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SHORT COMMUNICATION

Cu(BDC) as a catalyst for rapid reduction of methyl orange: room temperature synthesis using recycled terephthalic acid

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Abstract Terephthalic acid was recycled from waste PET bottles with a basic hydrolysis technique and characterized with UV and FTIR spectroscopy. Copper-based metal–organic framework Cu(BDC) was synthesized at room temperature without any additive; two different temperatures were chosen to activate the obtained material. Characterization studies were performed using XRD, N_2 physisorption, STEM and EDX. The obtained material was tested as a catalyst for the reduction of methyl orange with $NaBH_4$ in aqueous solutions. Thermal activation at 160 °C proved to be mandatory for catalytic activity; although higher temperature activation did not cause significant enhancement. Rapid dye removal was monitored by continuous photometry at λ_{max}. The results were quite satisfactory (about 85% removal in 5 min); even higher than the published results for precious metal (i.e., Au, Pt and Ag) nanoparticles. In an increased reaction scale, UV–visible spectra and mass spectrum were recorded to help elucidating the possible reaction mechanism. In addition, recycling experiment were performed in 100-ml scale without any kind of re-activation (washing or drying) to show the ability of Cu(BDC) as a stable catalyst for reductive dye removal (and probably similar reactions as well).

Keywords Cu(BDC) · Heterogeneous catalysis · Dye removal · Reduction · Terephthalic acid

Introduction

The discovery of new robust yet inexpensive catalysts for environmental applications has become a crucial topic in recent years (Centi et al. 2002). Industrial organic dyes are a major pollutant from textile industry (Reife et al. 1996). Various approaches have been used to remove such dyes from aqueous media using adsorbents (Crini 2006), microbes (McMullan et al. 2001), photocatalysts (Emrooz et al. 2017), oxidation catalysts (Shu et al. 2015) and reduction catalysts (Mondal et al. 2015).

As a major class of nanoporous materials, metal–organic frameworks (MOFs) have gained a lot of interest in a variety of applications (Furukawa et al. 2013), which include but are not limited to gas separation and storage, catalysts and biomedical usage (Farrusseng 2011). MOFs have been widely studied in the field of organic contaminate (Dias and Petit 2015) and pesticide (Dumée et al. 2017) removal over the past few years. One of the most interesting properties which make MOFs unique is their catalytic behavior which is a link between the well-known homogenous and heterogeneous metal-based catalysts (Luz et al. 2010). They can serve well as catalyst support for a variety of applications including CO_2 conversion (Maina

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et al. 2017), reduction reactions (He et al. 2015) and many others (Lee et al. 2009; Burrows et al. 2013).

Following the first report regarding copper terephthalate MOF (Carson et al. 2009), many researches have studied various aspects of this material; including but not limited to crystalline structure elucidation (Carson et al. 2014) and room temperature synthesis with the aid of triethylamine (Dikio and Farah 2013). It has also showed promising applications as photocatalyst support (Mohaghegh et al. 2015), oxidation catalyst (Dang et al. 2015), click-reaction catalyst (Luz et al. 2010), gas transport membrane (Kubica et al. 2016) and lithium-ion storage (Senthil Kumar et al. 2014).

In continuation of our quest studying different nanocatalysts for a variety of applications (Zonouzi et al. 2016), herein we present a simple room temperature synthesis route to obtain Cu(BDC) from $Cu(NO_3)_2$ and terephthalic acid (recycled from waste PET). This material can be used as a reduction catalyst for the removal of methyl orange (among other dyes) from aqueous solution by $NaBH_4$.

Experimental

Materials and methods

Copper nitrate, terephthalic acid, DMF, HCl, NaOH and methyl orange were purchased from Merck (Darmstadt, Germany), sodium borohydride was obtained from Dae-Jung Chemicals (Seoul, South Korea).

