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Studies on Improvement of Surface Characteristics and Stability of Cr, Cu and Zn based Metal Organic Frameworks (MOFs)

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ABSTRACT

"Metal Organic Frameworks" or MOFs is a term being associated to represent a class of novel adsorbents that has caught the attention of researchers owing to their great diversityin structures resulting from co-ordination bonds between inorganic metal atoms as nodes and organic ligands as linkers. They have high specific surface area (*ca*. 1000-5000 m^2/g), large pore volume (*ca*.0.7-2.5 cc/g) and low to moderate heat of adsorption (*ca*. 12 to 30 kJ/mol at moderate coverage). Proper selection of metal atoms and organic linkers leads to innumerable possibilities in the coordination geometry with wide variation in topology and functional groups. The tunable matrices or so-called tailor made structures has made it possible to design and synthesize materials meeting specific applications. Porosity, crystallinity and product purity are some of the keyfeatures of MOFs. Adsorptive gas separation/purification, gas storage and catalysis are some of the potential areas of study. We conceived our idea on present research work based on the discussions in the preceding paragraph. Our research objectives can be broadly divided into following sub-sections: Synthesis and characterization of Cu-BTC, Cr-BDC and Zn-BDC samples were successfully carried out in our present study. SEM images confirmed the authenticity of each of the MOFs. Cr-BDC and Cu-BTC were found octahedral in shape whereas Zn-BDC crystals appeared to be cubicinnature.

INTRODUCTION

Prelude

The concept of adsorption was conceived as early as eighteenth century by Scheele and Fontana when they observed porous solids to reversibly adsorb vapors but the practical applications of this propertylargelyremain unexplored. A few familiarpractical examples that werepracticed in earlier times include removal of moisture from gas streams using suitable hydrophilic agents in driers, removal of impurities such as H_2S and mercaptans from natural gas, removal of harmful organic pollutants from water etc. **[1, 2]**. The above processes are very much still in vogue and are classified as purification processes. Major advances in the field of adsorption took place in the latter half of the twentieth century with the advent of new adsorbents mainly *zeolites* and development of efficient process cycles.

Although first synthetic zeolite was synthesized by Milton at the Union Carbide Corporation but the history of this class of adsorbent goes dates back. It all started with the discovery of a mineral called "s*tilbite*" by a Swedish mineralogist Crönsted. The said mineral showed intumescence when heated in a flame and this new family of material was named "*zeolite*". The etymology of the word "zeolite" explains its origin from Greek words "zeo" and "lithos" meaning "to boil"and "stone".Since then for most of the times natural zeolite crystals were making their presence feltin"museums"to the amusement of the visitor still the advent of first man-made synthetic zeolites **[3]**. Simultaneously new and efficient process cycles were developed and adsorption established itself as one of the major unit operations in process industries.

All adsorption separation processes involve two principal steps. They are: (a) *adsorption*, when one component is being preferentially adsorbed onto the solid from its mixture and (b)*desorption* or *regeneration*, during which the adsorbent bed is cleaned to be used for the next cycle. Adsorptive separation processes can be categorized on certain principles. They are summarized as **[1]**:

Adsorbents of Importance

The success and failure of any adsorption based system largely depends on the selection of a proper adsorbent for a particular application. Although literature is crowded with examples of various adsorbents but only a few could last over the

ages of technological advances. Some well known adsorbents are: silica gel, activated alumina, activated carbon, carbon molecular sieves and zeolites. Each of these adsorbents has certain specific features that have been exploited in various applications rangingfrom adsorptive separation/purification, ion-exchange and catalysis.

Zeolites
Zeolites are crystalline alumino silicates of alkai or alkali earth elements, such as sodium, potassium and calcium. The chemical composition of zeolites can be represented by the following stoichiometry:
$M_{x/n}[(AlO_2)_x(SiO_2)_y].zH_2O$

Where *x* and *y* are integers with *y/x* equal to or greater than 1, *n* is the valance of cation *M*, and *z* is the number of water molecules in each unit cell **[1]**. The zeolite framework basically consists of an assemblage of SiO_4 and AlO_4 tetrahedral, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions. Since the crystal lattice determines the micropore structure, it results into pores of uniform size with no distribution, a feature very unique amongst adsorbents.

