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FULL PAPER

Synthesis, characterization and catalytic properties of tetrachlorocuprate(II) immobilized on layered double hydroxide

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Readily prepared copper(II) immobilized on layered double hydroxide has been found to effectively catalyse the 1,3-dipolar cycloaddition (CuAAC) of a variety terminal alkynes and benzyl azides generated *in situ* from sodium azide and benzyl halides furnishing the corresponding 1,2,3-triazoles in excellent yields. The advantages of the protocol are short reaction time, mild reaction conditions, reusability of the catalyst and applicability to a wide range of substrates.

KEYWORDS
azide–alkyne cycloaddition, copper, layered double hydroxide

1 | INTRODUCTION

1,3-Cycloaddition reactions of azides with olefins provide direct access to a wide range of 1,2,3-triazoles as useful heterocyclic systems with remarkably stable aromatic structures, which can serve, among other roles, as structural analogues of a peptide linkage.[1–10] Copper catalysts accelerate the cycloaddition reactions of azides with such terminal alkynes by a factor of at least 106 relative to the uncatalysed case[11] and copper-catalysed azide–alkyne cycloaddition (CuAAC) is a well-established methodology in modern organic synthesis.[12–20]

Layered double hydroxides (LDHs), also known as a class of synthetic two-dimensional nanostructured anionic clays, are a family of materials that have attracted increasing attention in recent years.[21–25] LDHs have anionic exchange capacity with the ability to capture organic and inorganic anions that makes them almost unique as inorganic materials for practical applications in catalysis,[26] adsorption,[27] pharmaceutics,[28] photochemistry[29] and other areas.[30] LDHs provide inexpensive and potentially recyclable catalyst supports due to their relative ease of synthesis, high versatility and readily tailored properties.[31–33]

We were inspired by an earlier report of Choudary *et al.*[34] who synthesized a LDH-supported Pd(0) catalyst via an exchange of $PdCl_4^{2-}$ followed by reduction with hydrazine hydrate. Herein, we report the synthesis of LDH-supported nanocopper(0) via the same method and its catalytic application in azide–alkyne cycloaddition in the presence of water and air leading to excellent yields.

2 | EXPERIMENTAL

2.1 | Materials

Chemicals and solvents were purchased from Merck and Fluka and were used without further purification. LDH of composition $Mg_{1-x}Al_x(OH)_2(Cl)_x{\cdot}zH_2O$ and Na_2CuCl_4 were prepared according to previously reported procedures.[34,35]

2.2 | Preparation of LDH-$CuCl_4^{2-}$

LDH (0.25 g) was suspended in a freshly prepared aqueous solution (15 ml) of Na_2CuCl_4 (0.063 g, 0.25 mmol) and stirred at 25 °C for 24 h under air. The solid catalyst was filtered, washed thoroughly with water and air-dried.

2.3 | Preparation of LDH-Cu^0

LDH-$CuCl_4^{2-}$ (0.3 g) was reduced with hydrazine hydrate (0.3 g, 6 mmol) in ethanol (10 ml) for 3 h at room temperature. The product was filtered and washed with ethanol to afford an air-unstable brown-black powder (0.21 g).

3 | RESULTS AND DISCUSSION

3.1 | Preparation of LDH-$CuCl_4^{2-}$

LDH was suspended in a freshly prepared aqueous solution of Na_2CuCl_4 and tetrachlorocuprate ($CuCl_4^{2-}$) was exchanged onto chloride-saturated (Mg/Al) LDH to obtain green-coloured LDH-$CuCl_4^{2-}$. The Cu(II) immobilized on LDH was then reduced with hydrazine hydrate, giving an air- unstable brown-black powder of LDH-Cu^0.[36,37] On exposure to air, LDH-Cu^0 is again oxidized to the LDH-Cu^{II} form as a green powder.

3.2 | Catalyst Characterization

The powder X-ray diffraction (XRD) patterns of the stable synthesized materials LDH and LDH-$CuCl_4^{2-}$ show peaks at 11.2°, 22.6° and 32.7° which fit well to LDH with basal reflections of (003), (006) and (009) without any crystalline impurity phases (Figure 1).[38] No peaks attributed to copper are observed in the XRD pattern of LDH-$CuCl_4^{2-}$. Elemental analysis confirms the presence of 9.6% copper in the LDH-$CuCl_4^{2-}$ sample.

