²⁴. Nevertheless, these catalysts often lacked reusability, require molecular oxygen or other chemical oxidants, use high copper loadings, and need both base and ligand that are indispensable for achieving high efficiency²⁵⁻²⁸. In addition, cross-coupling of two different terminal alkynes remains a challenging issue due to the competing homo-coupling reactions.^{13,29} Alkyne pre-functionalization, the presence of precious metals, and assistance of nitrogen based ligands were identified as crucial factors to promote the transformation^{30,31}. Moreover, current understanding of the exact mechanism of the copper mediated alkyne coupling reaction still remains unsatisfactory⁴. In spite of some efforts to describe the copper mediated coupling reaction still remains by computational techniques, proper design of catalytic active sites has not been done³²⁻³⁴. Therefore, considering the afore-mentioned disadvantages, design of copper based

heterogeneous catalyst with proper explanation of reaction pathways for alkyne coupling reactions is highly desirable. Ideally, the catalytic system will use air as the terminal oxidant, avoid the use of additives, allow low catalyst loading, withstand proper reusability and show high activity towards synthesis of symmetrical and asymmetrical diyne derivatives.

Synergistic–cooperative catalysis involving two metal centers is an exciting phenomenon in those organic transformations which cannot be accomplished by a single metal catalyst^{35,36}. Joint participation of dual metals having distinct properties is often required for achieving high activity. The biggest challenge in this field is to exploit the relative compatibility of the two metals in the same reaction medium. Mizuno et al. described a synergistic catalytic system for alkyne homo-coupling reactions using copper hydroxide on manganese oxide-octahedral molecular sieves (Cu(OH)_x/OMS-2)¹⁷. However, the catalyst was designed conceptually and no clear understanding of the active sites has been provided. It is also difficult to estimate if cross-coupling products would be obtained with similar efficiency to homo-coupling, since no example of cross-coupling has been reported.

Due to their intrinsic structural features, mesoporous nanostructured materials have been recognized as popular heterogeneous catalytic systems^{37,38}. They are ideal for providing a high surface area scaffold to which active metals can be tethered. Further, tunable pore size offers good flexibility for the transportation of organic moieties. Mesoporous manganese oxide materials prepared by a soft templated method are powerful heterogeneous catalysts for diverse oxidation reactions³⁹⁻⁴³. By tuning the nature of surface active manganese centers and the mobility of labile lattice oxygen, the catalytic activity can be promoted by several orders of magnitude. Herein, we designed mesoporous manganese oxide supported copper oxide for oxidative homo and cross-coupling of alkynes to 1,3-diyne derivatives. Use of air as the terminal

oxidant, no pretreatment by basic additives, high turnover numbers, proper reusability, and high functional group tolerability make our catalytic protocol superior to existing catalytic systems. The mechanistic pathways and kinetic analysis were studied in detail. Additionally, we performed density functional theory (DFT) computational techniques in order to establish a correlation with the experimental results towards disclosing the active catalytic centers and determined the role of manganese and labile lattice oxygen towards the activity.

2. Experimental Section

2.1 Synthesis of mesoporous Cu/MnO_x

The synthesis was performed following the synthetic procedure of University of Connecticut (UCT) mesoporous materials⁴⁴. Copper nitrate trihydrate (Cu(NO₃)₂.3H₂O) was selected as the dopant source in the synthesis. In a 120 mL beaker, 0.02 mol of manganese nitrate tetrahydrate (Mn(NO₃)₂.4H₂O), different amounts of Cu(NO₃)₂.3H₂O, and (0.134 mol) 1-butanol were added. To this solution (0.0034 mol) P123 (PEO₂₀PPO₇₀PEO₂₀, molar mass 5750 g mol⁻¹) and (0.032 mol) concentrated nitric acid (HNO₃) were added and stirred at room temperature until the solution became clear. The resulting clear blue solution was then kept in an oven at 120°C for 3 h under air. After reaction, the black material was washed with excess ethanol, centrifuged, and dried in a vacuum oven overnight. The dried black powder was then subjected to a heat treatment of 150°C for 12 h, cooled to room temperature, followed by heating at 250°C for 3 h under air (named as meso Cu/MnO_x).

2.2 Homo-coupling of terminal alkynes

In a typical homo-coupling reaction, alkyne (0.5 mmol), meso Cu/MnO_x (6 mol % with respect to alkyne) and toluene (5 mL) were put in a 25 mL round bottom flask (two necked flask for time dependent study, where the second neck was used as a sample port). The flask with the reaction

mixture with a reflux condenser attached was immersed in a silicone oil bath preheated to 105°C. The reaction mixture was refluxed under vigorous stirring (700 rpm) for the required time under an air balloon. After reaction, the mixture was cooled, the catalyst was removed by filtration, and Gas chromatography – mass spectra (GC-MS) was used to analyze the filtrate. The conversions were determined based on concentration of alkynes. The selectivity was calculated based on diyne as the only product. The products were isolated with silica gel column chromatography (n-hexane or a mixed solvent of n-hexane and dichloromethane was used as an eluent). Data of diynes are summarized in the supporting information.

2.3 Hetero-coupling of terminal alkynes

In a typical cross-coupling reaction, alkynes with the required molar amounts, meso Cu/MnO_x (6 mol % with respect to total alkyne amount), and toluene (5 mL) were put in a 25 mL round bottom flask. The flask with the reaction mixture with a reflux condenser attached was immersed in a silicone oil bath preheated to 105°C. The reaction mixture was refluxed under vigorous stirring (700 rpm) for the required time under an air balloon. After reaction, the mixture was cooled, the catalyst was removed by filtration, and GC-MS was used to analyze the filtrate. The conversions were determined based on the concentration of limiting alkynes.

