



New Nano-Structured Hybrid Materials-based Polyoxometalate for CH₄/H₂ Separation: A Computational Study

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Abstract

Global climate change is one of the most serious and formidable challenges in the world. After carbon dioxide that is well-known as the most important greenhouse gas, methane has been ranked the second. On the other hand, high-pressure separation of binary mixture of CH₄ and H₂ is relevant to hydrogen purification which absolutely play a vital role in many industrial processes. Thus, methane separation poses a big challenge that could be faced *via* various techniques such as adsorption. In this paper the capability of some of the recently synthesized structures of a new class of nano-porous materials, known as inorganic-organic hybrids based-Polyoxometalate (POM), have been examined for capturing methane from hydrogen stream. Grand Canonical Monte Carlo (GCMC) simulation has been used to predict pure methane and hydrogen and also their binary isotherms as well as CH₄ selectivity calculations over H₂ at two different concentrations of CH₄/H₂ mixture of 50/50 and 10/90. In addition, Ideal Adsorption Solution Theory (IAST) has been employed for the binary isotherms predictions and the results are compared with those of GCMC. The obtained results present that POMs could be introduced as a promising candidates for CH₄/H₂ separation in comparison with other conventional adsorbents such as Metal-Organic Frameworks (MOFs) and Covalent-Organic Frameworks (COFs) materials.

Keywords: Polyoxometalate, GCMC, Global warming, Methane capture, Adsorption process.

Introduction

Total worldwide energy consumption was estimated over 500 exa-joules in 2012, with about 90 percent derived from the combustion of various fossil fuels [1]. This immense amount of energy was produced from around 3 billion barrels crude oil, 3 trillion standard cubic meters natural gas and about 7 billion tons high quality coal, which emitted more than 30 billion tons carbon dioxide into our environment. Substitution of coal or even crude oil by natural gas (mainly CH₄) can drastically reduce the global carbon dioxide emission rate. On the other hand, hydrogen purification is an industrial process required after hydrogen generation. Over 50 million tons of H₂ are produced annually, that most of them come from steam reforming technology [2]. Carbon monoxide (CO: 1–3%), methane (CH₄: 3–6%) and carbon dioxide (CO₂: 15–25%) impurities [3] remain in the final output of this process that is very important to have an efficient technology for removing them from produced H₂. In this product stream



that is contaminated with CO, CH₄ and CO₂, CH₄ is the least adsorbing impurity because of its neutral nature. Unlike CO₂, which is a polar molecule and can be readily separated physically and/or chemically by using variety of nano-porous materials, methane is completely a non-polar molecule and interacts weakly with most porous solids. Therefore, the separation of CH₄ from H₂ is more difficult than CO₂/H₂ separation. It should be noted that due to low concentration of the CO contaminant, its separation is not very crucial as well as CH₄ and CO₂. Furthermore, capturing methane from a flue gas is very important since it is the second important greenhouse gas after CO₂ [4].

So with respect to the importance of methane storage and separation specially from hydrogen stream, many efforts have been paid for finding appropriate materials for separation of CH₄/H₂. Nevertheless, most of those materials, except some of the Metal-Organic Frameworks (MOFs) [5] have not shown very high selectivity [6-9]. Recently, in 2011, Wu et al., investigated more than one hundred MOF to select the best materials with the highest CH₄/H₂ selectivity [5]. They concluded that MOF materials are the most attractive adsorbents for CH₄/H₂ separation.

On the other hand, Polyoxometalate (POM) that are new class of porous materials, have found potential applications in many fields such as catalysis, ion exchange, magnetism, biological chemistry, medicine [10], and separation [11]. POMs are nanosized metal-oxide macroanions and can create nanostructured crystals in combination with appropriate molecular cations (macrocatations) [12,13]. Some inorganic-organic hybrids of POMs crystals sorb guest molecules in the crystal lattice, and the sorption properties are finely tuned by the choice of the organic ligands of the macrocatations. In this paper two newly synthesized Lanthanide inorganic-organic hybrids based-POM formulated as {Na(H₂O)₃[Ln(HCAM)(H₂O)₄]₃}[SiW₁₂O₄₀]•nH₂O (Ln = La, n = 15 (**1**) and Ln = Eu, n = 12 (**2**); H₃CAM = 2,6-dicarboxy-4-hydroxypyridine) are investigated for methane capture. Figure 1 shows the packing arrangements of **1**. The thermogravimetric analysis of these compounds shows that water molecules are released from the ambient to 300 °C without collapsing of the structures.