The surface structure information of LDH and supported copper particles was obtained using scanning electron microscopy (SEM) as shown in Figure 2. The SEM images of LDH-$CuCl_4^{2-}$ reveal the presence of many copper fine particles with an average diameter of 50–70 nm covering the surface of LDH. These results clearly show that $CuCl4^{2-}$ is successfully loaded on the surface of the LDH support, which is expected to improve the catalytic properties.

The transmission electron microscopy (TEM) images presented in Figure 3 show that the LDH-$CuCl_4^{2-}$ particles

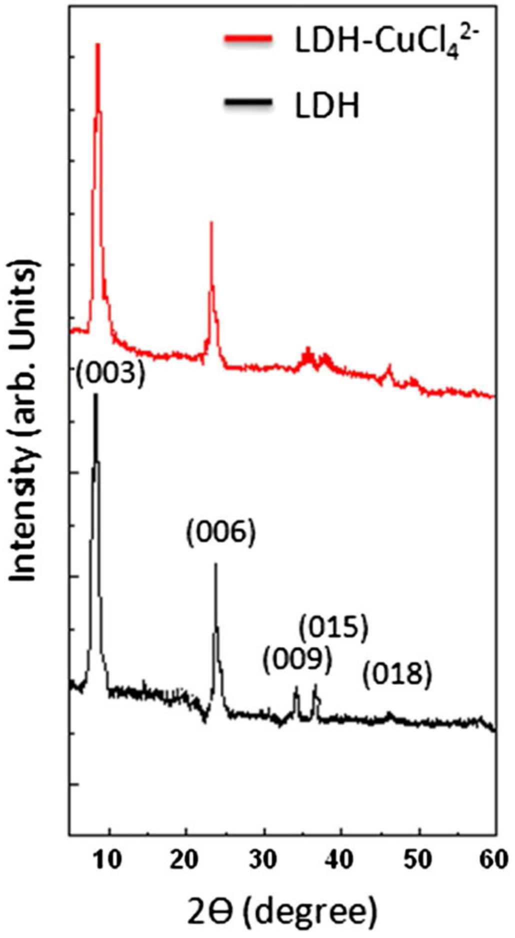


FIGURE 1 XRD patterns of LDH and LDH-$CuCl_4^{2-}$ nanoparticles

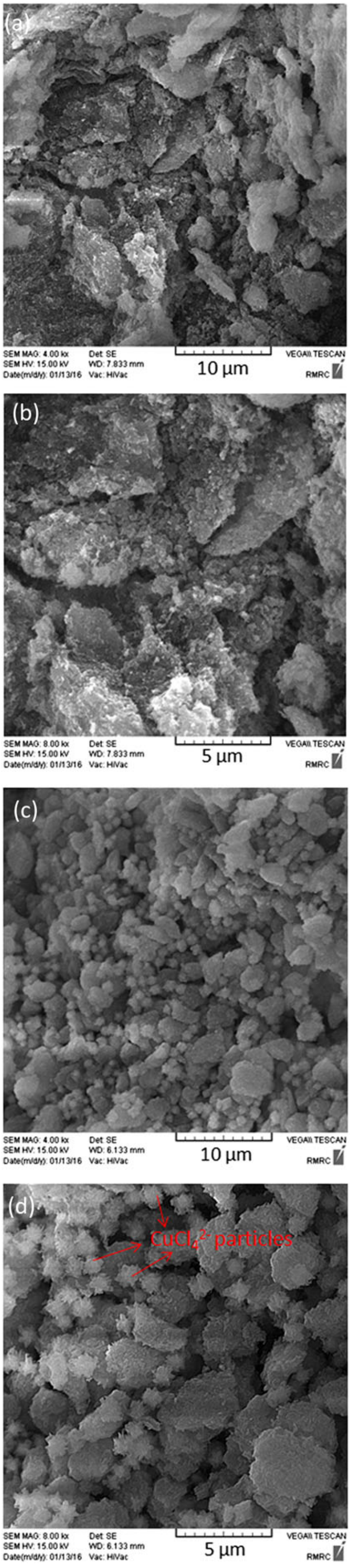


FIGURE 2 SEM images of (a, b) LDH and (c, d) LDH-$CuCl_4^{2-}$ nanoparticles

are largely spherical in shape with diameters ranging from 100 to 200 nm.

