Regulating thermal dynamics and gas transport of MOF glass through silver composites

Muhammad Yazid Bin Zulkifli¹, Ruiqi Chen¹, Rijia Lin², Yuqi Yao¹, Milton Chai¹, Dominique Appadoo³, Wupeng Wang¹, Zhong-Hua Zhu⁴, Kang Liang⁵, Vicki Chen⁶, and Jingwei Hou¹

¹University of Queensland ²Affiliation not available ³Australian Synchrotron ⁴The University of Queensland ⁵University of New South Wales South Western Sydney Clinical School ⁶University of Technology Sydney

July 23, 2023

Abstract

Metal-organic framework (MOF) glass is a versatile and processible material that retains its porous nature while transitioning between liquid and solid states. Incorporating composites into MOF glass can enhance its functionalities, but the effect on its state conversion remains understudied. This research explores the impact of silver ions on the properties of ZIF-62 glass, revealing their influence on phase conversion at varying ligand concentrations. The presence of silver enhances gas separation processes, particularly improving CO2 and hydrocarbon separation selectivity compared to pure ZIF-62 glass. These findings provide valuable insights for composite integration and highlight the potential of Ag-doped ZIF-62 glass in gas separation applications. Furthermore, this work paves the way for processing functional Ag-doped ZIF-62 glass films, enabling diverse applications such as gas separation, film catalysis, and antimicrobial glass.

Regulating thermal dynamics and gas transport of MOF glass through silver composites

Muhammad Yazid Bin Zulkifli, Ruiqi Chen, Rijia Lin, Yuqi Yao, Milton Chai^{*}, Dominique Appadoo, Wupeng Wang, John Zhu, Kang Liang, Vicki Chen and Jingwei Hou^{*}

M.Y.B Zulkifli, R. Chen, R. Lin, Y. Yao, M. Chai, W. Wang, V. Chen and J. Hou

School of Chemical Engineering, University of Queensland, St Lucia, QLD, 4072, Australia E-mail: mil-ton.chai@uq.edu.au; jingwei.hou@uq.edu.au

M.Y.B Zulkifli

Group Research & Technology (GR&T), Project Delivery & Technology (PD&T), PETRONAS Research Sdn Bhd, Block E, Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan Institusi Bangi, Kajang, 43000, Malaysia

D. Appadoo

Australian Synchrotron, 800 Blackburn Road, Clayton, VIC 3168, Australia

K. Liang School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

V. Chen

University of Technology Sydney, 15 Broadway, Ultimo, NSW 2007 Australia

Keywords: MOF glass, MOF composites, silver composite, gas separation membranes, light hydrocarbon separation

Abstract

Metal-organic framework (MOF) glass is a versatile and processible material that retains its porous nature while transitioning between liquid and solid states. Incorporating composites into MOF glass can enhance its functionalities, but the effect on its state conversion remains understudied. This research explores the impact of silver ions on the properties of ZIF-62 glass, revealing their influence on phase conversion at varying ligand concentrations. The presence of silver enhances gas separation processes, particularly improving CO_2 and hydrocarbon separation selectivity compared to pure ZIF-62 glass. These findings provide valuable insights for composite integration and highlight the potential of Ag-doped ZIF-62 glass in gas separation applications. Furthermore, this work paves the way for processing functional Ag-doped ZIF-62 glass films, enabling diverse applications such as gas separation, film catalysis, and antimicrobial glass.

1. Introduction

Silver (Ag) is an incredibly versatile material utilized in numerous applications, both in its ionic and elemental forms. Its exceptional catalytic properties have been demonstrated across a wide range of fields, including gas hydration, medical treatments, sensors, photovoltaics, drug delivery, textiles, paints, and imaging^[1-4]. Particularly in organic synthesis, silver has proven to be highly effective as a catalyst, contributing to its extensive application in chemical synthesis^[4-7]. Furthermore, silver ions and nanoparticles have shown significant potential in gas separation techniques, particularly when incorporated into membrane systems^[8-12]. To ensure precise control over silver nanoparticle size and prevent aggregation, researchers have developed encapsulation and stabilization methods. By utilizing high surface area, porous materials like metal-organic frameworks (MOFs) and zeolites, silver nanoparticles can be effectively encapsulated^[13-16]. Moreover, silver has been successfully incorporated as a dopant in diverse porous frameworks, thereby imparting its remarkable catalytic and antimicrobial properties to the porous structure ^[17-19]. This strategy allows for the synthesis of multifunctional materials with enhanced performance and applications in various industries.

MOF is one of the most studied porous materials due to it being a very versatile material owing to not onlitx exceptional porosity but also high tunability. MOF's capability to change its respective ligands and metal nodes within its structure allows for tunable pore characteristics to suit different applications.^[20] A recent study has shown a new phase of this highly tunable material, at which some species of zeolitic imidazolate frameworks (ZIFs), a family of MOF, can be melted to form a glassy phase.^[21,22] This highly processible material has been shown to have good applications in gas separation and has also been shown to be able to form excellent composites with other materials such as perovskite and other MOF for gas separation, photocatalysis and oxygen reduction reaction. The ease of processibility for this material also allows its application in coatings of previously hard-to-coat substrates such as non-functionalized carbon cloth.

One of the widely studied MOF glass is ZIF-62 due to its ultrahigh glass forming capabilities and large melting-to-decomposition temperature difference.^[21] Although ZIF-62 thermal behaviour and applications have been studied in the form of composites (with ionic liquid), metal substitution and ligand substitution, not much research has been done on the effect of functional guest molecules within its structure on its thermal and melting behaviour, as well as their gas separation applications.^[23–26] In this paper, we aim to understand and explore the effect of silver doping in ZIF-62 glass, its effects on dynamic thermal changes, and the resulting interactions of Ag within the glassy structure towards engineered gas separations.

2. Materials and Methods

Materials

All the materials were purchased from Sigma Aldrich unless otherwise stated. For the synthesis of different variations of zeolitic imidazolate frameworks (ZIF-62) the following chemicals were used: zinc nitrate hexahy-

drate $(\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, imidazole (Im), benzimidazole (bIm), All these chemicals were used as is without further purification. The following solvents were used either for chemical synthesis, dispersing synthesised particles, or washing: methanol and N, N-dimethylformamide (DMF). All these solvents were used as is without further purification. Polymers for the synthesis of mixed matrix membranes were purchased and used directly from suppliers. 6FDA-DAM ((4,4'-Hexafluoroisopropylidene) diphthalic dianhydride (6FDA) and 2,4,6-trimethyl-1,3-diaminobenzene (DAM)) is a type of polyimide that was obtained from Akron Polymer Sytems (USA) at a molecular weight of ~370k.

Synthesis of ZIF-62 and AgZIF-62

Generally, ZIF-62 particles were synthesised using solvothermal methods reported by Frentze-Beyme et al. with slight modifications.^[27] ZIF-62 particles are usually reported with an x value which represents the benzimidazole ratio in the particle according to the formula below:

$$x = 2c(bim)/(c(im) + c(bim))$$

whereby c is the molar concentration

Different amounts of $Zn(NO_3)_2 \cdot 6H_2O$, Im, bIm and DMF as per were measured into a Schott bottle and stirred until fully dissolved. Once fully dissolved, the Schott bottle was tightly sealed and left to react in a 130 °C oven for four days. The resulting solids were then soaked and washed with methanol three times before being dried in a 70 °C oven overnight before use.