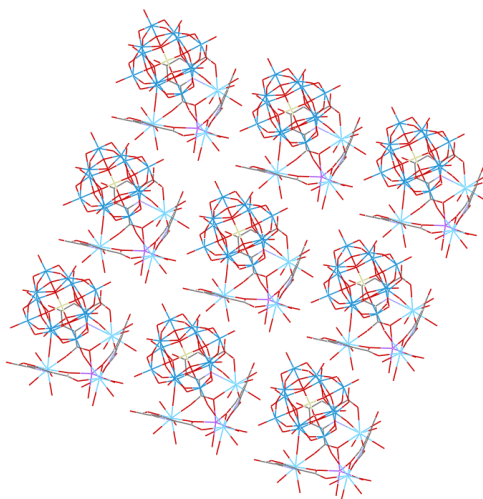


Figure 1. The packing arrangement of **1**. Lattice water molecules and H atoms are omitted for clarity.

Grand Canonical Monte Carlo (GCMC) simulation is employed in the entire work for investigating the ability of the POMs in CH₄/H₂ mixture separation field *via* selectivity calculations. This efficient tool, enable us to reduce dramatically experimental expenses as well as save time efficiently. Furthermore, single and various binary isotherms of CH₄ and H₂ are recovered *via* GCMC and compared with Ideal Adsorption Solution Theory (IAST). The



comparison of both GCMC and IAST performances reveals that IAST is a reliable method to mixture isotherm prediction in the case of small molecules such as CH₄ and H₂.

Models and Computational Method

All required simulations information of both POM structures were taken from their available CIF files which were generated by crystallographer during their syntheses. These information including unit cell dimension (length and angle), space group, cell volume and etc were utilized for all simulations. The crystal structure of **1** and **2** was used as a host after the removal of water molecules. Monte Carlo simulation in Grand Canonical (μ , V , T) ensemble was employed to calculate the equilibrium isotherms of both pure and mixture of CH₄ and H₂ by applying Lennard-Jones (LJ) interaction model¹. The LJ potential parameters for both structures atoms were taken from Universal Force field (UFF) while methane and hydrogen molecules were modeled as a united-atom (single center). All employed LJ parameters in these simulations are presented in Table 1. Meanwhile, all of the LJ cross interaction parameters were determined by the Lorentz-Berthelot mixing rules. Coulomb interactions were ignored in the presented simulations because both CH₄ and H₂ molecules are non-polar. Furthermore, a construction of (2×2×2) cells has been established for the simulations. Periodic boundary conditions in three-dimensions with cutoff radius equal to 12.5 Å was used for both samples.

Table 1. The LJ parameters used in this work

LJ Parameters	Structures atoms (1 & 2)							Methane	Hydrogen	
	W	O	C	N	Na	La	Si			Eu
δ (°Å)	2.73	3.03	3.47	3.26	2.80	3.14	3.80	3.11	3.73	2.96
ϵ/k_B (K)	33.73	48.16	47.87	38.96	251.71	8.56	156.06	4.03	147.90	36.70

Results and Discussion

In the adsorption separation processes, selectivity could be a good criterion of the ability of a porous material for separation of different components in a mixture. Several types of selectivity can be defined [14], however, in a general form, for component A relative to component B, that is defined as: $S = (x_A/x_B)(y_B/y_A)$. Where x and y are the mole fractions of each component in the adsorbed phase and bulk phase respectively. Evidently, for calculation of selectivity, binary equilibrium data of mixture is needed. Because of the difficulty of measuring adsorption equilibrium and process data of gas mixtures, we predicted binary isotherms via GCMC. So, first of all, single component isotherms of H₂ and CH₄ were simulated, then their binary mixture isotherms in two equimolar (CH₄/H₂:50/50) and non-equimolar (CH₄/H₂:10/90) levels were predicted. Accordingly, CH₄ selectivities over H₂ were calculated at two mentioned levels by resorting to simulated binary isotherms. Figures 2 and 3 show the simulated isotherms and calculated selectivities for both **1** and **2** structures, respectively. It should be noted that all calculations were performed at 298K.