The Fourier transform infrared (FT-IR) spectra of the prepared samples of LDH and LDH-$CuCl_4^{2-}$ are shown in Figure 4. A broad band at 3000–3600 cm^{-1} in both spectra is characteristic of O─H stretching of hydroxide basal layer and interlayer water. The main bands related to intercalated and adsorbed anions and the metal–oxygen ν(M─O─M) stretching modes are, respectively, observed at 1000–1800 and 400–1000 cm^{-1}.[39] The positions of all bands in the spectrum of LDH-$CuCl_4^{2-}$ are almost coincident with those in the spectrum of pure LDH, due to the fact that most bands of $CuCl_4^{2-}$ almost coincide with the bands of LDH.

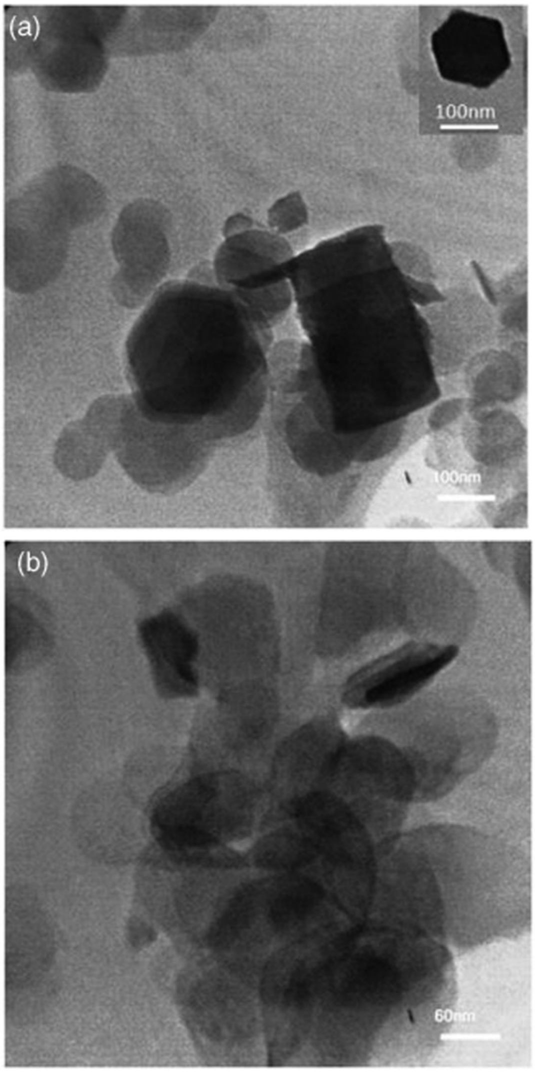


FIGURE 3 TEM images of LDH-$CuCl_4^{2-}$ nanoparticles

3.3 | Catalytic Effects

Synthetic utility of prepared materials LDH and LDH-$CuCl_4^{2-}$ was further explored as catalysts in the azide–alkyne cycloaddition reaction with the purpose of optimizing the reaction conditions for dipolar cycloaddition of phenylacetylene, benzyl chloride and NaN_3 as model substrates (Table 1). The investigation was initiated by comparing the activity of LDH and LDH-$CuCl_4^{2-}$. The control experiments in the absence of catalyst or pure LDH give no conversion at 70 °C in water, suggesting the role of copper-catalysing click reactions (entries 1 and 3). With increasing LDH-$CuCl_4^{2-}$ catalyst concentration from 0.001 to 0.004 g we observe 97% isolated yield of 1-benzyl-4-phenyl-1,2,3-triazole after 12 h (entries 4–6). The yield of reaction decreases to 70% when LDH-$CuCl_4^{2-}$ is replaced by Na_2CuCl_4 (entry 2). As indicated in Table 1, at lower temperatures a modest yield is achieved, but a significant increase in the product yield is observed at higher temperatures (entries 6–8). To determine the most effective solvent for 1,3-dipolar cycloaddition using LDH-$CuCl_4^{2-}$ as catalyst, the reaction of phenylacetylene, benzyl chloride and NaN_3 was carried out in various solvents such as acetone, chloroform, ethyl acetate, ethanol, methanol and acetonitrile (entries 9–14). Water is found to be the best solvent system for the azide–alkyne cycloaddition reaction in the presence of LDH-$CuCl_4^{2-}$. Also, according to Table 1 (entry 16), the reaction is completed within 6 h.

