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Short Communication

A synthesis of copper based metal-organic framework for *O*-acetylation of alcohols

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ABSTRACT

A novel metal-organic framework, Cu–BDC was synthesized by static hydrothermal method using innocuous solvents and characterized by several techniques such as powder XRD, ESR, TG–DTA, elemental analysis, ICP-AES, SEM, EDXS, FT-IR, BET surface area, pore volume and pore size. The catalytic performance of Cu–BDC was explored for *O*-acetylation of alcohols under *solvent-free* conditions at room temperature. The catalyst exhibited remarkable activity and reusability affording the desired products in excellent yields.

1. Introduction

Catalysis plays a dynamic role in achieving chemical conversions in an economically and commercially viable manner and is the foundational pillar of green chemistry as it offers a clear opportunity to provide realistic solutions to many environmental issues. In the present era, when pollution is a major problem, the focus is also on placing precincts to the use of conventional, corrosive and non-recoverable homogeneous catalysts and identifying robust, easy to handle, and recoverable heterogeneous catalysts. Metal-organic frameworks (MOFs) [1–4] belong to the class of materials that can fulfill the requirements for an environmentally viable heterogeneous catalyst and have potential to replace the traditional ones in the future. They have received a momentous attention in the area of inorganic–organic hybrid materials [5]. MOFs are porous polymeric are porous polymeric materials consisting of metal ions linked together by organic bridging ligands. After combination of solutions of these inorganic and organic components under stirring, the metal-organic structures are formed by self-assembly at temperatures starting at room temperature and up to solvothermal conditions at 200 °C.

Although the applications [6–10] of this new and emerging class of material have been significant in storage, separation and sensing; their catalytic properties have not been fully explored. The high metal content in MOFs, their insolubility in water and common organic solvents offer immense scope for their exploration as new heterogeneous catalysts. Also the possibility of incorporating various metal ions in variable valence states makes them excellent model systems for unraveling the electronic and matrix effects in catalysis. There are very few reports demonstrating the catalytic activity of MOFs [11–17]. Most of the work has been focused on the synthesis and characterization of MOFs providing catalysis as a supplementary study in short with the reactions unexplored with respect to the substrates. Thus, a detailed investigation on MOF as catalyst for organic transformation has been the subject of recent focus.

Acetylation of alcohols is a fundamental step in many organic syntheses. Hydroxyl groups are present in a number of compounds of biological and synthetic interest. Among the protecting groups for alcohols, the esters are the most important with acetate being the easiest of all. A wide range of homogeneous and some heterogeneous catalysts have been reported for this transformation [18–21]. A number of copper salts [18,22,23] have also been used in homogeneous catalyst for *O*-acetylation of alcohols but they suffer from the drawbacks of difficulty in catalyst/product separation and result in permanent deactivation of the catalyst which adds directly to the waste stream. Therefore, introduction of new methods and greener and better catalysts for the preparation of esters is still in demand.

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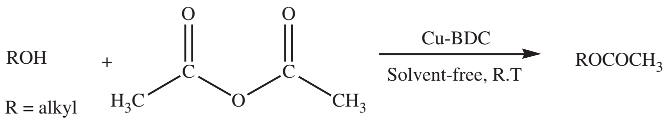


Scheme 1. *O*-acetylation of alcohol using acetic anhydride.

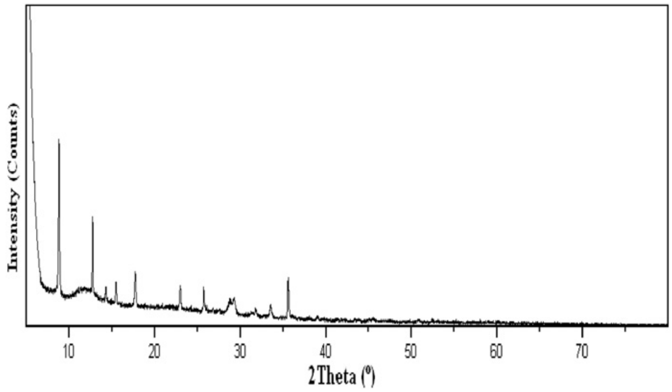


Fig. 1. X-ray powder diffraction pattern of Cu–BDC.

