Chapter 4

Highly Active Cu-MOF for Chemical / Electrochemical Reduction Reactions
4.1. Introduction

Metal-organic frameworks (MOFs) are very promising systems due to the virtually unlimited flexibility in their design. The generation of MOFs enables the tailoring of novel solids with regular porosity from micro to nanopore scale. Nowadays several hundred different types of MOFs are known. The self assembly of metal ions, which act as coordination centres, linked together with a variety of polyatomic organic bridging ligands, results in tailorable nanoporous host crystalline materials as robust solids with high thermal and mechanical stability. These hybrid organic-inorganic compounds exhibit rather low-dense and relatively robust three-dimensional architectures delimiting systems of well-defined cavities or tunnels and they offer new potential applications. Chui et al., reported that during the hydrothermal synthesis of copper benzene tricarboxylate (Cu$_3$(BTC)$_2$-MOF), each of the four coordination sites of three Cu$^{2+}$ ions are bound to twelve carboxylate oxygen atoms of the two BTC ligands to form a face centered crystal lattice with Fm3m symmetry which possesses a three-dimensional channel system with a bimodal pore size distribution based on their structural studies of Cu$_3$(BTC)$_2$. Further, the above authors have calculated the copper-copper distance as 0.263 nm with a pore diameter of 0.9 nm were formed from 12 paddle-wheel subunits forming a cubic octahedron.

The active copper species have free binding sites in the nanospaces, which facilitate the formation of adducts with electroactive molecule. Such unique properties may provide benefits that make a Cu-MOF a good candidate for catalytic reaction. Cu$_3$(BTC)$_2$ has widely been used as a heterogenous catalyst in acetalization of aldehydes with methanol, quinoline synthesis, $\alpha$-pinene oxide rearrangement, trimethylsilylazide addition to carbonyl compounds, oxidation of benzylic compounds with $t$-butyl
hydroperoxide,\(^6\) ring opening of epoxides with methanol,\(^7\) alkylation of amines with dimethyl carbonate,\(^8\) oxidation of cyclohexene to allylic products,\(^9\) cyclopropanation of styrenes and cycloaddition of phenyl acetylene with benzyl azide.\(^{10}\) Also Cu\(_3\)(BTC)\(_2\) along with TEMPO was proved to be a catalyst for i) the oxidation of benzylic alcohol\(^{11}\) and ii) heterogeneous chemoselective reduction of C-C multiple bonds on which the catalytic activity may depend on a) availability of significant numbers of accessible sites due to the open MOF crystal structure, b) reversible coordination of organic linkers with the metal atom and c) the influence of the electrostatic field in the cavity by the partially charged framework.\(^{12}\)

Conversion of CO\(_2\) to smaller useful organic molecules (or CO\(_2\) sequestration) has become an important issue, because of increment of CO\(_2\) level in the atmosphere leads to adverse impact on the environment. Recent research on CO\(_2\), mainly focused on electrochemical conversion and fixation of CO\(_2\) and has been reviewed in modern synthetic organic chemistry. Previous studies are reported on the conversion of CO\(_2\) into formic acid, methane, ethane, ethylene, propylene, methanol and ethanol under different electrocatalytic conditions in different solvents.\(^{13,14}\) Several methods are adopted for conversion and activation of CO\(_2\) such as chemical, thermochemical, photochemical, biochemical, electrochemical and hydrothermal methods.\(^{15,16}\) Among these, electrochemical method is an attractive technique, due to simple procedure and ambient operation conditions. The electrochemical reduction of CO\(_2\) occurs by the abstraction of proton from the solvents and yields various products.\(^{17}\) In recent year’s many investigators have studied the electrochemical reduction of CO\(_2\) on metallic electrodes and modified electrodes in aqueous, non-aqueous and ionic liquid medium at various temperatures.\(^{18,19}\) Particularly copper has been widely investigated for electroreduction of
CO$_2$ in protic and aprotic solvents like dimethyl sulphoxide, N,N-dimethylformamide, propylene carbonate, methanol and acetonitrile.$^{14}$ In non-aqueous medium, two competitive reaction pathways have been described; the first reaction pathway leads the formation of oxalate anion by 2-electrons reduction and dimerization. The second reaction pathway proceed through nucleophilic coupling of CO$_2^{-}$ radicals with CO$_2$(ads) and gave the product as CO and CO$_3^{2-}$.$^{20}$