CuAAC reactions were also carried out under optimized conditions with various aromatic and aliphatic benzyl halides and alkynes (Table 2). The presence of electron-donating and electron-withdrawing groups on the phenyl ring of the benzyl

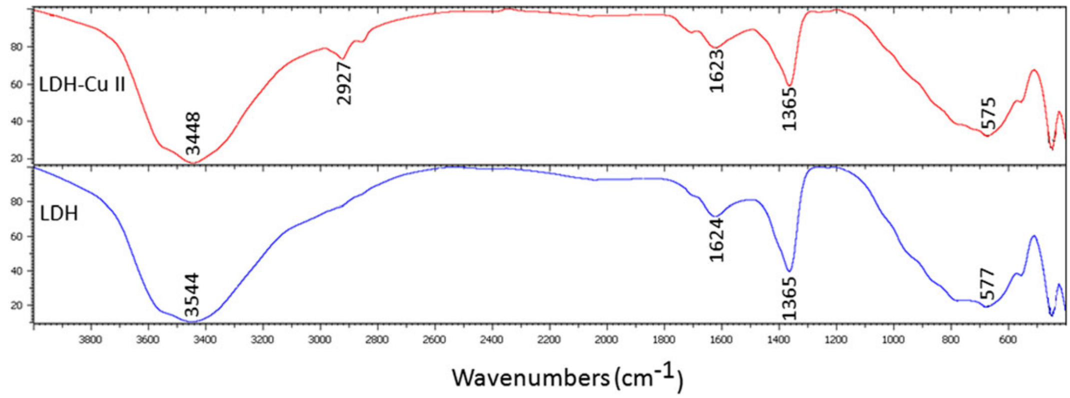


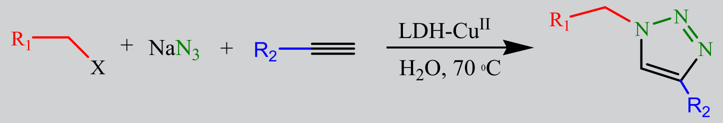
FIGURE 4 FT-IR spectra of LDH and LDH-$CuCl_4^{2-}$ nanoparticles

TABLE 1 Effect of reaction conditions on azide–alkyne cycloaddition

Entry	Catalyst	Catalyst amount (g)	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]
1	—	—	H_2O	70	12	0
2	Na_2CuCl_4	0.004	H_2O	70	12	70
3	LDH	0.004	H_2O	70	12	0
4	LDH-Cu^{II}	0.001	H_2O	70	12	58
5	LDH-Cu^{II}	0.003	H_2O	70	12	68
6	LDH-Cu^{II}	0.004	H_2O	70	12	97
7	LDH-Cu^{II}	0.004	H_2O	50	12	82
8	LDH-Cu^{II}	0.004	H_2O	r.t.	12	31
9	LDH-Cu^{II}	0.004	Acetone	70	12	90
10	LDH-Cu^{II}	0.004	CH_3Cl	70	12	Trace
11	LDH-Cu^{II}	0.004	EtOAc	70	12	Trace
12	LDH-Cu^{II}	0.004	C_2H_5OH	70	12	26
13	LDH-Cu^{II}	0.004	CH_3OH	70	12	22
14	LDH-Cu^{II}	0.004	CH_3CN	70	12	Trace
15	LDH-Cu^{II}	0.004	H_2O	70	4	86
16	LDH-Cu^{II}	0.004	H_2O	70	6	97

[a]Isolated yield.

