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Copper(II) SBA-15: A reusable catalyst for azide–alkyne cycloaddition Ibtissem Jlalia<sup>a</sup>, Florian Gallier<sup>b</sup>, Nancy Brodie-Linder<sup>b,c,\*</sup>, Jacques Uziel<sup>b</sup>, Jacques Augé<sup>b</sup>,

Nadège Lubin-Germain<sup>b,\*\*</sup>

<sup>a</sup> Laboratoire des Substances Naturelles, INRAP-Pôle Technologique, Sidi Thabet 2020, Tunisia

<sup>b</sup> Laboratoire de Synthèse Organique Sélective et Chimie bioOrganique, EA 4505, University of Cergy-Pontoise, F-95000 Cergy-Pontoise cedex, France

<sup>c</sup> Laboratoire Léon Brillouin, CEA Saclay, Bât. 563, F-91191 Gif-sur-Yvette, France

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### ABSTRACT

The azide–alkyne cycloaddition reaction was investigated under catalytic conditions involving a copper(II) loaded silica based mesoporous material. Cu(II) SBA-15 demonstrated a high catalytic effect in 1,4-triazoles synthesis in organic. No additives such as a base or a reductant are required. Quantitative yields were obtained and a mere filtration of the mesoporous material which retains copper(II) allows the recovery of the catalyst. In addition, up to 5 times recycling of the catalyst was achieved without loss of the activity affording 1,4-triazoles in a yield up to 98%.

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#### 1. Introduction

The copper-catalyzed azide-alkyne cycloaddition (CuAAC) is the landmark reaction in click chemistry and originates from the pioneering works of Sharpless et al. [1] and Meldal et al. [2]. Copper(I) catalysis accelerates dramatically the Huisgen 1,3-dipolar reaction and leads to a high regioselectivity in favor of the 1,4isomer of the triazole product. The copper(I) catalysts generally originate from copper(I) salts in presence of a base and/or a ligand, in situ reduction of copper(II) salts usually by ascorbate, and/or a mixture of copper(0) and copper(II) species [3]. Heterogeneous copper(I) sources have also been described as they present a great advantage concerning catalyst removal, recovery and recycling. Cu(I) salts have been supported on ionic resins [4-7], various polymeric backbones [8–16], silica [17–21], ionic liquids [22], montmorillonite [23], zeolites [24–27], or biopolymers [28,29]. The main drawback is that such solid catalysts frequently suffer from the thermodynamic instability of Cu(I) which is prone to oxidation or disproportionation. Therefore, Cu(II) has recently been immobilized on alumina [30,31], silica [32,33], anatase [34], various

\* Corresponding author at: Laboratoire Léon Brillouin, CEA Saclay, Bât. 563, F-91191 Gif-sur-Yvette, France.

\*\* Corresponding author. Tel.: +33 1 34 25 70 54; fax: +33 1 34 25 73 78. E-mail address: nadege.lubin-germain@u-cergy.fr (N. Lubin-Germain).

http://dx.doi.org/10.1016/j.molcata.2014.06.003 1381-1169/© 2014 Elsevier B.V. All rights reserved. polymeric backbones [35–37], heteropolyacids [38,39], minerals [40–43], or biooligomers [44–46] with or without the presence of a sacrificial reducing agent.

With respect to our work, we have already been concerned with controlling the regioselectivity of the reaction in microreactors such as micelles [47]. Herein we have explored the usefulness of mesoporous material and the potential role of the pores in the catalysis of the process. Indeed copper loaded on silica type materials as MCM-41 and SBA-15 have been shown to be very useful in selective catalytic experiments [48–50].

### 2. Experimental methods

# 2.1. Characterization of the mesoporous Cu(II) SBA-15

The SBA-15 material was prepared according to a wellestablished procedure [51]. This mesoporous silica (50 mg) was then suspended for 10 min at room temperature in 20 mL of a  $5 \times 10^{-2}$  mol/L aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O containing a particular amount of a solution of 28% (w/w) NH<sub>4</sub>OH in order to obtain pH 10.5 [52]. The material was then filtered, washed profusely with water to ensure the removal of all free Cu(II) ions and dried in an oven at 60 °C for 4 h to give a bluish solid. Control of the time and pH of impregnation is crucial for the copper loading.