In continuation of our research activities in nanocatalysis, greener synthesis and application of heterogeneous catalysts for various organic transformations [24–30] herein, we report the catalytic activity of copper based metal-organic framework material (Cu–BDC) for *O*-acetylation of alcohols under *solvent-free* condition at room temperature (Scheme 1). The MOF is prepared by simple static hydrothermal method employing non-hazardous solvents in an autoclave and using inexpensive precursors $Cu(NO_3)_2 \cdot 3H_2O$ and BDC (1,4-benzenedicarboxylic acid). Excellent yield of desired products was obtained and the catalyst was successively recycled for several runs with no significant loss in activity.

2. Results and discussion

2.1. Catalyst characterization

The powder XRD pattern of the Cu–BDC is depicted in Fig. 1, and the material appears to be crystalline. The average crystallite size (D) from X-ray line broadening was calculated using the Scherrer Eq. (1),

$$D = \frac{0.9\lambda}{\beta_{1/2}\cos\theta}, \tag{1}$$

where, λ is the wavelength of the X-ray beam, $\beta_{1/2}$ is the angular width at the half maximum intensity and θ is the Bragg's angle. The crystallite size of the material was found to be of the order of magnitude of 0.1–0.2 μm, at the extreme limit of applicability of the equation. Apart from crystallite size, results computed through Eq. (1) are sensitive to other peak broadening contributions, e.g. from the material's microstrained state. Indeed, considering that the MOF is prepared via a hydrothermal method, subject to high pressure and elevated temperature inside an autoclave, it may be expected that its crystallites are in a highly strained state. As a consequence, the calculated values for D should be regarded simply as a lower bound for crystallite size.

The powder XRD data of Cu–BDC could be indexed into a monoclinic cell as a = 3.099 Å, b = 18.520 Å, c = 11.750 Å, V = 571.555 $Å^3$ and β = 122.047°.

The appearance of the signal (g = 2.18) in ESR indicates the presence of copper in 2^+ oxidation state as the copper in 1^+ state is not EPR active because they lack unpaired electrons (Fig. 2).

The thermal gravimetric and differential thermal analyses were carried out from 30 °C to 800 °C at a heating rate of 5 °C per minute. It was observed that the MOF is thermally stable up to nearly 210 °C. The sample undergoes almost one half weight loss between 213 °C–434 °C. The onset of decomposition of the sample was found to be at 294 °C, which is confirmed, by both TG as well as DTA curves. The weight of the residue left at 434 °C is 48% and remains the same up to 800 °C.

Particle size and shape of Cu–BDC were observed using SEM. The images show a rod like shape of the particles with approximately 2.5 ± 1 μm in length and 0.4 ± 0.1 μm in width. Coupled with the above mentioned crystallite size, this is a clear indication of the polycrystalline nature of the particles. The different magnification images are as shown in Fig. 3(a), (b) and (c).

The EDXS data of Cu–BDC is summarized in Table 1, which is consistent with the ICP-AES and elemental analysis data.

FT-IR spectrum confirms the formation of Cu–BDC (Fig. 4). The bands observed at 471, 499, 563 and 628 cm^{-1} are probably due to

