FULL PAPER

Clinochlore-Supported Copper Nanoparticles as Green and Efficient Catalyst for Room-Temperature Synthesis of 1,2,3-Triazoles in Water

Mohammad Gholinejad,^{*,[a,b]} Erfan Oftadeh,^[a] José M. Sansano^[c]

Abstract: Acid activated clinochlore supported copper nanoparticles was prepared for the first time by immobilization of copper sulfate on clinochlore followed by in situ chemical reduction. This new material (AA-Clin@Cu) was characterized using SEM, TEM, TGA, FTIR, XRD, XPS, and EDX and it was applied as an efficient and inexpensive catalyst for the synthesis of 1,2,3-triazoles in water at room temperature. Using this catalyst, benzylic and aliphatic halides, as well as arylboronic acids were reacted successfully with sodium azide and alkynes. The easy synthesis and air-stable catalyst was recycled for four runs with small drops in catalytic activity. Characterization of the reused catalyst showed similar pattern to the fresh catalyst.

INTRODUCTION

In the past two decades, great attention has been paid for using heterogeneous catalysts in different organic transformations. The type of the catalyst support remarkably affects the overall performance of the catalytic reactions.^[1] Recently, green chemistry objectives have encouraged chemists for using less hazardous chemicals and economical processes in organic reactions.^[2] In this regard, the use of sustainable and heterogeneous catalysts is one of the most important aims of green chemistry. Clay minerals are one of the oldest materials of the earth which were used by ancient peoples for traditional medicines such as clay baths to cure skin and gastrointestinal diseases.^[3] In recent years, different properties of clays such as high surface area, water dispersibility, colloidal and swelling capacities, ion exchange and optimal rheological behavior have been found and applied in pharmaceutical and cosmetics industries, veterinary medicine, biomaterials, and biosensors.^[3] Also, an increasing attention has been paid to use clay minerals

as a catalyst or green supports for stabilization of transition metal catalysts.^[4] Among different types of clay materials, chlorite is an important constituent of the oceanic crust. It is also a major secondary mineral in low-grade metamorphism of rocks or hydrothermally altered mafic rocks, with the general chemical formula $(\text{Mg, Mn, Fe})_3(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2(\text{Mg, Mn, Fe, Al})_3(\text{OH})_6$.^[5] Clinochlore is an abundant and cheap member of the chlorite group found in low grade metamorphic terrains and it is a

secondary product of mafic minerals. It forms a solid solution series with its Fe^{2+} analog, chamosite.^[5]

1,2,3-Triazole derivatives are an important class of organic compounds showing different biological traits, such as anti-HIV properties^[6] and activity against Gram-positive bacteria^[7] as well as industrial applications such as dyes,^[8] corrosion inhibitors,^[9] photostabilizers, photographic materials,^[10] and agrochemicals.^[11] Traditional methods for the synthesis of 1,2,3-triazoles include thermal 1,3-dipolar cycloaddition of organic azides with alkynes (Huisgen reaction). The main drawback of this method was the formation of non-regioselective 1,4- and 1,5-disubstituted products.^[12] However, individual reports by Sharpless and Medal showed that these reactions produce regioselective 1,4-substituted-1,2,3-triazoles in the presence of Cu(I) under mild reaction conditions.^[13] In recent years, different heterogeneous and homogeneous copper catalysts have been applied to click reactions.^[14] However, few clay supported copper catalysts to date have been prepared and successfully used to the azide-alkyne cycloaddition reactions.^[14a-f]

In recent years, nanoparticles have been proven to be very effective in the catalyst design due to their high surface-to-volume ratio. Similar to many other catalytic processes, applications of nanoparticles in the context of click chemistry have received a great deal of attention. Along this line copper nanoparticles are recognized as efficient catalysts in synthesis of 1,4-substituted-1,2,3-triazoles.^[15]

Herein, for the first time, we have employed clinochlore as a very inexpensive and available support for stabilization of copper nanoparticles and its application as a recyclable catalyst in room temperature click reaction in water for the synthesis of 1,2,3-triazoles.

Results and Discussion

For the preparation of clinochlore supported copper nanoparticles, initially fresh clinochlore was treated with HCl (6 M) to obtain expanded clinochlore.^[16]

BET surface area analysis (a_s) showed increasing of surface area (S_{BET}) and pore volume (V_p) (Table 1) in acid activated clinochlore

[a] Dr. Mohammad Gholinejad, Erfan Oftadeh
Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), P. O. Box 45195-1159, Gavazang, Zanjan 45137-6731, Iran.
E-mail: gholinejad@iasbs.ac.ir

[b] Mohammad Gholinejad,
Research Center for Basic Sciences & Modern Technologies (RBST), Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran.

[c] Dr. Jose Sansano
Centro de Innovación en Química Avanzada (ORFEO-CINQA).
Universidad de Alicante, Apdo. 99, E-03080-Alicante, Spain.

