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Sonochemical Synthesis, FTIR, SEM–EDX, and XRD Characterization of a Calixarene-Based Cobalt Metal–Organic Framework

Calixarene-Based Cobalt Metal–Organic Framework

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Abstract—

The synthesis of porous coordination materials with tunable composition, available active centers, and adequate crystallinity poses challenges since the structural and morphological features of metal-organic frameworks (MOFs) largely depend on metal-ligand complexes and synthesis conditions. In spite of the possibility of using calixarene ligands due to their macrocycles, numerous oxygen donor sites, and adjustable coordination sphere, the study of cobalt-calixarene MOFs is still understudied with regard to the combination of their spectroscopic, morphological, elemental, and crystallographic characterization. In this paper, the synthesis and characterization of a cobalt-calixarene MOF (Co–CAR–MOF) are described. The material was synthesized by using a functionalized 4-tert-butylcalixarene, cobalt(II) chloride, and benzene-1,3,5-tricarboxylic acid in dimethylformamide at 40 °C at 30 kHz for 60 min in an ultrasonic sonicator. For characterization, Fourier-transform infrared spectroscopy, scanning electron microscopy combined with energy-dispersive X-ray spectroscopy, and powder X-ray diffraction were utilized. FTIR results have shown the existence of the calixarene-derived organic framework and the interaction of Co with oxygen atoms. SEM has shown that the material has irregular, rough, and agglomerated particles. Meanwhile, EDX has indicated that the framework consists of carbon, oxygen, and cobalt atoms. The existence of distinct PXRD reflections shows that there is an ordered, partly crystalline material, with an estimated crystallite size of 40.8 nm. It is apparent from the data that there has been a successful synthesis of a nanocrystalline cobalt-calixarene coordination material. This opens up a possibility for studying its porosity, stability, and possible applications in adsorption, catalysis, sensing, and environmental remediation.

Keywords—Calixarene; cobalt metal–organic framework; sonochemical synthesis; FTIR spectroscopy; SEM–EDX; powder X-ray diffraction.

I. INTRODUCTION

Metal-organic frameworks (MOFs) are crystalline coordination networks built up of metal ions or metal clusters coordinated by multitopic organic ligands. According to IUPAC [1], a metal-organic framework is defined as a coordination polymer that contains organic ligands and may have voids. This definition distinguishes MOFs from coordination compounds [2-11] by highlighting the structural features that confer porosity in MOFs. Rational design of metal nodes and organic ligands allows making MOFs with varied dimensionality, pore size, functional groups on surfaces, and chemical environment. This allows positioning MOFs among the most studied porous hybrid materials in contemporary materials chemistry [1]. The growing attention to MOFs is associated with such characteristics as high specific surface area, permanent or adjustable porosity, crystallinity, structural diversity, and chemical tunability [12]. As compared to many conventional porous solids like activated carbon and zeolites, MOFs allow systematic tuning of the nature of the inorganic node and organic ligands. This allows manipulation of parameters such as pore size, framework charge, hydrophilicity, catalytically active sites and host-guest interactions at the molecular level. This has enabled their utilization in applications related to gas storage and separations, heterogeneous catalysis, chemosensors, drug delivery, environmental clean-up, electrochemical energy storage, and molecular recognition [12].

MOFs' performance depends on the interaction between their metal centers, organic linkers, framework topology, pore architecture and their stability under the conditions of operation [13]. Metal ions serve as the structural nodes or secondary building units while the organic ligands are the bridging ligands that link the adjacent metal centers. Carboxylate, azolate, phosphonate, sulfonate and other donor groups are usually employed as they can form very strong and highly diverse metal-ligand complexes. Depending on the coordination geometry of the metal center and connectivity of the linker, the resulting framework can be one-, two- or three-dimensional. This approach enables molecular-level control over the properties of MOFs and allows correlation of their bulk characteristics with the underlying molecular structure

[13]. However, despite all those advantages, the synthesis of MOFs is still accompanied by certain scientific and technological difficulties. The formation of one specific crystal phase depends on such factors as the metal-to-ligand ratio, solvent, temperature, pH, reaction time, concentration, modulator, and way of activation. Even slight variations in any of those parameters can lead to a change in the coordination environment, formation of polymorphic forms, morphology of particles, or crystallinity degree. Moreover, a lot of MOFs demonstrate low hydrolytic, thermal, mechanical, or chemical stability. Contact with water or aqueous acidic and basic solutions can cause cleavage of metal-ligand bonds and lead to collapse of the pores, release of metal ions, or loss of crystallinity. This limits possibilities for reproduction, scaling up, reactivation, and application [14].