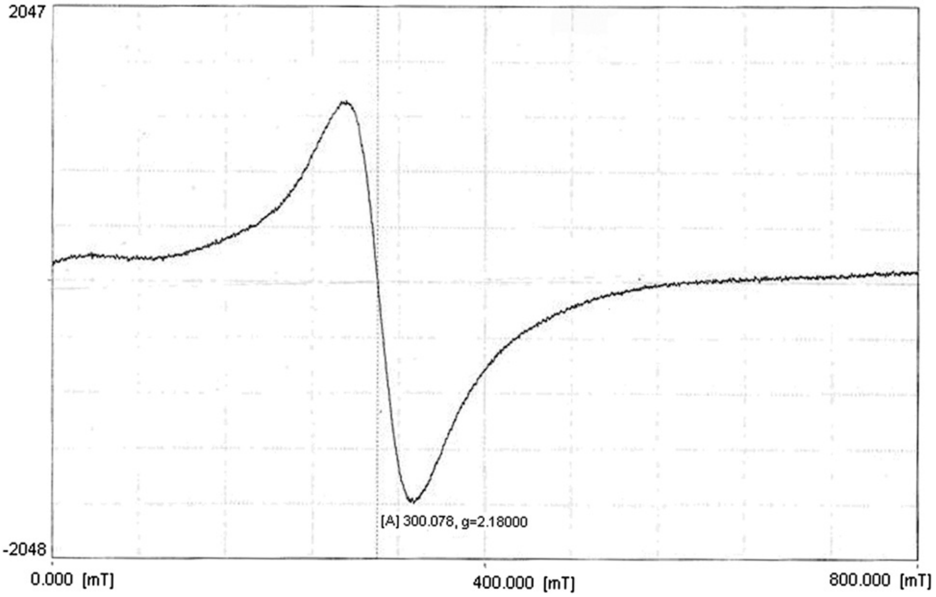
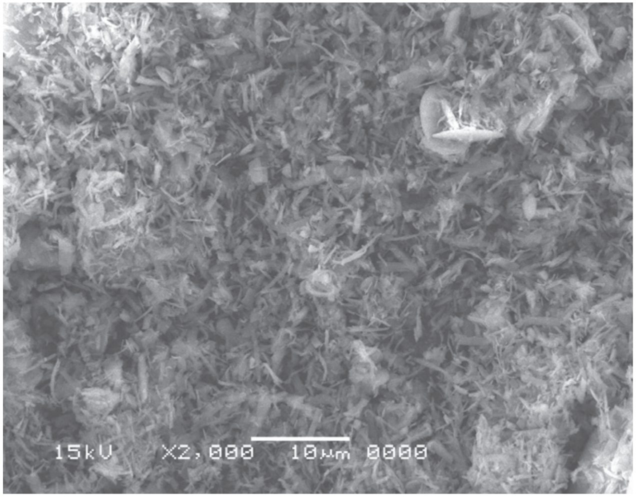
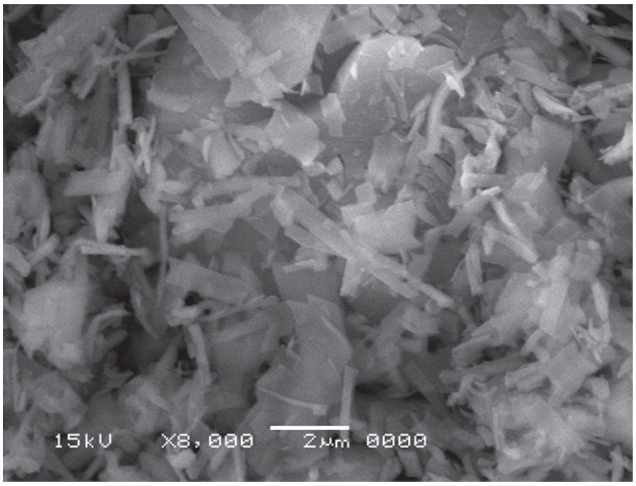


Fig. 2. ESR spectrum of Cu–BDC.

a) SEM of Cu-BDC at 10 μm



b) SEM of Cu-BDC at 2 μm



c) SEM of Cu-BDC at 1 μm.

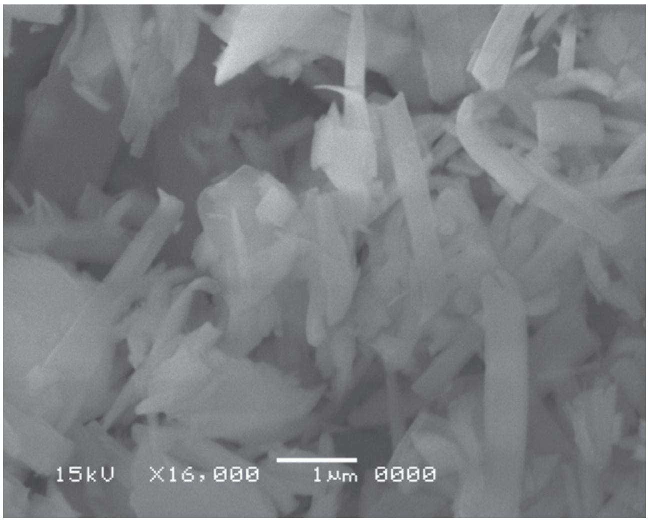


Fig. 3. (a) SEM of Cu–BDC at 10 μm. (b) SEM of Cu–BDC at 2 μm. (c) SEM of Cu–BDC at 1 μm.