Supporting information for this article is given via a link at the end of the document.

(AA clinochlore). Then, readily prepared AA clinochlore was treated with CuSO_4 in deionized water, followed by the addition of NaBH_4 as a reducing agent. The obtained new clay supported copper NPs is referred to as AA-Clin@Cu through the text. Using atomic absorption spectroscopy, the loading of copper in the AA-Clin@Cu NPs was found to be $0.0125 \text{ mmol g}^{-1}$. Also, results showed that both S_{BET} and V_p decreased in AA-Clin@Cu NPs compared to AA clinochlore indicating successful stabilization of Cu NPs (Table 1). In addition, the isotherms of clinochlore, AA clinochlore and AA-Clin@Cu exhibited type IV isotherm^[17], with a H3 hysteresis loop indicating mesopore and micropore structures (Figure 1 in ESI).

Table 1. The BET surface area and BJH pore volume for clinochlore, AA clinochlore and AA-Clin@Cu

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_p (mL g^{-1})
Clinochlore	7.066	0.040
AA clinochlore	42.74	0.277
AA-Clin@Cu	29.15	0.176

Scanning electron micrograph of AA-Clin@Cu showed the presence of sheet layers of clinochlore (Figure 2 in ESI).

The FTIR spectrum of clinochlore and AA clinochlore illustrated bands at 3571 cm^{-1} for O-H stretching and 3424 cm^{-1} for interlayered O-H stretching, 1634 cm^{-1} for H-O-H bending, 990 cm^{-1} for Si-O stretching, 768 and 672 cm^{-1} for (Al, Mg)-OH vibration, and 544 cm^{-1} along with 466 cm^{-1} for Si-O bending (Figure 3 in ESI).^[18]

In addition, the SEM-Map image of AA-Clin@Cu showed presence of Si and O as the major elements of chlorite (Figure 1a and 1b) and highly uniform dispersion of Cu nanoparticles over the clinochlore (Figure 1c and 1d). Furthermore, EDX spectra of the AA-Clin@Cu confirmed the presence of clay minerals and elements such as Fe, Mg, Al, Si, C, and O as well as Cu species (Figure 2).

Figure 1 SEM-Map image of AA-Clin@Cu; a) O, b) Si, c) Cu, and d) overlay image

Figure 2 EDS spectra of AA-Clin@Cu

X-ray powder diffraction (XRD) of AA-Clin@Cu was also studied (Figure 3). However, due to low loading weight of Cu on the support and also the overlap of clinochlore peaks^[19] with Cu, this diffractogram did not show any significant peaks for Cu NPs and a pattern which is very similar to clinochlore XRD was obtained.

Figure 3 XRD pattern of a) clinochlore and b) AA-Clin@Cu.

In order to further study the AA-Clin@Cu structure and trying to find information about the oxidation state of Cu, the X-ray photoelectron spectrum (XPS) was studied (Figure 4). XPS

spectrum in the Cu2p region showed a doublet peak located at approximately 932.9 and 952.9 eV which are attributed to Cu 2p_{3/2} and Cu 2p_{1/2} in Cu₂O, respectively (Figure 4).^[20] It should be noted that related peaks for Cu(0) species also appear in very close regions to Cu(I). One method to distinguish them is to study the LMM auger transition in the XPS spectrum, which has two peaks at 568 eV and 570 eV for Cu(0) and Cu(I), respectively.^[21] Results of our study showed the presence of a distinct peak at 570 eV confirming the presence of Cu₂O species (Figure 4 in ESI). Also, the doublet peaks with binding energies of 935.1 and 954.4 eV were assigned to Cu 2p_{3/2} and Cu 2p_{1/2} in CuO. On the other hand, two shake-up satellite peaks at 941.2 and 943.8 eV are related to Cu(II) species in the CuO form (Figure 4).^[20] Results indicated that 74.5% of copper is in Cu(II) form and 25.5% in Cu(I) form.

Figure 4 XPS spectra of AA-Clin@Cu in Cu 2p region.

The oxidation states of other clinochlore elements such as Si, Al, Fe, and Mg were also studied by XPS analysis (Figure 5). The binding energy (BE) value of Si 2p in silanol (Si-OH) and the silicone oxygen (Si-O) bond appeared at 102.9 and 103.7 eV, respectively (Figure 5a).^[22] Also XPS spectrum in the Al 2p region showed a broad peak between 72-76 eV deconvoluting into two main peaks at 74.2 and 74.60 eV, which are related to Al(III) in Al-OH and Al₂O₃ forms (Figure 5b).^[22-23] XPS spectra of Fe 2p region (Fe 2p_{3/2} and Fe 2p_{1/2}) showed two differentiated binding energy values at 711.2 and 725.0 eV related to Fe³⁺ species (Figure 5c).^[24] A peak at 1303.6 eV could be referred to the binding energies of Mg 1s in MgO form^[25] (Figure 5d).