Research Objectives
Our research objectives can be broadly classified into following sub-sections:

(A) Synthesizing MOF s of various stopologie sand tuning the synthesis route for better reproducibility
(B) Studying thermal and chemical stability of the synthesized materials
(C) Studying the surface characteristics of the synthesized materials

LITERATURE REVIEW

Metal Organic Frame works(MOFs)
Introduction
"Metal Organic Frameworks" or MOFsrepresent a class of novel materials that has caught the attention of researchers owing to their great diversity in structures resulting from co-ordination between inorganic metal atoms/ions and organic ligands as linkers. Proper selection of metal atoms/ions and organic linkers leads to innumerable possibilities in the co-ordination geometry with wide variation in structural architecture. A few very attractive motifs include honeycomb, brick wall, bilayer, ladder, herringbone, diamondoid, rectangular grid, and octahedral geometries **[5-12]**.The inorganic part in a MOF topology in variably (with a few exceptions)consists of first- row transition metals whereas organic links such as cyanide, glutamate, formate, triazole,oxalate, carboxylate, and squarates are well known **[5, 7-19]**. MOFs are crystalline porous solids composed of a 3-D network of metal ions held in place by multi dentate organic molecules where the spatial organization of these structural units results to a system of channel and cavities in the nanometer length scale. The 'tunable matrices' or so-called 'tailor made' structures of MOFs has made it possible to design and synthesize materials meeting specific applications.

Potential Research Areas
Ever since the first successful synthesis of a metal organic framework (MOF-5) there has been a continuous surge in research activities in this field. The concept of reticular design enables 'tailoring' a MOF structure with regular porosity at the nanometer scale. "Tunability' coupled with very high 'surface area' and 'pore volume' made metal organic frameworks a very interesting proposition for research in various fields. MOFs are highly crystalline with very low crystalline framework densities and interestingly most of the pores fall under IUPAC microporous regime i.e. < 2 nm and can be synthesized in very pure form. The salient features and beneficial traits shown by MOFs attracted researchers across the globe to exploit its potentials.

Description of Frame work Structures
In the following paragraphs we have illustrated the frame work architecture of Cu-BTC,Cr-BDC and Zn-BDC metal organic frameworks.

Cu-BTCorHKUST-1Framework
Cu-BTC [$Cu_3(BTC)_2$, BTC = 1,3,5-benzenetri carboxylate] also known as HKUST-1 is a widely studied MOF. It was first reported by Chui et al. **[44]** in 1999.
Cr-BDCorMIL-101Framework
Cr-BDC [BDC = 1,4-benzenedicarboxylate] framework or MIL-101 (an acronym for Material Institute Lavoisier) is a recent addition to the ever increasing list of metal organic frameworks. Frey et al. **[46]** first synthesized and reported this chromium-terephthalate based solid. The synthesized product showed a very high specific surface area and pore volume.