Table 1
EDXS data of Cu–BDC.

Element	Mass %	At %	K-ratio
C K	25.31	44.17	9.6845
O K	31.83	41.70	78.9263
Cu K	42.85	14.13	53.1718
Total	100.00	100.00	

Cu(II) – O vibrations in agreement with the literature reports [31,32]. In any compound containing –OH group, the molecules are connected by inter-molecular hydrogen bonding due to which a strong broad band of –OH in the region 3400–3200 cm^{-1} is usually obtained in the IR spectrum. However, when the compound is diluted, the extent of hydrogen bonding decreases or in any situation, where hydrogen bonding is not possible due to structural reasons, similar to the case of Cu–BDC, only free –OH group exists and the absorption is due to free –OH group which gives a sharp peak nearly in the region 3550–3450 cm^{-1}. In the case of Cu–BDC which is a solid co-ordination polymer, the –OH group is present in a rigid structure where hydrogen bonding is not possible and the absorption is due to free –OH group which gives a sharp absorption at 3611 cm^{-1} as seen in the IR spectrum of Cu–BDC.

Surface area of the material was found to be 58.8 m^2/g with a pore volume of 0.016 cm^3/g and pore diameter of 14.66 Å. The low surface area can be attributed to very small pore size of the material. The small pore size could also be the reason for the inability of the nitrogen molecules to access the pores of the particles resulting in a less surface area [33]. The nitrogen uptake by this class of material is also highly dependent on the activation procedure [6,34].

2.2. Reaction studies

The scope of MOF catalyzed *O*-acetylation of alcohols was explored by using 20 wt.% of Cu–BDC at room temperature under *solvent-free* condition (Table 2, entries 1–8). Various primary and secondary aliphatic alcohols underwent smooth acetylation with acetic anhydride providing high yield of desired products. The standard reaction of benzyl alcohol with acetic anhydride gave 87% yield of benzyl acetate (entry 1). Benzyl alcohol having electron donating and electron withdrawing groups reacted efficiently with acetic anhydride providing the desired product in excellent yields. The protocol was also applicable for acetylation of long chain aliphatic alcohols providing the desired products in good yields. Thus, the MOF showed excellent catalytic activity and was applicable for a wide variety of substrates.

The effect of temperature on *O*-acetylation of benzyl alcohol using acetic anhydride as acetylating agent was studied under *solvent-free* conditions (Table 3, entries 1–4). Notably, the yield of corresponding products was increased with an increase in temperature up to 80 °C. Further increase in temperature to 100 °C did not have much effect on the reaction yield. However, further studies were performed at room temperature.

The concentration–time study of the reaction was monitored using a gas chromatograph (Table 3, entries 5–8). Initially, the reaction proceeds comparatively fast and becomes slow at the later period. The probable reason may be that the ester competes with the reactant for similar surface sites of the catalyst thereby inhibiting its adsorption on the catalyst surface. Thus, an increase in product concentration decreases the reaction rate as few sites are available for the reactant to get activated.

Catalyst reusability was examined for the standard reaction of *O*-acetylation of benzyl alcohol at room temperature. The recycled catalyst after each run was separated by filtration, washed with diethyl ether and dried in air for 24 h. The catalyst was activated at 120 °C in air for 2 h prior to the next run and was reused up to three times with no significant loss in activity.