A Philips (Holland) PU 9624 instrument was used to record FTIR spectra. Melting points were measured by a Bernstein Electrothermal (UK) apparatus. UV spectra were measured by a Perkin Elmer (US) Lambda 25 spectrophotometer. Mass spectroscopy was performed on an Agilent (US) 5973 instrument at an ionization potential of 70 eV. X-ray diffraction patterns were recorded on a Philips (Holland) PW 1730 instrument using CuKα radiation with $\lambda = 1.54$ Å, N_2-physisorption isotherms were recorded on a BelSORP (Japan) mini II, Scanning Transmission Electron Microscopy (STEM) was performed on a FEI (US) Tecnai F30 microscope using holey carbon–nickel grid. A PG instruments (UK) T80+ double beam UV–Vis spectrophotometer was used for catalytic activity evaluation. Water droplet contact angels were measured by pressing a considerable amount of each sample between two glass slabs and then carefully poring 1 µl of distilled water on them with a micropipette (DragonLab, China) while taking pictures of the process with a digital still camera on burst mode and then analyzing the pictures.

Recycling of terephthalic acid

Terephthalic acid (1,4-benzenedicarboxylic acid) was obtained by modified basic hydrolysis of PET (Carta et al. 2003). In a typical procedure, 15 g of polyethylene terephthalate (PET) obtained by cutting down a mineral water bottle to 5 mm pieces was transferred to a BEP 280 buchi (Switzerland) stirrer laboratory autoclave with 400 ml of 5% aqueous NaOH solution. Temperature was set at 180 °C and pressure was increased to 5 bar. Reaction was carried out for 2 h during which the pressure was reached to 10 bar. The mixture was filtered off with a Whatman® no.1; the obtained filtrate is a basic solution of sodium terephthalate which is then treated with aqueous 5% HCl solution to precipitate terephthalic acid which is further washed with distilled water until reaching natural pH. The yield of this reaction was measured to be 96.4% by weight.

Synthesis of Cu(BDC)

In a typical synthesis procedure, 0.263 g of copper nitrate and 0.181 g of terephthalic acid were dissolved in 22 ml of DMF and transferred to a sealed 6-dram vial and kept in static conditions. The first crystallites precipitated in less than 2 h and the reaction was continued for 2 days to ensure completion. The light blue precipitate was centrifuged and washed with fresh DMF and then with water to remove any unreacted precursors. After drying at room temperature (code name **RT**), was divided into two equal parts; one part was activated at 160 °C (code name **RT160**) and the other was activated at 225 °C (code name **RT225**) to investigate the effect of temperature on the removal of DMF from the structure. These samples were used for XRD, N_2-physisorption, STEM, and catalytic reduction experiments as well.

Catalytic activity evaluation

Catalytic activity tests were performed by adding 0.1 mg of each catalyst, $NaBH_4$ (0.1 mg) and 2 ml of aqueous methyl orange solution (16.5 ppm) to a quartz cell and measuring the absorbance at $\lambda_{max} = 464$ nm, at kinetic mode (time resolution of 1 s). Recycling study was performed on **RT160** by adding 5 mg of the sample and 5 mg of $NaBH_4$ to 100 ml of methyl orange solution while stirring. 2 ml of this mixture was transferred to a quartz cell and UV–Vis spectrum was recorded every minute in the range $\lambda = 199$–599 nm (bandwidth was set to 5 nm to complete each spectrum in less than 1 min and record absorption at $\lambda_{max} = 464$ nm simultaneously). After 9 min the mixture was centrifuged and the sample was used without any kind of recovery step or drying by simply adding 100 ml of fresh methyl orange solution and 5 mg of $NaBH_4$; this procedure was repeated five times.

Results and discussion

Recycled terephthalic acid sample showed a melting point of 300 °C which proves its structure and purity. It was further characterized using FTIR (with KBr pallets) and compared with synthetic grade material from Merck; the results are presented in Fig. S1. This sample was also characterized using UV spectrophotometry in a 5% aqueous NaOH solution which also showed the same spectrum as synthetic grade material ($\lambda_{\max} = 242$ nm, Fig. S2).