The copper uptake was then determined by UV-visible spectroscopy. A sample of Cu(II) SBA-15 (10 mg) is suspended in 5 mL 2% (w/w) aqueous HNO<sub>3</sub> and stirred for 15 min at room temperature, vigorously in order to ensure the best homogeneity possible in solution and filtered. UV absorbance of the solution was measured and the copper content was calculated with the standard calibration curve.

Each batch of Cu(II) SBA-15 is further characterized by IR spectroscopy and N<sub>2</sub>-adsorption measurement. Detailed values of Pore volume and Pore diameter as well as the BET Surface area for the freshly prepared Cu(II) SBA-15, the Cu(II) SBA-15 after several runs (simply filtered after the last run) and the Cu(II) SBA-15 thoroughly rinsed after the last run can be found in the supporting information. Extensive characterization of this Cu(II) SBA-15 (elemental analysis, XRD, SAXS and TEM) has already been published elsewhere [52].

# 2.2. General procedure for Cu(II) SBA-15 azide–alkyne cycloaddition

Alkyne (0.5 mmol), azide (0.55 mmol) and Cu(II) SBA-15 (25 mg, 8 mol% Cu) were stirred in dichloromethane (2 mL) for 18 h. The mixture was filtered and the solid was washed twice with 2 mL of dichloromethane. The filtrate was concentrated by evaporation under vacuum. Excess of azide can be removed after immobilization on a triphenylphosphine resin. In the case of highly polar substrates, the solid was washed twice with 2 mL of acetonitrile.

# 2.3. General procedure for catalyst recycling

To a screw-capped vial were successively added ethyl propiolate ( $50 \mu$ L; 0.49 mmol), benzyl azide (73.2 mg; 1.15 eq.), dichloromethane (2 mL) and finally the Cu(II) SBA-15 (25 mg; 7.5% Cu, w/w; 6 mol%). The reaction was stirred overnight and the catalyst was recovered by filtration over a nylon membrane ( $0.45 \mu$ m, Millipore<sup>®</sup>) and washed with dichloromethane ( $2 \times 2 \text{ mL}$ ). The combined organic solvent was evaporated under vacuo yielding the desired triazole (97–110 mg; 87–97%). After the 5th run we recovered 23.9 mg of the catalyst (over the 25 mg used for the 1st reaction), hence a recovery of 93% over 5 runs (99% average recovery per run).

# 3. Results and discussion

#### 3.1. Catalysis

One of us recently reported the conditions for the controlled Cu(II) loading in SBA-15 materials from 6 to 20% Cu (w/w) [52]. It was shown that the amount of Cu(II) loaded on the SBA-15 surface could be controlled by a reaction in aqueous copper solutions at ambient temperature in 10 min. It was also shown that good copper dispersion over the surface was achieved. The cycloaddition between ethyl propiolate and benzyl azide was first investigated using an increasing amount of Cu(II) SBA-15 in dichloromethane. The conversion into the 1,4-disubstituted triazole was determined by <sup>1</sup>H-NMR spectroscopy after 2 h of reaction (Table 1). We were delighted to discover that a copper(II) catalyst could efficiently catalyze at room temperature such a reaction, without further addition of a reducing agent which would have allowed the existence of Cu(I) species. The reaction is totally regioselective as in the Cu(I) cycloaddition.

Next, we have checked the influence of the copper source as well as the solid support (Table 2). Without any copper source (entry 1–2) no reaction took place. The same goes for  $Cu(NO_3)_2 \cdot 3H_2O$  (entry 3) which is used for the Cu(II) SBA-15 catalyst preparation. In this case, as in the case of Cu(II) SBA-15 (entry 4), no reducing agent or base has been added.





Fig. 1. Cu(II) SBA-15 reusability.

In order to demonstrate the scope of this catalysis, various alkynes and azides were tested using a moderate amount (8 mol%) of the catalyst (Table 3). The reaction proceeded efficiently with ethyl propiolate (entries 1–5), 3,3-diethoxyprop-1-yne (entries 6–9) and 4-bromobut-1-yne (entries 10–14). The isolated yields are particularly high, sometimes quantitative (entries 1, 3, 12), with benzyl azides.