A probable mechanism for the reaction can be explained as follows [18]. The free metallic sites in the framework of Cu–BDC interact with the –CO– group of acetic anhydride thereby activating the acetyl group of the anhydride and enhancing the leaving ability of the acetate

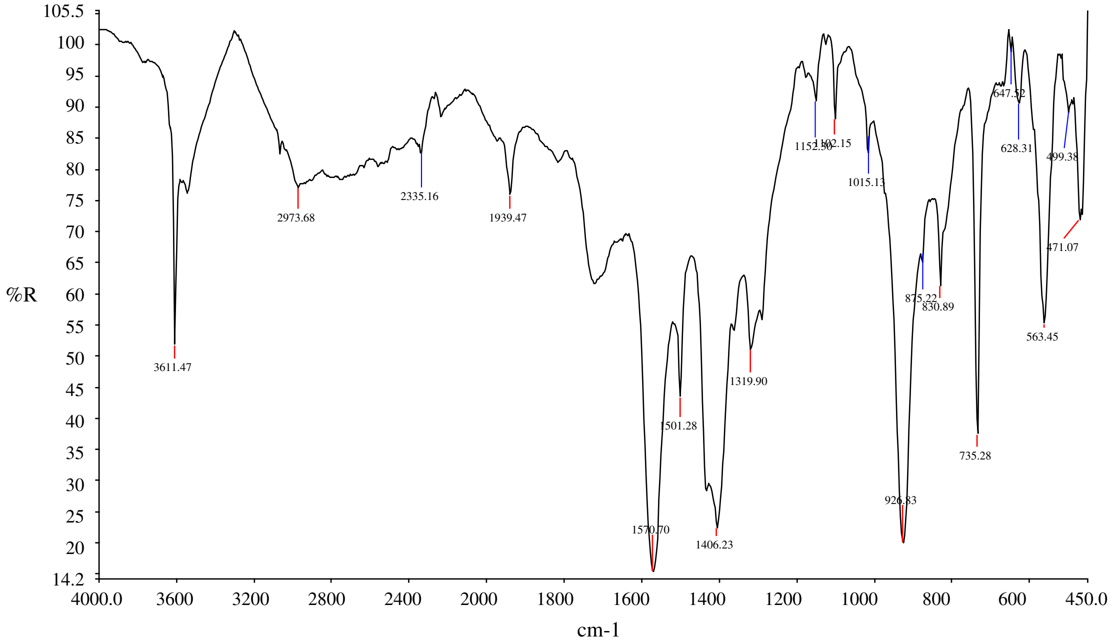


Fig. 4. FT-IR spectrum of Cu–BDC.

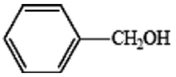
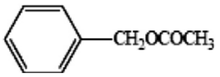
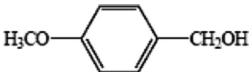
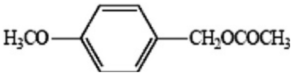
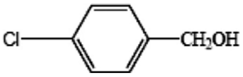
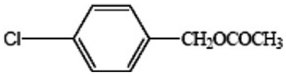
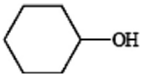
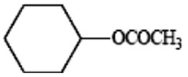
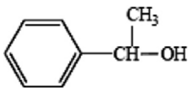
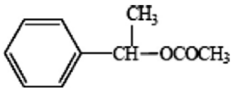
counterpart. The activated acetic anhydride on the catalyst surface further reacts with the alcohol to give ester as the product.

3. Experimental

3.1. General

All the chemicals purchased were of analytical grade and used without further purification. The powder XRD pattern was obtained with conventional powder diffractometer (Philips 1050) using graphite monochromatized Cu Kα radiation operating in Bragg–Brentano (θ/2θ) geometry. Thermal gravimetric and differential thermal analyses were performed with a Diamond TG/DTA analyzer (PerkinElmer). Elemental analysis was done on a model FLASH EA 1112 series (Thermo Finnigan). Percentage of copper was obtained by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on JY Ultima-2 (Jobin Yvon) instrument. Scanning electron microscopic (SEM) images were obtained on JEOL (JSM 6380-LA) and

Table 2
Liquid phase *O*-acetylation of alcohols catalyzed by Cu–BDC[a].

