



Valsartan metal complexes as capture and reversible storage media for methane

Liqaa H. Najim¹ · Gamal A. El-Hiti² · Dina S. Ahmed¹ · Alaa Mohammed³ · Mohammad Hayal Alotaibi⁴ · Emad Yousif³

Received: 11 May 2020 / Accepted: 29 May 2020 / Published online: 6 June 2020
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Abstract

Three valsartan metal (tin, nickel, and magnesium) complexes were examined as capture and storage media for methane under high temperature (323 K) and pressure (50 bar) conditions. The surface morphology of the complexes were examined using Field emission scanning electron microscopy and displayed porous structures comprising particles of different shapes and sizes. The narrow pore-size distribution of metal complexes makes them suitable materials for methane capture. The methane adsorption–desorption isotherms of the metal complexes were reversible. The tin(IV) and nickel(II) complexes exhibited type-III physisorption isotherms, while the magnesium(II) complex displayed a type-IV physisorption isotherm. Both types of isotherms are typical for mesoporous materials. The magnesium(II) complex was more efficient compared with the tin(IV) and nickel(II) complexes. It exhibited a remarkable methane uptake capacity of 71.68 cm³/g under optimized conditions.

Keywords Methane · Storage media · Adsorption capacity · Valsartan metal complexes · Methane · Adsorption–desorption isotherms

Introduction

Natural gas is an alternative energy source to petroleum and coal. Commercial natural gas contains methane (CH₄; 95%), ethane (3.2%), and other gas impurities (1.7%) [1]. Gas impurities have a negative effect on the CH₄ storage capacities of adsorbent materials. Compared to petroleum,

the combustion of natural gas produces intense heat and light energy, as well as low carbon emissions [2–4]. Two techniques are commonly utilized to measure the quantity of CH₄ adsorbed onto porous materials [5]. The first technique involves the measurement of weight changes in the adsorbent at various CH₄ pressures by gravimetry [5]. The second technique involves employing a volumetric method to record the changes in the volume of adsorbed CH₄ in porous materials under standard conditions [5]. The experiments conducted at high pressures are more complicated and generate errors compared to those performed at low pressures [6, 7]. The experimental errors can be effectively reduced by measuring the background CH₄ adsorption isotherms and subtracting the values from the actual experimental readings [8]. In addition, pure CH₄ should be used, since trace amounts of water and hydrocarbons can induce a large error in the adsorption measurements [8]. CH₄ capture is a slow process, because CH₄ is non-polar and its interaction with adsorbents is weak [9].

CH₄ is responsible for approximately 30% of global warming and climate change [9]. Consequently, various porous materials have been designed and tested as capture media for CH₄ [10–13]. The most common materials used for the adsorption of CH₄ are graphite, zeolites,

✉ Gamal A. El-Hiti
gelhiti@ksu.edu.sa

✉ Mohammad Hayal Alotaibi
mhhalotaibi@kacst.edu.sa

✉ Emad Yousif
emadayousif@gmail.com

¹ Department of Medical Instrumentation Engineering, Al-Mansour University College, Baghdad, Iraq

² Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, P.O. Box 10219, Riyadh 11433, Saudi Arabia

³ Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq

⁴ National Center for Petrochemicals Technology, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia

silica, metal–organic frameworks (MOFs), porous-organic polymers, polyphosphates, and activated carbons [14–16]. However, limited success has been achieved thus far. MOFs are potential effective materials for gas capture, and their pores can be tuned to improve their adsorption capacities [14]. In addition, the functional groups within MOFs control their gas-uptake capacity [15]. The adsorption and capture of gases over using new materials as storage media have received attention [17–21].

Recently, we reported the synthesis of various materials and their efficient applications as storage media for carbon dioxide [22–26] as a continuation of our general interest in designing and new materials for various applications [27–31]. For example, valsartan metal complexes were found to be very effective as carbon dioxide (CO₂) storage media [26]. Therefore, it is of interest to determine if these materials can be used to store CH₄. Valsartan is a stable, safe, and non-toxic medication that contains heterocyclic and aryl moieties [32, 33].

Materials and methods

Valsartan metal complexes **1–3** (Fig. 1) were synthesized, as previously reported, via the reaction of valsartan and metal chlorides in a 2:1 molar ratio [26]. Field emission scanning electron microscopy (FESEM) was conducted using a TESCAN MIRA3 LMU system. The CH₄ uptake was measured on an H-sorb 2600 high-pressure volumetric adsorption analyzer. The samples of complexes **1–3** (1.0 g) were degassed for 1 h at 50 °C in a vacuum oven to completely remove any trace of moisture or solvent trapped within the pores. Each CH₄ uptake experiment was repeated several times for pressure optimization.