2.4 Calculations of reactive species on catalytic copper manganese oxide surfaces

The choice of model complexes, used in these calculations and necessary for providing an adequate structural and energetic description of the active catalytic species, can be difficult, especially for fleeting species resting on a solid surface where structures are not especially well-defined. In these studies, the model compounds are simplified so that some ligands act as fixed lattice sites and influence the local Mn and Cu environments. Other ligands are reactant species or form short-lived species bonded to metal centers, and consequently, are optimized because of

their mobility and ability to follow a reaction pathway. The calculation details and geometries of the model compounds and transient intermediates are given in the supporting information. The model complexes, as herein described, should be able to provide a reasonably qualitative description of a catalytic pathways, or reaction mechanism, and are capable of explaining experimental results. The overarching goal of these calculations is to provide a qualitative description of the mechanism for the coupling of terminal alkynes.

3. Results

3.1 Physicochemical properties of meso Cu/MnO_x

Typically, UCT mesoporous materials are formed by aggregation of monodispersed nanoparticle in a random fashion, whereas the connection of the intraparticle voids is built the mesostructure⁴⁴. The presence of a low angle powder X-ray diffraction (PXRD) lines and a Type IV adsorption isotherms for meso Cu/MnO_x (**Figure 1A ad 1C**) indicate the preservation of mesoporous structure at various copper loadings. The wide angle PXRD patterns (**Figure 1B**) display diffraction lines corresponding to CuO at higher copper loading (10%), whereas no diffraction lines for manganese oxide have been observed. This indicates a poorly crystalline nature of manganese oxide at this calcination temperature (250°C). The surface areas were calculated as $227 - 290 \text{ m}^2\text{g}^{-1}$ (by Brunauer–Emmett–Teller (BET) methods) and 1% Cu containing sample exhibited the highest surface area of 290 m²g⁻¹ (**Table 1**). The Barrett-Joyner-Halenda (BJH) adsorption pore size distribution (**Figure 1D**) indicated a narrow monomodal pore size distribution for all the Cu containing materials. The pore diameters (**Table 1**) are within the mesoporous range (3.0 – 3.4 nm).



Figure 1. Structural characterization of meso Cu/MnO_x with different Mn/Cu molar ratio. PXRD patterns (A) Low angle $(0.5^{\circ} - 8^{\circ})$, (B) Wide angle $(5^{\circ} - 75^{\circ})$, (C) Nitrogen sorption isotherms and (D) BJH adsorption pore size distributions.

Mn/Cu	Surface Area	BJH ads.	Pore	EDX	Crystal
molar ratio	$S_{BET} (m^2 g^{-1})$	pore size	volume	Cu mol %	Structure
		(nm)	$(cc g^{-1})$		(PXRD)
n/a	200	2.8	0.153	n/a	Amorphous
100/1	290	2.9	0.244	1.0	Amorphous
50/1	227	3.4	0.202	3.8	Amorphous
10/1	270	3.4	0.301	6.0	CuO

Table 1. Structural parameters of meso Cu/MnO_x

n/a = not applicable.



Figure 2. The FE-SEM images of meso Cu/MnO_x with different Mn/Cu molar ratio (a) 100/1, (b) 50/1 and (c) 10/1.



Figure 3. (a, b and c) The TEM images and TEM-EDX elemental maps (d) Mn-L, (e) Cu-L and (f) O-L of meso Cu/MnO_x with Mn/Cu molar ratio 10/1.

Figure 2 shows the morphological features of meso Cu/MnO_x by field emission scanning electron microscope (FE-SEM) having various Cu loadings. The materials are composed of aggregated micron-sized rounded nanoparticles. Random packing of metal oxide particles was

also observed by Transmission electron microscopy (TEM) (**Figure 3**) of 10% meso Cu/MnO_x material. Energy dispersive X-ray spectroscopy (EDX) was used to analyze the concentration of each element in the material (**Table 1, Figure S1**). The high resolution TEM-EDX elemental map analyses of Mn, Cu, and O (**Figure 3**) indicated a homogeneous distribution of CuO over the MnO_x nanoparticle throughout the material.

In the case of metal oxide mediated oxidative reactions, oxidation states of active metals, and the nature of surface oxygen species are two important parameters to be considered. A Cu $2p_{3/2}$ binding energy of 933.3 eV and the presence of shake up satellite peaks from X-ray photoelectron spectra (XPS) studies confirmed the oxidation state of Cu as $2+^{17}$, which is in agreement with the PXRD data (**Figure 4a, Table S1**). The Mn 2p XPS signal consists of two peaks, which were assigned as Mn $2p_{3/2}$ and Mn $2p_{1/2}$ core levels (**Figure 4b**). The binding energies of 641.5 eV and 653.2 eV can be attributed to the Mn³⁺ oxidation state⁴⁰. On the other hand, deconvolution of O 1s spectra (**Figure 4c**) specified the existence of three different binding oxygen species, namely, structural or lattice oxygen (O_s), surface adsorbed oxygen (O_{ads}), and adsorbed water or hydroxyl groups (O_{mw}). In comparison to the reference catalyst (meso MnO_x), a shift of the O 1s peak at lower binding energy (530.2 eV in meso MnO_x and 529.2 eV in meso Cu/MnO_x) was observed (**Figure 4d**). This signifies an increase of mobility of lattice oxygen due to copper incorporation. The deconvolution O 1s spectra also suggest a predominance of lattice oxygen (O_s) near the surface of the catalyst.