XRD patterns for MOF samples (parts a and c of Fig. 1) clearly show the presence of the well-known main phase of Cu(BDC)(DMF), and the sample which was activated at 225 °C also shows the characteristic peaks of the high-temperature phase [i.e., Cu(BDC)]. The difference in the crystalline structure of these two phases has been conclusively investigated previously (Carson et al. 2014). Three more samples obtained by performing the reduction reaction in a 50-fold scale and centrifuging the catalyst which was then analyzed by XRD; the results (parts b, d and e of Fig. 1) represent the diffraction patterns for **RT160** and **RT225** after one run of reduction reaction and also for **RT160** after performing six runs of reaction. The results suggest a decrease in crystallinity of the sample after one run and amorphization after six runs of reaction.

Application of Scherrer's equation (Scherrer 1912) to the main peaks of the samples gave the average crystalline sizes of 570 nm for the synthesized **RT160** and 360 nm for the synthesized **RT225**. As can be seen thermal activation seems to decrease the crystallite sizes, also the crystallinity (which is apparent from the less sharp characteristic peaks and a heightened baseline at small diffraction angles, especially in the range $6 < 2\theta < 10°$. Furthermore, the average crystallite sizes decreased to 360 and 180 nm for the samples **RT160** and **RT225** after one run of reduction reaction, respectively. This is in agreement with the results of the recycling tests (Fig. 4). Contact angle data obtained for the samples prove that the wet ability of samples is enhanced by thermal activation which is a qualitative measure for surface energy, measured water droplet contact angles for **RT**, **RT160** and **RT225** are, respectively, 69°, 58° and 48°.

N_2-physisorption studies (Fig. S1) did not yield the expected values which may be attributed to the differences in instrumental settings. We tried several different methods (including the well-known solvothermal method) to obtain the literature values (Carson et al. 2014), while the XRD patterns of the samples were identical and the published data. But it is still comparable to the results published for nano-particulate catalyst used for the same purpose (Mondal et al. 2015).

STEM analysis was performed for the samples **RT160** and **RT225,** the results are presented in Fig. 2; there seems to be a decrease in particle size at higher activation temperature which is in line with crystallite size values deduced from XRD patterns. EDX spectra of rectangular areas designated by **1** in parts **e** and **g** are presented in parts **f** and **h**; they only show the peaks related to copper, oxygen and carbon.