When propargylamine was used, the reaction proceeded instantaneously but the triazole was recovered in very poor yield probably due to the amino complexation to copper (entry 20). This CuAAC rate acceleration by amino group complexation has already been observed [53]. The same observation could be made concerning alcohol-containing reactants in a less important manner (entries 15-19). Since no reaction was observed with octyne and 2,3,4,6tetra-O-benzyl-β-D-glucopyranosylacetylene (entries 21 and 22), it is supposed that the catalysis was impeded in these two cases by the size of the molecules (20 Å) compared to that of the pores (70 Å) which contain the copper catalytic species. Such an effect of the importance of the size of the pores was not observed with Cu(I)zeolites which accept any substrate [25]. Our observation opens the way to the possibility of tuning the size of the pores in concordance with the substrates. Concerning octyne, we can also take into account the hydrophilic character of the pores and we can postulate that the octyne preferred to remain outside in the organic phase.

# 3.2. Recycling of the Cu(II) SBA-15

The reaction was tested on ethyl propiolate with benzylazide and we demonstrated that it proceeded with the same yield for at least five times (Fig. 1). After each run, the catalyst can be almost quantitatively recovered by a mere filtration over a 0.45  $\mu$ m nylon membrane (See Section 2.3).

After the last catalytic cycle, a more thorough washing was performed and the material was analyzed in order to control the state of the catalytic surface. The IR spectra found in Fig. 2 indicates that no build-up of organic materials on the surface is occurring. This is also corroborated by N<sub>2</sub> volumetric adsorption analysis where only slight changes in the pore structure can be observed (*see Supporting Information*). In addition, the content of copper remained identical indicating that no leaching occurred.

# Table 1



Entry	Cu(II) SBA-15	Conversion*		
1	-	Traces		
2	4 mol%	34%		
3	8 mol%	75%		
4	16 mol%	100%		

\* Evaluated by <sup>1</sup>H-NMR.

# Table 2



Entry	Catalyst	Yield (%)
1	-	0
2	SBA-15 (20 mg)	0
3	CuNO <sub>3</sub> ·3H <sub>2</sub> O (8 mol%)	0
4	Cu(II) SBA-15 (25 mg, 8 mol% Cu)	67

# 3.3. Mechanistic studies

To our knowledge, the first example of the use of Cu(II) as the reactive catalytic species in the Huisgen reaction was described in

aqueous medium [54]. Later on, a di-copper(II) substituted silicotungstate was shown to catalyze both the oxidative alkyne-alkyne homocoupling and the Huisgen reaction; the high yield in 1,2,3triazoles in that reaction was proven to be due to the preformation

# Table 3

Scope and limitations of the catalyzed cycloaddition. Cu(II) SBA-15

р		(8 mol%, 10% Cu w/w)	
N	$\pm$ r n <sub>3</sub>		
1a-g	2а-е	CH <sub>2</sub> Cl <sub>2,</sub> RT, 16h	