Figure 4 XPS spectra of AA-Clin@Cu in a) Si 2p, b) Al 2p, c) Fe 2p, and d) Mg 1s regions.

Transmission electron microscopy (TEM) images of AA-Clin@Cu in different magnification showed the presence of very small and uniform copper NPs supported on clinochlore sheets (Figure 6 a-d). Comparing TEM images of AA-Clin@Cu with TEM image of Cu-free clinochlore (Figure 5 in ESI) confirms that dark particles in Figure 6 are copper NPs.

Figure 6 TEM images of AA-Clin@Cu NPs.

In order to study thermal stability of the catalyst, thermogravimetric analysis of AA-Clin@Cu NPs was studied. Results showed three main weight loss between 25-800 °C. First lost is referred to physically absorbed molecular water. The second one is attributed to losing of absorbed water molecules between the layers and third one is related to interlayer hydroxyl groups of the chlorite (Figure 7).^[26]

Figure 5 TG analysis of AA-Clin@Cu

The catalytic activity of AA-Clin@Cu NPs was assessed in the three-component synthesis of 1,4-disubstituted 1,2,3-triazoles. For optimizing the reaction conditions, coupling of benzyl bromide, sodium azide and phenylacetylene was selected as the benchmark reaction (Table 2). Initially, the reaction was performed using 0.1 mol% of the catalyst in different solvents at room temperature during 24 h (Table 2). Results indicated the formation of the desired triazole in EtOH, DMF, CH₃CN, CHCl₃ and toluene in low yields (Table 2, entries 1-5). However, results indicated the formation of desired products in 97% and 95% isolated yields in DMSO and H₂O as solvents, respectively (Table 2, entries 6 and 7). Formation of higher yields in DMSO and H₂O is may related to high solubility of sodium azide in these solvents. For further optimization studies, we selected water as the best green and cheap solvent to perform reactions using lower Cu loadings. Using 0.025 and 0.05 mol% of the catalyst, low to moderate yields were obtained (Table 2, entries 8 and 9). By increasing the catalyst loading to 0.075 mol%, the reaction proceeds efficiently in 94% isolated yield (Table 2, entry 10). Also, using 0.075 mol% of the catalyst and lowering the reaction time to 18 h and 12 h, lower yields were obtained (Table 2, entries 11 and 12). It should be noted that decreasing the catalyst amount to 0.05 or 0.025 mol% and increasing the reaction temperature did not afford desired excellent yield (Table 2, entries 13-15). Therefore, we selected 0.075 mol% of the catalyst and H₂O as the solvent at room temperature (25 °C) as an optimized reaction condition. It is worth mentioning that using trimethylsilyl azide instead of NaN₃ gave poor yields in water and THF solvents (Table 2, entries 16 and 17).

Table 2. Optimization of the reaction conditions for the reaction of benzyl bromide, sodium azide, and phenylacetylene^a

Entry	Solvent	Catalyst (mol%)	T (°C)	Yield(%) ^b
1	EtOH	0.1	25	10
2	DMF	0.1	25	20
3	CH ₃ CN	0.1	25	6
4	CHCl ₃	0.1	25	16
5	Toluene	0.1	25	12
6	DMSO	0.1	25	97
7	H ₂ O	0.1	25	95

8	H ₂ O	0.025	25	34
9	H ₂ O	0.050	25	57
10	H ₂ O	0.075	25	94
11	H ₂ O	0.075	25	80 ^c
12	H ₂ O	0.075	25	68 ^d
13	H ₂ O	0.050	40	75
14	H ₂ O	0.050	60	84
15	H ₂ O	0.025	60	62
16	H ₂ O	0.075	25	8 ^e
17	THF	0.075	25	25 ^e

^a Reaction condition: benzyl bromide (1 mmol), NaN₃ (1.5 mmol), phenylacetylene (1.5 mmol), and solvent (2 mL).

^b Isolated yields.

^c The reaction was performed during 18 h.

^d The reaction was performed during 12 h.

^e The reaction performed using trimethylsilyl azide instead of NaN₃.

