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Tuning of the Cross-Glaser Products mediated by Substrate-**Catalyst's Polymeric Backbone Interactions**

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Obtaining the hetero-selective product is the most challenging task in cross-Glaser reactions. So far this has been achieved mainly through the inherent reactivity of the substrates guided by metal catalyst. Here we report a novel catalyst based on copper-oxide (Cu^{1/II}O) nanoparticles with varying cellulose-polymeric backbone. The designed catalyst not only provides high hetero-selectivity but also allows tuning the homo/hetero products by modifying the catalyst cellulose-polymeric backbone either through chemical modification and/or by tweaking the catalyst-reactant interactions. The atomistic details of the hetero-selectivity is explored based on the ab initio Born-Oppenheimer molecular dynamics simulations.

The aerobic oxidation of terminal alkynes forming the C-C bond is a powerful reaction that enable dialkyne formation in a single step.¹ The dialkynes are quite important class of molecules not only available in numerous natural products,² but they also play major roles in materials exhibiting exotic electronic properties comprising of π -conjugated alkynes been utilised as advanced materials.³ Unlike Glaser homo-coupling, the Glaser cross-coupling reaction is challenging due to poor selectivity between homo- and cross-Glaser hetero-products that limits its wide applications.⁴ To address this issue various catalysts have been tried and achieved cross-heteroselectivity governed by inherent reactivity of substrates mediated by metal-catalyst.^{5,6} For examples, mesoporous Cu/MnOx catalyst^{6a} by Rossi and Suib et al. as well as bimetallic catalysts^{6b} by Wang et al. with 63-93% of hetero-selectivity's have been achieved. Shi et al. reported that good to excellent hetero-selectivity (57-93%) can be achieved for gold catalysed cross-Glaser coupling in the presence of PhI(OAc)₂ as an oxidant and 1,10-phenanthroline as an additive.^{6c} Yao et al. reported Cu/C₃N₄-composite as a recyclable catalyst for Glaser reactions.^{6d} Interestingly, Zhou and Yin et al. have reported that even simple Cu⁰ powder can catalyse the cross-Glaser reaction under simpler condition.^{6e} However, these catalysts suffer some limitations like using organic solvents, expensive metals, excess catalyst, oxidant, high temperature and longer reaction time,

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reactivation before reuse, etc. In some cases, it is accompanied by the formation of undesired side products. An alternative approach based on solid-support was investigated,⁷ but this method requires at least one alkyne to be used excessively along with additional detachment step from the resin. Transition metal based nanoparticles^{8,5a-c} has received considerable attention in recent years over noble metals^{5d} due to large abundance, high surface areas leading to high activity compared to bigger sized particles.



Fig. 1. (a) Structure of catalysts 1, 2 and 3 and (b) their synthetic pathway.

So far the hetero-selectivity was mostly achieved based on the inherent reactivity differences of differently substituted alkynes with the catalyst.^{2e,6,7} However, in addition to the reactivity, the polarity (H-bonding, hydrophobic, π - π or electrostatic interactions) is also inherently different for the cross-Glaserproducts, which are always among two homo-products, one is polar and the other is non-polar, whereas the hetero-product is medium-polar. This trend is more pronounced especially when one alkyne is highly polar (e.g. -OH, -NH₂ containing groups) and the other is non-polar (e.g. phenyl, alkyl, etc). Hence, we hypothesise that tuning the catalyst's backbone which can interact differently among homo- and hetero-products might influence the hetero-selectivity due to possible cooperative effects (non-covalent interactions). To test this hypothesis, we have designed the catalysts TC-S-Cu^{1/II}O 1, EC-S-Cu^{1/II}O 2, and C-