TABLE 2 Cycloaddition of alkyl halides with terminal alkynes in the presence of LDH-$CuCl_4^{2-}$ catalyst



Entry	R_1	X	R_2	Yield (%)[a]
1	Ph	Cl	Ph	96
2	4-CH_3Ph	Cl	Ph	91
3	2-CH_3Ph	Cl	Ph	80
4	4-NO_2Ph	Cl	Ph	96
5	Ph	Cl	4-CH_3OPh	94
6	Ph	Cl	4-CH_3Ph	95
7	Ph	Cl	$HOC(CH_3)_2$	62
8	Ph	Cl	$HOCH_2$	66
9	Ph	Br	Ph	96
10	Ph	Br	4-CH_3OPh	95
11	Ph	Br	4-CH_3Ph	95
12	Ph	Br	$HOC(CH_3)_2$	71
13	Ph	Br	$HOCH_2$	85

[a]Isolated yield.

halides and the phenylacetylenes does not greatly affect the yield of cycloaddition products. When aliphatic alkynes are coupled with benzyl halides (entries 7 and 8), a decrease in the yield of cycloaddition products is observed, but the reactions have good yields when the reaction time is extended to 12 h. Replacement of benzyl chloride with benzyl bromide does not have a decisive effect on the catalytic activity, as benzyl bromide reacts to give the corresponding 1,2,3-triazole product in almost quantitative yields (entries 9–11), except for aliphatic alkynes (entries 12 and 13).

The lifetime of a catalyst and its level of reusability are highly significant factors for the useful applications of such a heterogeneous system for organic reactions. Indeed the reusability of the LDH-$CuCl_4^{2-}$ catalyst was investigated for the cycloaddition of benzyl chloride, NaN_3 and phenylacetylene (Figure 5). The concentration of both catalyst and reactants were increased fivefold, and the experiment was performed under the previously optimized reaction conditions. After the first run, the product was extracted with ethyl acetate, and the residual catalyst was reused for a new cycle of the reaction under the same conditions. The results indicate that it is possible to recycle and reuse the catalytic system for a minimum of four cycles with relatively high catalytic activity. The small decrease in the activity of the catalyst from

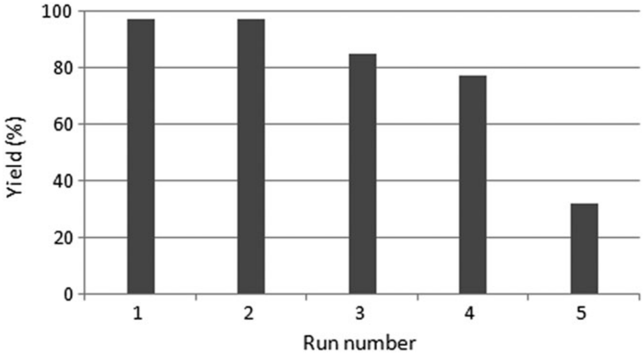


FIGURE 5 Recycling of LDH-$CuCl_4^{2-}$ catalyst for azide–alkyne cycloaddition

the first to the fourth cycle can be related to a small decrease of catalyst mass during the washing procedure.

To investigate the leaching of copper species into solution, after separation of the LDH-$CuCl_4^{2-}$ catalyst, the copper content of the residual mixture was measured using atomic absorption spectroscopy. The results show that the copper content of solution is significantly lower than the detection limit which confirms negligible leaching of copper from the catalyst.

To confirm the absence of catalyst leaching during reaction, the cycloaddition of benzyl chloride, NaN_3 and phenylacetylene as a model reaction was stopped at half the reaction time and the catalyst was completely separated from solution by centrifugation. With continuation of stirring (without catalyst) for another period of half the reaction time, it was observed that a trace amount of product is formed and therefore the catalyst really is heterogeneous.

4 | CONCLUSIONS

We have developed an efficient and simple protocol for the preparation of Cu(II) immobilized on LDH as a catalyst for the synthesis of 1,2,3-triazoles by 1,3-dipolar cycloaddition of terminal alkynes with benzyl azides generated *in situ* from sodium azide and various benzyl halides. This protocol has been performed efficiently to provide the desired products in excellent yields. Simple operation, easy separation, short reaction times, wide substrate scope, readily available starting materials and reagents, and recyclable and inexpensive catalyst are the salient features of this method.

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REFERENCES

[1] R. Huisgen, in *1,3-Dipolar Cycloaddition Chemistry* (Ed: A. Padwa), Wiley, New York **1984**, 1.

[2] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596.

[3] C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057.

[4] M. Meldal, C. W. Tornøe, *Chem. Rev.* **2008**, *108*, 2952.

[5] J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007**, *36*, 1249.

[6] H. C. Kolb, K. B. Sharpless, *Drug Discovery Today* **2003**, *8*, 1128.