Metal organic frameworks have unique properties like high surface area (500-6240 m$^2$ g$^{-1}$), wide range of pore size (3-3.5 Å), pore volume (0.4-3.6 cm$^3$ g$^{-1}$) and variety of functionalities,$^{21}$ these make a good catalytic material for number of organic reactions. For example MOF can be functionalized with variety of organic linkers, responsible for many catalytic organic reactions. Although a large number of MOFs have been examined as heterogeneous catalyst,$^{22}$ particularly MOF with carboxylate linkers have high surface area and wide range of pore size, which offers better catalytic performance.

In this chapter, we reported the optimized condition for the electrochemical synthesis of Cu$_3$(BTC)$_2$ by anodically dissolving copper ion to link/bind with BTC molecules (organic linker) by applying constant voltage using similar area of copper plates, as a cathode and anode with tetrabutylammonium tetrafluoroborate (TBATFB) as supporting electrolyte. The advantages of this synthetic protocol provides higher yield, high surface area and high purity than the earlier procedures and also demonstrate for the first time that Cu$_3$(BTC)$_2$ as a novel heterogeneous catalyst for reduction of $p$-nitrophenol (4-NP) as well as the uniform film of Cu$_3$(BTC)$_2$ on GC surface as an efficient electrocatalyst for the selective reduction of carbon dioxide.
4.2. Experimental Details

4.2.1. Materials

Cu-plates (John Mathew, India) with 99.9 % purity were used as electrode material. Benzene tricarboxylic acid (BTC), tetrabutylammonium tetrafluoroborate (TBATFB), sodium borohydride and 4-nitro phenol of analytical grade (Acros organics, India). Potassium chloride, acetone of analytical grade (Sisco Research Laborotories), methanol, N,N-dimethyl formamide of HPLC grade (Sisco Research Laborotories) were used as received.

4.2.2. Electrochemical Synthetic Procedure for Cu$_3$(BTC)$_2$ MOF

Two copper electrodes having similar area (10.5 cm$^2$) were used as an anode and cathode for the synthesis of Cu$_3$(BTC)$_2$. The organic linker (0.1 M BTC) and supporting electrolyte (TBATFB) were dissolved in 50 ml methanol solution in the electrolysis cell and stirred for 15 min for complete dispersion. Electrolysis was carried out in an electrochemical cell under constant voltage electrolysis for 2.5 h to complete the reaction. Finally the sky blue color precipitate of Cu$_3$(BTC)$_2$ was collected from the electrolysis cell and allowed to dry in a hot air oven at 120 °C for 12 h and activated at 200 °C for 2 h. The sky blue colour which appeared initially was changed to dark blue after activation, i.e., change in colour indicates that the co-ordination number of Cu in the complex state is changed from six to four.$^{23}$ A detailed flowchart is presented as Scheme 4.1. Further, optimization of experimental parameters like supporting electrolyte concentrations, applied voltage and reaction time were carried out in order to get good yield of highly crystalline Cu$_3$(BTC)$_2$. The yield of the product corresponding to the amount of weight loss in the copper anode is 97.51%.
4.2.3. Characterisation Techniques

The surface morphology and microstructure of synthesised samples were characterised by scanning electron microscope (SEM Hitachi S-3000H from Japan). The morphology and particle size was determined by using transmission electron microscopy (Philips CM 200). The synthesised product was characterised by XRD (‘Xpert PROPAAnalyticalPW3040/60’X’PertPRO’) using Cu–Kα radiation (λ = 1.5418 Å), with the voltage and current were held at 40 kV and 30 mA (2θ = 5–50°) at a scan rate of 1 min⁻¹. Fourier Transform Infrared spectrum has been recorded on a Nicolet 5DX-FTIR spectroscopy using KBr pellet in the range of 400 – 4000 cm⁻¹. The surface area and pore volume of the Cu₃(BTC)₂ are determined from BET adsorption isotherm of nitrogen at 77 K using a static volumetric apparatus Micromeritics, ASAP 2020 V3.00H.

