Catal Lett
DOI 10.1007/s10562-015-1625-1

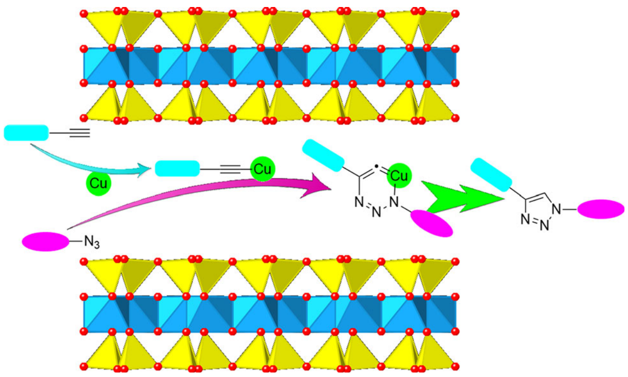
Copper(I) Confined in Interlayer Space of Montmorillonite: A Highly Efficient and Recyclable Catalyst for Click Reaction

Mohammed El Mehdi Mekhzoum[1,3] · **Hanane Benzeid**[2] · **Abou El Kacem Qaiss**[1] · **El Mokhtar Essassi**[1,3] · **Rachid Bouhfid**[1]

Received: 3 July 2015 / Accepted: 6 September 2015

Abstract Cu^{I}-exchanged solid based on montmorillonite material was investigated as catalyst in organic synthesis. The catalytic potential of this material was evaluated in the Huisgen [3 + 2]cycloaddition. This catalytic system has been examined and proved to be an efficient heterogeneous catalyst for this "click chemistry"-type transformation. The ensuing catalyst can be recycled and reused five times without dramatic yield loss.

Graphical Abstract



Keywords Click chemistry · Montmorillonite · Heterogeneous catalysis · Azide · Triazole

1 Introduction

1,2,3-Triazoles are an important class of heterocyclic compounds that received a huge attention from many pharmaceutical and organic chemists due to its broad spectrum of their biological and pharmaceutical properties [1]. Although these compounds are thus use in the making of dyes, corrosion inhibition, photostabilizers, and photographic materials [2]. Indeed, the main method for the synthesis of 1,2,3-triazoles is the Huisgen 1,3-dipolar cycloaddition reaction of azides with alkynes [3], which has been known as one of the most interesting synthetic tools essentially because of the convenient and reliable construction of 1,2,3-triazole derivatives [4]. However, unfortunately, the thermally induced 1,3-dipolar cycloaddition reaction requires an elevated temperatures and often gives a mixture of 1,4- and 1,5-

---

Electronic supplementary material The online version of this article (doi:10.1007/s10562-015-1625-1) contains supplementary material, which is available to authorized users.

✉ Rachid Bouhfid
r.bouhfid@mascir.com; gbouhfid@yahoo.fr

[1] Moroccan Foundation for Advanced Science, Innovation and Research (MAScIR), Institute of Nanomaterial and Nanotechnology (NANOTECH), Rabat Design Center, Rue Mohamed El Jazouli, Madinat Al Irfane, 10100 Rabat, Morocco

[2] Laboratoire de Chimie Analytique, Université Mohammed V de Rabat- Faculté de Médecine et de Pharmacie, BP 6203, Rabat, Morocco

[3] Laboratoire de Chimie Organique Hétérocyclique, Université Mohammed V de Rabat, Faculté des Sciences, Av. Ibn Battouta, BP 1014, Rabat, Morocco

triazole stereoisomers (nearly 1:1) when using asymmetric alkynes [5]. In this respect, the classic 1,3-dipolar cycloaddition fails as a true click reaction.

Alternatively, click chemistry represents an ideal set of near perfect reactions [6]. Historically, the Synthesis of triazolo conjugated compounds through click chemistry reaction has attracted attention in many fields and lots of interest in recent years [7, 8]. The click chemistry has many applications in synthetic and medicinal chemistry [9], bioconjugations [10], material sciences [11], and polymer chemistry [12], it's used increasingly in drug discovery [13]. Among the number of reactions that fulfill click chemistry's criteria, the copper-I catalyzed version of the Huisgen 1,3-dipolar cycloaddition between azides and alkynes is to date the most practical and useful "click" reaction, regioselectively affording 1,4-disubstituted 1,2,3-triazoles [14–17]. However, The catalyst could be Cu^I salt or Cu^I generated in situ by the reduction of Cu^{II} salts, usually in organo-aqueous media. Besides, The use of this catalytic Copper(I) accelerate the reaction resulting in the highly regioselective formation of 1,4-disubstituted triazoles [18, 19].