Having the optimized reaction conditions in hand, the click reaction of structurally different benzyl or alkyl halides as well as arylboronic acids with sodium azide and different alkynes was studied (Table 3). Reactions of benzyl halides with sodium azide and phenylacetylene proceed very well and the corresponding triazoles were obtained in high to excellent yields (Table 3, entries 1-8). Also, the reactions of benzyl bromide with 4-ethynyltoluene and 4-ethynylanisole were performed very efficiently and gave the corresponding products in 95% and 97% isolated yields (Table 3, entries 9 and 10). Furthermore, reactions of 4-bromobenzyl bromide and 4-nitrobenzyl bromide with sodium azide and propargyl alcohol as aliphatic alkyne proceed well and the desired products were obtained in 80% and 84% isolated yields, respectively (Table 3, entries 11 and 12). In the next step, we studied the reactivity of aliphatic alkyl bromides under the optimized reaction conditions. The obtained results indicated that the reaction of ethyl bromoacetate progressed very well and the corresponding product was achieved in 93% isolated yield (Table 3, entry 13). However reaction of other aliphatic alkyl bromides such as 2-bromoethylbenzene, 1-bromohexane and 1-bromobutane were slower than benzylic bromides and the corresponding triazoles were obtained in 80-86% isolated yields (Table 3, entries 14-16). Because the preparation of aryl azides from aromatic amines is not so straightforward, one-pot preparation of aryl azides from arylboronic acids or aryl halides and their click reaction with alkynes for the synthesis of triazoles is highly desirable. Along with this line, we studied the one-pot

FULL PAPER

reaction of arylboronic acids containing electron-donating and -withdrawing groups with sodium azide and alkynes. Results revealed that these reactions performed well and the products were obtained in high yields (Table 3, entries 17-21). Also, we have studied the reaction of prop-2-ynyl-4-nitrobenzoate and 1,3-dimethyl-5-(prop-2-ynyloxy)benzene with benzyl halides and sodium azide giving 1,2,3-triazoles in 80-90% isolated yields (Table 3, entries 22-24). Reaction of 2-(bromomethyl)pyridine as

a heterocyclic benzyl halide with sodium azide and propargyl alcohol was performed well and desired product obtained in 86% yield (Table 3, entry 25). Finally, reactions of two aryldiazonium tetrafluoroborates with sodium azide and phenylacetylene were proceed well and corresponding products were achieved in 89-94% yield (Table 3, entries 26-27).

Table 3. Multicomponent Synthesis of Triazoles at Room Temperature Using Water as Solvent and AA-Clin@Cu as catalyst^a

$R^1X + NaN_3 + R^2 \text{---} \xrightarrow[H_2O, 25^\circ C, 24 h]{AA-Clin@Cu} \begin{array}{c} R^1 \\ \\ N \text{---} N \\ \quad \backslash \\ C \quad N \\ \\ R^2 \end{array}$ <div style="display: flex; align-items: center; margin-top: 10px;"> <div style="border-left: 1px solid black; border-right: 1px solid black; padding: 0 10px; margin-right: 10px;"> $R^1 = \text{aryl, alkyl, benzyl}$ $X = \text{Br, Cl, B(OH)}_2, N_2^+BF_4^-$ $R^2 = \text{aryl, alkyl}$ </div> </div>					
Entry	R ¹ X	R ²	Product	Yields(%) ^b	TOF(h ⁻¹)
1		Ph	1a	94	52
2		Ph	1b	87	48
3		Ph	1c	90 ^c	50
4		Ph	1d	85 ^c	47
5		Ph	1a	90	50
6		Ph	1e	90	50

FULL PAPER

7		Ph		83	46
8		Ph		87	48
9		4-MeC ₆ H ₄		95	53
10		4-MeOC ₆ H ₄		97	54
11		-CH ₂ OH		80°	45
12		-CH ₂ OH		84°	47
13		Ph		93	52
14		Ph		83°	46
15		Ph		86	48
16		Ph		80	44
17		Ph		82	46

18		Ph		76	42
19		Ph		78	43
20		-CH ₂ OH		79	44
21		Ph		75	42
22				90°	50
23				87°	48
24				80°	45
25		-CH ₂ OH		86	41

26		Ph		94	51
27		Ph		89	49

^a Reaction conditions: R₁X (1 mmol), NaN₃ (1.5 mmol), alkyne (1.5 mmol), H₂O (2 mL) and catalyst (60 mg containing 0.075 mol% Cu).

^b Isolated yields.

^c Reactions performed in H₂O:EtOH (10:1)

In order to show a large-scale laboratory application of the catalyst, the reaction of benzyl bromide (10 mmol), sodium azide (15 mmol) and phenylacetylene (15 mmol) was studied under the optimized reaction conditions. The result of this study indicated that reaction was performed well and it was resulted the corresponding triazole in 92% isolated yield.

The proposed mechanism for the AA-Clin@Cu catalyzed click reaction is same as the known mechanism for the CuAAC synthesis of 1,2,3-triazoles. In the first step of reaction, terminal alkyne is reacted with Cu species and produced [Cu]-acetylide complex. In continue, organic azides is attached to [Cu]-acetylide followed by attack of the distal nitrogen of azide to the [Cu]-acetylide affording [Cu]-triazolide complex. In final step, [Cu]-triazolide is protonated and desired 1,2,3-triazole is obtained (Figure 8).^[14a, 27]

Figure 6 Plausible mechanism of AA-Clin@Cu NPs catalyzed click synthesis of 1,4-disubstituted 1,2,3-triazoles

From the economics and sustainability standpoints, recyclability of heterogeneous catalysts is an essential issue. Therefore, we studied the recycling of the catalyst for the reaction of benzyl bromide, sodium azide and phenylacetylene under the optimized reaction conditions. For this purpose, after 24 h the solid catalyst was removed from the reaction mixture by centrifugation and after washing and drying, it was used in another batch. Results of this study showed that the catalyst is recoverable and recyclable for 4 consecutive runs with a very small decrease of activity (Figure 9). AAS studding of copper leaching in second run indicated 10% leaching of copper from clay support.