X-ray photoelectron spectroscopic (XPS) analysis of synthesised sample has been investigated using VG electron spectroscopy, were recorded using an X-ray source (Al-Kα radiation) with a scan range of 0–1200 eV binding energy. The collected high-resolution XPS spectra were analyzed using XPS peak fitting software program. The energy scale was adjusted using carbon peak, C1s spectra at 284.5 eV. The EDX spectrum (Thermo Electron Corporation, USA) was collected at an accelerating voltage of 20.0 kV and a magnification of x700. Thermogravimetric analysis was performed using a Q 500 instrument manufactured by TA Instruments and experiments were conducted with a constant heating rate of 5 °C min⁻¹ in nitrogen atmosphere.

The cyclic voltammetric experiments and bulk electrolysis were performed using BAS IM6 Electrochemical Analyzer (USA). In a single comportment conventional three electrodes system, glassy carbon and a platinum foil were used as the working and counter electrodes, respectively. All potentials were recorded against SCE or Ag/Ag⁺
reference electrode. The Cu$_3$(BTC)$_2$ ink was prepared in acetone with Nafion® solution under ultrasonic condition. The electrochemically synthesised Cu$_3$(BTC)$_2$ was casted on glassy carbon electrode surface by drop dry method.

### 4.2.4. Chemical Catalysis

The catalytic reduction reaction was carried out in a standard quartz cell with a 1 cm path length and about 3 ml volume. The procedure entailed in mixing excess NaBH$_4$ (15 mM) with 4-nitro phenol (0.1 mM) solution in water in the quartz cell. Mixing leads to the colour change from light yellow to green yellow. The absorption spectra were recorded immediately after the addition of Cu$_3$(BTC)$_2$ (5 μl of 5 μg of Cu$_3$(BTC)$_2$ in aqueous dispersion) with a time interval of 30 seconds in a scanning range of 200-600 nm at 25 °C.

### 4.2.5. Electro-Catalysis

The bulk electrolysis was carried out in 5 ml (carbon dioxide saturated in 0.01 M TBATFB/DMF) batch in a three electrode single compartment electrochemical cell, by applying a constant potential of about -2.5 V vs. Ag/Ag$^+$ for 10 min. During the course of the experiment and after electrolysis an aliquot was taken out, FT-IR and GCMS experiments were carried out to monitor the formation of the products.

### 4.3. Results and discussion

#### 4.3.1. Optimisation of Electrolysis Conditions

Fig. 4.1a presents the effect of concentration of supporting electrolyte and applied voltage on the yield of the product, which clearly showed that while increasing the concentration and applied voltage the yield also increases. Fig. 4.1b depicts the yield vs.
reaction time and current vs. reaction time. The yield mainly depends on reaction time but as the reaction time goes on, the availability of BTC decreases and thereby current decreases. However, it is worthy to mention that, while increasing the concentration of TBATFB > 0.02 M and the applied voltage more than 15 V, the particles are agglomerated and cubic shapes are getting collapsed (the scanning electron microscope (SEM) image are shown in Fig. 4.2 a & b). Hence, the optimized experimental conditions are so important to get regular shapes without agglomeration with good yield of crystalline Cu₃(BTC)₂. Since all the parameters for the synthesis are electrochemically controllable, the above process is said to be scalable.

![Fig. 4.1](image)

**Fig. 4.1.** The plots corresponding to a) concentration of supporting electrolyte vs. yield and voltage vs. yield b) the yield vs. reaction time and current vs. reaction time.

The criteria for optimized electrochemical condition in order to get maximum yield, high surface area, controlled Cu dissolution and good crystallinity without agglomerisation for the synthesis of Cu₃(BTC)₂ is presented as Scheme 4.1.