Recent years have witnessed a phenomenal growth in the use of inorganic solids as reaction media for organic transformations [20–23], in this case, we propose to explore the use of copper exchanged montmorillonite for such catalytic application. Clays and modified clays are used to catalyze due to their high specific surface [24] various types of organic reactions such as addition, Michael addition, carbene addition and insertion, hydrogenation, allylation, alkylation, acylation, pericyclic reactions, epoxidation and several more [25]. Considering all these aspects, the objective of this research is to report a simple and efficient synthesis of a montmorillonite-supported, recyclable, and inexpensive copper catalyst. This system catalytic has been used especially in the reaction of click chemistry of azide with alkyne in aqueous media at room temperature to obtain 1,4-disubstituted triazole.

2 Experimental

2.1 General Remarks

Unless stated otherwise, all reagents and solvents were purchased from commercial suppliers and were used without further purification. Benzyl azide, azidoethanol, azidopropanol, 1-propargylthiabendazole, 3-phenyl-1-(prop-2-yn-1-yl)quinoxalinone and copper(I)-clay catalyst were prepared in our laboratory. 2-bromoethanol (95 %), 3-bromo-1-propanol (97 %) and sodium azide (99 %) are purchased from Sigma-Aldrich. Natural montmorillonite (trade name of Na-Cloisite Na-MMT) is purchased from Southern Clay Product Inc. (Gonzales, Texas). Na-MMT consists on fine particle powder with a cationic exchange capacity CEC = 96 mEq/100 g and an interlayer spacing $d_{001} = 1.17$ nm.

2.2 Preparation of Cu^I-Montmorillonite Catalyst

Cu^I-MMT was prepared from Na-MMT as follows: 2 g of the Na-MMT was dispersed in 300 ml of 1 M CuI aqueous solution for 24 h at room temperature under vigorous stirring. The dispersion was centrifuged at 10,000 rpm and washed several time with deionized water. Cu^I-MMT was dried overnight at 80 °C.

2.3 Preparation of 2-Azidoethanol and 2-Azidopropanol

These compounds were prepared as described in the literature [26, 27] from 2-bromoethanol, 3-bromo-1-propanol and sodium azide. *Caution*: special care should be taken to minimize the possible explosion in the preparation and handling of the azides compound.

2.4 Typical Experimental Procedure for the Synthesis of 1,2,3-Triazoles

To a glass bottle, was added a mixture of alkyne (1 mmol), Cu^I-MMT (5 mg) and the appropriate alkyl azide (1.2 mmol) in water (5 ml), the reaction mixture was stirred at room temperature for 2 h. The reaction was monitored by thin layer Chromatography. After completion of the reaction. Chloroform (25 ml) was added to the whole reaction mixture. The catalyst was removed by filtration and washed with $CHCl_3$ (10 ml), dried in vacuum at 80 °C and then stored in a desiccator before being reused in subsequent reactions to demonstrate its prolonged activity. The filtrate was dried over Na_2SO_4 to remove remaining water, conducting in filtration filter paper and the solvent was removed in vacuum. The products were purified by recrystallization or column chromatography and characterized by standard analytical techniques such as (^{1}H and ^{13}C) NMR, FTIR, mass spectroscopy, melting point determination and all gave satisfactory results (see supporting information).