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S-Cu^{I/II}O **3** which are different mainly in the amine spacer such as tris-(2-aminoethyl)amine (TREN)-functionalised cellulose (TC), ethylenediamine-functionalised cellulose (EC), and unfunctionalised cellulose (C), respectively (Fig. 1). The detailed synthetic procedures and characterisation of the catalysts 1, 2 and 3 have been described in Sections B and C, respectively in the Electronic Supplementary Information (ESI). Amino cellulose precursors for the synthesis of corresponding catalysts 1 and 2 have been prepared following the reported procedures starting from cellulose.⁹ Briefly, the synthesis of catalysts 1, 2 and 3 were achieved by two-steps processes (Fig. 1b, Scheme S1, ESI), i.e. (i) treatment of functionalised-celluloses (TC, EC, thioglycolic acid and C) with (S) mediated bv dicyclohexylcarbodiimide coupling agent to afford thiolfunctionalised celluloses (TC-SH, EC-SH, and C-SH),^{9,10} (ii) treatment of these celluloses with $CuCl_2$ in 1:1 EtOH/H₂O afforded Cu^{1/II}O nanoparticles (NP) anchored by thioglycolate part. It has been reported that thiol functionalised cellulose paper could efficiently reduce the copper (Cu) ions into copper(I) oxide NP.¹¹ Whereas in our case with microcrystalline celluloses modified with thiol groups provided Cu^{I/II}O (catalysts 1 to 3) nanoparticles which were characterised by various characterisation techniques (Section C, ESI).



Fig. 2. (a) XPS survey spectrum of TC-S-Cu^{I/II}O **1**. (b) XPS copper profile describing the coordination behaviour of Cu with TREN-Cellulose. (c) TEM images of TC-S-Cu^{I/II}O **1**. (d) Magnified view of the selected area showing the particle size less than 10 nm. (e) Their respective particle size distribution histogram.

Figs. 2a and 2b show the X-ray photoelectron spectroscopy (XPS) survey of the as-prepared TC-S-Cu^{1/II}O **1** and the presence of Cu₂O/CuO in 42:58 ratio, respectively.¹² The transmission electron microscopy (TEM) images of TC-S-Cu^{1/II}O **1** is showed that the spherical-shaped NP have been successfully deposited over the porous cellulose and the particles size distribution of the formed NP was found to be 1–7 nm (Figs. 2c–e). Further, the loading of Cu on TC-SH was found to be 36.2 wt%, as determined by inductively coupled plasma mass spectrometry (ICP-MS). Thus, these results suggest that TC-SH acts as a reducing agent as well as stabilizing agent for the synthesis of Cu^{1/II}O NP. After successful synthesis and characterisation of all the three catalysts, we chose catalyst **1** to test and optimise the reaction conditions to its catalytic activity in the Cu-catalysed homo-coupling of ethynylbenzene **1a** to form **2a** (Table S4,

Section D1 in ESI). Preliminary studies revealed that excellent yields were obtained when the homo-coupling was carried out with 1 mol% TC-S-Cu^{1/II}O **1**, 4 mol% TMEDA (N,N,N',N'-tetramethyl ethylenediamine) as ligand under air at 25 °C. We

tetramethyl ethylenediamine) as ligand under air at 25 °C. We have compared the turn-over-frequency (TOF) of TC-S-Cu^{I/II}O 1 with the commercially available Cu-TMEDA (Di-µ-hydroxobis[(*N*,*N*,*N*',*N*'-tetramethyl ethylene-diamine)copper(II)] chloride) catalyst showing 2909 and 139 h⁻¹, respectively (Table S5). To the best of our knowledge, the observed TOF of 2909 h^{-1} is ~20 times higher than reported TOF and the commercially available Hay-catalyst (Cu-TMEDA) (Table S7). Moreover, we examined the catalytic efficacy of TC-S-Cu^{1/II}O 1 using various amounts of catalysts down to 0.0001 mol% of Cu and the reaction was nearly quantitative (Table S6). It is noteworthy that the successful use of such an extremely low quantity of Cu under eco-friendly conditions for oxidative homo-coupling of ethynylbenzene is remarkable. Thus, it could be conferred that TC-S-Cu^{1/II}O 1/TMEDA has very high catalytic activity with exceptionally high TOF. Furthermore, to demonstrate catalyst 1, its practicality in a scalable reaction, 10 mmol scale of 1a was treated with 1 mol% of catalyst 1 and the corresponding diyne 2a (1.68 g) was obtained in 85% yield within 2 h.

After optimising the conditions, we investigated whether the catalyst **1** could be used for selective formation of heteroproduct in an aerobic oxidative cross-coupling of terminal alkyne reactions to produce asymmetric **1**,3-diynes (Table 1). We have chosen relatively non-polar (**1a-h**) and a polar (**1i**) terminal alkynes for cross-coupling reactions in order to see a clear polarity discrimination between the products which can be isolated by column chromatography. 2-Methylbut-3-yn-2-ol **1i** was successfully cross-coupled with various terminal alkynes to provide unsymmetric **1**,3-diynes (**3a-h**) in high yields (68– 85%, Table **1**, entries **1**–8), in addition to the corresponding homo-coupled **1**,3-diynes in very moderate yields.