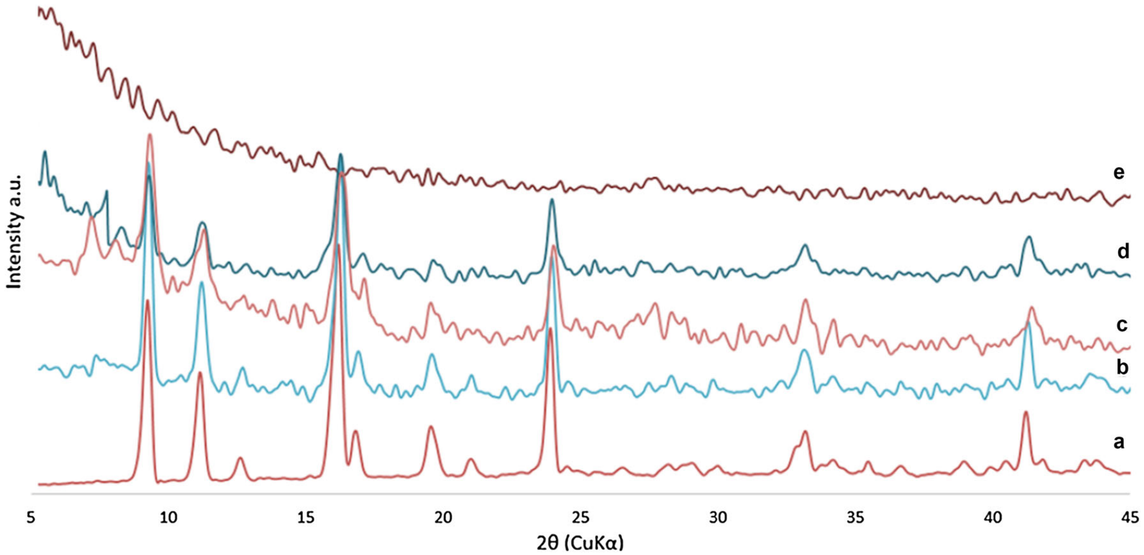


Fig. 1 XRD patterns for **RT160** (**a**), **RT160** after one run of reduction reaction (**b**), **RT225** (**c**), **RT225** after one run of reduction reaction (**d**) and **RT160** after six runs of reduction reaction