3 Results and Discussion

3.1 Preparation and Characterization of MMT-Cu^I

At first, the catalyst was efficiently prepared by cationic exchange of interfoliar cation Na^+ in saturated solution of CuI. The suspension was stirred 24 h at room temperature, followed by centrifugation, washed with deionized water, and finally drying overnight. Once the material was prepared, a systematic analysis was needed in order to correlate its structural, textural and morphological properties to its catalytic activity. A thorough characterization of the catalyst was done using different characterization techniques like XRD, FTIR, BET and thermal analysis. The X-ray diffraction patterns of the Na-MMT and Cu^{I}-MMT in the range of 2.5°–10° (2θ) were presented in (Fig. 1). The Na-MMT shows the peak corresponding to the reflexion of the (001) planes at $2\theta = 7.24°$, the basal spacing of this clay calculated to be 1.17 nm. After treatment of the parent Na-MMT with CuI the XRD studies of Cu^{I}-MMT showed that the layered structure is retained and the basal spacing of (d_{001}) was estimated to be 1.47 nm. On the other hand, the ionic radius for Cu^{I} is 0.96 Å which is similar to the Na of 0.95 Å; it seemed that Cu^{I} entered into the interlayer space of MMT as hydrated cation or composite cation that made planar distance increase. The increase in the basal plane distance from XRD may be caused by intercalation of Cu^{I} into the framework or swelling/hydration of the clay. Further, the incorporation of copper(I) in clays was not much studied due to its relative instability and the pH-dependent redox phenomena occurring inside the clay, even for copper(II). Clays that were cation exchanged with other metals were usually dispersed in aqueous solutions of the metal salt for long periods of time [28–30]. In our case, We decided to prepare Cu^{I}-MMT and washed with deionized water several times to remove the physisorbed copper onto the surface of clay keeping in mind that the copper salt may only be adsorbed or partially exchanged.

The FT-IR spectrum of both Na-MMT and Cu^{I}-MMT catalyst are shown in (Fig. 2). Most of the changes in the spectrum of copper-exchanged montmorillonite were noticed in the 3700–3000 cm^{-1} region, as the remaining part of the spectra is almost identical to the Na-MMT. These spectra present three bands absorption in the region 4000–1500 cm^{-1}. The band at 3625 cm^{-1} is assigned to the stretching vibration of structural (octahedral) hydroxyl (O–H) groups linked either to Al^{3+} or Mg^{2+}. The bands at 3370 and 1627 cm^{-1} is assigned to the hydroxy group of interlayer water molecules. The absorption bands at 1118, 980 and 925 cm^{-1} are attributed to the stretching vibration of Si–O, Si–O-Si and the deformation of hydroxyl linked to either Al^{3+} or Mg^{2+} or Fe^{3+}. On the other hand, as the Cu is exchanged with Na^{+} in MMT, the hydration peak intensity decreases in consistent with the fact that Na^{+} coordinates higher amount of water than the exchanged cation [31–34].

The TGA/DTG curves of Na-MMT and Cu^{I}-MMT were used to measure the thermal stability (Fig. 3). In the case of Na-MMT, two thermal decomposition steps are observed, one dehydration stage with the maximum peak at 82 °C in the range of 25–160 °C and the second stage at 663 °C in the range of 300–720 °C originate from the dehydroxylation of montmorillonite. Moreover, the catalyst showed one dehydration stage over the temperature range of 25–300 °C. The evolution of adsorbed and cation-coordinated water specie from Cu-MMT is represented by a peak centered at 65 °C and a shoulder at 160 °C, respectively. Three peaks at 369, 577 and 630 °C in the range of 300–870 °C signify the dehydroxylation process of Cu^{I}-MMT [35, 36]. Thus, the Na-MMT showed more absorption of water than Cu^{I}-MMT and can be explained by the exchanged of hydrate metal. Furthermore, many researchers agree that for temperatures up to 200 °C, Copper species migrate into hexagonal cavities and above 200 °C, they penetrate the octahedral sheets where they saturate the charge of the sheet [37–39].

The N_2 adsorption isotherms of Na-MMT and the catalyst are displayed in Fig. 4 and Table 1 shows their respective surface areas, pore volumes and areas. As can be depicted from Fig. 4, the shape of the isotherm gives a qualitative assessment of the porous structure of the materials. For both isotherms, the shape is approximately