Tabl	le 1:	Precursor	amount	for	ZIF-62	synt	\mathbf{hesis}
						•/	

Sample	Reported x value	$\operatorname{Zn}(\operatorname{NO}_3)_2 \cdot 6\mathrm{H}_2\mathrm{O},\mathrm{g}$	Imidazole, g	Benzimidazole, g	DMF, mL
ZIF-62-a	0.05	2.67	1.98	0.0267	200
ZIF-62-b	0.12	2.67	1.951	0.08	200
ZIF-62-c	0.24	2.67	1.867	0.231	200

The synthesised ZIF-62 particles were fully activated in the vacuum oven at 150 °C for 24 hours before Ag adsorption to ensure maximal adsorption of Ag^+ into the ZIF-62 pores. The activated particles were then lightly crushed and mixed using a small pestle and mortar to reduce possible agglomeration during activation and drying. The lightly ground ZIF-62 particles were then dispersed into a 0.05M methanol solution of AgNO₃ and stirred at 300 rpm using a magnetic stirrer for 1 hour. The resulting suspension was then centrifuged at 9500 rpm for 15 minutes using Cence H1850 high-speed centrifuge and dried at 70 °C for 5 hours before being stored in a dark and cool condition. The Ag-doped ZIF-62 can be further melted at a temperature ranging between 400 °C-450°C using a furnace with an Argon environment for 5 minutes to form the glassy/thermally treated version of these materials.

Synthesis of melted ZIF-62 and Ag-ZIF-62 mixed matrix membranes

In the formation of the 6FDA-DAM-based membrane, the polymer percentage in the solvent-polymer mixture was retained at 7.7 wt%. The melted ZIF-62 or Ag-ZIF-62 filler was first dispersed in chloroform for at least 12 hours before the addition of 6FDA-DAM. Occasional ultrasonication was also performed using an ultrasonic bath during the 12-hour filler dispersion period. This step is essential to ensure better dispersion of fillers and reduced chances of agglomeration before the addition of the polymer of choice. After filler dispersion, 3 wt% of the full amount of 6FDA-DAM (7.7 wt%) was added to the dispersed filler chloroform solution and left to stir for 24 hours. This step is important as a priming step to ensure full dissolution and dispersion of 6FDA-DAM polymer while having good contact with the fillers. Occasional ultrasonication was also performed using an ultrasonic bath during these 24 hours to ensure efficient dispersion and reduced agglomerates and then left to be stirred overnight. The highly viscous 6FDA-DAM-filler solution was then sonicated for 20-30

minutes to remove any remaining trapped air in the solution. The solution was then cast on a glass slide using a casting blade at the height of 500 μ m. The glass slide was then immediately covered in a solvent-saturated enclosed container and left to evaporate overnight slowly. The resulting membrane was then slowly peeled off and activated in a vacuum oven at 30 °C for 24 hours before use. A lower activation temperature of 30 °C was used for Ag-doped fillers to minimise the possibility of Ag nanoparticle formation during activation. All the drying/activation processes for Ag-doped fillers were also performed in a light-enclosed environment to minimise possible changes in the filler structure, such as further Ag nanoparticle formation.

Material characterization

SEM was used to analyze the morphology of particles and membranes in this study. SEM-EDS was performed to study the chemical composition within the Ag-ZIF-62 particles and membranes. Samples were prepared by mounting them onto an aluminium SEM sample stub using carbon tape. Particulate samples were dispersed onto a silicon wafer before being secured onto the SEM sample stub. The samples and the stub were dried in the oven overnight at 70 °C under a vacuum to remove any residual solvents. The samples were thinly coated with platinum for morphological analysis (FE-SEM and conventional SEM) (ca. 15 nm thickness) or carbon for Energy Dispersive Spectroscopy analysis (SEM-EDS) (ca. 30 nm thickness) using Quorum Q150T high-resolution sputter coater. Scanning Electron Microscopy was performed either using JEOL JSM-7001F or JEOL JSM-7100F for Field Emission Scanning Electron Microscopy (FE-SEM) and Hitachi SU3500-A for conventional SEM imaging. All SEM analysis for morphological analysis was performed under secondary electron imaging mode at 5kV and a working distance of 10mm. Point Energy Dispersive Spectroscopy (SEM-EDS) were performed using JEOL JSM-7100F and JEOL JSM-7001F. Mapping Energy Dispersive Spectroscopy (SEM-EDS) was performed using Hitachi SU3500-A. All SEM-EDS analyses were performed at 20 kV and a working distance of 10 mm.

FT-IR and synchrotron THz-IR analysis was performed to understand the underlying bonds within the particles and membranes. Fourier-Transform Infrared (FT-IR) spectra were obtained using Nicolet 6700 by Thermo Scientific equipped with a diamond attenuated total reflection (ATR) objective. All spectra were collected between 600 cm⁻¹ to 4000 cm⁻¹. THz/Far-IR absorption spectra were collected at the THz/Far-IR beamline at the Australian Synchrotron with a Bruker IFS 125/HR Fourier Transform (FT) spectrometer. The bolometer was cooled with liquid helium to reduce the background noise. A 6 μ m thick Multilayer Mylar beam splitter was applied. The measurement was performed with an attenuated total reflection (ATR) stage. Powder samples were mounted on the surface of the diamond crystal window. In situ spectra were gathered with the ATR heating stage under a flowing argon environment (ca. 20 mL min⁻¹). For data processing, the Extended ATR correction algorithms in the OPUS 8.0 software, together with NumPy module v1.15 together with Python v3.9, were applied for spectral data correction and peak fitting.

ICP-OES were performed to study the Ag to Zn ratios within the Ag-ZIF-62 particles. The Ag/Zn molar ratio of Ag-doped ZIF-62 was analysed with a Thermofisher iCap Pro inductively coupled plasma optical emission spectrometer (ICP-OES) instrument. The samples were digested with 35 wt% nitric acids before the ICP-OES test.

X-ray diffraction (XRD) was performed to analyse the crystalline and glassy structure of the ZIF-62 and Agdoped-ZIF-62. Room temperature X-ray diffraction measurements were carried out under ambient conditions with Rigaku Miniflex 600 Benchtop X-Ray Diffractometer and a Cu K_{α} ($\lambda = 1.5406$ Å) radiation source. Samples in particle or small solid form are ground using a pestle and mortar before being dispersed onto a zero-background holder. Membrane or film samples were cut into squares with a size of ca. 2 cm x 2 cm before being secured onto a zero-background holder using a blue tack on the edge of the holder. The secured samples were then mounted onto the sample stage for X-Ray diffraction measurements. The 2 ϑ range was 5° to 50°, with a step size of 0.03° and a 1.5° min⁻¹ scan speed.

In situ thermal XRD was also performed to understand the structural transformation between solid, liquid and cooling phases. In situ thermal x-ray diffraction was performed using Anton Paar BTS 500 benchtop heating stage to study the thermal dynamics of different particles and thin film MOFs. The particles were dispersed onto a zero-background holder before being secured onto the benchtop heating stage for analysis. The heating rate was fixed at 20 °C min⁻¹. All in situ thermal XRD analyses were performed under inert conditions via nitrogen gas flow. Samples within the benchtop heating stage were purged for 30 minutes before the temperature was increased for analysis. The collected XRD data were transformed into xy data format using PowDLL software (N. Kourkoumelis, ICDD Annual Spring Meetings (ed. Lisa O'Neill), Powder Diffraction, 28 (2013) 137-48) before being analysed using Excel. Literature comparison CIF data were obtained from the Cambridge Crystallography Data Centre (CCDC). The CIF data were processed using Mercury software obtained from CCDC, and the XRD data were extracted in xy data type format.

Thermogravimetric analysis was performed to understand the thermal decomposition behaviour of particles and membranes. Thermogravimetric analysis (TGA) was carried out using a METTLER TOLEDO TGA/DSC 1 STARe System. The sample was heated to 900 °C at a rate of 10 °C min⁻¹ under flowing air or nitrogen as required (20 mL min⁻¹).

Differential Scanning Calorimetry was used to study the melting temperature (T_m) and glassy transition temperature (T_g) of the samples. Differential scanning calorimetry (DSC) analysis was conducted using a separate Mettler Toledo DSC 1 STARe system. To determine the melting temperature (T_m) , the samples were heated from 40 °C to 450 °C at 20 °C min⁻¹ under a nitrogen atmosphere. For determining the glass transition temperature (T_g) , each sample was heated above the inherent T_g and then cooled back to room temperature at a ramping rate of 10 degC to eliminate the effect of thermal history on glass transition temperature (T_g) determination. Then the T_g was determined from the following up-scans.