Figure 7 Recycling of the catalyst for the reaction of benzyl bromide, sodium azide and phenylacetylene under the optimized reaction conditions.

TEM images of the reused catalyst after four runs shows presence very small aggregate nanoparticles and mostly uniform and mono-dispersed forms (Figure 10 a-b).

Figure 8 TEM images of reused catalyst after 4 runs.

Also, XPS study of the reused catalyst after the four runs in the Cu 2p region showed very similar pattern toward the fresh catalyst being Cu₂O and CuO the major copper species in the catalyst structure (Figure 11).

Figure 9 XPS spectra of reused catalyst after 4 runs in Cu 2p region.

Furthermore, XPS analysis showing major clinochlore elements such as Al(III), Si-O, Fe(III), and Mg(II) has remained intact and it is confirmed that the structure of clinochlore has not changed (Figure 12).

Figure 10 XPS spectra of reused catalyst after 4 runs in a) Si 2p, b) Al 2p, c) Fe 2p, and d) Mg 1s regions.

Comparison results about the catalytic activity of AA-Clin@Cu with some other heterogeneous catalysts in click reaction of benzyl bromide with sodium azide and phenylacetylene as a common reaction (Table 4), showed overall high catalytic efficiency of the presented catalyst using lower copper loading in water.

Table 4, Comparison of catalytic activity between some prepared catalysts

Catalyst	Catalyst (mol %)	T (°C)	Solvent	Time (h:min)	Yield (%)
Cu-IG@Fe ₃ O ₄ [28]a	1	70	H ₂ O	2.5	90
clay-Cu(II) [14ae]	5	rt	MeOH	4	96
CuO/SD [29]	6	rt	H ₂ O	0:15	95
CuI@HNTs-2 N-Sal [30]	0.48	rt	H ₂ O	0:12	98
2-pyrrolecabaldiminato-Cu(II) [31]	2.5	50	Ethanol	2	95

CoCuFe ₂ O ₄ [31b] ^b	5	rt	H ₂ O	1	99
CuNPs@agarose [14g]	0.05	40	H ₂ O	8	96
CuFe ₂ O ₄ @Starch [14aj]	0.1	30	H ₂ O	24	92
AA-Clin@Cu [This work]	0.075	rt	H₂O	24	94

^a Reaction performed in the presence of K₂CO₃.

^b Reaction performed using sodium ascorbate

Conclusions

In conclusion, we have used acid activated clinochlore as cheap and available clay for the stabilization of copper nanoparticles. This new material AA-Clin@Cu has shown excellent catalytic efficiency in the three-component synthesis of 1,2,3-triazoles in water. Structurally different benzylic or aliphatic halides and arylboronic acids were reacted efficiently with sodium azide and various alkynes at room temperature affording regioselective 1,4-disubstituted 1,2,3-triazoles in high to excellent yields. The catalyst was recycled for four runs without noticeable changes in the catalytic activity and structure.

Supporting information summary

General information, reaction procedures, N₂ adsorption-desorption isotherms, SEM images of catalyst, FT-IR spectra, auger LMM peak of Cu, TEM images of Cu-free clinochlore, spectral data, copies of ¹H and ¹³C NMR spectra of synthesized compounds can be obtained in the supporting information file.

Acknowledgements

The authors are grateful to Institute for Advanced Studies in Basic Sciences (IASBS) Research Council and Iran National Science Foundation (INSF-Grant number of 95844587) for support of this work. C. Nájera is also thankful for financial support to the Spanish Ministerio de Economía y Competitividad (MINECO) (projects CTQ2013-43446-P and CTQ2014-51912-REDC), the Spanish Ministerio de Economía, Industria y Competitividad, Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER, EU) (projects CTQ2016-76782-P and CTQ2016-81797-REDC), the Generalitat Valenciana (PROMETEOII/2014/017) and the University of Alicante. Special thanks to Ms. Dehghan Hesami for her technical assistant.