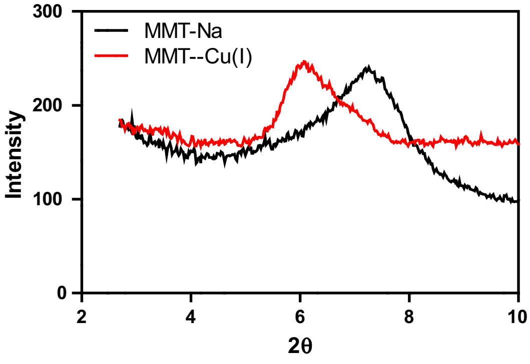


Fig. 1 XRD patterns of Na-MMT and Cu^{I}-MMT

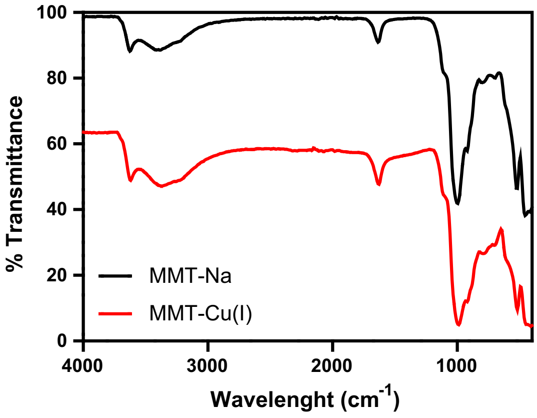


Fig. 2 FTIR spectra of Na-MMT and Cu^{I}-MMT

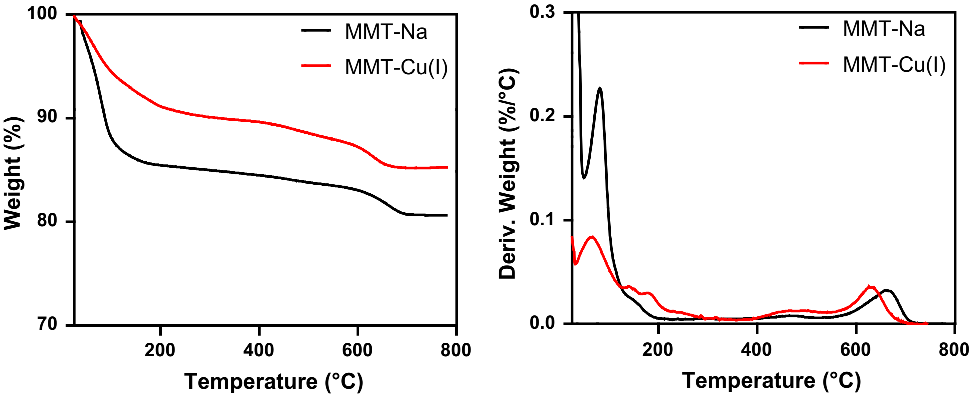


Fig. 3 TGA and DTG curves of Na-MMT and Cu^I-MMT

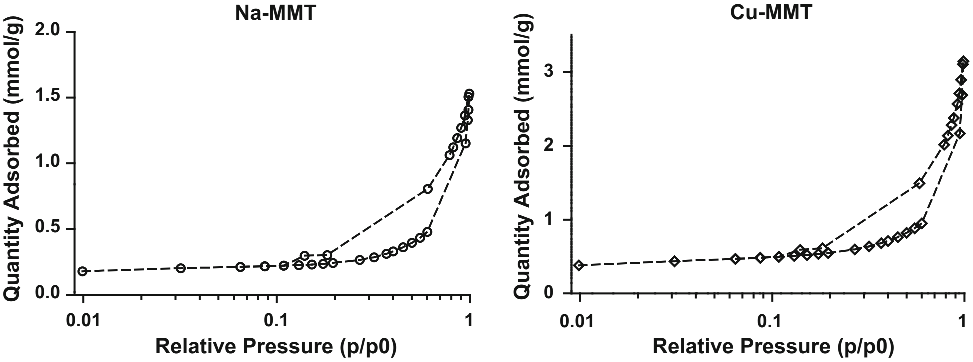


Fig. 4 N_2 adsorption/desorption isotherm of both Na-MMT and Cu^I-MMT

Table 1 Nitrogen physisorption data of both Na-MMT and Cu^I-MMT

	Surface area (BET) (m^2 g^{-1})	BJH total pore volume (cm^3 g^{-1})	BJH total pore area (m^2 g^{-1})
Na-MMT	18.9	0.053	30.92
Cu^I-MMT	42.6	0.111	55.78