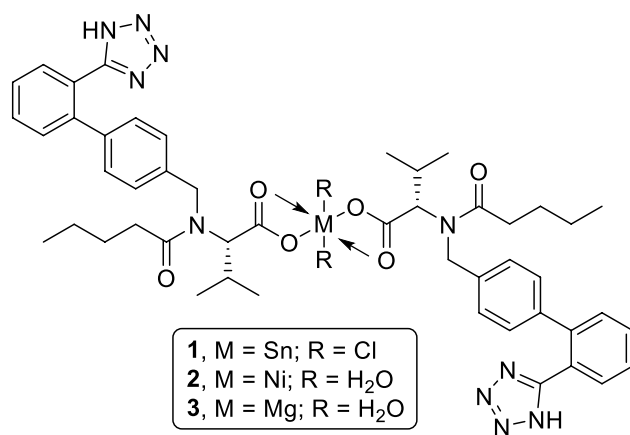


Fig. 1 Valsartan metal complexes **1–3**

Results and discussion

The surface morphologies of complexes **1–3** (Fig. 1) were examined by FESEM. The FESEM images of **1–3** (Fig. 2) show porous structures that are homogeneous and rough with irregular surfaces composed of loose agglomerates of tiny particles. In addition, the particles are of different shapes and contain crystals, and a number of cracks. The porosity of complexes was analyzed in terms of particles size. The pore volumes and diameters of complexes **1–3** were in the range of 0.011–0.108 cm³/g and 6.50–12.47 nm, respectively, and their surface areas were small (16.6, 22.8, and 16.0 m²/g, respectively) [26]. The narrow pore-size distribution of complexes **1–3** makes them suitable materials for CH₄ capture.

The CH₄ adsorption–desorption isotherms of complexes **1–3**, recorded at 323 K and 50 bar, are shown in Figs. 3, 4 and 5. The selected temperature and pressure were based on the performance of these complexes as storage media for CO₂ [26]. There was no overlap between the adsorption–desorption isotherms of **1** and **2**. However, the branches for the adsorption and desorption of **3** overlapped completely. Complexes **1** and **2** showed type-III physisorption isotherms (Figs. 3 and 4, respectively), while complex **3** exhibited a type-IV physisorption isotherm (Fig. 5). Both types of isotherms are typical for mesoporous materials, in which multilayers are not formed. The isotherms showed that the interaction between CH₄ and the complexes (**1–3**) was relatively weak, and the gas mostly adsorbed at the active site of each complex [34, 35]. It was evident that the CH₄ adsorption–desorption isotherms are roughly reversible.

The CH₄ uptake capacities of complexes **1–3** increased sharply with increase in pressure and were found maximum at 50 bar. Saturation was not achieved in the experiments attempted, which clearly indicated that a high adsorption capacity can be achieved at high pressures. The Mg(II) complex (**3**) was the most favorable, desirable, and practical medium for CH₄ capture. This complex could adsorb CH₄ even with exposure to the atmosphere and could release the gas from its cavities on releasing pressure. The CH₄ uptake capacities of complexes **1–3** at 323 K and 50 bar are presented in Table 1.

Complex **3** showed the highest CH₄ adsorption capacity (71.68 cm³/g; 5.15 wt%) compared to complexes **1** and **2** (10.47 and 3.76 cm³/g, respectively). In contrast, CO₂ adsorption of **1–3** under similar condition was mainly dependent on their surface area and the interaction with the gas [26]. Complex **2** which has the highest surface area ($S_{\text{BET}} = 22.75$ m²/g) was the most effective medium for CO₂ storage (6.8 wt%) compared to complexes **1** (16.63 m²/g; 5.4 wt%), and **2** (15.96 m²/g; 4.8 wt%)