Thus, choosing an appropriate organic linker plays an important role in designing a MOF that is both stable and functional. Classical ligands like terephthalic acid, trimesic acid, and imidazoles have already produced many frameworks. Nevertheless, they usually offer insufficient control over hierarchical environments and host-guest interactions. Macrocycles represent an alternative to traditional ligands. They are organic compounds with multiple coordination centers and molecular cavities. Their inclusion into coordination networks of extended coordination could cause structural hierarchy, preformed binding sites, and further supramolecular interaction within the framework. Macrocycle-containing MOFs have therefore been recognized as a very promising class of materials for molecular recognition, adsorption, sensing, catalysis, and controlled release [15]. From all the macrocyclic compounds, the calixarenes can be considered as the most promising ones in terms of building blocks. Calixarenes are phenolic macrocycles obtained by the reaction of phenols with formaldehyde in a basic medium [1]. “Calixarene” means vase or cup in Greek and refers to the typical bowl-like structure of such molecules. The most studied compound in this series is calixarene, which consists of four phenolic groups connected by methylene bridges. The rigid but flexible cavity of such a molecule, several phenolic hydroxyl groups, functionalizable rims, and capability of host-guest chemistry render calixarene a valuable platform in supramolecular and coordination chemistry [1]. Calixarenes have some structural properties useful in making MOFs. Firstly, phenolic oxygen atoms can be involved in metal coordination through direct coordination or deprotonation. Secondly, functionalization with carboxylate, phosphonate, sulfonate, pyridyl, or other coordinating groups of either upper or lower rims will result in increased connectivities and extension of the frameworks. Thirdly, the internal cavity can trap solvent molecules, ions, gases, and other guest molecules. Fourthly, aromatic walls can lead to π-π interaction and hydrophobic recognition. These properties make calixarene act both as a structural ligand, as a host molecule, and as a source of chemically active pores [2, 14].

The conformation of the calixarene also plays an important role in determining the structure of the final coordination framework. Cone, partial-cone, 1,2-alternate, and 1,3-alternate shapes are possible. Different conformations affect the orientation of the donor groups and the resulting dimensions, connectivities, and topologies of the framework.The structural flexibility of calixarene represents the advantage of chemical synthesis, but it raises a problem of predicting the end product on the basis of the formulas of initial materials only. The factors influencing the conformation and assembly include the metal used, additional ligands, solvent interaction, counter-ions, and other conditions of the reaction [2, 14]. Calixarene derivatives have already been successfully used as MOF linkers. Functionalisation of the upper rim of a calixarene dicarboxylic acid led to four MOFs formation, three of them being characterised by two- or three-dimensional structures [2, 14]. According to the modelled structure of the material, it was suggested that these materials might interact selectively with certain guest molecules. It has thus become clear that calixarene is not just a molecule filling pores in a material, but an active part of its construction.

The structure of calixarene-based coordination compounds has also been found to depend significantly on the metal ion and the auxiliary ligand [15]. Thiacalixarene tetraacetic acid complexed with cobalt salts and neutral linking ligands to form 3D networks of different topologies [15]. The cobalt ions formed secondary building units containing carboxylates, whereas auxiliary ligands such as 4,4’-bipyridine and others were responsible for extending the framework in another dimension [15]. Several of those compounds proved to be thermally stable up to 300 °C, showing the ability of the calixarene linkers to form strong coordination networks.

Co is an especially interesting metal node in terms of MOF construction. Cobalt can have several oxidation states, but mainly Co(II) and Co(III). Coordination geometries are different and include tetrahedral, square-pyramidal, octahedral, and distorted geometries. Such flexibility in coordination allows cobalt to connect oxygen- and nitrogen-donor ligands in networks of various dimensionalities. Redox function, Lewis acidity, magnetism, and catalysis can be additionally conferred to these metal centres. Consequently, cobalt-containing MOFs have found applications not just for adsorption purposes but also for catalysis, electrocatalysis, magnetism, chemical sensing, and as electrode materials [15]. The combination of cobalt and calixarenes may create synergistic effects on the structure and properties of resulting materials. Calixarenes can bring a rigid macrocyclic skeleton, oxygen-rich coordinating positions, an internal cavity, and functionalizable pore surfaces. Cobalt can bring a variety of coordination geometries and possibly active metal centers. The combination of these components may result in the formation of a porous hybrid where the macrocyclic cavity and voids in the framework act in tandem. Oxygen-coordinating atoms of a carboxylate or phenolate derivative of calixarene can form Co-O coordination bonds with cobalt ions, whereas the cavity of calixarene can participate in selective inclusion or adsorption of specific guest species [16-18]. Cobalt-calixarene frameworks have been known to possess structural diversity [16-18]. Cobalt sulfonylcalixarene coordination polymers have been examined in the context of gas adsorption, whereas cobalt-thiacalixarene assemblies containing phosphate, phosphite, or phenylphosphonate as anions yielded different structural assemblies [16-18]. In these compounds, cobalt-based secondary building units were connected through the presence of other anion-ligands, and antiferromagnetic interactions in the cobalt centres were identified. This demonstrates that cobalt and calixarene-related ligands can be used to construct extended coordination frameworks and that the resulting material can exhibit properties beyond just porosity [16-18].