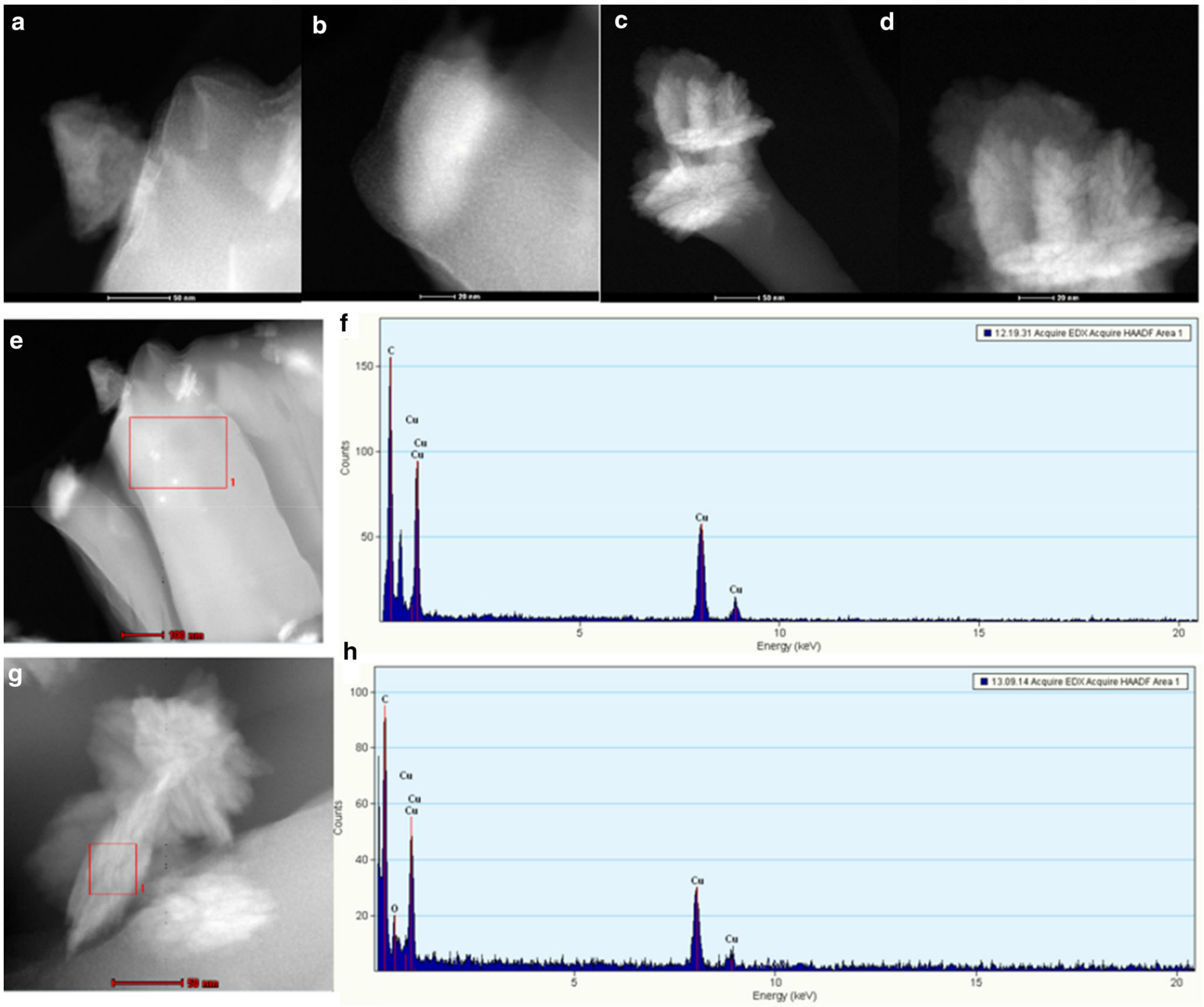


Fig. 2 Dark-field scanning transmission electron micrographs from the sample **RT160** (**a**, **b**, **e**) and the sample **RT225** (**c**, **d**, **g**). EDX spectra obtained from the area 1 of micrographs e and g are presented in parts **f** and **g,** respectively. Characteristic peaks related to grid (nickel) are omitted

Results of the time-dependent photometry test for **RT160**, **RT225**, **RT** and catalyst-free control ($NaBH_4$) are presented in Fig. 3. As can be seen, the two main samples are able to achieve 85% dye removal in about 5 min which is faster than the published results for cobalt (Mondal et al. 2015), gold, silver and platinum (Gupta et al. 2011) nanoparticles. Although the non-activated sample **RT** does not show considerable activity, the presence of high temperate Cu(BDC) crystalline phase does not seem to have a drastic effect on the catalytic activity; thus **RT160** was chosen to undergo recycling experiments (Fig. 4). The inset of this figure presents three further experiments with catalysts under study and dye solution but in the absence of $NaBH_4$ reducing agent and show the insignificance of dye adsorption in the systems under study.

To further elucidate the reaction, time-dependent studies were also performed in spectrum mode (Fig. S1a). The λ_{max} peak of methyl orange (at 464 nm in our study) is caused by its conjugated structure around the azo bond under the influence of electron-donating dimethylamino group. The other peak which can be spotted at about $\lambda = 280$ nm is due to the $\pi \rightarrow \pi^*$ transition of the aromatic moiety. As an attempt to monitor the un-catalyzed reduction, $NaBH_4$ was tested alone in the same reaction conditions. The results are presented in Fig. S1b. As can be deduced from the spectra, 60% reduction is achieved in 35 min (compared to about 85% in 5 min with both **RT160** and **RT225**).

The proposed mechanism for catalytic reduction of methyl orange is presented in Scheme 1. Copper-based