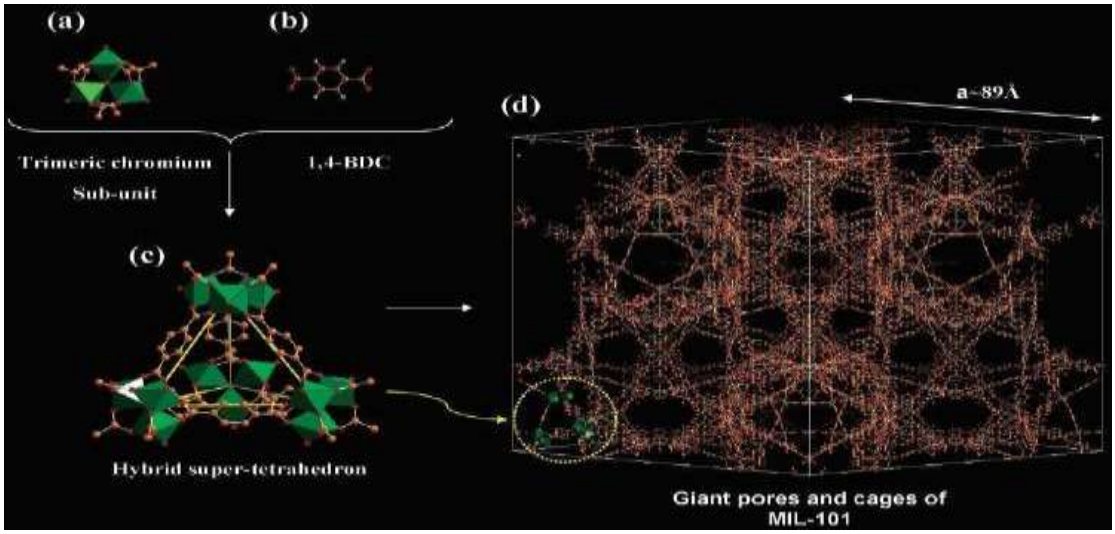

Figure 2.2: Schematic for Cr-BDC or MIL-101 Framework (a) Inorganic trimer (b) Benzene- 1,4-dicarboxylic acid (bdc) (c) Supertetrahedra made from the linkage of inorganic trimers and bdc (d) Schematic view of MIL-101 structure [46-47].

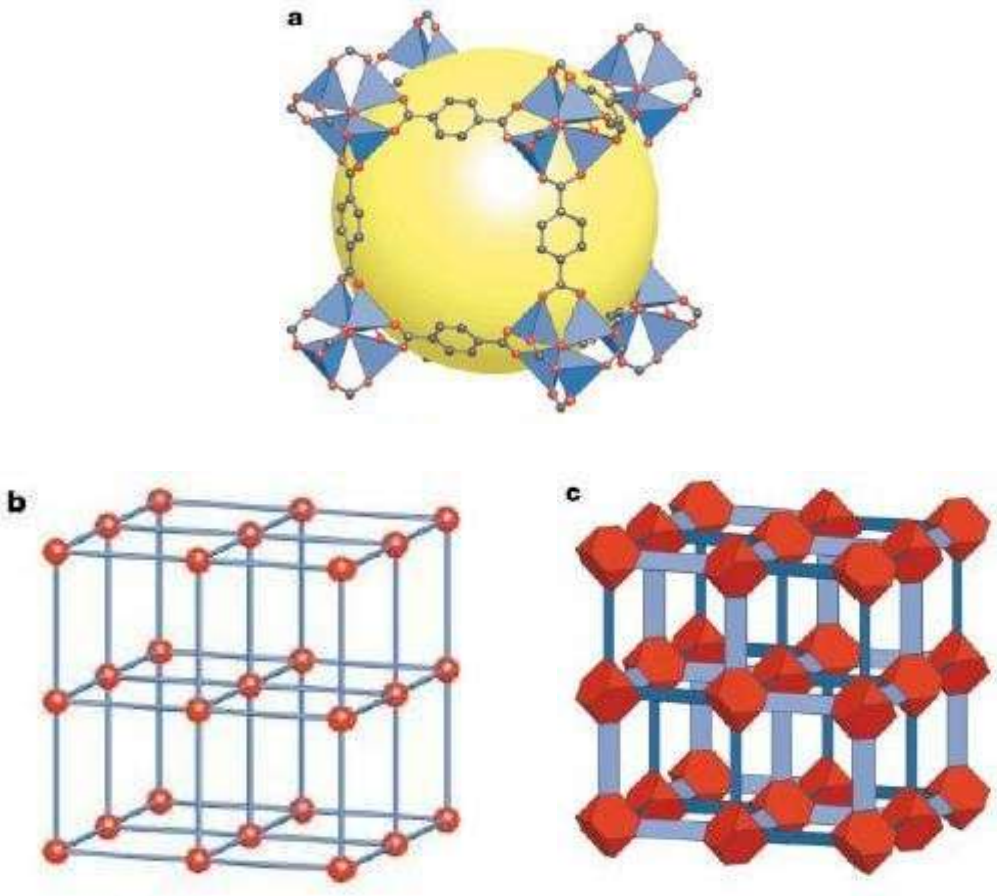

Figure 2.3: MOF-5 structure and topology. (a) The MOF-5 structure shown as ZnO_4tetrahedra (blue polyhedral) (b) The topology of the structure shown as a ball-and-stick model (c) The structure shown as the envelopes of the (OZn4)O12 cluster (red truncated tetrahedron) and benzene dicarboxylate (BDC) ion (blue slat) [5].

Literature Review on Cu-BTC, Cr-BDC and Zn-BDCMOFs

A comprehensive table has been prepared after going through literature on these said MOFs. The emphasis was put on the various synthesis procedures adopted by research groups and the final surface area and pore volume of the prepared samples. The complete list is given below.

