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Synthesis of nanoporous carbohydrate metal-organic framework and encapsulation of acetaldehyde

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ABSTRACT

Gamma cyclodextrin (γ-CD) metal organic frameworks (CDMOFs) were synthesized by coordinating γ-CDs with potassium hydroxide (KOH), referred hereafter as CDMOF-a, and potassium benzoate ($C_7H_5KO_2$), denoted as CDMOF-b. The obtained CDMOF structures were characterized using nitrogen sorption isotherm, thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). High surface areas were achieved by the γ-CD based MOF structures where the Langmuir specific surface areas (SSA) of CDMOF-a and CDMOF-b were determined as 1376 $m^2 g^{-1}$ and 607 $m^2 g^{-1}$; respectively. The dehydrated CDMOF structures demonstrated good thermal stability up to 250 °C as observed by the TGA studies. XRD results for CDMOF-a and CDMOF-b reveal a body centered-cubic (BCC) and trigonal crystal system; respectively. Due to its accessible porous structure and high surface area, acetaldehyde was successfully encapsulated in CDMOF-b. During the release kinetic studies, we observed peak release of 53 μg of acetaldehyde per g of CDMOF-b, which was 100 times greater than previously reported encapsulation in β-CD. However, aldol condensation reaction occurred during encapsulation of acetaldehyde into CDMOF-a. This research work demonstrates the potential to encapsulate volatile organic compounds in CDMOF-b, and their associated release for applications including food, pharmaceuticals and packaging.

1. Introduction

Cyclodextrins (CDs) are naturally synthesized from starch using glycosyltransferase enzymes. These cyclic structures exist in various forms including alpha (α), beta (β), gamma (γ) and delta (δ) form [1]. The difference among these forms is attributed to the numbers of 1,4-linked glucopyranose units which are attached in a cyclic arrangement. The α, β, γ, and δ forms have 6, 7, 8, and 9 glucopyranose units; respectively. As a result, the molecular weight of CDs varies from 972 to 1459 g mol^{-1} while their cavity diameter ranges between 0.47 and 0.83 nm; respectively [2]. One of the most remarkable properties of CDs is their ability to form inclusion complexes (ICs) with volatile organic compounds due to their hydrophilic exterior and hydrophobic interior. In such complexes, the volatile compounds are entrapped inside the hydrophobic CD pores due to secondary interactions. Such ICs have been widely explored because of their potential applications in pharmaceutical [3], chemical [4], food and packaging industries [5–7].

Several researchers have studied CD based ICs. The ability of CDs to host a guest molecule depends on various factors such as the size of the guest molecule, the pore size of the CDs, chemical interactions between functional groups of the guest molecule and hydrophobic pore interior. Veiga et al. [8] prepared tolbutamide urea (TBM) β-CD complexes using kneading, freeze-drying and co-precipitation. The study concluded increased solubility, dissolution and oral bioavailability of TBM due to the ICs. Almenar et al. [9] studied post-harvest fungal decay inhibition efficacy of acetaldehyde released from α, β or γ-CD acetaldehyde ICs. Effective fungal decay was observed when β-CD acetaldehyde IC was employed during the marketable period. In another study, Almenar et al. [10] also prepared hexanal and β-CD ICs in distilled water with different concentrations. The authors encapsulated a maximum of 1.40 ppb hexanal in β-CD, and reported that the released hexanal was effective against the growth of fungi. Although β-CD allows the encapsulation of organic compounds through ICs, the total amount that can be absorbed and later released is still relatively low.

Metal-organic frameworks (MOFs) are a new class of

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microporous coordination polymers, which consists of metal ions and organic linkers [11]. MOFs are well known for their high surface area, gas sorption, gas separation, selectivity and chemical sensing [12–15]. The structural properties of MOFs are unique among other materials including organic, inorganic and hybrid porous structures such as zeolite and activated carbon. These distinctive properties can be accredited to the high porosity of MOFs and their reticulate symmetrical structures, which allow them to host guest molecules like H_2, CO_2, N_2 and CH_4 [16–18].

Recently, cyclic macromolecules such as CDs [19–22], crown ethers [23], pillararenes [24] and cucurbiturils [25] with inherently large cavities have been utilized as organic struts for synthesizing MOFs. Such structures offer two porosity levels, the first one exists naturally in these cyclic macromolecules, and the second is created as the result of the chemical coordination between these struts and the metal ions. Gamma CD, a cyclic macromolecule, has been recently coordinated with earth metal ions (*e.g.,* K^+, Rb^+, Na^+, and Cs^+) to obtain cyclodextrin based metal organic frameworks (CDMOFs) [19]. Gassensmith et al. [20] utilized γ-CD and Rb^+ ions based MOF structure, also known as CDMOF-2, for sensing and quantification of CO_2 using electrochemical impedance spectroscopy. They credited reversible chemisorption of CO_2 to electrochemical sensing of CDMOF-2. Yoon et al. fabricated [21] metal/MOF/metal hetero-structures based memristors using single crystals of CDMOF-2 for storage of electrical information. The ability of these hetero-structures to work as resistive random-access memory (RRAM) was ascribed to the porous structure of MOFs, which allows transportation of ions when infused with electrolytes. The release of drug encapsulation in the γ-CD and K^+ ion MOF structure, generally known as CDMOF-1, has been studied for drug carrier applications using Monte Carlo simulations [22]. In their study, researchers observed strong interactions between the metal centers of the MOF and the carbonyl group present in the analgesic drug, ibuprofen [22].