XPS was performed to study the different elemental states on the surface of the ZIF-62 and Ag-ZIF-62 crystals and melted variations. X-ray photoelectron spectroscopy (XPS, AXIS Supra+, KRATOS Analytical) was performed using a mono Al X-ray gun with an emission current of 10.00 mA and pass energy 160 eV for survey scan and 20 eV for high-resolution spectra, respectively. The C–C peak position was set to 284.8 eV and used as an internal standard.

¹H liquid state NMR was performed to study the molar ratio of benzimidazole to imidazole in the as synthesised ZIF-62 particles. 5.0 mg of sample was digested in a mixture of DMSO-d6 (0.5 mL) and DCl/D₂O (35%; 0.1 mL). The ¹H NMR measurement was performed with a Bruker Avance 500 high-resolution NMR spectrometer interfaced to an 11.7 Tesla 51 mm bore magnet system.¹³C solid-state NMR was performed to study the molecular interaction surrounding carbon atoms within both the crystalline and melted variations of ZIF-62 and Ag-ZIF-62. Solid state NMR for ¹³C studies was performed using Bruker 300 MHz Avance III solid-state (SS) NMR spectrometer with 7.41 Tesla (300 MHz) wide bore superconducting magnet interfaced with a two-channel Bruker Avance III spectrometer.

Adsorption isotherms were measured using Micromeritrics TriStar II 3020. Samples were degassed for 24h under a high vacuum before adsorption analysis. CO_2 isotherms at 273K were performed from high vacuum up to 130 kPa through one adsorption-desorption cycle.



Figure 1: Flow diagram of gas permeation rig.

All pure gas membrane permeation tests were performed in a variable feed pressure and constant volume permeation system, as shown in Figure 1. All gas permeation tests were performed at room temperature. The membrane module utilizes a sealing o-ring directly onto the selective polymeric membrane surface. The membranes were secured in the gas permeation module before tests. The membranes were held under vacuum for approximately 5 minutes before being exposed to selected gas on the feed side at a selected pressure of around 2 bars. The permeate side of the membrane (including the buffer tank) was left in a vacuum before the start of the gas permeation test. The pressure of the feed and permeate side of the membrane were measured at intervals of 5 s, and the steady rate of pressure increase on the permeate side was calculated. The effective membrane area for each test was also recorded.

The permeation coefficient was calculated using the following equation:

$$P = \frac{273.15 \times 10^{10}}{760 \times A \times T} \frac{V \times L}{\frac{P_0 \times 76}{14.7}} \frac{\mathrm{dp}}{\mathrm{dt}}$$

Where P is the permeation coefficient in barrer (1 barrer $=1 \times 10^{-10}$ cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹), A is the effective area of the membrane (cm²), T is the absolute temperature (K), V is the dead-volume of the permeate side (cm³), L is the membrane thickness (cm), P₀ is the feed pressure (psi), and $\frac{dp}{dt}$ is the steady rate of pressure increase in the permeate side (mm Hg s⁻¹). All permeation values and error bars were obtained from multiple measurements of the samples.

The ideal selectivity for different gas pairs was calculated using the following equation:

$$\alpha = \frac{P_A}{P_B}$$

Where P_A and P_B are the permeation coefficient of pure gas A and B, respectively.

3. Results and Discussions

3.1. Silver adsorption and effects on ZIF-62 crystal structure

The pure ZIF-62 crystal structure was prepared in three different benzimidazole to imidazole ratios using a previously reported method with slight changes.^[27] This is to study the effects of silver interactions on the thermal dynamics of these structures at different melting points. Thermal dynamics in this context can be defined as the structural dynamics that occur upon the introduction/removal of heat. The as-synthesized ZIF-62 were labelled as ZIF-62-a, ZIF-62-b, and ZIF-62-c in increasing benzimidazole ratio within the structure. The benzimidazole (bIm) to imidazole (Im) ratio in ZIF-62 can usually be denoted in the form of $Zn(Im)_{2-x}(bIm)_x$. The actual benzimidazole to imidazole ratio was measured using liquid state NMR as per Table 2.

	Table 2:	Measured	benzimidazole to	imidazole rat	io for a	different	variation	of ZIF-62	via NMR
--	----------	----------	------------------	---------------	----------	-----------	-----------	-----------	---------

Sample	Benzimidazole ratio (x)	Imidazole ratio (2-x)
ZIF-62-a	0.0268	1.9732
ZIF-62-b	0.0936	1.9064
ZIF-62-c	0.225	1.775

Adsorption was chosen as the means to introduce silver ions into the ZIF-62 structure as it is one of the more straightforward methods to incorporate ions into porous structures. While some MOF encapsulation methods involve a one-pot in situ encapsulation during the synthesis of MOF, this method was not incorporated in this paper as the impact of silver ions on the formation of ZIF-62 during the normal synthesis route has not been studied well and will add complications which fall outside the scope of this study - which is to

understand the role of silver ions towards the dynamics of ZIF-62 thermal behaviour. Methanol was also chosen as the adsorption medium, both to dissolve silver ions and to disperse ZIF-62 crystals, even though silver ions (from AgNO₃ for this study) are much more soluble in aqueous conditions. This is because ZIF-62 crystals are highly hydrophobic and will not disperse well in water. A less toxic alternative such as ethanol was not chosen due to the possibility of the formation of an explosive byproduct when reacted with AgNO₃, such as the highly explosive silver fulminate^[28]. The as-synthesized ZIF-62 particles were activated overnight before silver adsorption to ensure that the pores were effectively vacant to maximize the silver adsorption efficiency. The morphology of the crystal between pure and silver-loaded ZIF-62 glass at different benzimidazole - imidazole ratio as seen in Figure 2 also shows that there was no clear morphological change in the shape of the resulting crystals.



Figure 2: SEM images showing the crystal ZIF-62 morphologies of a)ZIF-62-a, b)ZIF-62-b, c)ZIF-62-c, d)AgZIF-62-a, e)AgZIF-62-b, and f)AgZIF-62-c. Black scale bar represents 1µm.

The presence of silver ions within the structure was confirmed using SEM-EDS onto the resulting particles, as shown in Figure S 1. The peaks at around 1.1 keV, 8.6 keV and 9.5 keV show the presence of zinc, which is the metal node for the ZIF-62 framework. The two peaks around 3.0 keV and 3.1 keV show the presence of silver within the particles. The peak at around 1.8 keV represents silicon as the particles were dispersed onto a silicon wafer. This shows that zinc and silver are both present within the ZIF-62 structure indicating that silver has been successfully introduced into the structure.

Table 3: Measurement of Silver to Zinc ratio in silver-doped ZIF-62.

Sample	Ag:Zn ratio during adsorption	Ag:Zn ratio of resulting particles measured by ICP
AgZIF-62-a	0.507	0.523
AgZIF-62-b	0.516	0.541
AgZIF-62-c	0.532	0.569

ICP-OES was also used to further confirm the presence of silver ions in the structure and to measure the silver to zinc ratio, as can be seen in Table 3. The ratio of silver to zinc ions was shown to be around 0.5:1, which is very similar to the zinc to silver ratio during the adsorption process. Although the ratio calculated via ICP is slightly higher than the calculated ratio during adsorption, the difference is reasonably small and may have arisen from systematic and random errors throughout the experimental synthesis process. This





Figure 3: XRD patterns of pure ZIF-62 and silver-doped ZIF-62 crystals

A further probe into the structure of the resulting Ag-doped ZIF-62 was performed to understand the effect of silver adsorption onto the ZIF-62 structure. From the XRD results in Figure 3, it was found that there was no significant difference between synthesized ZIF-62 particles with the Ag-doped ZIF-62 particles, with the exception of the lower bIm ratio (ZIF-62-a). For the Ag-ZIF-62 at this lower bIm ratio, some small new peaks were seen, which may indicate the introduction of slight structural change, though the bulk ZIF-62 peaks are still present. This may also indicate that the silver interaction during adsorption towards the overall crystal structure of the ZIF-62 is dependent on the benzimidazole amount within the structure.