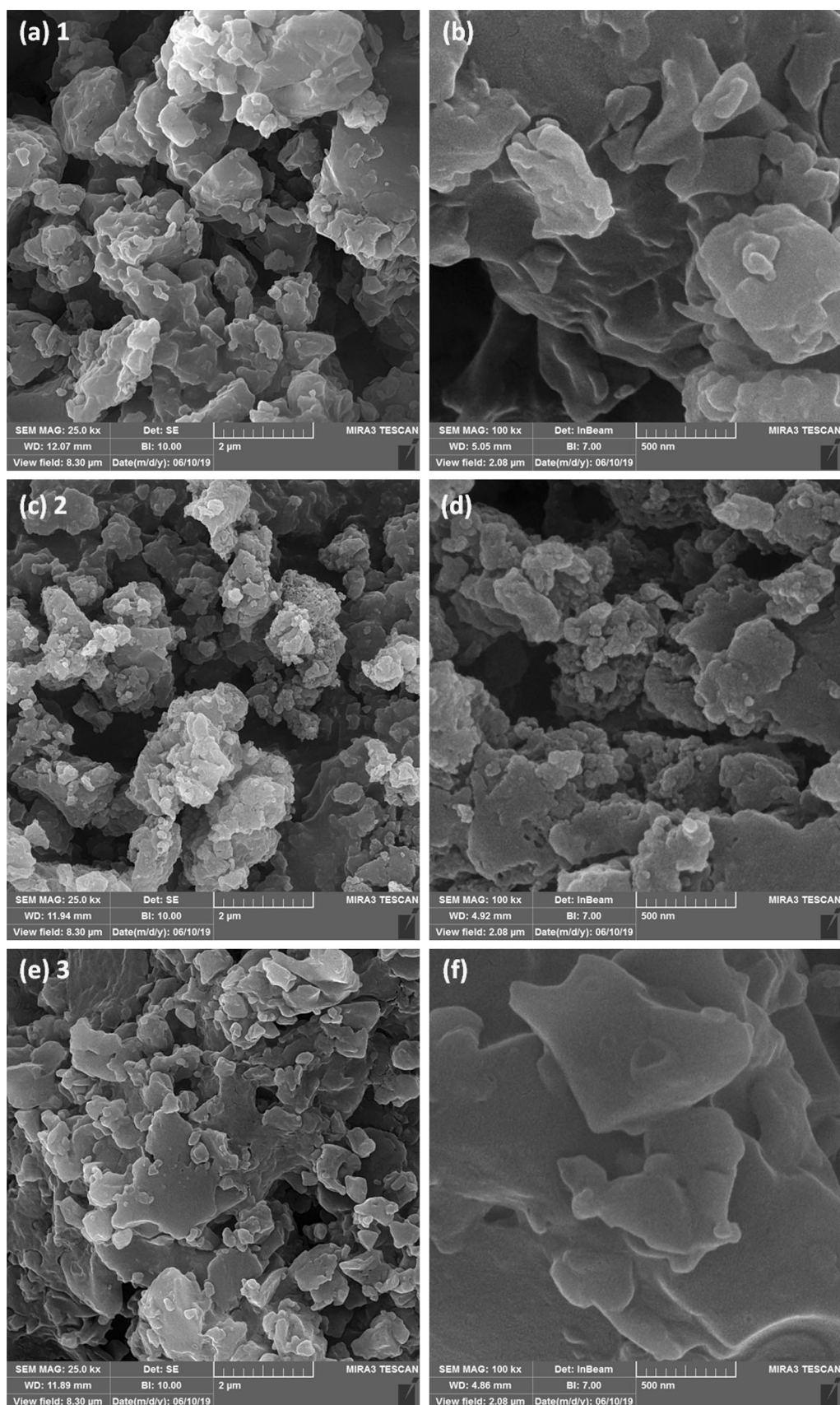


Fig. 2 FESEM images of complexes 1 (a 2 μm and b 500 nm), 2 (c 2 μm and d 500 nm), and 3 (e 2 μm and f 200 nm)