Entry	Alcohol	Product	Yield[b] (%)
1			87, 87, 85, 82[c]
2			93
3			85
4			72
5	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	$CH_3(CH_2)_3CH(C_2H_5)CH_2OCOCH_3$	86
6			70
7	$(CH_3)_2CHCH_2CH_2OH$	$(CH_3)_2CHCH_2CH_2OCOCH_3$	88
8	$CH_3(CH_2)_7OH$	$CH_3(CH_2)_7OCOCH_3$	90

[a] Reaction conditions: alcohol = 2 mmol; acetic anhydride = 4 mmol; catalyst = 20 wt.% (w.r.t. alcohol); time = 24 h under neat condition at room temperature.
[b] GC yield.
[c] Yield after fourth cycle.

Table 3
Effect of temperature and time on *O*-acetylation of benzyl alcohol[a].

Entry	Temperature (°C)	Time (h)	Yield[b] (%)
Effect of temperature			
1	40	2	58
2	60	2	75
3	80	2	95
4	100	2	98
Effect of time			
5	r.t.	2	35
6	r.t.	8	64
7	r.t.	15	75
8	r.t.	24	87

[a] Reaction conditions: alcohol = 2 mmol; acetic anhydride = 4 mmol; catalyst = 20 wt.% (w.r.t. alcohol) under neat condition.

[b] GC yield.

energy-dispersive X-ray spectroscopy (EDXS) data was collected from the model JED-2300 series (EX-2300BU). FT-IR spectrum was recorded on PerkinElmer model. BET surface area was determined using NOVA 1200 Quantachrome by nitrogen adsorption. The yield of the products for *O*-acetylation reaction was based on the analysis using capillary column equipped gas chromatograph (Chemito 1000). The products of the *O*-acetylation reaction were identified by GC/MS (Shimadzu, GCMS-QP 2010).

3.2. Catalyst preparation

$Cu(NO_3)_2 \cdot 3H_2O$ (19.5 g) and 1,4-benzenedicarboxylic acid (1.8 g) were dissolved in water (75 mL) and ethanol (75 mL) respectively. The two solutions were mixed and stirred for 20 to 30 min on a magnetic stirrer. The mixture was then transferred in an autoclave and allowed to react at 90 °C without stirring. After 18 h, the autoclave was allowed to cool at ambient temperature. A light blue colored material was collected by filtration and washed several times with water and hot boiling ethanol and dried in air overnight at 110–115 °C in an oven. The as synthesized material was found to be insoluble in water and common organic solvents such as acetone, ethanol, acetonitrile, pet ether, chloroform, ethyl acetate, dichloromethane, dimethylformamide (DMF), n-hexane, and diethyl ether. Elemental analysis revealed carbon and hydrogen content as 24.67% and 1.61% respectively. Copper content was analyzed by ICP-AES and was found to be 39.96%.

3.3. Typical procedure for O-acetylation of alcohols

Alcohol (2 mmol) and Cu–BDC (20 wt.% w.r.t. alcohol and preactivated at 120 °C for 1.5 h) were added to a 10 mL round bottom flask equipped with a magnetic stirrer. To this, acetic anhydride (4 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. After completion, the reaction mixture was diluted with diethyl ether (10 mL) and centrifuged. The supernatant liquid was decanted and diethyl ether (5 mL) was again added to the solid mass and centrifuged. The decanted aliquots were combined and washed with 10% sodium bicarbonate solution and then with water. The organic layer was dried using anhydrous sodium sulfate and concentrated to afford the crude product. The yields reported were based on GC analysis in comparison with an authentic sample. All compounds are known compounds and were characterized using GC–MS (Shimadzu QP2010).

4. Conclusion

In summary, a novel metal organic framework (Cu–BDC) has been hydrothermally synthesized using innocuous solvents and its catalytic activity is successfully demonstrated for the *O*-acetylation of alcohols at ambient conditions. The catalyst, heterogeneous by nature, showed excellent activity and reusability affording high yields of desired products under *solvent-free* condition. The ease of preparation of catalyst, high metal content and insolubility in common organic solvents make it an attractive alternative to the present range of conventional Lewis acid mediated reactions. Further work is in progress to extrapolate the catalytic activity of Cu–BDC for other organic transformations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.10.016.