Keywords: Clinochlore • Copper Nanoparticles • Click • 1,2,3-Triazoles • Water

- [1] a) D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem. Int. Ed.* **2005**, *44*, 7852-7872; b) M. J. Climent, A. Corma, S. Iborra, *RSC Adv.* **2012**, *2*, 16-58; c) Y. Xia, X. Yang, *Acc. Chem. Res.* **2017**, *50*, 450-454.
- [2] a) S. Kumar, P. Rath, K. Ameta, D. Kishore, *Green Chemistry Approach Using Heterogeneous Catalysts in the Heterocyclic Synthesis*, Springer, New Delhi, **2014**; b) R. S. Varma, *Green Chem.* **2014**, *16*, 2027-2041.
- [3] a) J. D. D. Moraes, S. R. A. Bertolino, S. L. Cuffini, D. F. Ducart, P. E. Bretzke, G. R. Leonardi, *Int. J. Pharm.* **2017**, *534*, 213-219; b) L. A. de Sousa Rodrigues, A. Figueiras, F. Veiga, R. M. de Freitas, L. C. C. Nunes, E. C. da Silva Filho, C. M. da Silva Leite, *Colloids Surf., B.* **2013**, *103*, 642-651; c) C. Viseras, P. Cerezo, R. Sanchez, I. Salcedo, C. Aguzzi, *Appl. Clay Sci.* **2010**, *48*, 291-295.
- [4] a) G. Nagendrappa, *Appl. Clay Sci.* **2011**, *53*, 106-138; b) A. Gil, S. A. Korili, M. A. Vicente, *Catal. Rev.* **2008**, *50*, 153-221; c) O. B. Ayodele, B. H. Hameed, *J. Ind. Eng. Chem.* **2013**, *19*, 966-974; d) R. B. Achma, A. Ghorbel, A. Dafinov, F. Medina, *Appl. Catal., A.* **2008**, *349*, 20-28.
- [5] a) N. O. Gopal, K. V. Narasimulu, J. L. Rao, *J. Phys. Chem. Solids* **2004**, *65*, 1887-1893; b) A. Steudel, R. Kleeberg, C. B. Koch, F. Friedrich, K. Emmerich, *Appl. Clay Sci.* **2016**, *132*, 626-634; c) G. Valdrè, S. Tosoni, D. Moro, *Am. Mineral.* **2011**, *96*, 1461-1466.
- [6] H. B. Lazrek, M. Taourirte, T. Oulih, J. L. Barascut, J. L. Imbach, C. Pannecouque, M. Witrouw, E. De Clercq, *Nucleos. Nucleot. Nucleic Acids* **2001**, *20*, 1949-1960.
- [7] K. Maji, D. Halder, *R. Soc. Open Sci.* **2017**, *4*, 170684.
- [8] T. Duan, K. Fan, Y. Fu, C. Zhong, X. Chen, T. Peng, J. Qin, *Dyes Pigm.* **2012**, *94*, 28-33.
- [9] Q. Ma, S. Qi, X. He, Y. Tang, G. Lu, *Corros. Sci.* **2017**, *129*, 91-101.
- [10] A. R. Katritzky, C. W. Rees, E. F. V. Scriven, *Comprehensive heterocyclic chemistry II*, Pergamon, **1996**.
- [11] T. F. Borgati, R. B. Alves, R. R. Teixeira, R. P. d. Freitas, T. G. Perdigão, S. F. d. Silva, A. A. d. Santos, A. d. J. O. Bastidas, *J. Braz. Chem. Soc.* **2013**, *24*, 953-961.
- [12] a) R. Huisgen, *Pure Appl. Chem.* **1989**, *61*, 613-628; b) R. Huisgen, G. Szeimies, L. Möbius, *Eur. J. Inorg. Chem.* **1967**, *100*, 2494-2507; c) J. H. J. Bastide, F. Texier, V. Q. Ven, *Bull. Soc. Chim. Fr.* **1973**, 2871-2887; d) J. H. J. Bastide, F. Texier, V. Q. Ven, *Bull. Soc. Chim. Fr.* **1973**, 2555-2579.
- [13] a) C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057-3064; b) V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708-2711; c) L. Li, S. Ding, Y. Yang, A. Zhu, X. Fan, M. Cui, C. Chen, G. Zhang, *Chemistry—A European Journal* **2017**, *23*, 1166-1172.
- [14] a) A. Banan, A. Bayat, H. Valizadeh, *Appl. Organomet. Chem.* **2017**, *31*, e3604; b) M. Chetia, P. S. Gehlot, A. Kumar, D. Sarma, *Tetrahedron Lett.* **2018**, *59*, 397-401; c) K. P. S. Cheung, G. C. Tsui, *Org. Lett.* **2017**, *9*, 2881-2884; d) Z. Dehbanipour, M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, *Polyhedron* **2017**, *138*, 21-30; e) S. Díez-González, *Catal. Sci. Technol.* **2011**, *1*, 166-178; f) E. Doustkhah, M. Heidarizadeh, S. Rostamnia, A. Hassankhani, B. Kazemi, X. Liu, *Mater. Lett.* **2018**, *216*, 139-143; g) M. Gholinejad, N. Jeddi, *ACS Sustainable Chem. Eng.* **2014**, *2*, 2658-2665; h) X. Guo, L. Zeng, Z. Wang, T. Zhang, C. He, C. Duan, *RSC Adv.* **2017**, *7*, 52907-52913; i) J. M. Holub, K. Kirshenbaum, *Chem. Soc. Rev.* **2010**, *39*, 1325-1337; j) S.