3.2. AgZIF-62 thermal and melting behaviour

The thermal decomposition behaviour of materials is an important property to be studied for glass-related research. This is because a number of ZIFs and MOFs such as ZIF-8 and ZIF-7 have a much higher melting point as compared to their decomposition point.^[29] This leads to the material not being able to melt before being decomposed. Thus, it is important to measure the thermal decomposition of AgZIF-62 variants to ensure that the decomposition temperature lies above the typical ZIF-62 melting temperature to ensure minimal decomposition from occurring during melting.



Figure 4: TGA analysis on AgZIF-62 variants in a) air and b) N₂ flow

Thermogravimetric analysis (TGA) was performed on the AgZIF-62 variants and compared with the assynthesised ZIF-62-a, as can be seen in Figure 4. The decomposition temperature of AgZIF-62 variants is much lower than ZIF-62-a when subjected to air, whereby the AgZIF-62 variants start to decompose at around 400°C as opposed to ZIF-62-a, which only starts to decompose at around 600 °C. However, when subjected to high temperature under N₂ flow, the decomposition of AgZIF-62 variants is almost similar to ZIF-62-a and does not significantly decompose below 500 °C. As the melting of ZIF-62 is usually performed under inert gas conditions, this TGA analysis shows that the AgZIF-62 variants can be treated with temperatures up to 500 °C without triggering significant decomposition. We then continue to check the thermal and structural behaviour of AgZIF-62 variants subjected to temperature to see if there are any observational changes towards its structural melting dynamics.



Figure 5: XRD on the thermal structural dynamics of a)ZIF-62-a and silver-doped ZIF-62 structures b)AgZIF-62-a, c)AgZIF-62-b, and d)AgZIF-62-c. Ag peak marked with asterisk (*), and ZIF-zni peak marked with hash (#).

A dynamic study of the thermal effects of Ag-doped ZIF-62 crystals was performed using in-situ thermal XRD in Figure 5 to further understand the structural changes in Ag-doped ZIF-62. For a lower bIm ratio, Ag nanoparticles start to form at a temperature of between 150 °C to 200°C. It is also interesting to note that ZIF-zni was formed for a lower bIm ratio and at a much lower temperature of below 200 °C than that previously reported for ZIF-4 and ZIF-62 via recrystallization ^[30,31]. ZIF-zni is a dense form of the imidazolate (Im) based ZIF and the presence of benzimidazolate (bIm) ligand usually prevents its formation due to the bulkier ligands preventing the complete collapse of the frameworks. The temperature of ZIF-zni formation here is close to the AgNO₃ melting point, which may indicate that the AgNO₃ molecules were mobilized at this temperature and started to interact with bIm in the structure. This caused the rearrangement of imidazole parts to form a ZIF-zni structure. However, at a higher bIm ratio, ZIF-zni formation was not observed, and the glass was able to be melted fully and become fully amorphous with Ag nanoparticle present. This shows that the Ag in the structure may have interacted with bIm in the structure during heating, leading to these observable changes. As the formation of ZIF-zni is seen in both AgZIF-62-a and AgZIF-62-b, future analysis will be only focused on AgZIF-62-a and AgZIF-62-c to compare and understand the interactions and functionality of ZIF-zni-forming and glass-forming AgZIF-62.



Figure 6: DSC heat flow analysis of pure and Silver doped ZIF-62 a)Initial upscan, and b) the second upscan. Small arrow indicating the melting peak (T_m) for the initial upscan and glass transition peak (T_g) for the second upscan. Highlighted region in a) indicates a possible region for Ag nanoparticle formation.

A DSC analysis (Figure 6) was used to further probe the behaviour of these particles. For the lower bIm ratio samples, there were additional peaks at temperatures ca. 179 °C and 238°C, which may indicate the interaction of Ag within the structure, leading to the formation of ZIF-zni. The dip at around 200 °C to 330 °C in Figure 6a may indicate the formation of Ag nanoparticles, which coincides with the previous XRD structure. These peaks are also not present in the pure ZIF-62, which further indicates the role of silver in the observation of this behaviour. It is also interesting to note that the peaks seen at earlier temperatures for

the lower bIm ratio of silver-doped AgZIF-62 were not observed at the higher bIm ratio, which may indicate the absence of ZIF-zni formation. The melting peak can be seen for all cases in the first DSC upscan, with each respective ZIF-62 and AgZIF-62 of the same benzimidazole ratio having an almost similar melting point. The ZIF-62-a and AgZIF-62-a can be seen to have a melting peak, with T_m at around 374 °C and 373°C, respectively, while ZIF-62-c and AgZIF-62-c have a melting temperature, T_m at 413 °C and 419 °C respectively. A clearer melting peak can also be observed for the higher benzimidazole ratio ZIF-62, which may indicate clearer and better melting at a higher benzimidazole ratio. An exothermic peak was also seen at around 373 °C for AgZIF-62-a, after the melting peak ends, which may indicate the recrystallisation back into the dense crystalline ZIF-zni phase right after the melting process occurs. This peak forms immediately after the observed melting point, which may also indicate an accelerated process of the conversion of the remaining ZIF-62 to ZIF-zni during melting, most probably due to the better flowability of silver interacting with the whole ZIF-62-a structure.

This analysis shows that the Ag to bIm ratio is very important to control the melting of ZIF-62, either to form a complete melt or to form a recrystallized and more thermodynamically stable ZIF-zni. It is also important to note that the Ag compounds in all AgZIF-62 variants start to form Ag nanoparticles at temperatures between 150°C to 200 °C.



3.3. Ag interaction with Zn ZIF-62 crystal and glass framework

Figure 7: In situ THz IR analysis on ZIF-62 and AgZIF-62 at a temperature range between 30°C to 300 °C for sample a) ZIF-62-a, b) ZIF-62-c, c) AgZIF-62-a, d)AgZIF-62-c. For each plot, from bottom to top, the sample is heated from 30°C to 300°C, before cooling back down to 30°C.

In order to further understand the silver interactions within the structure of the ZIF-62 and its role in the ZIF-62 structural transformation, the samples were probed using THz IR (Figure 7). There were not many changes or differences between different benzimidazole ratios of ZIF-62 particles with no silver loading (ZIF-62-a and ZIF-62-c). Only three main clear peaks can be observed in both cases, a peak at around 280-330 cm⁻¹ which indicates the Zn-N stretching movements, a peak around 650-700 cm⁻¹, indicating in-plane and out-of-plane aromatic ring deformations, and a peak at around 750-800 cm⁻¹ indicating C-H bending. In the presence of silver, however, some peak intensifies with new peaks forming at different benzimidazole ratio. For the lower benzimidazole ratio (AgZIF-62-a), the peaks responsible for all three groups present in the normal ZIF-62-a start to intensify greatly above 200°C. A clear peak broadening for the peaks responsible for Zn-N stretching movements (280-330 cm⁻¹) and C-H bending can be seen, which may indicate additional interaction

at these sites. Additional stronger peaks also start to emerge between 100-200 $\rm cm^{-1}$, which represents the 4-membered and 6-membered ring collective motions, especially with the peak around 150-200 cm⁻¹. This may indicate the formation of ZIF-zni-related interactions as this formation was not observed for AgZIF-62-c. AgZIF-62-c also undergoes similar intensification for the three main peaks observed for the normal ZIF-62-c. Some intensifications of the peaks between 400-600 cm⁻¹ may also indicate a stronger interaction with the benzimidazole ligand within the structure, as data from the literature shows no significant peak between this wavenumber region for Zn and Imidazole precursors.^[26] This may also indicate that the silver is strongly interacting with the benzimidazole ligands at higher temperatures, which further explains the change of thermal dynamics between lower and higher benzimidazole ratio AgZIF-62 (AgZIF-62-a forming ZIF-zni while AgZIF-62-c was able to fully melt). The stronger interaction of Ag with the benzimidazole ligand may have promoted the stacking of imidazolate ligand at a lower temperature, thus promoting the formation of ZIF-zni in the environment with a lower benzimidazole amount. An additional peak can also be seen for AgZIF-62-c at a wavenumber range between 650-700 cm⁻¹ at 300°C, which may indicate an additional interaction within the aromatic ring, leading to an additional aromatic ring deformation peak. This additional peak is highly likely to be attributed to the interaction of Ag within the AgZIF-62-c structure as this additional peak was not seen in any of the normal ZIF-62 structures (ZIF-62-a and ZIF-62-c), and also from THz data reported in the literature on ZIF-62 variants.^[26] This proves that Ag is strongly interacting with the ligand structure within the AgZIF-62 crystals, but at different sites depending on the final formation results (ZIF-zni for AgZIF-62-a and fully melted ZIF for AgZIF-62-c).