Figure 4. XPS of meso Cu/MnO_x (10% Cu): (a) Cu 2p (* indicates the shake up satellite peaks), (b) Mn 2p, (c) deconvoluted O 1s and (d) comparison of the O 1s transitions of meso Cu/MnO_x and meso MnO_x .

3.2 Optimization of reaction condition

The oxidative homo-coupling of phenylacetylene was selected as the model reaction for developing the optimal reaction conditions. The bare mesoporous manganese oxide was totally inactive suggesting the absence of active sites for the coupling reaction. An increase of conversion from 4 to 70% was observed by increasing the copper concentration from 1% to 10% in the MnO_x (**Figure S2**). The selectivity in all the cases were 100% as 1,3-diyne was the only product. The 10% Cu incorporated sample was then selected for further studies. Changing the

oxidant source from air (45% conversion) to oxygen (55% conversion) resulted in an increase of activity [Entry 1 and 2, Table 2], whereas, reaction under nitrogen atmosphere displayed much lower conversion (24%) [Entry 3, Table 2]. A significant enhancement of conversion (70%) was achieved by addition of base [Entry 4, Table 2] and the combination of oxygen and base displayed the best (85% conversion) activity [Entry 5, Table 2]. We then conducted the homocoupling experiment with varied the amount of base (K₂CO₃) and found 1 equivalent of base as the optimal amount (**Table S2**). On the other hand, the reaction did not proceed at all in the presence of an acid [Entry 6, Table 2]. However, performing catalytic reactions under aerobic conditions without any additives is much more desirable in terms of green and sustainable chemistry. While performing further optimizations, an increment of catalyst loading from 3 to 6 mol% with respect to alkyne yielded the desired divne quantitatively within 40 min (TOF 24.7) [Entry 8-9, Table 2] without any additives under an air balloon. The reaction also proceeded under nitrogen, though having a much lower TOF value of 3.9 [Entry 10, Table 2]. Therefore the best optimized reaction conditions [Entry 9, Table 2] were used for the rest of the work. The catalyst precursor $Cu(NO_3)_2$. 2H₂O and other Cu salts (CuCl, CuCl₂, CuSO₄.5H₂O) [Entry 1-4, Table S3] and commercial Cu oxide (CuO, Cu₂O) [Entry 5-6, Table S3] did not produce

any coupling product. No reaction proceeded with a physical mixture of CuO and meso MnO_x [Entry 7, Table S3]. To determine the role of MnO_x in the reaction, we selected mesoporous Cu/TiO₂ (prepared by the same UCT method, see supporting information for details) as a reference catalyst for comparison. In contrast to meso Cu/MnO_x (>99 % conversion), meso Cu/TiO₂ displayed much lower conversion (7 %) [Entry 8-9, Table S3], under identical conditions. No reaction happened in the absence of catalyst [Entry 10, Table S3]. Therefore, the

 highly dispersed copper oxide species on mesoporous manganese oxide is indispensable for the present aerobic oxidative coupling of terminal alkynes.

Entry	Cu (mol%)	Oxidant	Additives	Time	Conversion ^b	TOF ^c
				(min)	(%)	(h^{-1})
1	3	Air	None	180	45	3
2	3	O_2	None	180	55	6
3	3	N_2	None	180	24	2.7
4	3	Air	$K_2 CO_3^{d}$	180	70	7.8
5	3	O_2	$K_2 CO_3^{d}$	180	85	9.4
6	3	Air	PTSA ^e	180	0	0
7	3	Air	None	360	80	8.9
8	6	Air ^f	None	45	94	21
9	6	Air	None	40	>99	24.7
10	6	N_2	None	180	70	3.9

Table 2. Optimization of reaction conditions^a

^a Reaction conditions: phenylacetylene (0.5 mmol), catalyst (different mol% of meso Cu/MnO_x), toluene (5 mL), balloon of air/O₂/N₂, 105°C. ^b Conversions were determined by GC-MS and based on phenylacetylene. ^c TOF = TON/ time (h), TON = no of moles of phenylacetylene converted per mol of Cu in the catalyst. ^d 1 equivalent of K₂CO₃ was used. ^e PTSA (p-Toluenesulfonic acid, 1 equivalent). ^fOpen to atmosphere.

3.3 Oxidative homo-coupling of terminal alkynes

The methodology worked well for diverse alkyne derivatives such as aromatic [Entry 1-8 and 13, Table 3], aliphatic [Entry 9-12, Table 3], heterocyclic [Entry 8, Table 3], olefinic [Entry 7, Table 3], and silylic [Entry 10, Table 3]. In all cases, the reaction exhibited >99% selectivity, as the corresponding 1,3-diyne was the only observed product. The isolated yields of the1,3-diyne derivatives are given in Table 2 along with their ¹H NMR and ¹³C NMR data (see supporting information). Alkynes with electron releasing [Entry 2-4, Table 3] or electron