References

[1] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705.
[2] J.L.C. Rowsell, O.M. Yaghi, Microporous Mesoporous Mater. 73 (2004) 3.
[3] M.J. Rosseinsky, Microporous Mesoporous Mater. 73 (2004) 15.
[4] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 38 (2005) 176.
[5] S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334.
[6] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, J. Am. Chem. Soc. 126 (2004) 5666.
[7] T. Duren, L. Sarkisov, O.M. Yaghi, R.Q. Snurr, Langmuir 20 (2004) 2683.
[8] Y. Li, R.T. Yang, J. Am. Chem. Soc. 128 (2006) 726.
[9] A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi, J. Am. Chem. Soc. 128 (2006) 3494.
[10] Q.M. Wang, D. Shen, M. Bulow, M.L. Lau, S. Deng, F.R. Fitch, N.O. Lemcoff, J. Semanscin, Microporous Mesoporous Mater. 55 (2002) 217.
[11] K. Tanaka, S. Oda, M. Shiro, Chem. Commun. (2008) 820.
[12] D. Jiang, T. Mallat, F. Krumeich, A. Baiker, J. Catal. 257 (2008) 390.
[13] F.X.L. Xamena, O. Casanova, R.G. Tailleur, H. Garcia, A. Corma, J. Catal. 255 (2008) 220.
[14] S. Cho, B. Ma, S.T. Nguyen, J.T. Hupp, T.E. Albrecht-Schmitt, Chem. Commun. (2006) 2563.
[15] K. Schlichte, T. Kratzke, S. Kaskel, Microporous Mesoporous Mater. 73 (2004) 81.
[16] J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim, Nature 404 (2000) 982.
[17] S.D. Rosa, G. Giordano, T. Granato, A. Katovic, A. Siciliano, F. Tripicchio, J. Agric. Food Chem. 53 (2005) 8306.
[18] K. Jeyakumar, D.K. Chand, J. Mol. Catal. A Chem. 255 (2006) 275.
[19] A.R. Gholap, K. Venkatesan, T. Daniel, R.J. Lahoti, K.V. Srinivasan, Green Chem. 5 (2003) 693.
[20] J.R. Satam, M.B. Gawande, S.S. Deshpande, R.V. Jayaram, Synth. Commun. 37 (2007) 3011.
[21] T.S. Reddy, M. Narasimhulu, N. Suryakiran, K.C. Mahesh, K. Ashalatha, Y. Venkateswarlu, Tetrahedron Lett. 47 (2006) 6825.
[22] K.L. Chandra, P. Saravanan, R.K. Singh, V.K. Singh, Tetrahedron 58 (2002) 1369.
[23] R.K. Khunger, Synlett (2006) 327.
[24] S.J. Singh, R.V. Jayaram, Tetrahedron Lett. 49 (2008) 4249.
[25] S.J. Singh, R.V. Jayaram, Catal. Commun. 10 (2009) 2004.
[26] S.J. Singh, S.R. Kale, R.V. Jayaram, Curr. Catal. 2 (2013) 130.
[27] M.B. Gawande, D.B. Bonifacio Vasco, R. Luque, P.S. Branco, R.S. Varma, Chem. Soc. Rev. 42 (2013) 5522.
[28] M.B. Gawande, P.S. Branco, R.S. Varma, Chem. Soc. Rev. 42 (2013) 3371.
[29] M.B. Gawande, P.S. Branco, I.D. Nogueira, C.A.A. Ghumman, N. Bundaleski, A. Santos, O.M.N.D. Teodoro, R. Luque, Green Chem. 15 (2013) 682.
[30] M.B. Gawande, A. Rathi, I.D. Nogueira, R.S. Varma, P.S. Branco, Green Chem. 15 (2013) 1895–1899.
[31] G. Cordoba, R. Arroyo, J.L.G. Fierro, M. Viniegra, J. Solid State Chem. 123 (1996) 93.
[32] E.M. Fixman, M.C. Abello, O.F. Gorriz, L.A. Arrua, Appl. Catal. A 319 (2007) 111.
[33] A.B.M. Danna, S.E. Iyuke, A. Fakhrul-Razi, T.G. Chuah, M.A. Atieh, M.F. Al-Khatib, Environ. Info. Arch. 1 (2003) 597.
[34] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature 402 (1999) 276.