- Jang, Y. J. Sa, S. H. Joo, K. H. Park, *Catal. Commun.* **2016**, *81*, 24-28; k) K. Kacprzak, I. Skiera, M. Piasecka, Z. Paryzek, *Chem. Rev.* **2016**, *116*, 5689-5743; l) A. Kafle, S. T. Handy, *Tetrahedron* **2017**, *73*, 7024-7029; m) S. Li, L. Wang, F. Yu, Z. Zhu, D. Shobaki, H. Chen, M. Wang, J. Wang, G. Qin, U. J. Erasquin, *Chemical Science* **2017**, *8*, 2107-2114; n) X. Liu, N. Novoa, C. Manzur, D. Carrillo, J.-R. Hamon, *New J. Chem.* **2016**, *40*, 3308-3313; o) M. M. Heravi, M. Tamimi, H. Yahyavi, T. Hosseinejad, *Curr. Org. Chem.* **2016**, *20*, 1591-1647; p) H. Naeimi, Z. Ansarian, *Inorg. Chim. Acta* **2017**, *466*, 417-425; q) V. Nejadshafee, H. Naeimi, *Turk. J. Chem.* **2017**, *41*, 700-709; r) B. Ourri, O. Tillement, T. Tu, E. Jeanneau, U. Darbost, I. Bonnamour, *New J. Chem.* **2016**, *40*, 9477-9485; s) N. Sareen, A. S. Singh, V. K. Tiwari, R. Kant, S. Bhattacharya, *Dalton Trans.* **2017**, *46*, 12705-12710; t) J.-A. Shin, S.-J. Oh, H.-Y. Lee, Y.-G. Lim, *Catal. Sci. Technol.* **2017**, *7*, 2450-2456; u) A. Tăbăcaru, B. Furdul, I. O. Ghinea, G. Cârâc, R. M. Dinică, *Inorg. Chim. Acta* **2017**, *455*, 329-349; v) M. Tireli, S. Maračić, S. Lukin, M. J. Kulcsár, D. Žilić, M. Cetina, I. Halasz, S. Raić-Malić, K. Užarević, *Beilstein J. Org. Chem.* **2017**, *13*, 2352-2363; w) C. Wang, D. Ikhlef, S. Kahlal, J.-Y. Saillard, D. Astruc, *Coord. Chem. Rev.* **2016**, *316*, 1-20; x) C. Wang, F. Yang, Y. Cao, X. He, Y. Tang, Y. Li, *RSC Adv.* **2017**, *7*, 9567-9572; y) Z. Weng, W. Wu, J. Wang, Y. Wang, Y. Huang, Y. Tan, *Angew. Chem.* **2017**, *56*, 10612-10616; z) X. Xiong, Z. Tang, Z. Sun, X. Meng, S. Song, Z. Quan, *Appl. Organomet. Chem.* **2018**, *32*, e3946; aa) B. J. Borah, D. Dutta, P. P. Saikia, N. C. Barua, D. K. Dutta, *Green Chem.* **2011**, *13*, 3453-3460; ab) J.-L. Cao, G.-S. Shao, Y. Wang, Y. Liu, Z.-Y. Yuan, *Catal. Commun.* **2008**, *9*, 2555-2559; ac) N. Touj, I. Özdemir, S. Yaşar, N. Hamdi, *Inorg. Chim. Acta* **2017**, *467*, 21-32; ad) B. Kaboudin, R. Mostafalu, T. Yokomatsu, *Green Chem.* **2013**, *15*, 2266-2274; ae) N. Dubey, P. Sharma, A. Kumar, *Synth. Commun.* **2015**, *45*, 2608-2626; af) M. Navid Soltani Rad, S. Behrouz, S. Jafar Hoseini, H. Nasrabadi, M. Saberi Zare, *Helv. Chim. Acta* **2015**, *98*, 1210-1224; ag) M. E. M. Mekhzoum, H. Benzeid, A. E. K. Qaiss, E. M. Essassi, R. Bouhfid, *Catal. Lett.* **2016**, *146*, 136-143; ah) B. A. Dar, A. Bhowmik, A. Sharma, P. R. Sharma, A. Lazar, A. Singh, M. Sharma, B. Singh, *Appl. Clay Sci.* **2013**, *80*, 351-357; ai) S. Ghosh, S. Saha, D. Sengupta, S. Chattopadhyay, G. De, B. Basu, *Ind. Eng. Chem. Res.* **2017**, *56*, 11726-11733; aj) R. Bonyasi, M. Gholinejad, F. Saadati, C. Najera, *New J. Chem.* **2018**, *42*, 3078-3086; ak) C. Beto, E. Holt, Y. Yang, I. Ghiviriga, K. Schanze, A. Veige, *Chem. Commun.* **2017**, *53*, 9934-9937.
- [15] a) F. Alonso, Y. Moglie, G. Radivoy, *Acc. Chem. Res.* **2015**, *48*, 2516-2528; b) S. Shaabani, A. Tavousi Tabatabaei, A. Shaabani, *Appl. Organomet. Chem.* **2017**, *31*, e3559.