withdrawing [Entry 5-6, Table 3] groups reacted smoothly to give the corresponding 1,3-diynes with excellent yields. The position of the methyl group in the aromatic ring did not affect the reaction rate [Entry 3-4 Table 3]. No dehalogenated product was observed in the case of halogen substituted alkynes [Entry 5-7, Table 3]. The dimerization of a heterocyclic substituted alkyne [Entry 8, Table 3] was conducted to afford high yield and selectivity but a much longer reaction time (12 h) was required. Excellent activity (>99% conversion, >99% selectivity) in oxidative coupling of an enyne (1-ethynylcyclohexene) [Entry 9, Table 3] revealed the superior chemo-selectivity nature of the meso Cu/MnO_x, since no reaction at the double bond was identified by GC-MS. Moreover, aliphatic alkynes were successfully converted to the corresponding diynes with similar turnover numbers (16.7) to the aromatic alkynes [Entry 10-11, Table 3]. Great functional group tolerability was also observed with silylated alkyne [Entry 12, Table 3] and substrates containing reactive ester groups [Entry 13, Table 3].

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Entry	Substrate	Time (h)	Conversion (%)
1		1	>99(97)
2	MeO-	3	>99(85)
3		2	>99(83)
4		2	>99(91)
E		1	> 00/08)
5	F-{	1	>99(98)
6	ci-	8	90(82) ^d
7	Br	6	95(87) ^e
8		12	>99(85)
9		2	>99(91)
10		2	>99(82)
11	n-C ₆ H ₁₃ ==	6	>99(87)
12		2	>99(93)
13	0, ´	4	>99(96)

Table 3. Aerobic oxidative homo-coupling of terminal alkynes^a

^a Reaction conditions: alkynes (0.5 mmol), meso Cu/MnO_x (6 mol% Cu with respect to amount of alkyne), toluene (5 mL), 105°C, air balloon. ^b Conversion was determined by GC-MS based on the concentration of alkynes. Selectivity in all cases were 100% to diynes. Numbers in parenthesis refer to yields of isolated products. ^c TON (no. of moles of alkynes converted / moles of copper in catalyst) = 16.7. ^d TON = 15.0, ^e TON = 15.8.

3.4 Cross coupling of alkynes

Table 4.	Aerobic	oxidative	cross	coupling	of	terminal	alkvnes ^a
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	II. I	' ^ا	meso Cu/MnO	× P			-P.
	R ₁	К ₂ ———Н —	Air, toluene, 105°C, 3 h	- N ₁			N2
Entry	R ₁	R ₂	Rel.	Conv ^b	Cou	pled prod	ucts
			ratio	(%)	sel	ectivity (%)
					$R_1 - R_1$	$R_1 - R_2$	$R_2 - R_2$
1			1/1	>99	17	52	23
2	F-		1/2	>99	38	50	12
3			1/3	80	12	54	36
4			1/3	92	11	57	32
5		$n-C_6H_{13}$	1/3	>99	20	62	18
6	F-{	MeO-	≡ 1/1	>99	20	45 ^d	35
7			1/1	>99	20	55 ^e	25

^a Reaction conditions: alkynes total amount (0.5 mmol), meso Cu/MnO_x (6 mol% Cu with respect to total amount of alkynes), toluene (5 mL), 105°C, 3 h, air balloon. ^b Conversion was determined by GC-MS based on the concentration of limiting reagent. ^c Selectivity was calculated by GC-MS. ^d Isolated yield was 82% ^e Isolated yield was 87%.

As illustrated in **Table 4**, the catalyst was able to produce the desired asymmetrical dignes by selecting two different terminal alkynes with good selectivity. We performed a conditional screening with a focus on the molar ratio of partner alkynes to get the maximum selectivity towards the asymmetric dignes [**Table S4**]. The catalyst exhibited cross-coupling between terminal alkynes of different types including aromatic and aromatic [Entry 1, 2, 6 and 7, Table 4], aromatic and aliphatic [Entry 3 - 5, Table 4], and aromatic and olefinic [Entry 4, Table 4].

Page 17 of 34

ACS Catalysis

The best selectivity to asymmetrical diyne was obtained by selecting an excess of the aliphatic alkynes over aromatic alkynes. On the other hand, selecting an equal molar amount of two aromatic alkynes produced the maximum selectivity to the asymmetric diyne. We also compared the cross-coupling activity of our system with the best known copper based heterogeneous catalyst [Cu(OH)_x/OMS-2] for alkyne coupling. As observed in table S5, meso Cu/MnO_x displayed better selectivity (62%) to the asymmetric diyne compared to Cu(OH)_x/OMS-2 (40%) in cross-coupling of phenylacetylene and 1-octyne.

3.5 Reusability and heterogeneity

Stable reusability and negligible leaching of active species are two important factors for an efficient heterogeneous catalytic system. We selected oxidative homo-coupling of phenylacetylene as the model reaction for a reusability study. After the reaction, the catalyst was retrieved by filtration and was washed with excess solvent and ethanol (>90% recovery). Prior to reuse the catalyst was reactivated at 250°C for 30 min to remove any adsorbed organic species. **Figure S3a** shows that the catalyst can retain activity and selectivity even after the 8th reuse. Moreover, no change in the PXRD pattern after the 8th cycle was observed (**Figure S3b**), which confirms that the catalyst can retain the crystal structure even after multiple reuse cycles. To verify any possible leaching of active Cu species in the solution, the catalyst was filtered and the filtrate was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). A trace amount of Cu (1.9 ppb) and Mn (7.0 ppb) were detected in the filtrate. All of these results signified the truly heterogeneous nature of our catalyst, which is active, stable, as well as recyclable.