4.3.2. Characterisations of Cu$_3$(BTC)$_2$ MOF

Fig. 4.2c shows the morphological structure (SEM image) of the electrochemically synthesised Cu$_3$(BTC)$_2$ sample under optimized experimental condition. Morphological studies clearly shows the synthesised Cu$_3$(BTC)$_2$ is highly porous in nature and the inset in the above figure represents higher magnification of the SEM image exhibiting a uniform decoration of cubic shaped particles of the Cu$_3$(BTC)$_2$. Transmission electron microscopy (TEM) analysis is used to find out the individual particle size of the cubic structure of Cu$_3$(BTC)$_2$ are shown in Fig. 4.3, with different magnification. Inset in the TEM image of Fig. 4.3b shows the SAED pattern, in which the bright circular rings representing the highly polycrystalline nature of the synthesised Cu$_3$(BTC)$_2$ particles, which is in good agreement with the electron diffraction results. As
can be seen in the TEM image, 10-20 nm Cu$_3$(BTC)$_2$ particles form a network structure in cubic shape of 0.2-0.5 µm due to Van-der walls forces. Higher magnification image (Fig. 4.3c) clearly shows that the nanocrystals of 10 nm particles closely bound together forms the cubic shape. Hence, SEM, TEM and SAED pattern unambiguously proved that the discrete state as well as the Cu$_3$(BTC)$_2$ nanoparticles were formulated in cubic manner.

**Fig. 4.2.** Scanning electron microscope image of Cu$_3$(BTC)$_2$ synthesised using a) 18 V as applied potential, b) 0.2 M TBATFB as supporting electrolyte and c) optimized reaction condition at lower magnification and higher magnification (inset).

**Fig. 4.3.** Transmission electron microscopy image of Cu$_3$(BTC)$_2$ a) Lower magnification, b) and c) Higher magnifications images, Inset - selected area diffraction pattern (SAED).

The powder X-ray diffraction pattern of synthesised Cu$_3$(BTC)$_2$ is shown in Fig. 4.4. The diffraction peaks of electrochemically synthesised sample are well consistent with available literature$^{24,25}$ and the simulated pattern published by Chui et al.,$^1$ calculated
using single crystal data are comparable. The observed XRD peaks are very sharp indicates that highly crystalline nature of the synthesised material. These peaks correspond to the face centered cubic structure of Cu$_3$(BTC)$_2$ nanoparticles.\textsuperscript{24} Moreover, it is interesting to note that the synthesised Cu$_3$(BTC)$_2$ from optimized experimental condition does not exhibit any peaks corresponding to CuO (2$\theta$ = 35.5 and 38.7$^\circ$), Cu$_2$O (2$\theta$ = 36.43$^\circ$) and impurities peak at 2$\theta$ = 11.0$^\circ$ as observed by Hartmann et al. who synthesised Cu$_3$(BTC)$_2$ by hydrothermal method\textsuperscript{26} which confirms that higher purity Cu$_3$(BTC)$_2$ was obtained from the present method using optimized electrochemical experimental conditions.

![Graph](image)

**Fig. 4.4.** Powder X-ray diffraction pattern of electrochemically synthesised Cu$_3$(BTC)$_2$. 

Therefore, electrochemically synthesised Cu$_3$(BTC)$_2$ under optimized experimental condition exhibits the highly crystalline structure of Cu$_3$(BTC)$_2$ in which twelve carboxylate oxygen atom from two BTC molecules (electrochemically reduced at
cathode) and each of the three \( \text{Cu}^{2+} \) ions (electrochemically oxidised from Cu anode) forms \( \text{Cu}_3(\text{BTC})_2 \) like structure with paddle-wheel units of fcc lattice.\(^1\) The formation of \( \text{Cu}_3(\text{BTC})_2 \) is shown in reaction Scheme 4.2.

![Reaction Scheme 4.2](image)

**Scheme 4.2.** Reaction Scheme for the synthesis of \( \text{Cu}_3(\text{BTC})_2 \) from 1,3,5-Benzene tricarboxylic acid.