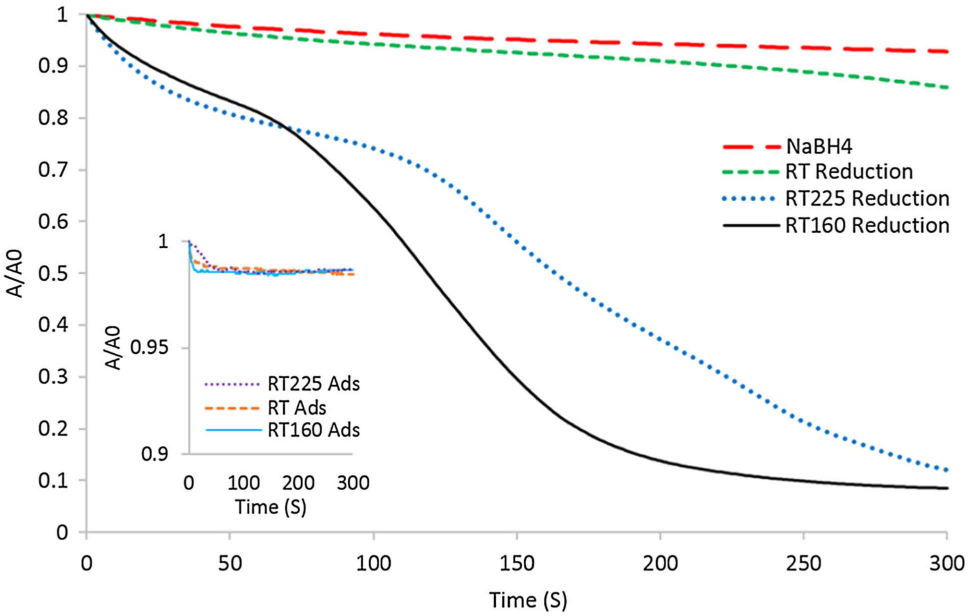


Fig. 3 Time-dependent photometry results for the reduction of methyl orange by $NaBH_4$ without catalyst and with the samples under study. Inset: time dependent photometry results for the samples in the absence of $NaBH_4$ as a measure for dye adsorption at the same conditions. Time resolution was set to 1 s

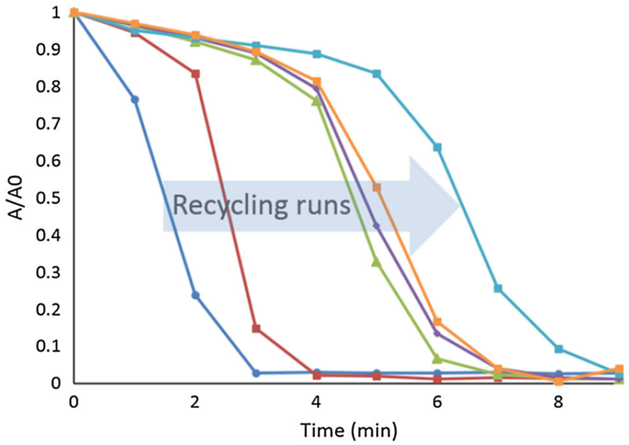
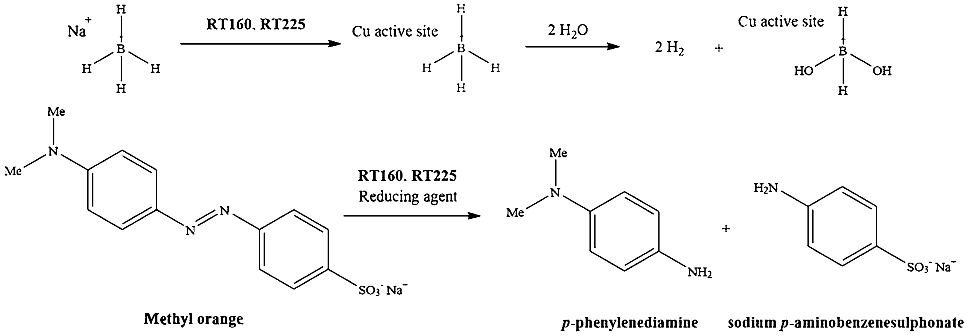


Fig. 4 Results of the recycling tests for **RT160**

catalysts act by increasing the rate of hydrogen generation by $NaBH_4$ and transfer the obtained reducing agents to dye molecules. In this manner, the liberated hydrogen reduces the azo group and the products would be sodium *p*-aminobenzenesulphonate and *N*,*N*-dimethyl-*p*-phenylenediamine. These fragments are also confirmed by mass spectral data. Figure S5 shows the mass spectrum for a concentrated solution after removing the catalyst from the reaction mixture. As can be seen, a trace amount of unreacted methyl orange is still detectable. The fragments related to reduction products can be assigned according to table S1. On the other hand, sodium *p*-aminobenzenesulphonate has a reported characteristic peak at $\lambda = 246$ nm (Fan et al. 2009) which is identically observed to intensify for both un-catalyzed and catalyzed reactions over time.

Recycling tests were performed to study the long-term stability of **RT160** over six identical reaction runs without any kind of re-activation, washing or even drying. The obtained spectra (Fig. S2) show identical peak behaviors, but in different times during the course of reaction. As can also be seen from the summarized results (Fig. 4), it is apparent that while the first run is incredibly fast, next runs tend to become slower and slower; nonetheless, the overall removal efficiency remains almost constant.