However, there are still relatively few studies concerning the controlled preparation and comprehensive physicochemical characterization of the cobalt MOFs derived from calixarenes. Most of the described calixarene-based coordination materials employ thiacalixarenes, mixed metal systems, additional bridging ligands or structurally complex solvothermal compounds. For many of them, the dependence of the properties of the ligand (its functional groups), the presence of cobalt ions, morphological features, and the crystallization process is not yet clarified. Moreover, most of the research concerns the structure of the single crystals rather than the whole phase.

This is a significant knowledge gap. The material may display a realistic FTIR profile and cobalt peak in EDX testing but not show a conclusive framework. Similarly, a crystalline XRD profile does not necessarily provide information on the precise nature of coordination and porosity of the compound. An integrated approach to characterization should therefore be adopted. FTIR spectroscopy can detect the functional group(s) and changes due to coordination of the ligands and metal ions. SEM can provide information on the particle shape, texture, and porosity. Energy dispersive X-ray spectroscopy (EDX) can confirm the presence of cobalt and other elements. PXRD can examine the crystalline properties of the material and, where applicable, the average crystallite size using the Scherrer formula.

This research helps to bridge the research gap by investigating the synthesis and characterization of a cobalt-based metal–organic framework using calixarene. This new material aims to combine the pre-organized nature of calixarenes with the coordination capability and possible functionality of the cobalt centers. More emphasis will be placed on demonstrating the formation of the organic-inorganic framework using spectroscopic, microscopic, elemental, and diffraction techniques. The correlation between the functional groups, elemental composition, surface morphology, crystallinity and domain size will also be considered.

The novelty of the research is concerned with the preparation and characterisation of the Co-based MOF, whose unique feature is in its calixarene derivative ligands, and specifically in the detailed characterisation of its molecular, morphological, elemental, and crystalline structure. Even though coordination complexes of Co and calixarene have already been studied [14], our study stands out in terms of the consideration of the synthesised material as a potential nanocrystalline MOF and the linking of FTIR, SEM-EDX, and XRD data. The employment of calixarene means the formation of a macrocyclic cavity along with the presence of various oxygen-rich coordination sites, which might result in a unique MOF structure compared to the traditionally used dicarboxylates or azolates.

The rationale behind this research can be linked to the persistent demand for porous materials, which should have tunable chemical composition, accessibility of active sites, and adjustable host-guest interactions. Traditional adsorbents may have a large specific surface area but lack control of pore chemistry, and some MOFs can have outstanding structural features, but not enough stability or a complicated synthesis procedure. Calixarene-based cobalt metal-organic frameworks may fill this gap by creating one structure out of a functional macrocycle and transition metal node.

Thus, the aim of this research is the synthesis and characterization of the calixarene-based cobalt metal-organic framework. It is anticipated that the study will serve as the basis for further study of physicochemical properties of calixarene-based cobalt frameworks and assessment of the possibility of their use in various applications. In other words, synthesis and characterization of the material is a critical initial stage of producing calixarene-based cobalt MOFs with desirable properties.

II. Materials And Methods

A. Materials

The reagents employed in this study, including 4-tert-butylcalixarene, benzene-1,3,5-tricarboxylic acid, ethyl bromoacetate, triethylamine, and cobalt (II) chloride, were acquired from Sigma-Aldrich and were analytical grade reagents. They were used in their purchased form without any further purification. Solvents used in the experiment were sourced from Bristol Scientific, Nigeria.