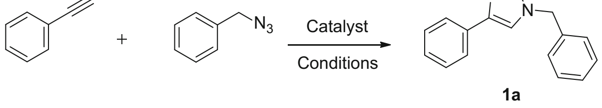
the same. The isotherm powder shows a significant hysteresis pattern but does not show a plateau at high P/Po like the Type IV isotherm. The adsorption–desorption isotherm was of type-IIB which reflects predominance of macropores with a H3 hysteresis pattern indicates presence of slit-like pores. The isotherm shape indicates that the material contains fine and larger mesopores, which is responsible for the hysteresis and macropores, which results in the absence of the plateau. Furthermore, the strong adsorption at low relative pressures ($P/P_o < 0.01$), characteristic for microporous materials, is, however, very low indicating that the material has negligible or non-existent micropores. The surface area and pore volume of Na-MMT was found to be 18 m^2 g^{-1} and 0.053 nm and that for catalyst was found to be 42 m^2 g^{-1} and 0.111 nm, respectively. The incorporation of copper into the framework of the MMT is apparent here, as it leads to 57 % increase in surface area as well as 52 % increase in pore volume. This gives first indication of chemical interaction between Cu^I and MMT. The insertion of copper cation into MMT reduces the number of small mesopores and thus, the exchange process results in significant increase in the surface areas of Cu-montmorillonite with respect to the Na-montmorillonite. These findings suggest that the copper ion is introduced inside the interlayer of the clay mineral not only by cation exchange at the planar sites, but also through the interaction with the aluminosilicate sheets. The above results indicate that the exchanged ion affect the surface characteristics of MMT in some manner that appears to be related to the size and interlayer arrangement of the exchanged ion in the clay [40].

3.2 Preparation and Characterization of 1,4-Disubstituted Triazoles

After synthesis and characterization of copper(I)-exchanged montmorillonite. The model reaction of phenylacetylene and benzyl azide was used to investigate the efficiency of this Cu^I -modified montmorillonite. Although acetonitrile was often used as solvant for click reaction (because many early experiments were performed in acetonitrile). First, it should be noted that the reaction without any catalyst, did not occur in acetonitrile at room temperature, but led to a 1:1 mixture of regioisomers after a extended reaction time at reflux (36 h; 70 %). At room temperature, using CuI alone as the catalyst, the reaction was still very slow but yielded a single regioisomer with incomplete conversion (36 h, 70 %). In sharp contrast, the modified montmorillonite Cu^I-MMT had a significant effect on catalytic activity and gave the expected adduct **1a** even at room temperature (12 h; 72 % only the 1,4-adduct pure was formed and isolated after complete conversion). Refluxing acetonitrile, good yield was also obtained (6 h; 76 %). Given the above experimental data, the Cu^I catalytic activity is significantly enhanced in the presence of modified montmorillonite. In order to get the best result that involves the reaction yield, we started with optimizing the reaction conditions keeping in mind the greener conditions. Various reaction conditions were examined namely: catalyst loading, time, and different solvent systems. Initially, the influence of the solvent nature was first studied on the synthesis of **1a** to adjust the reaction conditions, the model reaction was carried out in ACN, ACN/water (1:1) and then water at room temperature. In general, the yields obtained are privileged 80–98 % (Table 2). More polar solvent such as ethanol and tetrahydrofuran including the increase of catalyst loading and varying reaction time provided as well the corresponding compound **1a,** the yield was lower than the one in water. However, the reaction was less clean with detectable formation of byproducts [41] and thus, water proved to be the best solvent.

The regioselectivity of this 1,3-dipolar cycloaddition reaction was confirmed by ^{13}C NMR spectrum, according to a recent study release by Creary et al. [42] concerning the difference between 1,4- and 1,5-disubstituted triazoles, the 1,4-disubstituted-1*H*-1,2,3-triazoles can easily be distinguished from the isomeric 1,5-disubstituted-1*H*-1,2,3-triazoles by the large bond C–H coupling constant in the gated decoupled ^{13}C NMR spectrum. Depending on the substituents within the triazole ring, The C-5 signal of 1,4-appears at $\delta = 120$ ppm, whereas the C-4 signal of 1,5 appears at $\delta = 133$ ppm. In this respect, the ^{13}C NMR signal of the 1,4 isomer was more shielded than the 1,5 isomer. In our case, ^{13}C NMR spectrum showing the characteristic signal at ~124 ppm assigned to C-5 triazolyl carbon, which confirm that the 1,4-regiosmers has been obtained exclusively in the presence of Cu^I-MMT catalyst.

Table 2 Screening of catalyst optimization studies for the cycloaddition of phenylacetylene to benzyl azide



Entry	Solvent	Yield (%)
1	ACN	80
2	ACN: H_2O	86
3	H_2O	98

Reaction condition [Cu^I-MMT] (5 mg); stirred at room temperature; ACN/H_2O (1:1); ACN; H_2O; 2 h