- [16] P. Komadel, J. Madejová, *Chapter 7.1 Acid Activation of Clay Minerals, Vol. 1*, Elsevier, Amsterdam, **2006**.
- [17] F. Rouquerol, J. Rouquerol, K. Sing, *Adsorpt. by Powders Porous Solids. Elsevier, London* **1999**, 439-447.
- [18] a) N. Gopal, K. Narasimulu, J. L. Rao, *J. Phys. Chem. Solids* **2004**, *65*, 1887-1893; b) C.-M. Hristodor, N. Vranceanu, A. Pui, O. Novac, V.-E. Copcia, E. Popovici, *Environ. Eng. Manag. J.* **2012**, *11*, 573-578.
- [19] G. N. Hemanthkumar, G. Parthasarathy, R. P. S. Chakradhar, I. Omkaram, J. L. Rao, Y. C. Ratnakaram, *Phys. Chem. Miner.* **2009**, *36*, 447-453.
- [20] a) P. Wang, Y. H. Ng, R. Amal, *Nanoscale* **2013**, *5*, 2952-2958; b) L. Pandolfi, P. Cafarelli, S. Kaciulis, A. A. G. Tomlinson, *Microporous Mesoporous Mater.* **2008**, *110*, 64-71.
- [21] a) T. Ghodselahi, M. A. Vesaghi, A. Shafiekhani, A. Baghizadeh, M. Lameii, *Appl. Surf. Sci.* **2008**, *255*, 2730-2734; b) J.-Y. Park, Y.-S. Jung, J. Cho, W.-K. Choi, *Appl. Surf. Sci.* **2006**, *252*, 5877-5891.
- [22] Y. Zhang, X. He, J. Ouyang, H. Yang, *Sci. Rep.* **2013**, *3*, 2948.
- [23] V. Dalmoro, J. H. Z. dos Santos, I. M. Baibich, I. S. Butler, E. Armelin, C. Alemán, D. S. Azambuja, *Prog. Org. Coat.* **2015**, *80*, 49-58.
- [24] W.-J. Liu, K. Tian, H. Jiang, H.-Q. Yu, *Green Chem.* **2014**, *16*, 4198-4205.
- [25] J. Li, Y. Jiang, G. Bai, T. Ma, D. Yang, Y. Du, M. Yan, *Appl. Phys. A* **2014**, *115*, 997-1001.
- [26] a) B. Velde, *Introduction to clay minerals: chemistry, origins, uses and environmental significance*, Chapman and Hall Ltd, **1992**; b) R. C. Mielenz, N. C. Schieltz, M. E. King, *Clays Clay Miner.* **1953**, *2*, 285-314.
- [27] a) T. S. Rodrigues, A. G. da Silva, L. C. de Oliveira, A. M. da Silva, R. R. Teixeira, P. H. Camargo, *Tetrahedron Lett.* **2017**, *58*, 590-595; b) F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless, V. V. Fokin, *J. Am. Chem. Soc.* **2005**, *127*, 210-216.
- [28] Z. Dolatkhah, S. Javanshir, A. Bazgir, A. Mohammadkhani, *ChemistrySelect* **2018**, *3*, 5486-5493.
- [29] F. Faeghi, S. Javanshir, S. Molaei, *ChemistrySelect* **2018**, *3*, 11427-11434.
- [30] N. Bahri - Laleh, S. Sadjadi, M. M. Heravi, M. Malmir, *Appl. Organomet. Chem.* **2018**, *32*, e4283.
- [31] a) X.-Y. Huo, L. Guo, X.-F. Chen, Y.-T. Zhou, J. Zhang, X.-Q. Han, B. Dai, *Molecules* **2018**, *23*, 1344; b) F. Matloubi Moghaddam, R. Pourkaveh, M. Ahangarpour, *ChemistrySelect* **2018**, *3*, 2586-2593.

Table of Contents Entry:

For the first time acid activated clinochlore was used for stabilization of copper nanoparticles. Characterization of this new material was carried out by various techniques and also the catalytic activity of this material investigated in the synthesis of triazole compounds. Using this new reusable catalyst, the wide ranges of benzylic and aliphatic halides, as well as arylboronic acids and diazonium salts were participated successfully in the synthesis of triazole derivatives in water as the solvent at room temperature.