In order to confirm the nature of bonding between benzene tricarboxylic acid and \( \text{Cu}^{2+} \), vibrational spectral analyses was carried out and are shown in Fig. 4.5. The band observed around 1715 cm\(^{-1}\) can be significantly assigned to acidic C=O stretching vibration present in the BTC, which after complexation with \( \text{Cu}^{2+} \) is shifted to 1665 cm\(^{-1}\) suggesting that deprotonated has happened in acidic C=O. This unambiguously indicates that the carboxylate ion participates in the complex formation. The absence of peaks at 410, 500, 610 and 615 cm\(^{-1}\) indicates that the synthesised materials are free from CuO and \( \text{Cu}_2\text{O}^{27} \) crystals during the nucleation of \( \text{Cu}_3(\text{BTC})_2 \). Moreover, the characteristic vibration at 714 cm\(^{-1}\) may be attributed to Cu-O stretching vibration, in which the oxygen atom is coordinated with Cu. The broad band observed at 2500 – 3300 cm\(^{-1}\) region in benzene tricarboxylic acid is due to O-H stretching in carboxylic group, which is shifted to 3100 – 3600 cm\(^{-1}\) region in the complex indicating the presence of loosely bound water molecules in \( \text{Cu}_3(\text{BTC})_2 \).
To find out the exact specific pore volume and surface area of electrochemically synthesised and activated Cu$_3$(BTC)$_2$, the BET nitrogen gas adsorption/desorption isotherm studies were carried out. The nitrogen adsorption data yield a specific pore volume of 0.43 cm$^3$ g$^{-1}$ and surface area of 1498 m$^2$ g$^{-1}$. While comparing the reported values of Cu$_3$(BTC)$_2$, the specific surface area is almost similar 1510 m$^2$ g$^{-1}$, 1587 m$^2$ g$^{-1}$ and pore volume value is also similar with the results of Pradip Chowdhury et al., (0.425 cm$^3$ g$^{-1}$) and Chui et al., (0.333 cm$^3$ g$^{-1}$). Nanoporous nature is also confirmed from the steep rise at the high relative pressure in the isotherm.

X-ray photoelectron spectroscopy is carried out on particles recovered after complete evaporation of solvent, separating the supporting electrolyte and starting materials if any, which is shown in Fig. 4.6. The main peaks observed in the survey scan as C1s, Cu2p$_{3/2}$, Cu2p$_{1/2}$ and O1s centered at 284.5, 934.14, 954.27 and 531.1 eV.
The binding energy of C1s emission peak observed at 284.5 eV, which was used as the reference in the present XPS measurements. In Cu2p core level photoelectron spectra for Cu₃(BTC)₂ displayed doublets i.e., Cu2p₃/2 and Cu2p₁/2 at 934.14 and 954.27 eV respectively. The Cu2p₃/2 and Cu2p₁/2 main doublets were separated by ~20 eV and their satellite peaks at ~8 eV from the main peaks were also observed. Further, the similar satellite peaks were also observed in CuO indicating that Cu in the synthesised MOF is in divalent nature, which is consistent with our FT-IR and XRD results. The binding energy of O1s core level is observed at 531.1 eV corresponds to the characteristics of O^{2-} ions in the crystalline network. These results are in good agreement with the previously reported work.

![X-ray photoelectron spectrum of a) Cu2p region and b) O1s region of the synthesised Cu₃(BTC)₂.](image)

**Fig. 4.6.** X-ray photoelectron spectrum of a) Cu2p region and b) O1s region of the synthesised Cu₃(BTC)₂.

The chemical composition and the purity of electrochemically synthesised Cu₃(BTC)₂ was determined using energy dispersive X-ray analysis. It clearly shows the Cu without any impurities other than carbon and oxygen. The effective atomic weight percentage of Cu, C, and O are listed in the Table-3.1. Since there are no peaks
corresponding to boron and fluoride, we conclude that electrochemically synthesised Cu$_3$(BTC)$_2$ does not contain any impurities of supporting electrolyte.

Scheme 4.3. Schematic representation of co-ordinated and deco-ordinated forms of water in Cu$_3$(BTC)$_2$.

The nature of thermal stability and the molecules that are desorbed or buried in the synthesised Cu$_3$(BTC)$_2$ with respect to temperature was studied by TGA and compared with literature and is presented in Fig. 4.7. The synthesised Cu$_3$(BTC)$_2$ was heated in nitrogen atmosphere with a heating rate of 5 °C min$^{-1}$. The thermogram shows three different regions viz., 1) the first weight loss (19.5%) region between 50 and 120 °C indicating the loss of moisture 2) the region between 120 to 293 °C corresponding to the loss of two water molecule from the MOF with the weight loss of 6%. It is interesting to note that Cu co-ordination has been reduced from six to four takes place at this stage (Scheme 4.3), which was confirmed by the colour change during activation$^{23}$ and 3) the third region starts at 293 °C, at that temperature the structure of MOF collapse and the organic linker is buried. This weight loss is completed at 438 °C and stable up to 800 °C and the residue is found to be 35% which is comparatively higher than the reported value of 24% and is ascribed to the availability of Cu$^{2+}$ in the open structure for catalysis. While
comparing the results of Harman et al.,\textsuperscript{25} they observed that the trapping of supporting electrolyte methyltributylammoniummethyl sulphate (MTBS) in the pores of Cu$_3$(BTC)$_2$, but in the present case the supporting electrolyte namely TBATFB is not trapped inside the pores of the Cu$_3$(BTC)$_2$, which can be explained from the higher Cu$^{2+}$ content and lower weight loss of the organic linkers.