B. Instrumentation

A sonochemical preparation of the calixarene-cobalt metal organic framework, labeled as Co-CAR-MOF, was performed using the Elementrix ultrasonic bath. The functional groups in the MOF sample were studied by means of FTIR Spectroscopy with the aid of a PerkinElmer Spectrum 100 FTIR Spectrometer and an attenuated total reflectance (ATR) accessory. The powder X-ray diffraction (PXRD) analysis of the samples was carried out using the X-ray diffractometer. The surface morphology and elemental analysis of the product were determined by means of scanning electron microscopy with energy-dispersive X-ray spectrometry using the JEOL JSM-5800LV Scanning Electron Microscope (SEM).

C. Sonochemical Synthesis of the Co–CAR–MOF

The Co-CAR-MOF was synthesized through the sonochemical technique described by Omosun *et al.*[19]. In this method, 4-tert-butylcalixarene functionalized (0.38 g, 0.5 mmol), $CoCl_2$ (0.065 g), and benzene-1,3,5-tricarboxylic acid (0.11 g, 0.5 mmol) were added to a reaction flask containing 10 mL of DMF. The mixture was magnetically stirred for 30 mins to ensure its homogenization and initial interaction of the metal salt with organic substances. The prepared mixture was placed into an Elementrix ultrasonic bath and subjected to sonochemical treatment at 40 °C and 30 kHz for 60 min. The purpose of sonochemical irradiation was to help mix, mass transport, nucleation, and growth of the coordination framework. After the reaction had ended, the resulting suspension was centrifuged to get the solid product. The collected solid was repeatedly washed with a water–ethanol (1:1, v/v) mixture in order to remove DMF, unreacted ligand, excess cobalt salt, and other soluble compounds formed in the reaction. The obtained solid material was dried overnight at 70 °C to obtain Co-CAR-MOF as a dry powder.

III. Results And Discussion

FTIR spectrum of the prepared Co-CAR-MOF is shown in Fig. 1.

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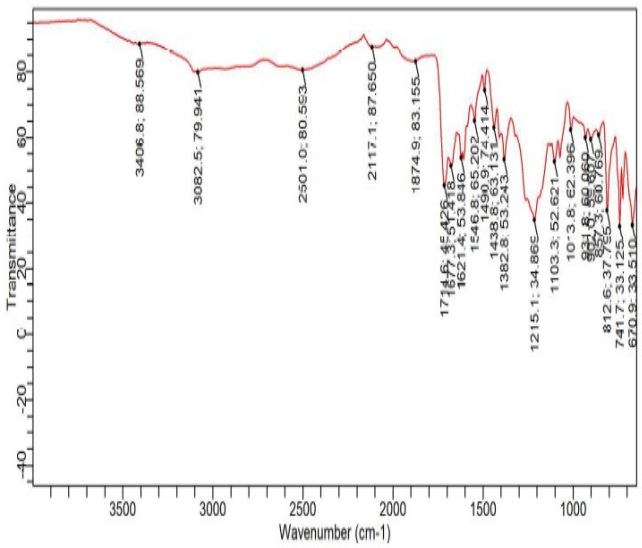
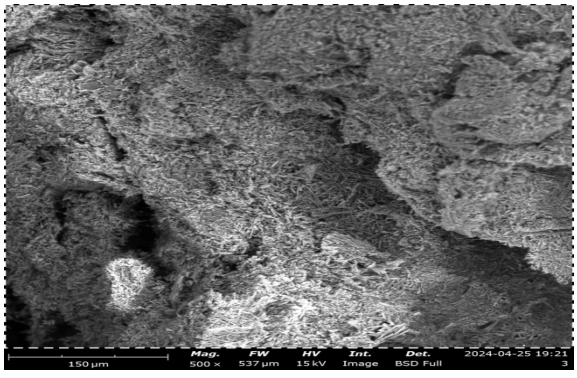


Figure 1: FTIR of Co–CAR–MOF

An intense absorption band at 3406 cm-1 corresponded to O–H stretching vibrations for hydroxyl groups. Similar to the results of our earlier publication [19], this band is red-shifted in comparison with the known O–H absorption band of the corresponding 4-tert-butylcalixarene compound at 3386 cm^{-1}, which could suggest phenolic hydroxyl groups participation in complex formation. The band at 3082 cm^{-1} corresponds to aromatic C–H stretching vibrations related to the calixarene core of ligands. An intense band at 1714 cm^{-1} corresponds to C=O stretching vibrations of carboxylic acid/carboxylate groups. The similarity of this band with the free ligand at 1715 cm^{-1} [19] indicates the absence of coordination of the carbonyl moiety. Absorption bands in the region of 1300–1500 cm^{-1} are related to aromatic calixarene core vibrations, including C=C aromatic stretching and C–O/C–C vibrations. The low-frequency band at 670 cm^{-1} is related to Co–O vibrations. The Co- O band has been observed at 668 cm^{-1} for cobalt-based MOF systems [17, 18], indicating that cobalt-oxygen bonds have been formed. The FTIR spectrum clearly shows that the calixarene-derived organic portion is present in the compound, which provides strong evidence for cobalt-oxygen bonds.