3.6 Kinetic study

Kinetics of the reaction were then determined by conducting a time dependent study of the model reaction (oxidative coupling of phenylacetylene). Periodic sampling was undertaken at specific time intervals and conversion was determined by GC-MS. Kinetic experiments depicted a first order rate equation with respect to alkyne (Figure S4) having a rate constant of 0.093 min⁻ ¹. Kinetically relevant elementary steps in the reaction pathways were measured by changing the acetylenic H to D in phenylacetylene. The obtained kinetic isotope effect (KIE) value was 0.9 (Figure S5), which signified that abstraction of the acetylenic proton of alkyne was very fast.

3.6 Role of manganese oxide

A significant lower conversion (7% in air and 5% under nitrogen) was achieved when meso Cu/TiO₂ was selected instead of meso Cu/MnO_x (94% in air and 28% under nitrogen). We used XPS to probe the oxidation state of Cu and Mn in the unreacted catalysts and after reaction in air and nitrogen atmospheres (Figure S6 and Table S6). The oxidation state of Cu was estimated as 2+ in both of the untreated materials (pink and blue lines), as shown in **Figure S6**. The oxidation state of Cu persisted at 2+ (red and black lines) for meso Cu/MnO_x irrespective of the reaction environments (air or nitrogen). In contrast, reduction of Cu was observed (absence of satellite peaks), when the Cu/TiO₂ material was subjected to react under nitrogen (green line). These results confirmed the re-oxidation of reduced Cu species occurs in the presence of MnO_x even under nitrogen atmosphere. To further establish the re-oxidation of reduced Cu species, we tested the oxidation state of Mn in the meso Cu/MnO_x before and after reaction. As revealed from XPS (Figure S7), no change of oxidation state of Mn was detected when the coupling reaction was performed under air, whereas a lowering of Mn oxidation state was observed (Table S6), when the reaction was performed under nitrogen.

3.7 Comparison between experimental and calculated results

3.7.1. Cu sites on the meso Cu/MnO_x surface

Because acetylenes have two π orbitals, $\pi - [L_4Cu(II)(H-C\equiv C-H)]^{2+}$ complexes are capable of exhibiting enhanced stability. Tatsumi et al.⁴⁵ showed that the Dewar-Chatt-Duncanson model⁴⁶ can be applied to both double bonds, $\pi_{\perp}, \pi^{*}_{\perp}$ and $\pi_{\parallel}, \pi^{*}_{\parallel}$, which play an important role in bonding to mononuclear transition metal complexes. The $\pi - [L_4Cu(II)(H-C\equiv C-H)]^{2+}$ complex, as shown in **Figure 5a**, appears to be more stable than the corresponding Cu(I) complex, which is quite reasonable because the d_z^2 orbital is now only partially filled and can interact with the first π system, i.e. $\pi_{\parallel}, \pi^{*}_{\parallel}$. The $\pi_{\parallel} - d_z^2$ is a three-electron stabilizing interaction, together with further stabilization from a favorable interaction with π^{*}_{\parallel} . The π^{*}_{\perp} orbital from the second π system stabilizes a matched filled Cu d_{π} orbital. This corresponds to the transformation of $\pi - [L_4Cu(II)(H-C\equiv C-H)]$ when H⁺ is abstracted to an $\pi - [L_4Cu(II)(^-C\equiv C-H)]$ complex, shown in **Figure 5b** which can then couple with a neighboring acetylide anion (H-C≡C⁻).



Figure 5. (a) $\pi - [L_4Cu(II)(H-C \equiv C-H)]^{2+}$, and (b) $\pi - [L_4Cu(II)(C \equiv C-H)]^+$ complexes. The stability of the complex (a) relative to the separate components is 6.2 kcal mol⁻¹. The acetylide anion ($-C \equiv C-H$) in (b) was unstable with respect to a DFT calculation using a 6-31g* basis set,

and prevented the determination of relative stability, but its value is larger than (3a). L stands for H_2O .

3.7.2 Mn sites on the meso Cu/MnO_x surface

Vacant Mn sites on the Cu/MnO_x surface play a complementary role with respect to the Cu sites, especially when they are adjacent to one another. The Mn sites absorb O₂, form stable L_nMnO_2 intermediates, and are capable of abstracting H⁺ from neighboring Cu sites bonded to H–C=C–H molecules. In the case of Mn surface sites with L_nMnO_2 intermediate, it is important to keep track of the spin on the Mn atom. The $[L_nMn(II)(O_2)]$ (d⁵ : S = 6) complex is not stable, whereas $[L_nMn(III)(O_2)]^+$ (d⁴ : S = 5) forms a stable complex as shown in **Figure 6a.** The O₂ abstraction of H⁺ by $[L_nMn(III)(O_2)]^+$, does not alter the electronic configuration of the Mn(III) in the complex. The complex $[L_nMn(III)(O_2H)]^{2+}$ (d⁴: S = 5) remains stable as shown in **Figure 6b** below, eventually releasing the OOH⁻ ion. The remaining $[L_nMn(III)]^{3+}$ site is eventually reduced to $[L_nMn(III)]^{2+}$.



Figure 6. (a) $[L_nMn(III)(O_2)]^+$, and (b) $[L_nMn(III)(O_2H)]^{2+}$, complexes. The stability of the complex (a) relative to the separate components is 59.4 kcal mol⁻¹. The hydroperoxyl anion

 (O_2H^-) was unstable with respect to a DFT calculation using a 6-31g* basis set, and prevented the determination of relative stability, but its value is larger than (4a). L stands for H₂O.