Figure 8: FTIR analysis on ZIF-62 and AgZIF-62 particles

FTIR analysis was also performed on the pure ZIF-62-a and ZIF-62-c, as well as the silver-loaded AgZIF-62-a and AgZIF-62-c and their melted components (denoted as the mAgZIF-62) (Figure 8). The FTIR analysis shows peaks for the C-C in-plane and out of plane bending (600-700 cm⁻¹), C-H out of plane bending (700-1000 cm⁻¹), C-H in-plane bending (1100-1300 cm⁻¹), C-N stretching (1300-1370 cm⁻¹), and C=C stretching (1390-1650 cm⁻¹), which are all present in the ligands used for the formation of ZIF-62. However, no clear FTIR peak changes between the silver-loaded ZIF-62 (AgZIF-62-a and ZIF-62-c), its melted components (mAgZIF-62-a and mAgZIF-62-c), and pure ZIF-62 variants (ZIF-62-a and ZIF-62-c) can be seen. Thus, it is most likely that these interactions were not impacted by the presence of silver ions/molecules in the structure. An extra peak for mAgZIF-62-a that is present at 775cm⁻¹ could be attributed to the out-of-plane deformation of the imidazolate linker contributed by the presence of ZIF-zni. This extra peak was also present in FTIR data reported in the literature for the ZIF-zni phase.^[32]

An XPS analysis was also performed to understand the bonding occurring on the surface of the particles.

The wide scan XPS analysis, as can be seen in Figure S 2a, shows no obvious new peaks between all the crystalline and melted variations, except for the variations containing Ag. This is consistent with the sample and demonstrates that the Ag has been successfully embedded within the sample. The intensity of Ag peaks relative to other peaks was also diminished in the melted sample when compared to the crystalline sample, which indicated that the Ag species may be embedded within the ZIF-62 melted structures rather than being on the surface. This is because XPS is usually a surface-sensitive analysis, and with the same penetration power, the XPS will not penetrate as deeply into the denser melted/zni forms when compared to the crystalline forms, thus reading less Ag that is situated deeper within the structure. The summary of the XPS peaks found for different species can be found in Figure S 3. No clear changes can be seen for all other species except for Ag. A deeper look into the Ag peak shifts can also be seen in Figure S 2b, in which the non-melted AgZIF-62 variants indicate that the Ag may exist in an ionic AgNO₃ form, while the melted mAgZIF-62 variants show a possible oxidised Ag. This may be due to the exposure of Ag on the surface to air, thus resulting in the formation of AgO on its surface. As explained above, the lower penetration depth and surface sensitivity of XPS into the denser heat-treated ZIF-62 may be a reason for the lack of Ag nanoparticle peaks, as the Ag nanoparticle may be deeper embedded within the structure. Thus, the actual state of silver within the melted/zni particles should closely resemble the results seen in previously collected XRD data which shows the conversion of silver ions into silver nanoparticles only at higher temperatures (above 150° C).



Figure 9: ¹³C solid-state NMR on ZIF-62 and silver-loaded ZIF-62 a)crystals and b)glasses.

Solid State NMR has also been performed to help probe the interaction of the carbon atoms within the ZIF-62 structure in the presence of silver. The chemical shift at 125 ppm and 137 ppm could be attributed to the carbon atoms available in the imidazole ligands, while the additional peaks at 115 ppm, 120 ppm, 149 ppm and 160 ppm can be attributed to the carbon atoms present in the benzimidazole ligands. This can be clearly seen in both crystal and melted ¹³C solid-state NMR in Figure 9, at which the peaks responsible for the benzimidazole ligands are much more pronounced in higher benzimidazole ratio ZIF-62 variants. The ¹³C solid-state NMR do not show a clear difference between the detected C bonds, except for the case of mAgZIF-62-a, at which an additional peak appears around 123 ppm. This peak can be attributed to the presence of the ZIF-zni structure in the system of mAgZIF-62-a. This is as, according to literature, when ZIF-4 was melted into ZIF-zni, a new set of peaks appeared around the region between 127.8 ppm – 128.3 ppm, which is slightly higher than the other imidazole-related peak in ZIF-4 around 123.9 ppm – 125.8 ppm.^[33] As this peak exists very close to the peak responsible for carbon atoms in the imidazolate ligand, it indicates that the presence of Ag may have strongly interacted with the imidazolate ligand during melting/heating for the lower benzimidazole ratio ZIF-62-a).

A quick probe into the porosity behaviour of the synthesised ZIF-62 silver composites was also performed. CO₂ adsorption behaviour was studied as previous reports for ZIF-62 have stated that limited N₂ adsorption can be seen for ZIF-62 glasses due to their relatively small pore windows and cavities.^[21] From the CO_2 adsorption behaviour seen in Figure S 4, it can be seen that only a slight adsorption behaviour can be seen when silver was doped into the ZIF-62 glass, indicating that minimal pore size change occurred after silver adsorption. The slight increase of CO_2 adsorption for ZIF-62-a variation when silver was added may be due to the disruption of ultra-dense ZIF-zni structure by the silver composite, which formed additional pores allowing for some extra pore formation allowing for extra CO_2 adsorption. The slight decrease of CO_2 adsorption capacity in the ZIF-62-c variation upon the addition of silver composites may be due to the filling up of some pores in the amorphous ZIF-62 glassy structure by silver composite, leading to lower CO_2 adsorption.

3.4. Utilisation of Ag Zn-ZIF-62 for gas separation processes

In order to study the practical applicability of the synthesised Ag-doped glassy materials, its capability to selectively separate gases was tested. Silver in its different states, such as Ag ionic liquid, Ag salts, Ag nanoparticles and even AgO, have been shown to have the capability of selectively transporting different gas pairs such as CO_2/N_2 and olefin/paraffin.^[9,34–36] In this section, we attempt to demonstrate the accessibility of the silver nanoparticles embedded within the glassy matrix by studying the gas separation performance in a mixed matrix membrane set. 6FDA-DAM was chosen as the polymer matrix due to its good capabilities in separating CO_2/N_2 , as well as its relatively good selectivity for olefin/paraffin-based separation.^[37–39] The melted AgZIF-62 and ZIF-62 particles were dispersed in a 6FDA-DAM polymer solution before being cast and activated.

The membranes were characterised to understand their intrinsic properties. SEM and SEM-EDS were used to study the contact between the dispersed particles and the polymer matrix as can be seen in Figure S 5. As can be seen in Figure S 5a and d, the contact between the filler particles and the polymer matrix is considerably good. No clear void was observed between the AgZIF-62 fillers with the 6FDA-DAM polymer matrix. SEM-EDS showed the presence of the fillers embedded within the membrane, with reasonable particle dispersion and particle size of around 5-10µm. The silver atoms were also seen to be well dispersed within the regions at which Zn is present, indicating that the Ag is well embedded in the ZIF-62 glass/zni and does not leach into the main polymeric section of the membrane. This would allow any improvement to be mainly attributed to the filler rather than any leached silver ions in the 6FDA-DAM matrix.