METHODOLOGY

This chapter revolves around discussing various synthesis procedures on MOFs of our interest (hydrothermal/ solvo thermal) and their detailed characterization.

Materials

All materials wereused as supplied bythevendors without furtherpurification. Thelist ofall the chemicals with their formula and manufacturer are shown in the respective parenthesis:

Chromium (III) nitrate Nonahydrate [Cr $(NO_3)_3.9H_2O$, LobaChemie], Copper (II) Nitrate Trihydrate [Cu $(NO_3)_2.3H_2O$ (Merck)], Zinc (II) Nitrate Hexahydrate $Zn(NO_3)_2.6H_2O$ [Merck], 1,4-benzene dicarboxylic acid [$C_8H_6O_4$, LobaChemie], Hydrofluoric acid [HF, Merck], 1, 3, 5- benzene tricarboxylic acid (commonly known as trimesic acid) [Merck], N, N-dimethyl formamide [Merck], Ethanol [Merck] and Methanol [Merck].

SYNTHESIS PROCEDURES

SynthesisofCu-BTCorHKUST-1

Cu-BTC or HKUST-1 was first reported by Chui et al. **[44]**. This present method was reportedby Liu et al. **[48]** and was a modification of previous works by Rowsell and Yaghi**[53]**. 1, 3, 5- benzenetri carboxylic acid (1.0 g) was dissolved in 30 ml of a 1:1 mixture of ethanol/*N, N*- dimethyl formamide (DMF). In another flask, Copper (II) Nitrate trihydrate (2.077 g) was dissolvedin15mlwater.

SynthesisofCr-BDCorMIL-101

In a typical synthesis procedure, Cr-BDC or MIL-101 was synthesized hydrothermallyfollowing the published work of Férey et al. **[46]**. The reaction was carried out in a Teflon lined stainless steel autoclave where a stoichiometric mixture of Cr $(NO_3)_3.9H_2O$ (1 gm), de-ionized water (12 ml),1,4-benzenedicarboxylic acid (0.4 gm) and HF (0.125ml)wasplacedfor8 hrs at 493K.

Characterization

Thermal analysis of Cu-BTC, Cr-BDC and Zn-BDC samples were carried out in detail in a TGA apparatus, SHIMADZU (DTG 60 H). The morphologies of the synthesized Cu-BTC, Cr-BDC and Zn-BDC products were characterized using a scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with an energy dispersive X-ray spectrometer (EDX). The different batches of synthesized MOF samples were analyzed by comparing images taken in an optical microscope (Hund Wetzlar H600).

The synthesized samples were subjected to X-ray diffraction by a diffractometer (XRD, Philips Analytical, PW-3040) equipped with the graphite mono chromatized Cu Ka radiation (λ=1.5406Å) in 2θ angles ranging from 5^o to 75^o with a step sizeof0.05degree and scanning rate 1 minute.

RESULT AND DISCUSSION

Surface Morphology of Cr-BDC

The scanning electron microscopy images of various batches of Cr-BDC metal organic framework is shown in the following figure.