Considering the above result, the best yields were obtained when the reaction was terminated after 2 h. Prolonging the reaction time had no distinguishable effect on the progress of the reaction. Furthermore, when the click reaction was conducted at room temperature the increase of the temperature up to reflux affect slightly the reaction yield. It has been found that water is the most suitable solvent for this reaction process. Among the examined solvents, when water was used alone, the yield increase until 98 % for **1a**. According to a recent DFT calculations study [43], the coordination of the alkyne to the Cu(I) species was calculated to be slightly endothermic in acetonitrile. However, with water, the displacement process becomes exothermic. This is in good agreement with our experimental results that the reaction proceeds much faster in aqueous solution and does not require an amine base to form the corresponding triazole products in excellent yields. Moreover, there was no difference in yield and reaction time when catalyst loading was reduced to 30, 10 and 5 mg. As a result; we decided to use 5 mg of the catalyst for further studies. On the other hand, using 5 mg as the amount of catalyst Cu^I-MMT afforded the satisfactory results of **1a**. Shabber et al. [44] developed a highly efficient and economical one-pot protocol for synthesis of 1,4-disubstituted 1,2,3-triazoles at room temperature using a heterogeneous clay supported CuO nanoparticles which is recyclable, environmentally friendly. Using others support catalytic as chitosan [45] or silica [46] based-copper(I), the authors reported a green and recyclable heterogeneous catalyst for the Huisgen 1,3-dipolar cycloaddition.

To illustrate the scope of this method, the optimized reaction condition to azides and other alkynes cyclo additions were extended to obtain a novel 1,4-disubstituted 1,2,3-triazole derivatives. As the results indicate, the catalyst gave good yields for most synthesized triazoles that were isolated by a simple filtration to separate the catalyst and by solvent evaporation. The products were isolated in a pure form without traces of copper and thus the Cu^I-MMT proved to be a useful catalyst for [3 + 2] Huisgen cycloaddition between azides and alkynes. As show (Table 3) a various compounds **1a–i** were regioselectively obtained as 1,4-disubstituted-1,2,3-triazoles in excellent yields.

The recyclability of our catalyst was investigated in the cycloaddition of phenylacetylene and benzyl azide. The catalyst was recovered by a simple filtration technique after each experiment. The recovered catalyst was washed with

Table 3 Scope of the catalytic system

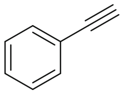
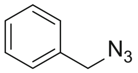
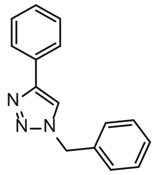
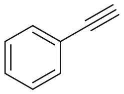
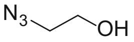
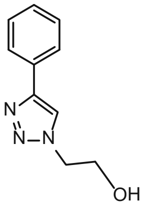
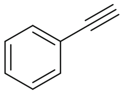
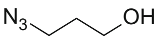
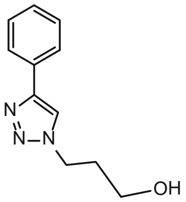
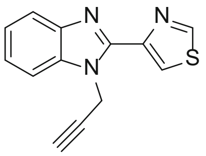
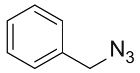
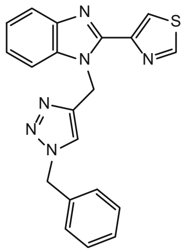
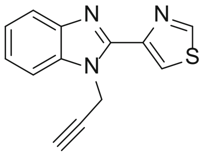
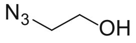
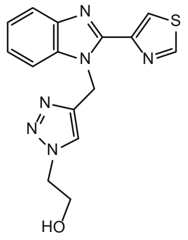
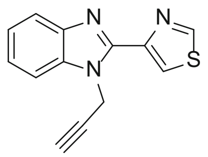
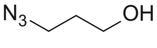
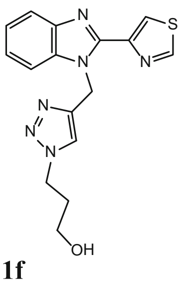
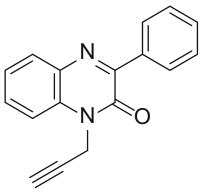
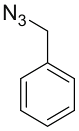
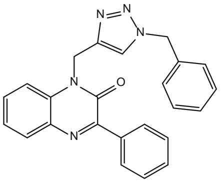
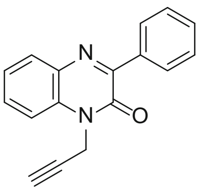
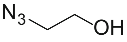
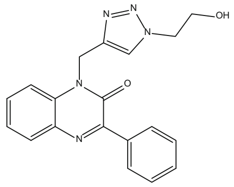
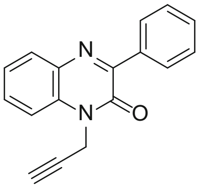
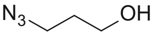
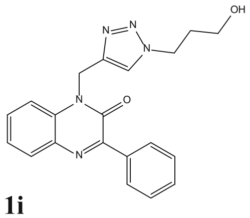
Entry	Alkyne	Azide	Product	Yield (%)
1			 **1a**	98
2			 **1b**	94
3			 **1c**	94
4			 **1d**	96
5			 **1e**	90