An analysis using XRD has also shown the successful incorporation of different fillers at different loadings into the 6FDA-DAM matrix as can be seen in Figure S 6a, as the filler retains its characteristic peaks within the 6FDA-DAM matrix, with its intensity increasing with respect to its loading in the membrane. As can be seen in Figure S 6b, all the FTIR peaks present in pure 6FDA-DAM polymers over the range of 600 cm⁻¹ to 4000 cm⁻¹ were present in all of the membranes, indicating that there were no significant changes in the chemical bonds and structure of the polymer matrix were seen. However, in the range between 600 cm⁻¹ to 850 cm⁻¹, a few new peaks were seen in the MMMs. A peak between 610 cm⁻¹ to 615 cm⁻¹ was present only in AgZIF-62 variants of MMMs, which may indicate the interaction of Ag with the polymer matrix. This is as the lower region peaks are usually attributed to the interaction of metal nanoparticles/ions with an organic ligand (typically seen in MOFs). A peak at 665 cm⁻¹ was seen in all AgZIF-62 and ZIF-62 loaded MMMs, which comes from the ZIF-62 particles themselves. Two peaks at about 775cm⁻¹ and 835 cm⁻¹ were seen only in AgZIF-62-a loaded MMMs, which is also present in the AgZIF-62-a particles due to the presence of dense ZIF-zni phase.^[32]

A TGA analysis, as can be found in Figure S 6c, demonstrates the membrane decomposition in air at around 500 °C, which shows that the 6FDA-DAM polymer has a thermal decomposition behaviour similar to the previous TGA analysis of the filler particles. The 6FDA-DAM neat polymer has a remaining weight of about 2%, while the 10%, 20% and 30% loaded mAgZIF-62-a membranes all have a residual weight of 5%, 12% and 21%, respectively. The 20% mZIF-62-a membrane has a slightly lower remaining weight of 9.5% when compared to the Ag-loaded variation of similar loading, which is also consistent with the previous particle TGA analysis due to the absence of Ag nanoparticles in the resulting weight. This demonstrates that these membranes are relatively stable up to 500 °C and can be considered for higher temperature-based gas separation in the future.

1400 CO₂/N₂ Permeability (Barrer) 30 1200 CO₂/CH₄ lectivity Factor (SF 1000 CO₂ 20 800 N_2 600 CH_4 80 10 40 10% magth sta 0 20% magth s2.8 30% magth sta Pure of DA. DAM Membrane b 200 Selectivity Factor (SF) Permeability (Barrer) Ethylene/Ethane 150 Ethane 100· Ethylene 50· Nolo magth set a 20% magth st.a 30% magth 62.8 PureoFDADAM 0 Membrane С 250 Permeability (Barrer) 10 Selectivity Factor (SF) Propylene/Propane 200 Propane Propylene 150 40 20 30% magtr 52.8 not not not the state Pure of DA.DAM 20% magth 52.3 0 Membrane

Figure 10: Gas separation performance for AgZIF-62-a at different composite loading for a) CO_2 , N_2 , and CH_4 based separation, b)ethylene/ethane based separation, and c) propylene/propane-based separation

а

The activated ZIF-62@6FDA-DAM membrane was then tested for different gases, including CO₂, N₂, CH₄, ethane, ethylene, propane, and propylene. As mentioned in earlier sections, silver, both in the elemental and ionic state, has been shown in the literature to improve gas separation performance. In the case of CO_2/N_2 and CO_2/CH_4 separation, silver nanoparticles embedded in Pebax mixed matrix membrane have been shown to consistently help towards CO_2 permeance improvements and selectivity.^[40] Similar behaviour can be seen in this experiment, too, as per Figure 10 and Figure 11, whereby the addition of mAgZIF-62 continually increases the permeability of CO_2 and increases CO_2/N_2 selectivity until a maximum loading of 20%. At 20% loading, a maximum CO_2/N_2 selectivity of 27.1±1.7 and CO₂ permeability of 864.3±4.4 barrer were achieved, which is significantly higher than pure 6FDA-DAM with a selectivity of 17±0.9 and CO₂ permeability of 642.4±4.8 barrer. This corresponds to a selectivity increase of 60% and permeability of 34.5% as compared to a pure 6FDA-DAM membrane. However, an increase to 30% loading starts to lower the selectivity significantly despite a continual increase in permeability, which may be caused by aggregation of mAgZIF-62 particles in the membrane at higher loading and the possible formation of interfacial voids. However, no clear increase in CO_2/CH_4 selectivity can be seen, which may be caused by proportionally similar permeance improvements for both CH₄ and CO₂ with increase loading.

Other than CO₂-targeted separation, silver nanoparticles have also been demonstrated to help with light hydrocarbon separation. Although silver ions have been shown to result in good selectivity for olefin/paraffinbased separation, they are unstable over an extended period of time.^[41] The utilisation of silver nanoparticles has been shown in the literature to be more stable over longer periods, with good selectivity of olefin over paraffin.^[10,42] This behaviour is also consistent with our data, as can be seen in Figure 10 and Figure 11. Like previous CO₂ – targeted separation, the selectivity for ethylene/ethane and propylene/propane both increases until mAgZIF-62 loading of 20% before dropping, with a maximum selectivity of 3.57 and 10.21, respectively. This corresponds to ethylene/ethane and propylene/propane selectivity increases of 32.8% and 17.2% when compared to the pure 6FDA-DAM membrane. The permeability of both ethylene and propylene also increases by 29.3% and 18.4% to a value of 44.4 and 31.1 barrer respectively at 20% loading. а 30 1400 Separation Factor (SF) CO_2/N_2 Permeability (Barrer) 1200 CO₂/CH₄ 20 1000 CO_2 800 N_2 600 CH_4 10 80 40 0 20% magtheste 20% magth st.2 20% matra2.2 Pure of DA DAM Membrane b 200· Selectivity Factor (SF) Ethylene/Ethane Permeability (Barrer) 3 150 Ethane Ethylene 100 50· 20% magth st.s 0 20% maglifield Pure of DA. DAM 20% ndf sta n Membrane С 250 Permeability (Barrer) 200 Selectivity Factor (SF) Propylene/Propane Propane 150 Propylene 100 50 20 10 20% magtreste 0 Pure of DA.DAM 20% million 7 20% magtraza

Membrane

Figure 11: Gas separation performance for AgZIF-62 at different composite states (ZIF-zni vs ZIF glass) for a)CO₂, N₂ and CH₄ based separation, b)ethylene/ethane-based separation, and c)propylene/propane-based

separation.

Further analysis of the effect of Ag-loaded thermally treated ZIF type (ZIF-zni and amorphous ZIF glass) on gas separation performance was also studied, as can be seen in Figure 11. The performance of the presence of Ag nanoparticles in ZIF-62 glass was also compared to pure ZIF-62 glass. The selectivity of all gas pairs studied shows no significant increase when the pure 6FDA-DAM polymer was loaded with mZIF-62-a, despite an increase in gas permeability. This may be attributed to possible void formation between mZIF-62-a towards its surrounding 6FDA-DAM polymer matrix. The gas performance of all gas pairs for 6FDA-DAM mixed membrane systems loaded with silver nanoparticles (mAgZIF-62-a and mAgZIF-62-c) consistently show improvements in both selectivity and permeability no matter the ZIF types (ZIF-zni or amorphous ZIF glass). This demonstrates the accessibility of silver in thermally treated ZIF-62 irrespective of phase, which is important to ensure that the silver can be accessed for other applications too. The accessibility of silver for both ZIF-zni and amorphous ZIF glass also demonstrates that silver nanoparticle immobilisation/functionalisation can be applied for both ZIF material types to suit their respective future applications.



Figure 12: Demonstration of reverse hydrocarbon selectivity for olefin species with the presence of silver nanoparticles.