3aa-gb sole regioisomer

Entry	Alkyne 1: R	Azide <b>2</b> : R′	Product <b>3</b> : Yield <sup>*</sup>
1	1a: COOEt	<b>2a</b> : PhCH <sub>2</sub>	<b>3aa</b> : 98%
2	1a: COOEt	<b>2b</b> : EtOCOCH <sub>2</sub>	<b>3ab</b> : 76%
3	1a: COOEt	<b>2c</b> : <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	<b>3ac</b> : 99%
4	1a: COOEt	<b>2d</b> : 2-oxolan-CH <sub>2</sub>	<b>3ad</b> : 87%
5	1a: COOEt	2e: HOCH <sub>2</sub> CH <sub>2</sub>	<b>3ae</b> : 64%
6	<b>1b</b> : CH(OEt) <sub>2</sub>	<b>2a</b> : PhCH <sub>2</sub>	<b>3ba</b> : 83%
7	<b>1b</b> : CH(OEt) <sub>2</sub>	<b>2b</b> : EtOCOCH <sub>2</sub>	3bb: 66%
8	<b>1b</b> : CH(OEt) <sub>2</sub>	<b>2d</b> : 2-oxolan-CH <sub>2</sub>	3bd: 56% <sup>(a)</sup>
9	<b>1b</b> : CH(OEt) <sub>2</sub>	2e: HOCH <sub>2</sub> CH <sub>2</sub>	3be: 35%
10	1c: CH <sub>2</sub> CH <sub>2</sub> Br	<b>2a</b> : PhCH <sub>2</sub>	<b>3ca</b> : 67%
11	1c: CH <sub>2</sub> CH <sub>2</sub> Br	<b>2b</b> : EtOCOCH <sub>2</sub>	3cb: 72%
12	1c: CH <sub>2</sub> CH <sub>2</sub> Br	<b>2c</b> : <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	3cc: 98%
13	1c: CH <sub>2</sub> CH <sub>2</sub> Br	<b>2d</b> : 2-oxolan-CH <sub>2</sub>	3 cd: 57%
14	1c: CH <sub>2</sub> CH <sub>2</sub> Br	2e: HOCH <sub>2</sub> CH <sub>2</sub>	3ce: 52%
15	1d: CH <sub>2</sub> OH	<b>2a</b> : PhCH <sub>2</sub>	<b>3 da</b> : 68%
16	1d: CH <sub>2</sub> OH	<b>2b</b> : EtOCOCH <sub>2</sub>	3db: 65%
17	<b>1d</b> : CH <sub>2</sub> OH	<b>2c</b> : <i>p</i> -F-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	3dc: 72%
18	<b>1d</b> : CH <sub>2</sub> OH	<b>2d</b> : 2-oxolan-CH <sub>2</sub>	3dd: 46%
19	1d: CH <sub>2</sub> OH	2e: HOCH <sub>2</sub> CH <sub>2</sub>	3de: 26%
20	1e: CH <sub>2</sub> NH <sub>2</sub>	<b>2a</b> : PhCH <sub>2</sub>	<b>3ea</b> : 17%
21	<b>1f</b> : <i>n</i> -C <sub>6</sub> H <sub>13</sub>	<b>2b</b> : EtOCOCH <sub>2</sub>	3fb:-
22	<b>1 g</b> : 2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl	<b>2b</b> : EtOCOCH <sub>2</sub>	3gb:-

\* Isolated yield.

<sup>a</sup> Isolated as the aldehyde.

58



Fig. 2. IR spectra of Cu(II) SBA-15 materials before and after 5 catalytic cycles.



Fig. 3. Cycloaddition under O<sub>2</sub> atmosphere.

of a Cu(I) acetylide [38]. With Cu(OAc)<sub>2</sub> as catalyst, a fast reaction occurred with organic azides capable of chelation-assisted copper coordination at the alkylated nitrogen position [55–57].

# 3.3.1. Oxidation state of copper

In these cases, the authors suggest that Cu(II) undergoes reduction to Cu(I) *via* alcohol (solvent) oxidation and/or alkyne homocoupling; they gave experimental evidence of the formation of a mixed-valency dinuclear copper (I/II) species. They proposed that the copper centers function as a Lewis acid to enhance the electrophilicity of the azido group, whereas the other one is a two-electron reducing agent in oxidative metallacycle formation [58].

At this stage of discussion, we must remember that, as early as 2002, Sharpless et al. noted that even Cu(0) could be used as a source of the catalytic process, although these reactions took longer to proceed to completion [1,59]. Recently Cu(0) nanoparticules as nanocatalysts were proved to be particularly active in the process [59]. Copper (II) has been reported to be the reactive catalytic species in other cases as well [60].

Our copper source was loaded onto a solid support which hampers direct observation of the oxidation state; therefore indirect measurement might give information about the mechanism. No spectroscopic evidences concerning the formation of the homocoupling 1,3-diyne were found, either by NMR or GC–MS. Thus, reduction to Cu(I) seems unlikely.

In order to probe the oxidation state of the copper ions, we studied the influence of an atmosphere of molecular oxygen. Air oxidation of Cu(I) to Cu(II) is generally fast (thus explaining the instability of Cu(I) ions) and has been proven here when copper(I) iodide was introduced into vials that were successively flushed (for 5 min) and kept (for ½h) separately under either O<sub>2</sub> or Ar atmosphere. Complexation by addition of NH<sub>4</sub>OH solution occurs readily in the case of oxygen producing a blue solution (characteristic for Cu<sup>II</sup>(NH<sub>3</sub>)<sub>n</sub> ions). In the case of argon, this blue solution was observed only after few minutes. We have then performed the cycloaddition under O<sub>2</sub> atmosphere and shaded from the light (Fig. 3). In that case, if Cu(II) again. This reaction was monitored



by GC–MS and the conversion is complete within 24 h, just as the classical conditions.