The SEM- EDX micrograph of Co-CAR-MOF (Figure 2) indicates the existence of a particulate, irregular, and apparently porous surface structure.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	67.16	59.03
8	O	Oxygen	32.02	37.50
27	Co	Cobalt	0.58	2.50
50	Sn	Tin	0.03	0.28
25	Mn	Manganese	0.05	0.20
30	Zn	Zinc	0.04	0.18
22	Ti	Titanium	0.03	0.12
19	K	Potassium	0.04	0.11
13	Al	Aluminium	0.04	0.09
20	Ca	Calcium	0.00	0.00
15	P	Phosphorus	0.00	0.00
12	Mg	Magnesium	0.00	0.00
26	Fe	Iron	0.00	0.00
11	Na	Sodium	0.00	0.00
14	Si	Silicon	0.00	0.00
16	S	Sulfur	0.00	0.00
17	Cl	Chlorine	0.00	0.00
29	Cu	Copper	0.00	0.00
24	Cr	Chromium	0.00	0.00

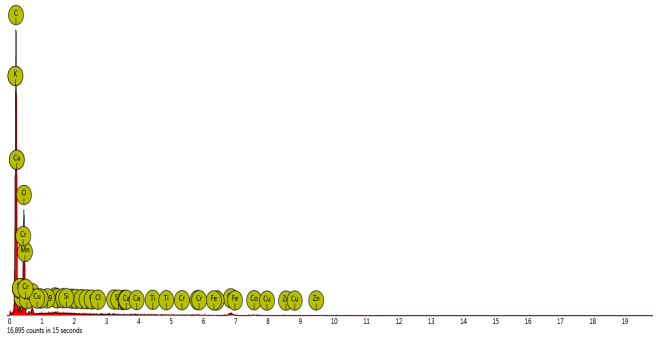


Figure 2: The SEM-EDX micrograph of Co-CAR-MOF

The particles are agglomerated and have a rough appearance, suggesting that crystallites or particles have been formed through assembly processes during the synthesis. It is possible to have such kind of an irregular and heterogeneous morphology when making MOFs using calixarene due to factors like metal-to-ligand ratio, solvent, pH, reaction time, and temperature, which influence deprotonation of the ligand, metal ion coordination, nucleation, kinetics of crystal growth, and the dimensionality of the coordination network [20-21]. Previous literature [14, 22] shows that a functionalized calixarene dicarboxylic acid can give rise to MOFs which have both two- and three-dimensional coordination networks, showing that the topology and pore structures depend upon the metal ion and coordination environment. Similar studies [22-23] have also indicated that calixarenes have the potential of generating MOFs with different structures like two-dimensional layers and three-dimensional porous networks.

The presence of voids and surface roughness on the particles may be advantageous for adsorption or catalysis because such characteristics favor interaction between the external surface and the molecules. However, SEM alone is not sufficient for the determination of any permanent microporosity or quantitative measurement of surface area. Nitrogen adsorption-desorption studies should be carried out to confirm the porosity of the substance.

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From the EDX analysis results, it is clear that the major elements detected are carbon and oxygen, whose concentrations are 59.0% and 37.5%, respectively. This composition confirms that there is a rich carbon-based framework of calixarene with oxygen-containing functional groups. It is noted that cobalt exists at 2.5%, which confirms the existence of cobalt in the area analysed and that the cobalt has been incorporated successfully. This low cobalt concentration can be attributed to the fact that EDX analysis is surface sensitive and hence it cannot give information on the bulk cobalt stoichiometry, especially in an organic ligand framework. The small traces of Sn, Mn, Zn, Ti, K and Al could be due to contaminants, inorganic species from reagents or glassware, sample holder or coating materials. This is because EDX analysis gives information from only small areas of the analysed material, and hence it has low reliability in detecting light elements like carbon and oxygen. For future experiments, elemental mapping and repeated spot analysis should be done.