Another observation was that with similar carbon content, alkene/olefin always has a much higher permeability than its alkane/paraffin counterpart. This can be explained by the π -Ag complexation allowing the alkene bond (C=C) to overlap with the 5s and 4d orbitals present in Ag.^[10,42,43]However, as can be seen in Figure 12, the permeability trend with increasing carbon amount differs with the presence of silver nanoparticles. An expectation of the permeability trend of molecules with very similar physical and chemical properties is that it should follow the trend of smaller particles having higher permeability than their bigger counterpart. This trend can be seen for paraffin molecules despite loading type and amount (CH₄ > C₂H₆ > C₃H₈). However, in the presence of silver, the permeability of alkene increases with an increase in molecular size (C₃H₆ > C₂H₄), while the reverse of that behaviour was seen in membranes and mixed matrix membranes with no silver composites ($C_3H_6 < C_2H_4$). Although this behaviour has been shown in terms of adsorption with the presence of silver ions, to our knowledge, it has never been demonstrated for silver nanoparticles and in terms of membrane permeability.^[43] The adsorption capacity data of olefins for Ag⁺ decorated particles from literature also follows the order of $C_3 > C_2 > C_1$, which was explained to be due to the decreasing sequence of the light hydrocarbon's critical temperatures (T_c). However, this behaviour was also reported to be similar for paraffins, which is not the case for our silver loaded mixed matrix membranes. Thus, this may demonstrate a facilitated diffusion-based transport in our silver loaded membrane system, at which the silver complexation helps improve the diffusion of olefin over paraffin without strongly bonding to the olefin molecules.

A possible explanation for the observation of this behaviour may come from the transport mechanism of the olefin itself. As each of the propylene and ethylene has only one alkene bond (C=C), and the system has a constant amount of π bond site available on the Ag surface; theoretically, the molar amount of π -Ag complexation that is able to be achieved by both propylene and ethylene should be relatively similar. The π -Ag complexation also occurs in the same electron orbital for both propylene and ethylene, and thus, the complexation energy (for adsorption and desorption) should be relatively close. Propylene has a higher molecular weight and consequentially higher gas density when compared to ethylene. Thus, when measured on a weight or volume basis, a larger amount of propylene will be adsorbed than ethylene (when considering that a similar molar amount was adsorbed for both species). This higher weight/volume amount of propylene-Ag complex formed can then be translated to a higher facilitated transport rate by weight/volume when compared to ethylene, which is consistent with the result seen in Figure 12. However, more experiments will have to be performed to confirm this theory as many other factors also come into play, such as the effect of propylene vs ethylene sizes which may reduce the molar adsorption density on the Ag nanoparticle surface, and possible differences of (C=C) π -Ag complexation energies due to the presence of extra alkyl chain in propylene when compared to ethylene.

4. Data Availability and Reproducibility Statement

All plotted numerical data (XRD, TGA, DSC, THz-IR, FTIR, 13C SSNMR, Gas permeation data, SEM EDS, XPS, and CO_2 adsorption data) as shown in Figures 3 – 12, and Figures S1, S2, S4 and S6 can be found in the Supplementary Information. All data has been either calibrated, or corrected to calibration where required, according to widely practiced data analysis for specific techniques, such as carbon peak calibration for XPS data, XRD sample calibration, and background data removal for spectroscopic measurements. Where error bars are presented, repeat of the analysis measurements were made and the mean value was used, with the standard deviation reported as the error range/bar.

5. Conclusion

The presence of silver as guest molecules has been shown to provide a significant impact on the melting behaviour of ZIF-62. The benzimidazole ratio within the ZIF-62 structure was shown to directly impact the resulting dynamic thermal behaviour. At a lower benzimidazole ratio, the ZIF-62 tends to form ZIF-zni at a much lower temperature, while at a higher benzimidazole ratio, ZIF-62 was able to melt fully into an amorphous glass without any resulting ZIF-zni. An additional look into the Ag interaction using THz-IR shows that the Ag may have significant interaction with the ligands, especially the benzimidazole ligand, which may explain the difference in behaviour at a lower benzimidazole ratio. This chemical interaction analysis, coupled with solid-state NMR, also indicates that the Ag may have interacted at different sites within the ZIF-62 structure based on the initial benzimidazole ratio amount in the structure. The resulting Ag-doped thermally treated ZIF-62, both in ZIF-zni and amorphous glass form, forms accessible Ag nanoparticles within the thermally treated ZIF-62 framework. This was shown by good gas separation performance when the materials were applied as a gas separation membrane in a mixed-matrix membrane setting. The gas separation analysis also shows Ag nanoparticles' capability to reverse the alkene selectivity as its size increase ($C_3H_6 > C_2H_4$), which has never been demonstrated before in a membrane.

The success in the formation of functional thermally treated ZIF-62 in both ZIF-zni and amorphous ZIF-62

when doped with silver demonstrates the suitability of this material to be composited with other functional metallic molecules. The ease of processibility of these meltable ZIFs also opens its usage in the form of a thin film for a variety of real-life applications such as for gas separation or film-based catalysis and functional films (eg. antimicrobial glass).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

J.H would like to acknowledge the financial support from the Australian Research Council (FT210100589), the Foundation Research Excellence Award of the University of Queensland, and UQ Dow Centre. This research was undertaken on the THz/Far-IR beamline at the Australian Synchrotron, part of ANSTO. This research was supported by the AINSE Ltd. Early Career Researcher Grant (ECRG).

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

References

[1] M. A. Islam, M. V. Jacob, E. Antunes, Journal of Environmental Management 2021, 281, 111918.

[2] A. Syafiuddin, Salmiati, M. R. Salim, A. Beng Hong Kueh, T. Hadibarata, H. Nur, *Journal of the Chinese Chemical Society***2017**, *64*, 732.

[3] O. Gherasim, R. A. Puiu, A. C. Bîrcă, A.-C. Burduşel, A. M. Grumezescu, Nanomaterials (Basel) 2020, 10, 2318.

[4] O. Nashed, S. M. Youssouf, A. M. Shariff, S. Sufian, B. Lal, K. M. Sabil, IOP Conference Series Materials Science and Engineering (Online) 2018, 458, 6.

[5] M. Li, W. Wu, H. Jiang, ChemCatChem 2020, 12, 5034.

[6] Y.-C. Wu, Y.-T. Xiao, Y.-Z. Yang, R.-J. Song, J.-H. Li, ChemCatChem 2020, 12, 5312.

[7] K. Sekine, T. Yamada, Chem. Soc. Rev. 2016, 45, 4524.

[8] L. Cheng, G. Liu, W. Jin, Discover Chemical Engineering2020, 1, 1.

[9] M. Kim, S. W. Kang, Scientific Reports 2019, 9, 4266.

[10] S. W. Kang, D. H. Lee, J. H. Park, K. Char, J. H. Kim, J. Won, Y. S. Kang, *Journal of Membrane Science* **2008**, *322*, 281.

[11] Y. Xiao, M. L. Chng, T.-S. Chung, M. Toriida, S. Tamai, H. Chen, Y. C. J. Jean, *Carbon* **2010**, *48*, 408.

[12] S. Kasahara, E. Kamio, R. Minami, H. Matsuyama, Journal of Membrane Science 2013, 431, 121.

[13] P. Zhuang, P. Zhang, K. Li, B. Kumari, D. Li, X. Mei, Molecules 2019, 24, 2442.

- [14] Q.-L. Zhu, Q. Xu, Chem **2016**, 1, 220.
- [15] A. Dhakshinamoorthy, H. Garcia, Chem. Soc. Rev.2012, 41, 5262.
- [16] D. Farrusseng, A. Tuel, New J. Chem. 2016, 40, 3933.
- [17] J. Abdi, Colloids and Surfaces A: Physicochemical and Engineering Aspects 2020, 604, 125330.
- [18] S. Ban, K. Long, J. Xie, H. Sun, H. Zhou, Ind. Eng. Chem. Res. 2018, 57, 2956.
- [19] Z. Rahmati, J. Abdi, M. Vossoughi, I. Alemzadeh, Environmental Research 2020, 188, 109555.

[20] Introduction to Metal–Organic Frameworks, Chem. Rev.2012, 112, 673.

[21] A. Qiao, T. D. Bennett, H. Tao, A. Krajnc, G. Mali, C. M. Doherty, A. W. Thornton, J. C. Mauro, G. N. Greaves, Y. Yue, *Sci Adv* **2018**, *4*, eaao6827.