[7] S. Chuprakov, S. W. Kwok, V. V. Fokin, *J. Am. Chem. Soc.* **2013**, *135*, 4652.

[8] M. Zibinsky, V. V. Fokin, *Angw. Chem. Int. Ed.* **2013**, *52*, 1507.

[9] A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Chem. Rev.* **2013**, *113*, 3084.

[10] J. C. Jewett, C. R. Bertozzi, *Chem. Soc. Rev.* **2010**, *39*, 1272.

[11] F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless, V. V. Fokin, *J. Am. Chem. Soc.* **2005**, *127*, 210.

[12] A. Akbari, N. Arsalani, M. Amini, E. Jabbari, *J. Mol. Catal. A* **2016**, *414*, 47.

[13] M. Amini, A. Bayrami, M. N. Marashi, A. Arab, A. Ellern, L. K. Woo, *Inorg. Chim. Acta* **2016**, *443*, 22.

[14] M. Faraji, M. Amini, A. P. Anbari, *Catal. Commun.* **2016**, *76*, 72.

[15] S. Díez-González, S. P. Nolan, *Angew. Chem. Int. Ed.* **2008**, *47*, 8881.

[16] L. K. Rasmussen, B. C. Boren, V. V. Fokin, *Org. Lett.* **2007**, *9*, 5337.

[17] L. Zhang, X. Chen, P. Xue, H. H. Y. Sun, I. D. Williams, K. B. Sharpless, V. V. Fokin, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 15998.

[18] S. Díez-González, E. D. Stevens, S. P. Nolan, *Chem. Commun.* **2008**, 4747.

[19] D. Wang, N. Li, M. Zhao, W. Shi, C. Ma, B. Chen, *Green Chem.* **2010**, *12*, 2120.

[20] S. Messaoudi, M. Gabillet, J-D. Brion, M. Alami, *Appl. Organometal. Chem.* **2013**, *27*, 155.

[21] V. Rives, *Layered Double Hydroxides: Present and Future*, Nova Science, New York **2001**.

[22] Z. An, W. Zhang, H. Shi, J. He, *J. Catal.* **2006**, *241*, 319.

[23] X. Jin, K. Taniguchi, K. Yamaguchi, N. Mizuno, *Chem. Sci.* **2016**, *7*, 5371.

[24] J. Feng, Y. He, Y. Liu, Y. Du, D. Li, *Chem. Soc. Rev.* **2015**, *44*, 5291.

[25] L. Li, L. Dou, H. Zhang, *Nanoscale* **2014**, *6*, 3753.

[26] G. Fan, F. Li, D. G. Evans, X. Duan, *Chem. Soc. Rev.* **2014**, *43*, 7040.

[27] J. Das, B. S. Patra, N. Baliarsingh, K. M. Parida, *Appl. Clay Sci.* **2006**, *32*, 252.

[28] Q. Wang, D. O'Hare, *Chem. Rev.* **2012**, *112*, 4124.

[29] B. Velde, *Clays and Clay Minerals in Natural and Synthetic Systems*, Elsevier, Amsterdam.

[30] T. Selvam, A. Inayat, W. Schwieger, *Dalton Trans.* **2014**, *43*, 10365.

[31] L. Liu, W. Wang, Y. Hu, *RSC Adv.* **2015**, *5*, 97458.

[32] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* **1991**, *11*, 173.

[33] B. F. Sels, D. E. de Vos, P. A. Jacobs, *Catal. Rev.* **2001**, *43*, 443.

[34] B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2002**, *124*, 14127.

[35] T. P. F. Teixeira, S. F. Aquino, S. I. Pereira, A. Dias, *Braz. J. Chem. Eng.* **2014**, *31*, 19.

[36] M. Amini, R. Hassandoost, M. Bagherzadeh, S. Gautam, K. H. Chae, *Catal. Commun.* **2016**, *85*, 13.

[37] A. Kumar, A. Saxena, A. De, R. Shankar, S. Mozumdar, *RSC Adv.* **2013**, *3*, 5015.

[38] F. P. Jiao, X. Q. Chen, L. Liu, Z. D. Hu, Y. H. Hu, Y. H. Wang, *J. Mol. Struct.* **2010**, *964*, 152.

[39] H. D. Lutz, K. Wussow, P. Kuske, *Z. Naturforsch. B* **1987**, *42*, 1379.

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