![Thermo-Gravimetric Analysis of Cu$_3$(BTC)$_2$.](image)

**Fig. 4.7.** Thermo-Gravimetric Analysis of Cu$_3$(BTC)$_2$.

### 4.3.3. Chemical Reduction of p-Nitrophenol

Due to the enhanced properties of the synthesised Cu$_3$(BTC)$_2$, as a proof of concept, an attempt is being made to demonstrate Cu$_3$(BTC)$_2$ as an effective catalyst for the chemical reduction of p-nitrophenol. Cu$_3$(BTC)$_2$ was used in the reduction of p-nitrophenol in water along with excess NaBH$_4$ (see reaction Scheme 4.4).

The process of reduction was monitored by measuring UV-Vis spectra recorded at different time t. Every 30 seconds UV spectrum was recorded and presented in Fig. 4.8a. The absorption peak of p-nitrophenol undergoes a red shift from 317 to 401 nm immediately upon addition of aqueous NaBH$_4$ solution (15 mM) with an associated
colour change from light yellow to yellow-green (corresponding to the generation of \( p \)-nitrophenolate anion).\(^{31}\) The absorption peak at 401 nm remains unchanged for extended periods of time showing that even an excess concentration of NaBH\(_4\) is unable to bring out reduction of \( p \)-nitrophenolate anion. Interestingly, addition of very small aliquots [5 \( \mu \)l i.e., (5 \( \mu \)g)] of Cu\(_3\)(BTC)\(_2\) dispersion (1 mg of MOF was dispersed in 1 ml of acetone) in to the above solution was found to cause fading and finally decoloration of the yellow-green colour of \( p \)-nitrophenolate in aqueous solution. This is clearly proved by the gradual disappearance of absorption peak at 401 nm after the addition of Cu\(_3\)(BTC)\(_2\) MOF, with a concurrent appearance of two new peaks at 310 nm and 230 nm, corresponding to the formation of \( p \)-aminophenol as shown in Fig. 4.8b (corresponding plot of \( \ln(A) \) vs. time for the disappearance of \( p \)-nitrophenol absorption at 401 nm upon reduction in the presence of excess borohydride in solution).

![Scheme 4.4: Reduction scheme of \( p \)-nitrophenol to \( p \)-aminophenol using synthesised Cu\(_3\)(BTC)\(_2\).](image)

**Scheme 4.4.** Reduction scheme of \( p \)-nitrophenol to \( p \)-aminophenol using synthesised Cu\(_3\)(BTC)\(_2\).

Thus, the kinetics of the reduction reaction can be treated as pseudo-first-order with respect to \( p \)-nitrophenol concentration. Here the ratio of the absorbance \( A(t) \) at a given time \( t \) to the absorbance \( A_0 \) measured at \( t = 0 \) is directly proportional to the ratio of the \( c/c_0 \). From this, the rate constant of \( p \)-nitrophenol reduction reaction is calculated to be \( 8.69 \times 10^{-2} \) s\(^{-1}\). The rate constant obtained from slope of the kinetic curves has been related to catalyst concentration. That is, as the concentration of the catalyst increases
(more surface area for the reaction to occur) the rate is also found to increase. The concentration of NaBH$_4$ was chosen to exceed the concentration of $p$-nitrophenol by far, because the chemical conversion of nitrophenol to aminophenol takes place only in the presence of excess NaBH$_4$.\cite{32} In the absence of BH$_4^-$ ions, the reaction does not happen even noble metal catalyst like Pt used for this reaction.

![Fig. 4.8.](image)

**Fig. 4.8.** a) UV-Vis absorption spectra recorded at different times $t$ using Cu$_3$(BTC)$_2$ (a-0 sec, b-30 sec, c-60 sec, d-90 sec, e-120 sec) and b) A plot of concentration with respect to time (i.e., ln(A) vs. time plot).