Scheme 1 Proposed mechanism for catalytic methyl orange reduction

Conclusions

In summary, we presented a basic hydrolysis procedure to terephthalic acid from waste PET bottles; the sample was analyzed with UV and FTIR spectroscopy and compared with synthetic grade terephthalic acid. Using the recycled compound, we successfully synthesized Cu(BDC) MOF in a room temperature, additive free procedure; activation was performed in two different temperatures (160 and 225 °C). The obtained samples were characterized using powder XRD, N_2-physisorption, water droplet contact angle, STEM and EDX. The samples were also tested as catalyst for the reduction of methyl orange dye with $NaBH_4$. This reaction was monitored using time-dependent spectrophotometry. Mass spectral data were interpreted based on the literature to propose a mechanism for dye reduction. Thermal activation proved to be crucial for catalytic activity toward this reaction, although the presence of high-temperature phase did not have a significant impact on activity. Recycling tests were performed five times without any kind of re-activation; the total turnover of the catalyst remained constant at 9 min, but the rate of reduction decreased over re-use. XRD patterns for the samples after one reaction run proved no significant phase change but amorphization took place after several reaction runs.

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References

Burrows A, Lamberti C, Pidko E, Minguez IL, de Vos D, Hupp JT, Juan-Alcaniz J, García H, Palkovits R, Kapteijn F (2013) Metal organic frameworks as heterogeneous catalysts. R Soc Chem. eISBN:978-1-84973-758-6

Carson CG, Hardcastle K, Schwartz J, Liu X, Hoffmann C, Gerhardt RA, Tannenbaum R (2009) Synthesis and structure characterization of copper terephthalate metal–organic frameworks. Eur J Inorg Chem 2009:2338–2343. doi:10.1002/ejic.200801224

Carson CG, Brunnello G, Lee SG, Jang SS, Gerhardt RA, Tannenbaum R (2014) Structure solution from powder diffraction of copper 1, 4-benzenedicarboxylate. Eur J Inorg Chem 2014:2140–2145. doi:10.1002/ejic.201301543

Carta D, Cao G, D'Angeli C (2003) Chemical recycling of poly (ethylene terephthalate) (PET) by hydrolysis and glycolysis. Environ Sci Pollut Res 10:390–394. doi:10.1065/espr2001.12.104.8

Centi G, Ciambelli P, Perathoner S, Russo P (2002) Environmental catalysis: trends and outlook. Catal Today 75:3–15. doi:10.1016/S0920-5861(02)00037-8

Crini G (2006) Non-conventional low-cost adsorbents for dye removal: a review. Bioresour Technol 97:1061–1085. doi:10.1016/j.biortech.2005.05.001

Dang GH, Vu YT, Dong QA, Le DT, Truong T, Phan NT (2015) Quinoxaline synthesis via oxidative cyclization reaction using metal–organic framework Cu (BDC) as an efficient heterogeneous catalyst. Appl Catal A 491:189–195. doi:10.1016/j.apcata.2014.11.009

Dias EM, Petit C (2015) Towards the use of metal–organic frameworks for water reuse: a review of the recent advances in the field of organic pollutants removal and degradation and the next steps in the field. J Mater Chem A 3:22484–22506. doi:10.1039/C5TA05440K

Dikio ED, Farah AM (2013) Synthesis, characterization and comparative study of copper and zinc metal organic frameworks. Chem Sci Trans 2:1386–1394. doi:10.7598/cst2013.520

Dumée LF, Maina JW, Merenda A, Reis R, He L, Kong L (2017) Hybrid thin film nano-composite membrane reactors for simultaneous separation and degradation of pesticides. J Membr Sci 528:217–224. doi:10.1016/j.memsci.2017.01.041

Emrooz HBM, Rahmani AR, Gotor FJ (2017) Synthesis, characterisation, and photocatalytic behaviour of mesoporous ZnS nanoparticles prepared using by-product templating. Aust J Chem. doi:10.1071/CH17192