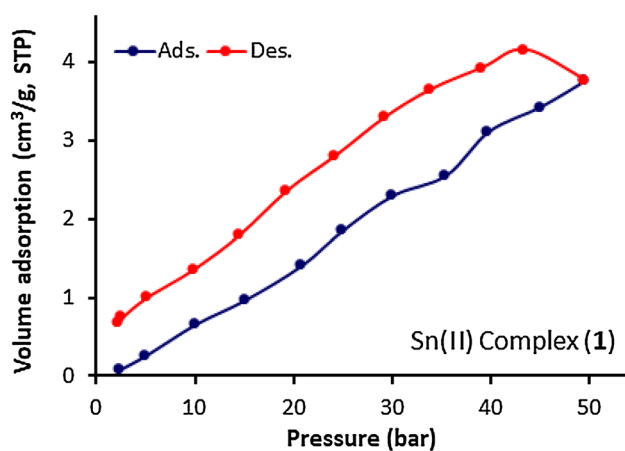


Fig. 3 CH₄ adsorption–desorption isotherms of 1

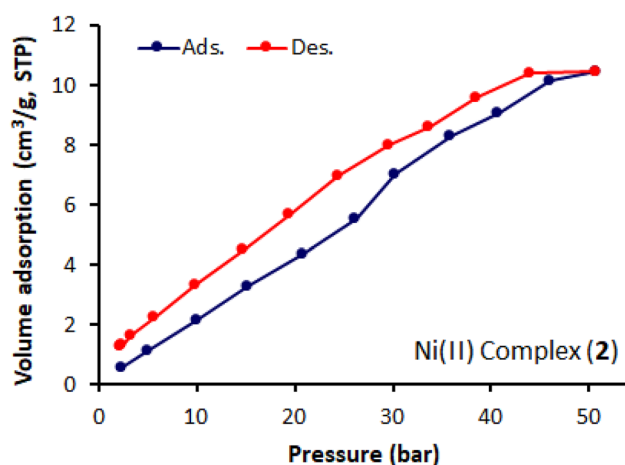


Fig. 4 CH₄ adsorption–desorption isotherms of 2

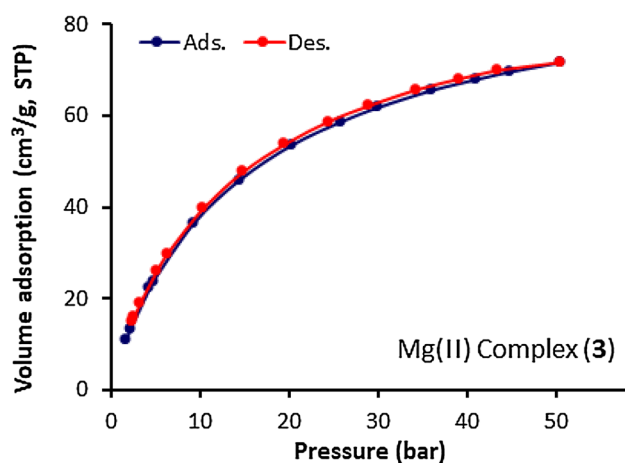


Fig. 5 CH₄ adsorption–desorption isotherms of 3

Table 1 Methane uptake capacities of complexes 1–3 at 323 K and 50 bar

Complex	CH ₄ uptake capacity		
	cm ³ /g	mmol/g	wt%
Sn(IV) complex 1	3.76	0.16	0.26
Ni(II) complex 2	10.47	0.46	0.74
Mg(II) complex 3	71.68	3.19	5.15

[26]. The variation in the CH₄ capture capacities of 1–3 depends mainly on the strength of the interaction between the gas and adsorbent materials. Regardless of the pressure (either low or high), the capture of CH₄ occurs more effectively in particles with tuned pore sizes and volumes. It has been reported that the modification of MOF pores, though incorporation with magnesium-decorated fullerenes, can increase the gas-adsorption capacity significantly [36]. This process results in tuned pores and increases the enthalpy of adsorption. Carboxylic acid and heterocycles are the most common units utilized in the construction of MOFs [37]. These units are hydrophobic enough to enhance the CH₄ uptake of and interaction with the MOFs, as well as increase the moisture stability of the framework [37, 38].

In addition to the surface area, the tuned pore volume and size play significant roles in controlling the gas-adsorption capacity of adsorbent materials. In the current work, the Ni(II) complex has a larger surface area than the magnesium complex; however, it is less efficient as a storage medium for CH₄. The enthalpy of adsorption can be increased through the incorporation of coordinatively unsaturated metal sites within the MOFs [39]. In addition, the doping of MOFs with a transition metal or alkali can improve their gas-adsorption capacities [40]; however, only few examples have been successful for CH₄ capture [41].

Conclusions

Three valsartan metal complexes were investigated as potential capture and storage media for CH₄. The complexes exhibited different adsorption–desorption isotherms depending on the type of metal. The magnesium complex was more effective than the other two as a storage medium for CH₄. A remarkable CH₄ uptake capacity (71.68 cm³/g) was achieved using the magnesium–valsartan complex.

Acknowledgements The authors are grateful to the Deanship of Scientific Research, King Saud University for funding through Vice Deanship of Scientific Research Chairs. We thank Al-Nahrain University for the technical support.

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