3.7.3 Molecular analogues of reactive surface species

Several model systems can be used to illustrate the oxidative coupling of alkynes on the Cu/MnO_x surface, and three are shown in **Figure 7**. For the models, it is assumed that nearby Mn sites are capable of interacting with catalytically active Cu sites, and have the capability of producing a coupled alkyne product. The model in **Figure 7a** is considered favorable because the Mn atom, squeezed between two active Cu atoms, and bonded to two acetylide anions, is capable of interacting with the approaching anionic fragments (H–C=C: \rightarrow :C=C–H), stabilizing the incipient repulsive interaction, and subsequently absorbing the two discarded electrons, resulting from the oxidation of the acetylide anions, into an available Mn(d) orbital. An advantage of considering the model in Figure 7b is that the Cu sites are adjacent to each other (Mn sites are also presumed to be adjacent to each Cu site), allowing direct coupling of the acetylide anions and electron exchange with Mn atoms. Model Figure 7b is also analogous to an intermediate in the solution-phase Glaser-Hay reaction. Finally, the model in Figure 7c is similar to that in Figure 7b, but now includes O_2 as the bridging ligand between Cu atoms. O_2 is plentiful under the experimental conditions, when air and O₂ are available above the Cu/MnO_x surface. A dominant structure, supported by Cu atoms, may include the side-on $\mu - \eta^2 : \eta^2$ -peroxo motif⁴⁷⁻⁴⁹ shown in Figure 7c which provides some degree of confidence that this is a reasonably valid model.



Figure 7. Model systems [(a) Mn atom, squeezed between two active Cu atoms, (b) Cu sites are adjacent to each other and (c) O_2 as the bridging ligand between Cu atoms] on the Cu/MnO_x surface capable of oxidative coupling of alkynes.

4. Discussion

This study features the design of mesoporous copper incorporated manganese oxide material as an efficient heterogeneous catalyst for aerobic oxidative coupling of alkynes to 1,3-diynes. The material was synthesized by an inverse micelle templated sol-gel synthesis procedure using copper nitrate as the copper source. In this process, a pluoronic surfactant (P123) along with the metal source (Mn and Cu) randomly packed in an acidic alcoholic solution (HNO₃ + butanol) to build the mesostructure. The nitrate ions pulled the positively charged manganese and copper oxo-clusters into the core of the inverse micelles. The formation of NO_x (by thermal decomposition of nitrates) controls the whole sol-gel process. Control of the dopant amount is

crucial, since high amounts of dopants can destabilize the reaction gel and cause the surfactant to precipitate. We have successfully employed 1 -10 mol % incorporation of copper without disturbing the solution gel. The reaction system was then treated at 120° C for 3 h, followed by extracting the surfactant with ethanol to get the mesoporous material (meso Cu/MnO_x). Chemisorbed species (nitrates and carboxylates) were removed from the material by a heat treatment at 150° C for 12 h and 250° C for 3 h consecutively.

As illustrated in Table 3, our system indicates excellent substrate scope and functional group tolerability, giving the desired homo-coupling product in excellent yields. For aromatic alkynes, excellent activity was observed for both electron donation and electron withdrawing groups. Halogen substituted aromatic alkynes gave the desired product with excellent selectivity (>99%) without any dehalogenation, though dehalogenation and oxidative addition of halogen substituted aromatic compounds has been shown to occur in copper mediated systems⁵⁰. The longer reaction time (15 h) to achieve efficiency for a heteroatom containing substrate can be attributed to the poisoning of the active copper sites of the catalyst by coordination with Nheteroatoms⁵¹. Homo-coupling reactions with long chain aliphatic alkynes are known to be relatively difficult and higher copper loading or longer reaction times are essential, as mentioned in previous studies^{17,22,52}. However, meso Cu/MnO_x exhibited excellent performance in the reaction with the long chain, inactive 1-octyne with no drop in turnover number versus aromatic alkynes. The easy diffusion and transportation of 1-octyne in the mesoporous network may be the reason behind the high activity. Excellent selectivity was also observed with a reaction of an envne, though manganese oxides are known to oxidize the double bond in catalytic conditions⁵³. The excellent selectivity was also demonstrated by the homo-coupling reaction of a silvlated derivative without oxidation of the Si-H bond⁵⁴.

In cross-coupling of alkynes, discrimination of partner alkynes to metal acetylide formation has been considered the most important feature³⁰. We hypothesized that proper choice of relative alkyne amounts might provide the discrimination effect toward different alkynes. There were no significant differences in the rate of the homo-coupling of aromatic alkynes. Therefore, by selecting an equal amount of aromatic alkynes, we observed the maximum selectivity towards the asymmetric diynes. As observed in previous studies, aliphatic alkynes reacted faster to form the metal acetylide species to provide the discrimination effect⁴⁰. Similarly in our study, asymmetric diynes were synthesized with good to excellent selectivity when aliphatic alkynes were used in excess over aromatic alkynes.