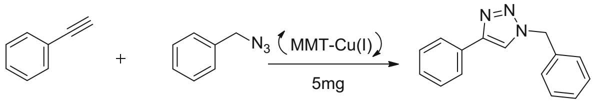
Table 3 continued

6			 **1f**	88
7			 **1g**	93
8			 **1h**	90
9			 **1i**	91

Reaction conditions 5 mg of Cu^I-MMT, rt, H_2O, 2 h

Chloroform, dried in a desiccator and reused directly with fresh reaction mixture without further purification for the desired 1,2,3-triazole synthesis up to the 5th run. The catalyst showed catalytic activity in five consecutive reactions and it can be stated that in all experiments there was a small loss in the amounts of catalyst initially introduced in the first reaction. Despite the high activity of catalyst, there is a slight decrease of its activity after the recycling experiments that may be related to the decrease in the amount of copper in the MMT after the recycles. As the results in (Table 4) indicate, the obtained conversions for five successive runs are 97, 96, 96, 94 and 92 % respectively. The reused catalyst was further characterized by ICP-AES analysis in order to evaluate

Table 4 Recycling of Cu^I-MMT catalyst



1a

No of cycles	Yield
1	97
2	96
3	96
4	94
5	92

Recycling experiments 1.2 mmol of benzyl azide, 1 mmol of phenylacetylene, recovered Cu^I-MMT, H_2O, rt, 2 h the catalyst leaching degree in the reaction. The metal leaching was studied of the catalyst before and after the 5th reaction cycle. The reuse studies show a slight decrease in yields from 97 to 92 % which may be due to Cu leaching. The weight percentage of copper was found to be 28.9 wt.%. After the reaction the Cu concentration was found to be 27.7 wt.%, and thus we observed that the amount of copper present in the spent catalyst after 5 reuses is almost same with that of the fresh catalyst as estimated by ICP-AES, which further confirms the true heterogeneity of the catalyst. After 5 recycles, a negligible amount of leached Cu was detected by ICP-AES (3.9 %). The above results of the recycle experiments followed by the ICP-AES analysis, confirmed the feasibility of using montmorillonite as supports for copper(I) in catalysis, which displayed merits of the heterogeneous (excellent recyclability) catalysis.

4 Conclusion

In summary, we explained the synthesis and characterization of Copper(I) modified montmorillonite as a highly active heterogeneous catalyst, this material was found to efficiently catalyze the formation of several 1,4-disubstituted 1,2,3-triazoles from organic azides and various terminal alkynes. Using this catalytic system, with the best conditions found, specially water as solvent, 1,4-disubstituted-1,2,3-triazole adducts are mainly obtained, in good to excellent yields, this result often referred to as "Green Chemistry". Cu^{I}-MMT was approved as a stable catalyst that can be reused for many consecutive trials without a significant decline in its reactivity.

Acknowledgments This work was supported by Hassan II Academy of Science and Technology, and Moroccan Foundation for Advanced Science, Innovation and Research (MAScIR).