As we originally hypothesised the observed high selectivity of the TC-S-Cu^{1/II}O 1 towards the hetero-products (Table 1) might be attributed due to catalyst backbone polarity/ interactions (H-bonding, hydrophobic, etc) facilitating moieties which may selectively favour the similar polar nature of the cross-coupled product (Fig. S47).^{13,4a} To investigate the role played by TREN moiety in 1 on hetero-selectivity, catalysts EC-S-Cu^{1/II}O 2^{8b} and C-S-Cu^{1/II}O 3^{10,9} in which TREN is replaced by ethylenediamine and no TREN, respectively were also examined under similar conditions for a model reaction between 1a and 1i (Fig. S47a, Table 2, entries 1, 4, and 7). Both catalysts 2 and 3 showed reduced selectivity of 59 and 25%, respectively, towards hetero-product 3a as compared to 85% for catalyst 1. It was observed that the selectivity towards the hetero-product decreases as the amine part decreases in the catalysts similar to the polarity/H-bonding interacting order of the catalysts 1>2>3. To verify further, we changed the polarity/H-bonding interacting part in 1, i.e. TREN moiety by adding additive compounds with either polar (-COOH) or non-polar (dodecyl chain) moieties for the same model reaction (Table 2, entries 2, 3, 5, 6, 8, and 9). In both cases, we chose carboxylic acidcontaining additives such as dodecanoic acid (DDA, non-polar) and benzene-1,3,5-tricarboxylic acid (BTC, polar) because they

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would bind with TREN moiety as it contains tertiary amine, thus changing the polarity/H-bonding environment favoured atoms in the catalyst's backbone to non-polar and polar, respectively. It was found that catalyst 1 alone showed 85% selectivity for medium-polar hetero-product 3a (entry 1, Table 2). Whereas, upon addition of DDA, the major compound observed was nonpolar 2a with 76% yield (entry 2). Interestingly, upon addition of polar-additive BTC, the catalyst showed selectivity towards polar homo-product 2i with 76% yield (entry 3). More evidently, the similar significant effect was not observed in the case of catalyst 2 and 3 which contain no-tertiary amine in the catalyst backbone (entries 4-9, Table 2). In addition, catalyst 2 containing ethylenediamine moiety favoured moderate heteroproduct selectivity (50 - 61%). Whereas the catalyst 3 containing no-amine spacer favoured non-polar homo-product selectivity (59 - 65%). These experimental results indicate that TREN moiety in TC-S-Cu^{1/II}O 1 is responsible for high selectivity towards hetero-product and polarity does play a role which in turn might be governed by the forces like non-covalent interactions (Section F, ESI). Further, the fact that the effect of additives is so prominent which implies that the catalyst backbone largely controls the selectivity with very little effect of chemo-selectivity caused by inherent reactivity of substrates.

 Table 1. Aerobic oxidative cross-coupling of terminal alkynes.^a

| K1 | 1a-h TC-S-Cu ^{VII} O 1, TMEDA | R1-=== | -R1 + R1 | — (он • но-) | | н | | | | | | |
|----------------------------------------------------------------------------------------------------|----------------------------------------|--------|---------------------|-------------------------------------------|---------|----|--|--|--|--|--|--|
| $HO \xrightarrow{1}_{11} = H^{1:1} EIOHM_2O, 25 \text{°C, air} \qquad 2a-h \qquad 3a-h \qquad 2i$ | | | | | | | | | | | | |
| en | Substrate R ₁ | Tim | Conversi | Selectivity ^c (%) ^d | | | | | | | | |
| try | 1a–h | e (h) | on [,] (%) | 2a-h | 3a-h | 2i | | | | | | |
| 1 | | 0.08 | 99 | 10 | 85 (79) | 5 | | | | | | |
| 2 | | 0.75 | 99 | 13 | 81 (75) | 6 | | | | | | |
| 3 | ^ ۱c | 0.75 | 99 | 20 | 72 (70) | 8 | | | | | | |
| 4 | F | 0.33 | 95 | 14 | 83 (78) | 3 | | | | | | |
| 5 | | 4 | 99 | 15 | 76 (73) | 9 | | | | | | |
| 6 | ^{Br} → 1f | 4 | 96 | 18 | 78 (72) | 4 | | | | | | |
| 7 |) | 5 | 94 | 12 | 84 (73) | 4 | | | | | | |
| 8 | _Si–≹ ∕ 1h | 0.33 | 98 | 23 | 68 (65) | 9 | | | | | | |

^oReaction conditions: **1a-h** (0.20 mmol), **1i** (0.26 mmol), TC-S-Cu^{(*J*)I}O **1** (1 mol%), TMEDA (4 mol%), 1:1 EtOH/H₂O (3 mL), air, 25 °C. ^bconversion and ^cselectivity were determined by GC-MS analysis. ^disolated yields based on **1a-h** are given in parentheses.