The role of excess NaBH$_4$ is only to change the solution pH form neutral to more than 12 and to remove or abstract the acidic proton from nitrophenol to nitrophenolate. After that, the catalyst (Cu$_3$(BTC)$_2$-MOF) will catalyse the chemical reduction of nitrophenolate to aminophenolate. So whenever the availability of catalyst is more, obviously the rate of conversion is also more, because reaction behaves like pseudo first order kinetics. The obtained value of the rate constant is higher than the rate of reduction of $p$-nitrophenol (0.1 mM) in aqueous NaBH$_4$ in the presence of Au(NP)/PEDOT/PSS and Au(NP)/PMMA was found to be 0.0439 and 0.0073 s$^{-1}$ respectively.\cite{31,32}
4.3.4. Electrochemical Behaviour of Cu$_3$(BTC)$_2$ MOF

Cyclic voltammetric responses of Cu$_3$(BTC)$_2$ coated on GC electrode is crucial in order to find out the electrochemical stability of the compound and is compared with CV response of Cu foil in 0.1 M KCl at a scan rate of 20 mV s$^{-1}$ under nitrogen atmosphere are illustrated in Fig. 4.9. In general a good experimental reproducibility indicates that the mechanical stability of the frame work structure is high. The resulting cyclic voltammogram (Fig. 4.9a) shows distinct redox peak potentials at -0.14 and +0.02 V vs. SCE indicating the reversible oxidation and reduction of Cu$^{II}$/Cu$^{I}$. The another reduction peak at -0.45V vs. SCE and corresponding sharp oxidation peak at -0.102V vs. SCE indicates the redox couple of Cu$^{0}$ to Cu$^{I}$. The cyclic voltammetric response of Cu$_3$(BTC)$_2$ indicated that the copper is in the Cu$^{2+}$ ionic state which is consistent with XPS and XRD results, where as such a redox peak behavior was not observed for Cu electrode in 0.1 M KCl solution (Fig. 4.9b). The stability of the Cu$^{II}$ and Cu$^{I}$ form is very important in catalysis.

Fig. 4.9. Cyclic voltammogram for a) Cu$_3$(BTC)$_2$ coated GC (redline represents GC background), b) Copper foil recorded in 0.1 M KCl at a scan rate of 20 mVs$^{-1}$. 
4.3.5. Electrochemical Reduction of CO$_2$

So far, most of the studies discussed in literature on MOF have focused on gas adsorption with particular emphasis on molecular hydrogen, methanol and carbon dioxide, and as on date, there are no reports available on electro-reduction of carbon dioxide.\textsuperscript{34} Herein we demonstrate for the first time that the electrochemically synthesised Cu$_3$(BTC)$_2$ exhibit catalysis towards sequestration as well as electro reduction of CO$_2$ simultaneously. While purging the CO$_2$ through DMF solution for several minutes, no precipitate was formed which proves that CO$_2$ does not react with DMF. The maximum concentration can be built to 0.199 M in DMF solution.\textsuperscript{35} Therefore, CO$_2$ can be considered to be physically dissolved, i.e., under intact form in the DMF/TBATFB solution.

![Fig. 4.10. a) Cyclic voltammogram 1) bare GC, 2) bare GC in presence of CO$_2$, 3) Cu$_3$(BTC)$_2$ coated GC and 4) Cu$_3$(BTC)$_2$ coated GC in presence of CO$_2$, in a solution containing 0.01 M TBATFB/DMF at a scan rate of 50 mV s$^{-1}$ b) FT-IR spectra of I) Oxalic acid (authentic) and II) Oxalic acid (synthesised).](image)