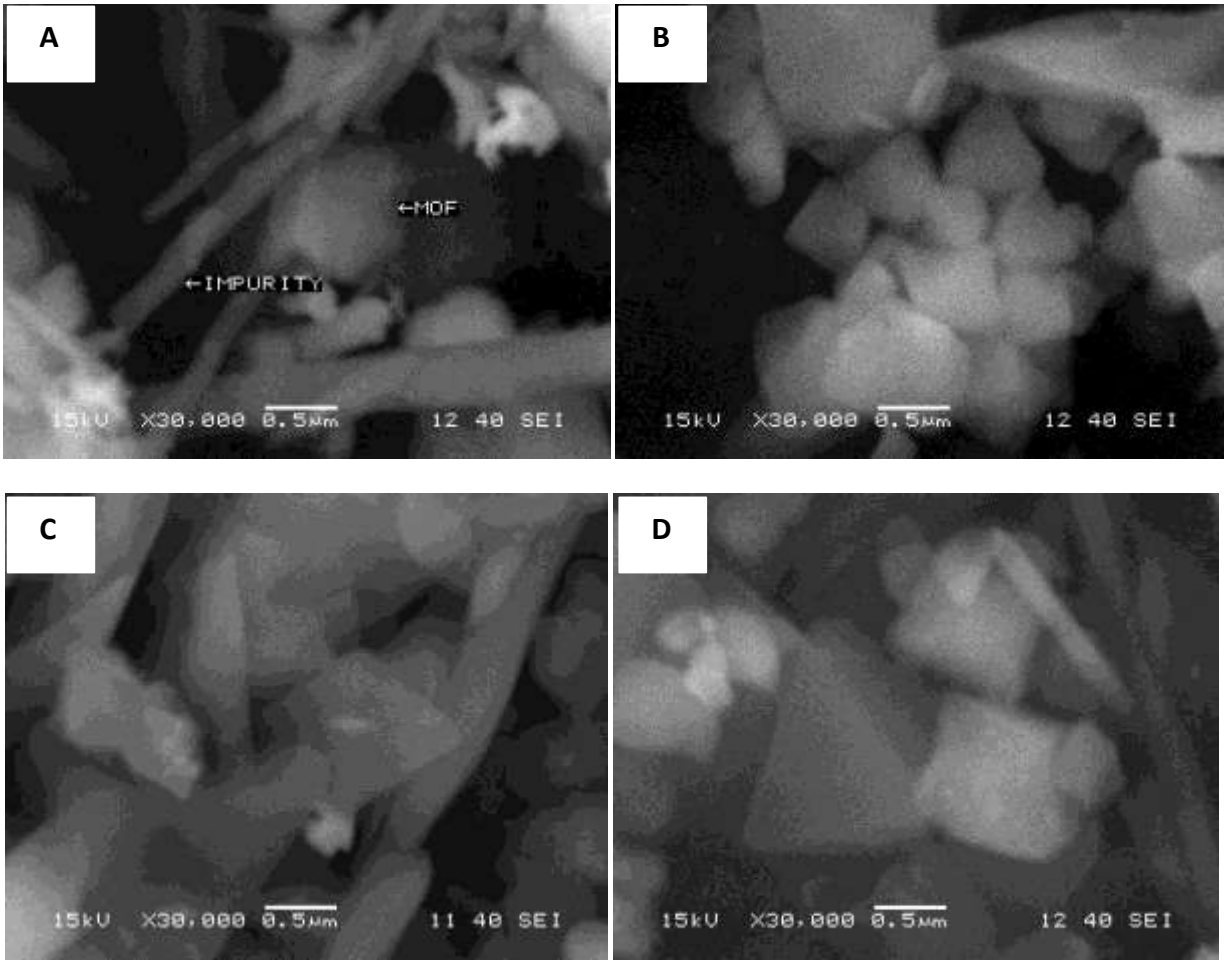

Figure 4.1: **SEM images of Cr-BDCsamples:(A) Impure Cr-BDC(B)DMF washed (C) Cold Ethanol treated (D) Hot Ethanol treated**

Synthesis of Cr-BDCat Other Reaction Conditions

The ideal condition for synthesis of Cr-BDC is at 220^{o}C for 8 hours. We tried to bring down the reactiontemperatureto200^{o}C orlesswiththeaim toget abetterproduct (sincehigh temperature tend to produce by-products) and to prolong the longevity of the Teflon lining of the high pressure autoclave. The various permutations and combinations with the temperature, time and reactant concentrations are already shown in table 3.1.

CONCLUSIONS

Synthesis and characterization of Cu-BTC, Cr-BDC and Zn-BDC samples were successfully carried out in our present study. SEM images confirmed the authenticity of each of the MOFs. Cr-BDC and Cu-BTC were found octahedral in shape whereas Zn-BDC crystals appeared to be cubic in nature. The presence of impurities was not uncommon in MOF synthesis and here as well we had seen reactions leading to the formation of impure by-products. Post synthesis treatments in different organic environments were particularly important in removal of these impurities. Powder XRD patterns validated the crystalline nature of the products formed and thereby degree of purity in various batches owing to different solvent treatments.

TGA patterns were typical of specific MOFs synthesized. However, a shift towards low thermal stability had been observed for cases where solvents eliminated impurities. Although it appeared that elimination of impurities decreased the thermal stability of the products but if not, eventually it would lead to reducing the effective surface area which is most crucial in any gas adsorption study. The packing density data nicely corroborated the TGA analysis.

The concept of tuning the pores of a membrane using 'surface modification technique' is also gaining momentum and our present study can very well lead to improvising the surfaceproperties of membrane which would on the other hand be useful in 'Nano-filtration' operations.

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