The powder XRD diagram presented in Figure 3 demonstrates that the prepared Co-CAR-MOF consists of crystalline phases.

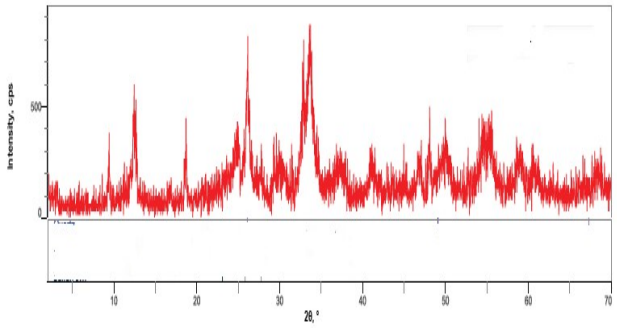
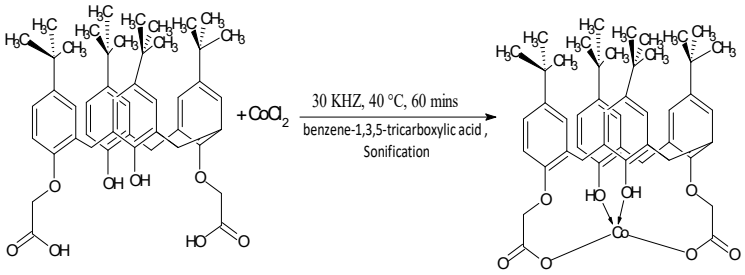


Figure 3: XRD pattern of Co-CAR-MOF

It is assumed that the presence of diffraction peaks proves that the solid obtained is an ordered structure and not an amorphous compound composed of cobalt-calixarene elements. The presence of diffraction peaks suggests that the compound is ordered, crystalline, at least partially, but not an entirely amorphous compound of cobalt-calixarene elements. In metal-organic frameworks based on cobalt, low-angle reflections correspond to the periodicity of pore or framework structures, while medium and high-angle 2θ reflections come from other crystallographic planes of the metal-ligand complex [24]. Certain reflections have been identified for the cobalt-terephthalate MOFs, which were considered proof of crystallinity of the framework structure [24]. Similar cobalt-calixarene coordination frameworks have been structurally identified, proving that calixarenes may create crystalline cobalt-containing structures [23, 24]. However, the presence of the peaks does not define the MOF topology unambiguously, as there should be a comparative analysis of the simulated PXRD diagram and unit-cell refinement. The presence of 40.8 nm means nanometer scale crystals. Therefore, the material should be referred to as a nanocrystalline material. It should be noted that one has to differentiate the crystal size determined using the XRD technique from the particle size determined using the SEM method. Crystal size obtained from the Scherrer equation refers to the coherent scattering domains, which could be much smaller than particles seen using SEM. A single SEM particle could consist of several crystallites, and hence the irregular micron-scale agglomerates seen in SEM do not conflict with a 40.8 nm crystal size.

Scheme 1 has been proposed based on the FTIR, SEM-EDX, and XRD techniques for the reaction equation of Co-CAR-MOF synthesis.



Scheme 1: Synthesis of Co-CAR-MOF

IV. Conclusion

The preparation of calixarene-based cobalt metal-organic framework through a milder sonochemical process was successful and characterized by means of FTIR, SEM-EDX, and PXRD. From the FTIR result, the existence of the calixarene derived organic framework is confirmed, and supporting evidence of Co-O coordination is achieved. From the SEM study, irregular, rough, and agglomerated morphology is found. With EDX, cobalt is confirmed to be incorporated into the carbon- and oxygen-rich material. The finding of trace amounts of minor elements shows the necessity of purification, elemental mapping, and compositional studies of the material. From the PXRD analysis, the existence of discrete peaks proves that the material has ordered crystalline domains. It can be said that a crystallite size of 40.8 nm means that the material is nanocrystalline; however, this crystallite size refers to the coherently diffraction domain but not to the larger agglomerate seen in the SEM image. Overall, all the results indicate that the material is a partially crystalline cobalt-calixarene coordination material. The results, however, cannot prove that it has unique topology, permanent porosity, or specific bulk composition. Consequently, further experiments with nitrogen adsorption/desorption measurements, thermal gravimetric analysis, elemental analysis, inductively coupled plasma analysis, crystallographic refinement, and stability tests are recommended. Such an investigation would provide a better understanding of the properties of this material in relation to adsorption, catalysis, sensing, and environmental applications.

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