[22] C. Zhou, L. Longley, A. Krajnc, G. J. Smales, A. Qiao, I. Erucar, C. M. Doherty, A. W. Thornton, A. J. Hill, C. W. Ashling, O. T. Qazvini, S. J. Lee, P. A. Chater, N. J. Terrill, A. J. Smith, Y. Yue, G. Mali, D. A. Keen, S. G. Telfer, T. D. Bennett, *Nature Communications* **2018**, *9*, 5042.

[23] R. Lin, Y. Yao, M. Y. B. Zulkifli, X. Li, S. Gao, W. Huang, S. Smart, M. Lyu, L. Wang, V. Chen, J. Hou, Nanoscale 2022, 14, 2221.

[24] J. Hou, C. W. Ashling, S. M. Collins, A. Krajnc, C. Zhou, L. Longley, D. N. Johnstone, P. A. Chater, S. Li, M.-V. Coulet, P. L. Llewellyn, F.-X. Coudert, D. A. Keen, P. A. Midgley, G. Mali, V. Chen, T. D. Bennett, *Nature Communications* **2019**, *10*, 2580.

[25] Hou Jingwei, Chen Peng, Shukla Atul, Krajnc Andraž, Wang Tiesheng, Li Xuemei, Doasa Rana, Tizei Luiz H. G., Chan Bun, Johnstone Duncan N., Lin Rijia, Schülli Tobias U., Martens Isaac, Appadoo Dominique, Ari Mark S', Wang Zhiliang, Wei Tong, Lo Shih-Chun, Lu Mingyuan, Li Shichun, Namdas Ebinazar B., Mali Gregor, Cheetham Anthony K., Collins Sean M., Chen Vicki, Wang Lianzhou, Bennett Thomas D., Science 2021, 374, 621.

[26] J. Hou, M. L. Ríos Gómez, A. Krajnc, A. McCaul, S. Li, A. M. Bumstead, A. F. Sapnik, Z. Deng, R. Lin, P. A. Chater, D. S. Keeble, D. A. Keen, D. Appadoo, B. Chan, V. Chen, G. Mali, T. D. Bennett, J. Am. Chem. Soc. 2020, 142, 3880.

[27] L. Frentzel-Beyme, M. Kloß, P. Kolodzeiski, R. Pallach, S. Henke, J. Am. Chem. Soc. 2019, 141, 12362.

[28] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, J. Chem. Educ. 1986, 63, 1016.

[29] L. Longley, S. M. Collins, S. Li, G. J. Smales, I. Erucar, A. Qiao, J. Hou, Doherty Cara M., A. W. Thornton, A. J. Hill, X. Yu, N. J. Terrill, A. J. Smith, S. M. Cohen, P. A. Midgley, D. A. Keen, S. G. Telfer, T. D. Bennett, *Chem. Sci.* **2019**, *10*, 3592.

[30] T. D. Bennett, D. A. Keen, J.-C. Tan, E. R. Barney, A. L. Goodwin, A. K. Cheetham, Angewandte Chemie International Edition2011, 50, 3067.

[31] V. Nozari, C. Calahoo, L. Longley, T. D. Bennett, L. Wondraczek, J. Chem. Phys. 2020, 153, 204501.

[32] D. Tocco, C. Carucci, D. Todde, K. Shortall, F. Otero, E. Sanjust, E. Magner, A. Salis, *Colloids and Surfaces B: Biointerfaces* **2021**, 208, 112147.

[33] E. F. Baxter, T. D. Bennett, C. Mellot-Draznieks, C. Gervais, F. Blanc, A. K. Cheetham, *Phys. Chem. Chem. Phys.* **2015** ,17 , 25191.

[34] D. Ji, Y. S. Kang, S. W. Kang, Scientific Reports 2015, 5, 16362.

[35] X. Wu, X. Li, L. Xu, W. He, Z. Zhou, W. Liu, F. Zhang, Z. Ren, Journal of Chemical Technology & Biotechnology **2021**, n/a.

[36] B. Jun Kim, S. Wook Kang, Journal of Industrial and Engineering Chemistry 2022, 106, 311.

[37] R. L. Burns, W. J. Koros, Journal of Membrane Science 2003, 211, 299.

[38] M. Rungta, C. Zhang, W. J. Koros, L. Xu, AIChE Journal2013, 59, 3475.

[39] L. M. Robeson, Journal of Membrane Science 2008, 320, 390.

[40] T. Zhou, L. Luo, S. Hu, S. Wang, R. Zhang, H. Wu, Z. Jiang, B. Wang, J. Yang, Journal of Membrane Science 2015, 489, 1. [41] Z. D. Pozun, K. Tran, A. Shi, R. H. Smith, G. Henkelman, J. Phys. Chem. C 2011, 115, 1811.

[42] S. W. Kang, K. Char, Y. S. Kang, Chem. Mater.2008, 20, 1308.

[43] J. Yan, B. Zhang, L. Guo, Z. Wang, J. Phys. Chem. C2019, 123, 575.

Supporting Information

Regulating thermal dynamics and gas transport of MOF glass through silver composites

Muhammad Yazid Bin Zulkifli, Ruiqi Chen, Rijia Lin, Yuqi Yao, Milton Chai, Dominique Appadoo, Wupeng Wang, John Zhu, Kang Liang, Vicki Chen and Jingwei Hou

The numerical data for the plots in Figures 3 - 12, and Figures S1, S2, S4 and S6 are provided in a compressed ZIP file called "Data for publication" in the Supplementary Information. The numerical data are in an excel spreadsheet format, and the files included are:

- Figure 3, Figure S6a XRD at room temperature (particles and membrane)
- Figure 4, Figure S6c TGA Data (Air and N2, particle and membrane)
- Figure 5 In-situ thermal XRD data
- Figure 6 DSC plot data
- Figure 7 THz-IR data
- Figure 8, Figure S6b FTIR data (particles and membrane)
- Figure 9 Solid State NMR 13C data
- Figure 10, Figure 11, Figure 12 Membrane gas permeation performance data
- Figure S1 SEM point EDS plot data
- Figure S2 XPS data
- Figure S4 CO2 adsorption data from Micromeritrics Tristar



Figure S 1: SEM-EDS analysis of Silver doped ZIF-62 crystal and glass. The X mark indicates the location of point EDS. The scale bar indicates a length of 1μ m.



Figure S 2: a) Wide scan XPS analysis for all ZIF-62 and melted ZIF-62 composites. Ag3d peaks region were marked with the star symbol for samples containing Ag. b) Focused XPS scan on Ag3d peak region for samples containing Ag.

Sample	XPS Binding Energy Peak Values (eV)	XPS Binding Energy Peak Values (eV)	XPS Bind
	C1s	N1s	O1s
ZIF-62-a	284.8	398.9	531.5
ZIF-62-c	284.8	398.8	531.4
mZIF-62-a	284.8	398.7	531.4
mZIF-62-c	284.8	399.1	531.6
AgZIF-62-a	284.8	398.9	531.9
AgZIF-62-c	284.8	398.9	531.7

Sample	XPS Binding Energy Peak Values (eV)	XPS Binding Energy Peak Values (eV)	XPS Bindi
mAgZIF-62-a	284.8	398.7	531.3
mAgZIF-62-c	284.8	399	531.5

Figure S 3: XPS peaks calculated by peak fitting from collected peaks (C1s binding energy (eV) calibrated to 284.8).



Figure S 4: CO₂adsorption data of different melted ZIF-62 and ZIF-62 composites



Figure S 5: SEM and EDS images of 20% mAgZIF-62-a @ 6FDA-DAM on the top layer (a, b, and c), and 20% mAgZIF-62-c @ 6FDA-DAM on the bottom layer (d, e, and f). a) and d) are SEM secondary electron images. b) and e) are Zn EDS scans. c) and f) are Ag EDS scans.



Figure S 6: a)XRD analysis of melted mZIF-62 and mAgZIF-62 loaded into 6FDA-DAM at different loading, b)FTIR analysis of the loaded membranes, and c) TGA analysis of filler loaded 6FDA-DAM.

а