Dashed lines in the Figures (1&2) present the IAST predictions of binary isotherms and then selectivities. This theory that was presented by Myers and Prausnitz [15] can be used for mixture isotherm estimations from pure component isotherm data. As it can be observed, good agreement between GCMC simulation and IAST calculation indicates that IAST is an efficient alternative for calculations of adsorption selectivities in POMs.

Furthermore, Figure 4 compares CH₄ selectivity of the POMs over H₂ with some of the reported data in literatures [5]. Obviously, both POMs are one of the most promising candidates for CH₄/H₂ mixture separation. Note that in Figure 4, **1** and **2** structures are shown as KHC325 and KHC369 respectively.

¹ LJ interaction model: $U(r_{ij})=4\epsilon_{ij}[(\delta_{ij}/r_{ij})^{12} - (\delta_{ij}/r_{ij})^6]$

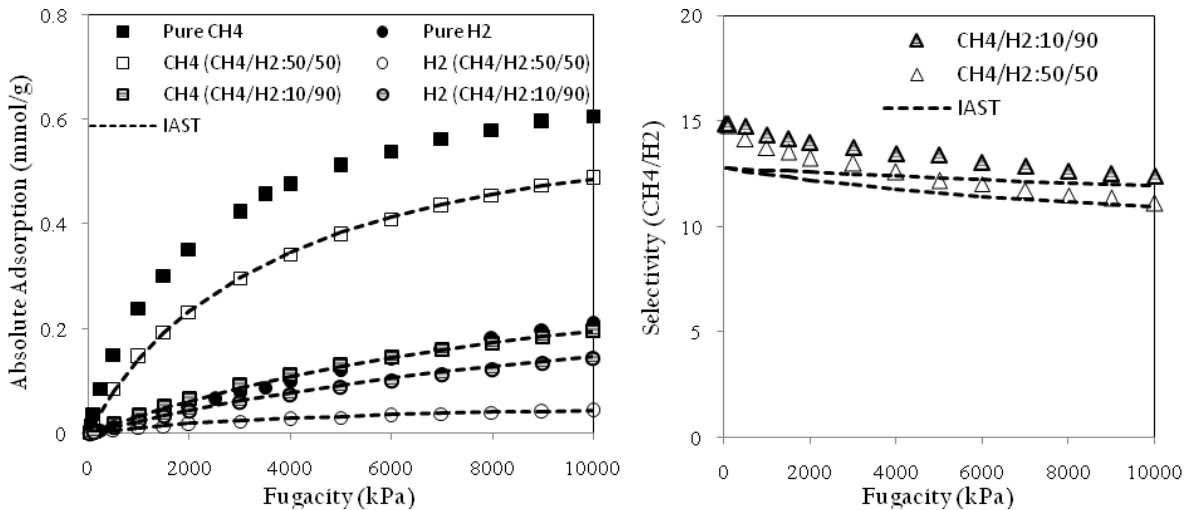


Figure 2: Simulated single and mixture isotherms of CH₄ and H₂ at 298K (left), calculated selectivities of CH₄ at different pressures up to 10Mpa (right) for 1.