#### 3.3.2. Kinetic study

In this kinetic study, we are not comparing the direct catalytic activity between Cu(I) and Cu(II). We are taking into consideration the particular catalytic system where the reduction of Cu(II) in the SBA material is not expected to be a minor secondary reaction if at all. As we want to create a scenario for possible Cu(I) catalysis in our reaction, as proposed by Sharpless and co-workers [1] or Meldal and co-workers [2], and in order to have similar reaction conditions (especially involving a solid catalyst) copper(I) iodide was chosen as the Cu(I) catalyst and no base was added. Reactions were carried out in CDCl<sub>3</sub> under similar condition using Cu(II) SBA-15 (6 mol%) and Cul (0.3 mol%) and monitored by GC-MS at given times (Fig. 4). At this loading of catalyst, the rate of the reaction involving Cu(II) SBA-15 is much higher than the one of CuI (around 4 times). So if the copper(I) ions are the only one involved in the catalysis, 20% of the total amount of the Cu(II) bound to the surface of SBA-15 has to be reduced to Cu(I), which is highly unlikely to occur. Therefore, copper(II) is believed to play a crucial role for this reaction.

# 3.3.3. Acetylide copper intermediate

Deuterium exchange experiments can also give us insights into the reaction mechanism. We have first prepared ethyl deuteropropiolate under basic classical conditions. GC–MS showed deuterium incorporation over 99% (Fig. 5). This deuterated alkyne was then submitted to the usual cycloaddition conditions. No deuterium was incorporated into the triazole ring (confirmed either by <sup>1</sup>H-NMR and GC–MS) thus indicating the cleavage of the C–D bond and the formation of a copper–carbon bond can be postulated. Therefore, Lewis acidic mechanism (as exemplified with zeolites [26]) can be ruled out.

#### 3.3.4. A dinuclear mechanism

Although copper(II) reduction to Cu(I) by a hydrogenabstraction/proton-delivery/electron-gain mechanism is a remote possibility [60], the previous set of experiments led us to hypothesize the formation of the triazole through the following mechanism involving only Cu(II) species (Fig. 6). The complete



Fig. 5. Deuteration experiment.



Fig. 6. Simplified mechanism of the Cu(II) SBA-15 catalyzed Huisgen reaction.

1,4-regioselectivity is rationalized through a covalent bond between copper and the alkynes.

It was observed that dinuclear alkynyl copper complexes exhibit superior reactivity toward organic azides compared to their monomeric counterparts [61]. Such complexes were supposed to be involved in the recent description of the copper catalyzed Huisgen reaction [40,57,60], and were recently unveiled [62]. Since the pore surface of the catalyst is covered with copper (II) atoms, approximately 2 Cu(II) atoms per nm<sup>2</sup>, we can presume that the formation of a dinuclear complex is not out of the question. Since we have not detected alkyne oxidative homocoupling products, we can hypothesize that the formation of a Cu(II) acetylide complex (Fig. 6) is a key and rate-determining step [40,60,62]. Once the dinuclear alkynyl copper complex is formed, it can undergo a classical evolution *via* a metallacycle [40,57,60,62]. Protodemetallation can subsequently occur through internal proton delivery from the residual silanol groups of the surface.

Two supplementary experiments were performed using Cu(II)-SBA 15 with different porosity or Cu loading (Fig. 7).



Cu(II) SBA-15 (5.5% w/w;  $\varnothing$  7nm)

Fig. 7. Loading and sizes of the pores.

In addition, the pore size may have a great effect on the reactivity as the reaction is believed to occur inside the pores (as corroborated by  $N_2$  volumetric adsorption of the catalyst without washing). The influence of these parameters is currently under investigation and will be reported in due time.

# 4. Conclusion

We have shown herein that our Cu(II) SBA-15 material can be used successfully as a reusable catalyst for an azide–alkyne cycloaddition reaction without degradation. The conversion can be as high as 99% and a total regioselectivity is obtained. To our knowledge, this is the first time that a copper(II) SBA-15 material has been shown to be active as a reusable catalyst for azide–alkyne cycloaddition reactions.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.06.003.

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