There are many existing hypotheses, but the alkyne coupling mechanism proposed by Bohlmann et al. is considered as the most reasonable and acceptable⁵⁵. Based on their understanding, initially, a π co-ordination species between the triple bond and copper (I) is established, which further forms a dinuclear copper (II) acetylide species, and essentially collapses to give the coupled product. However, considered as an oxidative reaction, little has been discussed about the role of dioxygen in the mechanistic details. In general, copper undergoes a one electron reduction and forms a Cu-acetylide species, which dimerizes to give the corresponding diyne ⁵⁶. As elucidated from DFT calculations, a schematic diagram, showing how the energy decreases as the two separated acetylide anions for model **Figure 7b** readily couple to form a coupled acetylene product is given in **Figure S8**. The relative energy (-84.6 kcal mol⁻¹) of the final optimized coupled product is reasonable for the formation of the C-C bond in H–C=CC-C=C-H, which is the bond joining the two acetylide fragments.

However, no change in copper oxidation state of meso Cu/MnO_x was observed after the reaction by XPS. Therefore, re-oxidation of reduced copper species has been included in the

Page 25 of 34

ACS Catalysis

present oxidative coupling. The re-oxidation is well supported by disappearance of the satellite peaks of Cu 2p in meso Cu/TiO₂, confirmed the reduction of Cu(II) to Cu(I) in the present homocoupling reaction under nitrogen atmosphere (**Figure S6**). In contrast, the re-oxidation was efficiently promoted by MnO_x even under nitrogen atmosphere. A reduction of Mn oxidation state was also observed by XPS (**Figure S7**) which complemented the re-oxidation of reduced Cu(I) species by Mn(III) species. On the other hand, under an aerobic atmosphere, the reduced Mn species can effectively reoxidize⁵⁷.

The homo-coupling reaction did not proceed with an internal alkyne (diphenylacetylene), suggesting that the copper species is likely binding to terminal alkyne to form the copperacetylide species. Since the addition of a base is unnecessary in our system, the catalyst itself must have the ability to abstract the alkyne proton. An incremental increase of catalytic performance was observed when the catalyst was subjected to a heat treatment from 250°C to 450°C, whereas, the activity again decreased at 550°C (Figure S9). As revealed from the XRD studies, when the material was calcined at 250° C to 450° C, the manganese support was poorly crystalline but transformed to highly crystalline Mn₂O₃ phase at 550°C (Figure S10). Temperature programmed desorption (TPD) experiments were performed in order to determine the nature of oxygen species of the material, as crystallinity has a remarkable effect in accessibility of lattice oxygen of manganese oxides³⁹. The material calcined at 250°C to 450°C showed an oxygen desorption peak around 500°C which can be ascribed as desorption of lattice oxygen (Figure S11). A transformation to lower temperatures of the lattice oxygen peak was also observed with rising calcination temperature by O₂-TPD, which was complemented by thermogravimetric (TGA) analyses (Figure S12). Thus, the effect of calcination temperatures on catalytic performance can be correlated with the accessibility of labile lattice oxygen. Therefore,

the role of labile lattice oxygen of copper manganese oxide is probably relevant to the abstraction of alkyne hydrogen to from the alkynyl species. This results are also supported from the models derived by DFT calculation, where the Mn sites of the catalyst can absorb O_2 , forming stable intermediates, which are capable of abstracting H⁺ from neighboring Cu sites bonded to H–C=C–H molecules (**Figure 6**).

Based on experimental findings, we propose a mechanism for oxidative coupling of alkynes by meso Cu/MnO_x (Scheme 1). First, the lattice oxygens of meso Cu/MnO_x abstract an alkyne proton to form the Cu(II) acetylide species (formed by weak π coordination between alkyne triple bond and copper center), which dimerizes to give the corresponding divide and generates Cu(I) species. The surface active Mn centers simultaneously involves a one electron reduction and re-oxidizes the Cu(I) species to Cu(II). Under catalytic turnover conditions, the reduction of active Mn species can lead to facile release of lattice oxygen⁵⁸. The labile lattice oxygen reoxidizes the Mn center back with production of H₂O₂, which could easily be decomposed over manganese oxide and form water⁵⁸⁻⁶⁰. The supply of oxygen is crucial for the catalytic activity, as loss of lattice oxygen should be replenished by oxygen from the air. This also was supported by the observation that using a dinitrogen atmosphere instead of air diminished the reaction rate. A kinetic isotope effect was hardly observed in the homo-coupling of phenylacetylene ($k_{\rm H}/k_{\rm D}$ = 0.9) indicating that the abstraction of the alkyne proton is not the rate determining step. Therefore, the re-oxidation of reduced copper species is probably the rate determining step in the present coupling reaction.



Scheme 1. Proposed mechanism of aerobic oxidative coupling of alkynes by meso Cu/MnO_x.

The reaction mechanism was further validated by DFT calculations. A basic assumption for any credible mechanism presumes that Cu atoms are randomly distributed on the Cu/MnO_x surface and are intertwined with neighboring Mn atoms, forming bonds with O atoms.

Air environment

1. Initially, the neutral H–C=C–H molecule forms a weakly bound $\pi - [L_4Cu(II)(C_2H_2)]^{2+}$ complex (L = H₂O).

2. Concomitantly, an adjacent $L_nMn(III)^{3+}$ species reacts with O₂ to form $[L_nMn(III)(O_2)]^+$. The $[L_nMn(III)(O_2)]^+$ intermediate is able to directly abstract an H⁺ and yield a $[\pi-L_4Cu(II)(C\equiv CH)]^+$ and a $[L_nMn(III)(O_2H)]^{2+}$ complex. L_nMn sites exhibit a twofold role in enhancing catalysis, by both changing its oxidation state and by yielding an acetylide anion.