Since, Cu and Cu$_3$(BTC)$_2$ coated electrodes are behaving differently as indicated in the CV studies, here we have compared current potential response of GC and Cu$_3$(BTC)$_2$ coated GC electrodes in both solution without CO$_2$ (1 & 3 respectively) and
the CO₂ saturated DMF containing TBATFB solution (2 & 4 respectively) and presented in Fig. 4.10a. As can be seen from cyclic voltammograms, the direct reduction potential of CO₂ starts at potential more positive in Cu₃(BTC)₂ coated GC electrode (-1.12 V vs. Ag/Ag⁺) than bare GC electrode (-1.75 V vs. Ag/Ag⁺), i.e. potential shifts to less anodic side and also cathodic evolution current density is increased from 2.27 mA cm⁻² to 19.22 mA cm⁻². This clearly indicates that carbon dioxide reduction at the electrode is the main electrochemical process at these potentials and also brings out the electrocatalytic activity behaviour of Cu₃(BTC)₂ on CO₂ reduction. This may be due to the tendency of absorbing more CO₂ in the pores of Cu₃(BTC)₂ and there is a possibility of reducing the compressed gas inside the pores electrochemically via heterogeneous electron transfer between Cu₃(BTC)₂ and CO₂ molecule. Further it is also proved that the catalytic activity of the Cu(II)-complex might be attributed to their immediate reduction to Cu(I) species. As in the case of CO₂ reduction using cobalt(I) complex, provided as an intermediate and a five-coordinate Co(I)-CO₂ adduct which was isolated from the reaction,³⁶ here activated Cu(II)-MOF present as four coordinated, which is acting as a Lewis acid and forms adduct with CO₂. Hydrogen bonding between the coordinated CO₂ inside the MOF pores is important in stabilizing the adduct. Cu(I) which is formed at potential -0.62 V vs. Ag/Ag⁺ in the CO₂ saturated DMF solution is catalyzing the reduction³⁷ (See inset Fig. 4.10a). In literature, two main competitive reaction pathways have been described for the reduction of CO₂ in non-aqueous media.²⁰ The mechanism of reduction, resulting in oxalate anion by dimerization of CO₂⁻ formed from the 2-electrons reduction of CO₂ presented as follows.

\[
\begin{align*}
2\text{CO}_2 & \quad + 2e^- \quad \xrightarrow{\text{Dimerisation}} \quad 2\text{CO}_2^- \\
\text{COO}^- & \quad + 2\text{H}^+ \quad \xrightarrow{} \quad \text{COOH}
\end{align*}
\]
As a first report, we demonstrate the synthesised Cu based MOF as a uniform film on GC electrode electrochemically reduce CO$_2$ saturated DMF solution in the presence of supporting electrolyte to oxalate anion through the formation of carbon dioxide radical anion. This oxalate anion abstracts proton from solvent to form the oxalic acid. FT-IR spectrum was taken during the course of reaction confirmed the formation of oxalic acid (Fig. 4.10b). The resultant spectrum also compared with that of oxalic acid (commercial sample) and was consistent. From the bulk electrolysis, the conversion and product selectivity of CO$_2$ to oxalic acid was also confirmed through GCMS analysis. GCMS study clearly confirms the formation of oxalic acid with 90% purity, and the Faradaic efficiency was calculated as 51%.

4.4. Conclusions

The problem associated with the scalable synthesis is unveiled here by optimizing the electrochemical parameters as well as by selecting the suitable supporting electrolyte in order to get pure Cu$_3$(BTC)$_2$. The yield corresponding to the electrochemical dissolution of Cu is 97.51%. The advantage of the present synthetic route is that the Cu content is about 32% than the previously reported value of 22% and the thermal stability of the Cu$_3$(BTC)$_2$ is as high as 293 °C. The surface area and pore volume of the synthesised Cu$_3$(BTC)$_2$ were found to be 1469 m$^2$ g$^{-1}$, 0.43 cm$^3$ g$^{-1}$ respectively. Finally, it was demonstrated that the presence of high Cu content (exposed open structured Cu which is Lewis acidic in the paddle wheel structure of Cu$_3$(BTC)$_2$) is responsible for highly effective conversion of $p$-nitrophenol to $p$-aminophenol. The rate constant corresponding to $p$-nitrophenol reduction reaction is as high as $8.69 \times 10^{-2}$ s$^{-1}$. Cu$_3$(BTC)$_2$ continuous film formed on GC surface shows electrochemically active Cu(I) species formation. This Cu(I) forms adduct with carbon dioxide and forms oxalate acid by
electrochemically, which is confirmed through bulk electrolysis and analysis using GCMS. The above results were published in peer reviewed journals 1. Microporous and Mesoporous Materials and 2. Electrochemistry Communications.
References