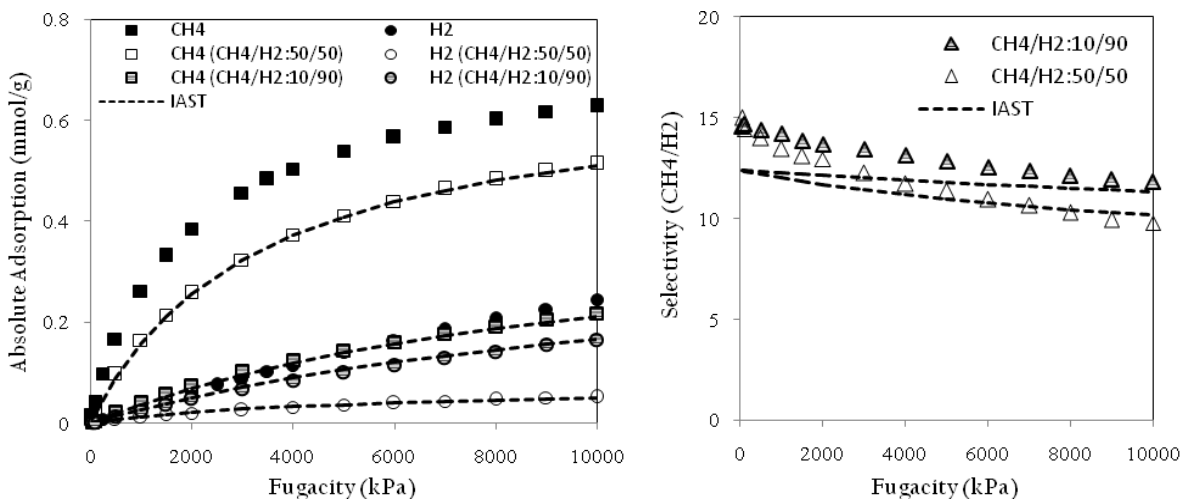


Figure 3: Simulated single and mixture isotherms of CH₄ and H₂ at 298K (left), calculated selectivities of CH₄ at different pressures up to 10Mpa (right) for 2.

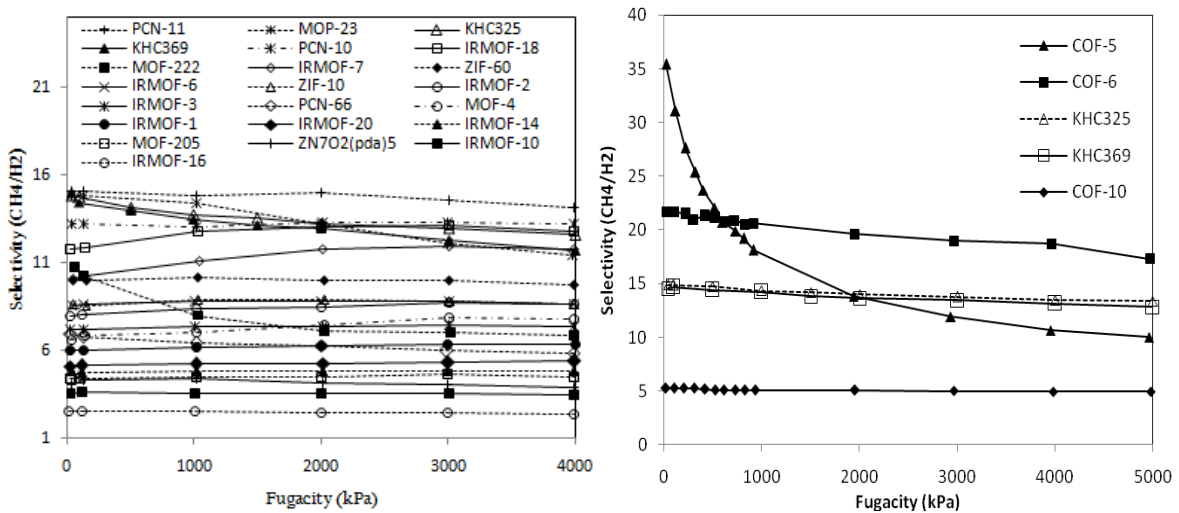


Figure 4: CH₄ Selectivity, Left: in the equimolar (CH₄/H₂:50/50) and Right: non- equimolar (CH₄/H₂:10/90) mixtures at 298 K in 1 and 2 in comparison with other data borrowed from literature [5].



Conclusions

The main conclusion from this work is that the CH₄ selectivity over H₂ in the two selected POM structures known as **1** and **2** [16] is comparable to most known MOF and COF materials. In other words, to the best of our knowledge, inorganic–organic hybrids based-POM could be one of the best candidates for methane separation from hydrogen stream in medium concentration (5-75%) sources.

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