Fan J, Guo Y, Wang J, Fan M (2009) Rapid decolorization of azo dye methyl orange in aqueous solution by nanoscale zerovalent iron particles. J Hazard Mater 166:904–910. doi:10.1016/j.jhazmat.2008.11.091

Farrusseng D (2011) Metal-organic frameworks: applications from catalysis to gas storage. Wiley. doi:10.1002/9783527635856

Furukawa H, Cordova KE, O'Keeffe M, Yaghi OM (2013) The chemistry and applications of metal-organic frameworks. Science 341:1230444. doi:10.1126/science.1230444

Gupta N, Singh HP, Sharma RK (2011) Metal nanoparticles with high catalytic activity in degradation of methyl orange: an electron relay effect. J Mol Catal A: Chem 335:248–252. doi:10.1016/j.molcata.2010.12.001

He L, Dumee LF, Liu D, Velleman L, She F, Banos C, Davies JB, Kong L (2015) Silver nanoparticles prepared by gamma irradiation across metal-organic framework templates RSC. Advances 5(14):10707–10715. doi:10.1039/C4RA10260F

Kubica P, Wolinska-Grabczyk A, Grabiec E, Libera M, Wojtyniak M, Czajkowska S, Domański M (2016) Gas transport through mixed matrix membranes composed of polysulfone and copper terephthalate particles. Microporous Mesoporous Mater 235:120–134. doi:10.1016/j.micromeso.2016.07.037

Lee J, Farha OK, Roberts J, Scheidt KA, Nguyen ST, Hupp JT (2009) Metal–organic framework materials as catalysts. Chem Soc Rev 38(5):1450–1459. doi:10.1039/B807080F

Luz I, i Xamena FL, Corma A (2010) Bridging homogeneous and heterogeneous catalysis with MOFs: "Click" reactions with Cu-MOF catalysts. J Catal 276:134–140. doi:10.1016/j.jcat.2010.09.010

Maina JW, Pozo-Gonzalo C, Kong L, Schutz J, Hill M, Dumee LF (2017) Metal organic framework based catalysts for CO_2 conversion. Mater Horizons 4(3):345–361. doi:10.1039/C6MH00484A

McMullan G et al (2001) Microbial decolourisation and degradation of textile dyes. Appl Microbiol Biotechnol 56:81–87. doi:10.1007/s002530000587

Mohaghegh N, Kamrani S, Tasviri M, Elahifard M, Gholami M (2015) Nanoporous Ag_2O photocatalysts based on copper terephthalate metal–organic frameworks. J Mater Sci 50:4536–4546. doi:10.1007/s10853-015-9003-3

Mondal A, Adhikary B, Mukherjee D (2015) Room-temperature synthesis of air stable cobalt nanoparticles and their use as catalyst for methyl orange dye degradation. Colloids Surf A 482:248–257. doi:10.1016/j.colsurfa.2015.05.011

Reife A, Reife A, Freeman HS (1996) Environmental chemistry of dyes and pigments. John Wiley & Sons ISBN: 978-0-471-58927-3

Scherrer P (1912) Bestimmung der inneren Struktur und der Größe von Kolloidteilchen mittels Röntgenstrahlen. Springer, Kolloidchemie Ein Lehrbuch, pp 387–409

Senthil Kumar R, Nithya C, Gopukumar S, Anbu Kulandainathan M (2014) Diamondoid-structured Cu–dicarboxylate-based metal–organic frameworks as high-capacity anodes for lithium-ion storage. Energy Technol 2:921–927. doi:10.1002/ente.201402076

Shu QW, Lan J, Gao MX, Wang J, Huang CZ (2015) Controlled synthesis of CuS caved superstructures and their application to the catalysis of organic dye degradation in the absence of light. CrystEngComm 17:1374–1380. doi:10.1039/C4CE02120G

Zonouzi A, Afjei S, Rahmani A, Ng S (2016) Novel synthesis of some 2-aminochromene derivatives using nano-sized zirconium oxide as catalyst. Org Prep Proced Int 48:45–54. doi:10.1080/00304948.2016.1127099