3. $[L_nMn(III)(O_2H)]^{2+}$ loses O_2H^- to form an $[L_nMn(III)]^{3+}$ complex.

4. In the final step, two acetylide anions from $[\pi - L_4Cu(II)(C \equiv CH)]^+$ species react to form a divide molecule (e.g., H $-C \equiv C - C \equiv C - H$) and residual L₄Cu(II) surface species.

The overall equations for the postulated mechanism are given below:

$$2 [\pi - L_n Cu(II)C_2H_2]^{2+} + 2 [L_n Mn(III)(O_2)]^+ \rightarrow 2 [\pi - L_n Cu(II)(C \equiv CH)]^+ + 2[L_n Mn(III)(O_2H)]^{2+}$$

$$2 [L_n Mn(III)(O_2H)]^{2+} \rightarrow 2 [L_n Mn(III)]^{3+} + 2 OOH^-$$

$$2 OOH^- \rightarrow H_2O + 1/2O_2 + 2e^-$$

$$2 [\pi - L_n Cu(II)(C \equiv CH)]^+ \rightarrow 2 [L_n Cu(I)]^+ + H - C \equiv C - C \equiv C - H$$

Nitrogen environment

Surface sites containing reactive species such as $[L_nMn(III)=O]+$, are assumed to always be available on the Cu/MnO_x surface under nitrogen environments.

1. $[L_nMn(III)=O]^+$ reactive species abstracts an H⁺ from $[\pi-L_nCu(II)(C_2H_2)]^{2+}$ to form $[\pi-L_nCu(II)(C=CH)]^+$ and $[L_nMn(III)(OH)]^{2+}$.

2. $[L_nMn(III)(OH)]^{2+}$ decomposes to $[L_nMn(III)]^{3+} + OH^-$.

3. Two acetylide anions from $[\pi-L_4Cu(II)(C=CH)]^+$ species react to form the coupled product (H - C=C-C=C-H).

The yield of coupled alkyne product is reduced, when the Cu/MnO_x surface is exposed to nitrogen environments, and may be related to the formation of a weak $[L_nCu(II)(N_2)]^{2+}$ complex which inhibits the formation of the neutral $[\pi-L_nCu(II)(C_2H_2)]^{2+}$ complex (Figure S13). Complex formation with nitrogen competes with H–C=C–H for Cu(II) sites and decreases catalytic activity. Similar to the $L_nCu(II)$ sites, the $L_nMn(III)$ sites can also form weakly bound complexes with N₂ which may hinder catalytic reaction of alkynes under nitrogen atmosphere (Figure S14).

5. Conclusions

In summary, we report the fabrication of thermally stable and reusable mesoporous copper supported manganese oxide materials (meso Cu/MnO_x) for aerobic oxidative coupling of

Page 29 of 34

ACS Catalysis

alkynes. The material was composed by aggregation of rounded nanoparticles with high surface area (as high as 270 m²g⁻¹) and uniform mesoporous size (3.0 - 3.4 nm) distribution. The alignment of copper over the manganese oxide was shown by PXRD refinement showing a copper (II) oxide (CuO) phase at higher copper doping. Elemental mapping analysis by TEM-EDX confirmed a uniform distribution of copper oxide over the manganese oxide. Broad substrate scope and excellent functional group tolerability were demonstrated for the oxidative homo and cross-coupling of terminal alkynes. While unravelling the mechanistic details, a synergistic effect between copper and manganese has been established along with the contribution of labile lattice oxygen. The high catalytic activity can be attributed to an electron transfer pathway between dioxygen and alkyne through manganese and copper oxide. In addition, we performed DFT calculations to provide a reasonably qualitative description of the catalytic pathway by building model compounds in four/five or six - fold coordination to manganese and copper atoms, together with their ligands and constrained by bonds in the lattice. In case of copper active sites, a π coordination between the alkyne triple bond and copper enhancing the acidity of alkyne proton has been shown, resembling the classical Bohlmann mechanism. The proton was abstracted by the complex formed between manganese active sites and dioxygen, which can be correlated with the experiments, where an exchange mechanism between labile lattice oxygen and aerial oxygen was shown to be the factor behind the deprotonation. After deprotonation, the copper (I) acetylide species was dimerized to produce the divne products as observed by the relative energies of the coupling of two acetylide moieties. Therefore, the design of copper and manganese active sites along with the validity of the coupling reaction mechanism was strengthened from both experimental and theoretical perspectives. Finally, using air as the terminal oxidant, avoidance of additives, no pretreatment

of catalysts, high turnover numbers for aliphatic and aromatic alkynes, superior reusability, and excellent selectivity to both homo and cross-coupling of alkynes, make our catalytic protocol superior over the best heterogeneous copper based catalytic systems reported to date. This combined experimental and theoretical study can serve as a benchmark for the oxidative coupling reactions and opens up a new avenue to design and identify supported copper based heterogeneous catalysts for potential applications in other complex oxidative coupling reactions.

ASSOCIATED CONTENT

Supporting Information:

This material is available free of charge via the Internet at http://pubs.acs.org.

List of chemicals, catalyst characterization procedures, calculation details and geometries of the model compounds, EDX measurement, effect of base, comparison of different catalysts, optimization of cross-coupling condition, reusability test, kinetic and isotopic study, change of oxidation state measurement, XRD, O₂-TPD, CO₂-TPD, TGA and catalytic activity of the catalyst at different calcination temperatures, and ¹H NMR and ¹³C NMR of typical products.

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