References

1. Lee T, Cho M, Ko SY, Youn HJ, Baek DJ, Cho WJ, Kang CY, Kim SJ (2007) Med Chem 50:585
2. Buckle DR, Outred DJ, Rockell CJM, Smith H, Spicer BA (1983) J Med Chem 26:251
3. Huisgen R (1989) Pure Appl Chem 61:613
4. Huisgen R (1984) In: Padwa A (ed) 1,3-dipolar cycloadditional chemistry. Wiley, New York
5. Moses JE, Moorhouse AD (2007) Chem Soc Rev 36:1249
6. Kolb HC, Finn MG, Sharpless KB (2001) Angew Chem Int Ed 40:2004
7. Shi Q, Chen X, Lu T, Jing X (2008) Biomaterials 29:1118
8. Sudhir VS, Venkateswarlu C, Musthafa OTM, Sampath S, Chandrasekaran S (2009) Eur J Org Chem 13:2120
9. Zhou CH, Wang Y (2012) Curr Med Chem 19:239
10. Link AJ, Tirrell DA (2003) J Am Chem Soc 125:11164
11. Hawker CJ, Fokin VV, Finn MG, Sharpless KB (2007) Aust J Chem 60:381
12. Evans RA (2007) Aust J Chem 60:384
13. Kolb HC, Sharpless KB (2003) Drug Discov Today 8:1128
14. Aucagne V, Leigh DA (2006) Org Lett 8:4505
15. Parrish B, Breitenkamp RB, Emrick T (2005) J Am Chem Soc 127:7404
16. Dichtel WR, Miljanic OS, Spruell JM, Health JR, Stoddart JF (2006) J Am Chem Soc 128:10388
17. Bouhfid R, Joly N, Massoui M, Cecchelli R, Lequart V, Martin P, Essassi EM (2005) Heterocycles 65:2949
18. Hong V, Presolski SI, Ma C, Finn MG (2009) Angew Chem Int Ed 48:9879
19. López-Ruiz H, de la Cerda-Pedro JE, Rojas-Lima S, Pérez-Pérez I, Rodríguez-Sánchez BV, Coreño O (2013) ARKIVOC iii:139
20. Laszlo P (1987) In: Laszlo P (ed) Preparative chemistry using supported reagents. Academic, San Diego
21. Clark JH (1994) Catalysts of organic reactions by supported inorganic reagents. VCH, New York
22. Nikalze MD, Phukan P, Sudalai A (2000) Org Prep Proced Int 32:1
23. Izumi Y, Urabe K, Onaka M (1992) Zeolite, clay and heteropoly acids in organic reactions. VCH, New York
24. Nagendrappa G (2002) Resonance 7:64
25. Nagendrappa G (2011) Appl Clay Sci 53:106
26. Zhang J, Li C, Wang Y, Zhuo R, Zhang X (2011) Chem Commun 47:4457
27. Hooper N, Beeching LJ, Dyke JM, Morris A, Ogden JS, Dias AA, Costa ML, Barros MT, Cabral MH, Moutinho AMC (2002) J Phys Chem A 106:9968
28. Carrado KA, Wasserman SR (1996) Chem Mater 8:219
29. Morillo E, Undabeytia T, Maqueda C (1997) Environ Sci Technol 31:3588
30. Ennajih H, Gueddar H, El Kadib A, Bouhfid R, Bousmina M, Essassi EM (2012) Appl Clay Sci 65:139
31. Madejová J, Arvaiová B, Komadel P (1999) Acta Part A 55:2467
32. Heller-Kallai L, Mosser C (1995) Clays Clay Miner 43:738
33. Van der Marel HW, Beutelspacher H (1976) Atlas of infrared spectroscopy of clay minerals and their admixtures. Elsevier, Amsterdam
34. Farmer VC (1979) In: Van Olphen H, Fripiat JJ (eds) Data handbook for clay materials and other non-metallic minerals. Pergamon Press, Oxford
35. Tabak A, Afsin B, Aygun SF, Icbudak H (2005) J Therm Anal Calorim 81:311
36. Olson CG, Thompson ML, Wilson MA (2000) Phyllosilicates. In: Sumner ME (ed) Handbook of soil science. CRC, Boca Raton
37. Stadler M, Schindler PW (1993) Clays Clay Miner 41:288
38. Mosser C, Michot LJ, Villieras F, Romeo M (1997) Clays Clay Miner 45:789
39. Kloprogge JT, Mahmutagic E, Frost RL (2006) J Colloid Interface Sci 296:640
40. Slade PG, Stone PA, Radoslovich EW (1985) Clays Clay Miner 33:51
41. Goyard D, Praly JP, Vidal S (2012) Carbohydr Res 362:79
42. Creary X, Anderson A, Brophy C, Crowell F, Funk Z (2012) J Org Chem 77:8756
43. Himo F, Lovell T, Hilgraf R, Rostovtsev VV, Noodleman L, Sharpless KB, Fokin VV (2005) J Am Chem Soc 127:210
44. Mohammed S, Padala AK, Dar BA, Singh B, Sreedhar B, Vishwakarma RA, Bharate SB (2012) Tetrahedron 68:8156
45. Nasir Baig RB, Varma RS (2013) Green Chem 15:1839
46. Shamim T, Paul S (2010) Catal Lett 136:260