Synthesis and Characterization of Gamma Cyclodextrin Metal Organic Framework and Encapsulation of Ethanol

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Introduction
Various porous materials, including metal organic frameworks (MOFs), have been extensively researched in the recent years for different applications. MOFs are synthesized by the coordination of metal ions with organic binders. Different molecules can be incorporated into the pores of MOFs. This host-guest chemistry can be used to absorb established active organic compounds. The prolonged release of such active species can be used to optimize the shelf life of food products. EDH has been known as a preservative because of its antifungal and antimicrobial effects and is safe for human consumption when taken in small quantities. Direct addition of these compounds to food and packaging structures can be problematic due to their rapid release and volatility. To manipulate the stability and release, these antimicrobials can be encapsulated in a carrier matrix or metal organic framework. Recently, gamma-cyclodextrin (γ-CD) and alkali metal based MOF structures (γ-CDMOF) have been in focus because these porous frameworks can be easily synthesized from completely non-toxic, naturally occurring raw materials, that can potentially host active molecules.

Objective
The purpose of this study is to develop suitable carriers for ethanol to temporarily contain and protect this antimicrobial volatile, as well as to manipulate its release behavior for active packaging applications.

Methodology
γ-CDMOF were synthesized through vapor diffusion of 100 mL methanol in a solution of 1.30 g γ-CD and 0.45 g KOH in 20 mL deionised water. γ-CDMOFs were activated in a low temperature oven to remove residual methanol and deionised water and open up the pores of the crystals in preparation for encapsulation. SEM and XRD were used to characterise the activated crystals. Ethanol was subsequently encapsulated into the γ-CDMOF crystals through vapor diffusion and analysed using TGA, DSC and FTIR to determine whether encapsulation took place.

Results
The γ-CD building units are connected by potassium ions, in aqueous medium at ambient temperature and pressure in a bodycentred cubic structure.

XRD was performed to determine the crystal structure and chemical composition of γ-CDMOFs. The XRD pattern in Fig. 6 clearly shows peaks that indicate the crystallinity, which confirms the inclusion complex formation. The ethanol loading process did not destroy the crystallinity of the material. TGA is used to characterise materials by measuring their change in mass as a function of temperature. These results are used to analyse whether encapsulation has taken place and to determine the approximate quantities. From the results, shown in Fig. 7, it can be concluded that the encapsulation of ethanol γ-CDMOF was successful. The TGA results show that γ-CDMOF can encapsulate ~30% ethanol in the crystals. It can be concluded that the capacity of γ-CDMOF is triple the capacity of γ-CD, since γ-CD can only encapsulate 7% EtOH.

DSC is a useful tool for confirming whether guest molecules are included inside the CD cavities. The absence of the ethanol peak in the DSC curve (Fig. 8) is due to its encapsulation in the host γ-CDMOF. The complete disappearance of the endothermic DSC signal corresponding to the guest is a strong evidence of the total inclusion of the ligand inside the cavity of γ-CD and γ-CDMOF.

The use of infrared spectra is important to determine structural information about a molecule and to verify if structures are identical or not. The FTIR results in Fig. 9 confirm the conclusions obtained from TGA and DSC. Therefore it can be concluded again that γ-CDMOF successfully encapsulates ethanol.

Conclusion
In this study, stable high surface area microporous MOF structure was synthesized using a vapor diffusion process. γ-CDMOF analyzed before and after synthesis using SEM and XRD indicated that γ-CDMOF crystals retained the crystal structure after the complex formation. Ethanol was encapsulated using vapor diffusion process; the crystal adsorbed around 20% ethanol, as observed by TGA. The crystals retained their crystal structure after adsorbing ethanol. Ethanol was successfully encapsulated in γ-CD and γ-CDMOF, as supported by the TGA, DSC and FTIR studies. This study helps in advancing our understanding of ethanol-CDMOF host-guest interactions.

References