We infer that Cu^{1/II}O NP in these catalysts bind preferentially with the similar polar nature of alkynes possibly due to various cooperative factors like H-bonding, electrostatic, and van der Waals interactions, etc., which in turn lead to the formation of different homo- and hetero-products. In order to obtain a comprehensive understanding of hetero-selectivity of the catalyst **1**, the detailed investigations of the mechanism of the chemical reaction with atomistic and electronic structures details are indispensable. We have performed the *ab initio* molecular dynamics (AIMD)^{14a} simulations to explore the possible interactions between the catalyst **1** and substrates and also the formations of products. Tris2-aminoethylamine (TREN)- cellulose (TC) functionalised with thioglycolic acid (S) anchored on the CullO-111 surface, was used to model the/catalyst AVP assembly (see Fig. 3a). To investigate the hetero-selectivity, alkynes **1a** and **1i** were investigated by forming the copper- σ acetylide complexes with Cu(I/II)-atoms on the CuO surface as proposed in the previous mechanistic study.^{13a} Complete details of the modelling of the catalyst and the copper (I/II)– σ – acetylide complexes along with the computational methods are given in Section F in ESI. The unit cell of CuO was optimised using density functional theory^{14b} with Perdew-Burke-Ernzerhof¹⁴ exchange correlation functional as implemented in the VASP code.^{14d} A time step of 1 fs was set for the AIMD simulations. The dynamics were performed for all the three possibilities of the coupling reaction; two homo-coupling reactions and the cross-coupling reactions. The alkynes were anchored on the surface by means of copper (I/II)–σ–acetylide complex formation. For sake of simplicity, we will use σ-complex instead of Cu $(I/II)-\sigma$ -acetylide complex throughout our discussion.

Table 2. Effect of amine spacer and additives on aerobic oxidative cross-coupling of terminal alkynes.^a

| Ph-== | ≡—H | | | | | | |
|-------------------------|---------------------------|--------------|------------|---------------------|--------------------------|----|----|
| | 1a h Cat (Cu) | TMEDA | | n — — /a | | | 1 |
| но | 1:1 EtOH/H ₂ C | , 25 °C, air | Pn + 2a | 3a (0) | | 2i | |
| 10 / ₁₁ - 11 | | r | non-polar | medium-polar | polar | | |
| En | Catalyst | additi | Time | Conversi | Product | | |
| try | | ve | (min) | on [,] (%) | selectivity ^c | | |
| | | | | | 2a | 3a | 2i |
| 1 | 1 | none | 10 | 99 | 10 | 85 | 5 |
| 2 | 1 + DDA | DDA | 10 | 97 | 76 | 18 | 6 |
| 3 | 1 + BTC | BTC | 10 | 96 | 3 | 20 | 76 |
| 4 | 2 | none | 30 | 99 | 33 | 59 | 7 |
| 5 | 2 + DDA | DDA | 30 | 96 | 43 | 50 | 6 |
| 6 | 2 + BTC | BTC | 30 | 96 | 30 | 61 | 8 |
| 7 | 3 | none | 60 | 98 | 62 | 25 | 12 |
| 8 | 3 + DDA | DDA | 60 | 96 | 65 | 24 | 10 |
| 9 | 3 + BTC | BTC | 60 | 96 | 59 | 27 | 13 |

^oReaction conditions: **1a-h** (0.20 mmol), **1i** (0.26 mmol), Cu-catalyst (1 mol%), TMEDA (4 mol%), 1:1 EtOH/H₂O (3 mL), air, 25 °C. ^bconversion and ^cselectivity were determined by GC-MS analysis.