In this study, we synthesized two different γ-CD-K^+ ions based MOFs using potassium hydroxide and potassium benzoate as sources of K^+ ion, referred hereafter as CDMOF-a and CDMOF-b; respectively. Gamma-CDs were chosen as linkers due to their bio-based nature as well as their unique ability to form ICs. These CDMOFs were synthesized because of the non-toxic nature of alkali metals, presence of polar groups, open metal sites and the ability of various CDs to form ICs [26–28]. The main objectives of this study were: a) to synthesize CDMOF-a and CDMOF-b; b) to determine the physical and thermal characteristics of CDMOF-a and CDMOF-b crystals; and c) to run a proof-of-concept of the ability of CDMOFs to encapsulate and release a selected organic compound, acetaldehyde, which is known for its anti-fungal activity [9]. To the best of the authors' knowledge, no study has focused on encapsulation and release kinetics of acetaldehyde in CDMOFs.

2. Methodology

2.1. Materials

Gamma CD (purity $>99\%$, food grade) was donated by Wacker Chemical Corporation (Adrian, MI, USA). Potassium hydroxide (KOH) pellets (ACS reagent, purity $\geq 85\%$), and potassium benzoate ($C_7H_5KO_2$) were purchased from Columbus Chemical Industries, Inc. (Phoenix, AZ, USA). Anhydrous methanol (purity $>99.8\%$) and acetaldehyde (purity $\geq 99\%$, FCC) were purchased from Sigma-Aldrich Corp. (Saint Louis, MO, USA). Distilled and deionized water was purchased from Avantor Performance Materials (Center Valley, PA, USA). All materials were used as received unless otherwise indicated.

2.2. Synthesis and activation of CDMOF

The CDMOFs were synthesized as per Smaldone et al. [26]. One mmol (1.30 g) of γ-cyclodextrin and 8 mmol (0.45 g) of KOH were dissolved in 20 mL of deionized water and labeled in this work as CDMOF-a. On the other hand, 1.6 mmol (0.256 g) of $C_7H_5KO_2$ and 0.2 mmol (0.26 g) of γ-CD were diluted in 5 mL of deionized water to synthesize CDMOF-b. The solutions were stirred continuously for 6 h at 500 rpm followed by slow vapor diffusion of methanol over a period of 3 to 7 d. After the CDMOF crystals were produced in the solution with an average yield of 1.25 g for the CD and KOH, and 0.30 g for the CD and $C_7H_5KO_2$, the crystals were washed with methanol to remove unreacted potassium ions and then filtered (samples were labeled as as-synthesized). After synthesis, the CDMOFs were activated in a vacuum oven at 23 °C for 10 h at 4 kPa (30 mmHg). Then, the temperature was increased to 45 °C and maintained for an additional 12 h under the same vacuum pressure 4 kPa (samples were labeled as activated).

2.3. Surface area and pore size

The gas sorption experiments were conducted using an iQMicropore-XR (Quantachrome Instruments, Boynton Beach, FL, USA). The surface area, pore sizes and diameters of the CDMOFs were calculated using the Brunauer-Emmett-Teller (BET) and Langmuir methods. Samples weighing 0.05 g of each synthesized CDMOF-a and CDMOF-b crystals were dehydrated for 10 h of vacuum pressure at 0.133 kPa (1 Torr) at 25±0.1 °C followed by heating at 45 °C for 12 h under the same pressure. The specimens were then transferred to the sorption station where the N_2 adsorption took place at 77.3 K and N_2 gas sorption at a relative pressure varying from 10^{-5} to 0.99 [29].

2.4. Thermogravimetric analysis (TGA)

Thermal stability of CDMOF-a and CDMOF-b crystals were evaluated using a TGA model 2950, from TA Instruments (New Castle, DE, USA). A sample weight of 5 mg of activated CDMOF-a and CDMOF-b were utilized to perform the studies. Samples were heated from 25 to 450 °C at a rate of 10 °C min^{-1}. Data were collected and analyzed using the Universal Analysis software version 2000 from TA Instruments.

2.5. X-ray diffraction (XRD)

The CDMOF-a and CDMOF-b activated crystals were examined using a Bruker D8 advance X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) using Cu Kα ($\lambda=0.154$ nm) radiations at 40 kV, 40 mA. The samples were studied using 1.2 mm primary beam slit, and 2.0 mm detector slit over 3 to 40° 2 theta angles with increments at 0.02° per min.

2.6. Scanning electron microscopy (SEM)

To study the topography, activated CDMOF-a and CDMOF-b crystals were sputter coated with approx. 8 nm thick platinum coating. The coated specimens were examined using a JEOL JSM 6410 LV (JEOL Ltd., Tokyo, Japan) SEM, equipped with a tungsten filament, at 10 kV accelerating voltage.

2.7. Encapsulation and release method

Acetaldehyde encapsulation was carried out after activating the CDMOF-a and CDMOF-b. First, 1 g of activated CDMOF-a or CDMOF-b was placed in a small aluminum pan that was placed in a 2 L glass jar. Acetaldehyde (1 mL), previously stored in a