The snapshots at different stages during the progress of the reaction are captured and few selected snapshots are shown in Fig. 3b. The simulations revealed that the σ-bonded (nearby) Catoms from two different alkynes (1a and 1i) come within the bonding proximity and re-hybridisation of their electron densities facilitates the formation of the C-C bonds between the alkynes in the cost of the σ -complexes. A detailed description from electronic structure point of view is given in Section F5, ESI. This is the key step of the coupling reactions, however, the formation of the $\sigma\text{-bonded}$ complexes in the neighbourhoods is the prime conduction for such heterogeneous chemical reactions. The detailed study about the mechanism of formation of the activated σ -complex will be reported elsewhere. The AIMD simulations also revealed the relaxation process of the activated product states to the ground state of the product. This occurs upon dissipating the electronic and thermal energies through the configurations and conformational changes along with the changes in the catalyst backbone-product interactions which indeed remarkably different between the catalyst backbone-reactant interactions. The AIMD simulations within sub-picosecond timescale convincingly describes the formation of C-C bond that results in the coupled hetero-product **3a** from the σ -bonded alkynes **1a** and **1i** (see Fig. 3). This indeed qualitatively matches with the experimental observations of the hetero-selectivity. We further

COMMUNICATION

Page 4 of 5

investigated the role of the catalysts in the hetero-selectivity process, and realised that the H-bonding interaction (-NH…OH) between the amide N-H atom of the catalyst and the oxygen atom in O-H of 3a play the central role in the selectivity process. This H-bond formation influences the formation of the σ-bonded complex near to the catalyst anchored sites. The nonpolar alkyne **1a** will have ample possibilities to form σ -bonded complexes within the bonding proximity of the 1i and that lead to hetero-product 3a. However, the same H-bond guided grafting of 1i alkyne cannot promote the polar homo-product 2i. This is simply because of the bulkiness of the catalysts and the directional grafting of the 1i σ-complex makes fewer probable configurations of having another $1i \sigma$ -complex within the bonding proximity. The variation of the possible H-bonding distances along the MD trajectory, shown in Fig. 3b clearly depicts that there is no H-bonding interaction present in this case. Due to the absence of polar group no such interaction is present in case of non-polar homo-product 2a.



Fig. 3. (a) The optimised TREN-backbone on the CuO-(111)-surface along with the copper (I/II)-σ–acetylide complexes formed by alkynes **1a** and **1i**. The formation of the alkyne σ -complexes on the neighbouring Cu-atoms is one of the crucial steps for the coupling reactions occurred on the surface.¹³ (b) Progress of the coupling reactions are captured in the snapshots at different time steps of the AIMD trajectory. The formation of the C—C bond and the H-bond occurs simultaneously. (c) The plots describe the H-bonding distances between the amide –NH and O atom of –OH group of polar homo- (inset) (**2i**) and hetero-products (**3a**). In case of hetero-product (**3a**) formation, the H-bonding interaction changes from moderate to strong as the reaction proceeds. The strength of the H-bond is represented by the thickness of the broken H-bond in blue in (b). Different chemical entities involved in the reaction are denoted as follows. The large spheres represents CuO substrate (Cu in tan and O in red). The stick model represent the TREN-backbone without H atoms. Colour Code: grey: C (TREN-backbone), cyan: C (for alkynes), red: O (TREN-backbone and alkynes) blue: N, yellow: S and white: H.

In conclusion, Cu^{1/II}O NPs anchored by cellulose polymer functionalised with TREN and thiol groups TC-S-Cu^{I/II}O **1**, served as an effective water-soluble catalytic system for the homo- and cross-Glaser-couplings of terminal alkynes under greener conditions. The comparison studies of catalysts backbone and carboxylic acid-based additives and the AIMD simulations reveals the interactions between the catalyst backbone and reactants, that play the key fundamental role in facilitating the hetero-selectivity. Thus, any modifications in the catalytic centres that tune such interactions will affect the heteroselectivity. Though the designed catalyst not providing 100% hetero-product, but the approach is highly promising as the desired goal could be achieved by playing with the catalyst- 14 backbone and substrates interactions. Further, we showed easy recyclability by one-step conversion of soluble catalyst 1 to magnetically separable heterogenous catalyst 4 by grafting on to Fe₃O₄ NPs (for details see, section G, ESI).

Notes

View Article Online The authors declare no competing financia, interest C9CC08565C

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Tuneable selectivity in cross-Glaser products is achieved by tweaking the catalyst-backbone. The interaction responsible for this is unravelled.