# Insights into hydrogen and methane storage capacities: Grand canonical Monte Carlo simulations of SIGSUA

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# ABSTRACT

In the pursuit of sustainable energy solutions, the development of materials with efficient hydrogen and methane storage capacities is imperative, particularly for advancing hydrogen-powered vehicles. Metal–organic frameworks (MOFs) have emerged as promising candidates to meet the stringent targets set by the Department of Energy for both hydrogen and methane storage. This study employs Grand Canonical Monte Carlo simulations to investigate the usable hydrogen and methane gravimetric and volumetric storage capacities of the recently synthesized SIGSUA. A comparative analysis encompasses the selected MOFs with similar metal compositions, those with comparable density and average pore radius, and classical benchmarks, such as IRMOF-15 and IRMOF-20, all evaluated at room temperature and moderate pressures ranging from 25 to 35 MPa. The results reveal that SIGSUA demonstrates noteworthy gravimetric and volumetric storage capacities for both hydrogen and methane, rivaling or surpassing those of the selected MOFs for analysis. These findings underscore the potential of SIGSUA in advancing clean energy storage technologies.

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## I. INTRODUCTION

Human activities have been altering the climate since ancient times. A significant turning point occurred in the eighteenth century, marked by extensive deforestation for agriculture and the onset of the industrial revolution. Subsequently, the escalating demand for energy has driven an increase in both fossil fuel consumption and the emission of pollutants, such as  $CO_2$  or CO. Addressing the rising demand for energy while minimizing environmental impact has become a pressing challenge in the contemporary world. Among the various sectors contributing to the consumption of fossil fuels, transportation emerges as a significant player. As societies continue to rely on conventional modes of transport, the need for sustainable energy alternatives becomes increasingly evident.

In the quest for a sustainable energy future, hydrogen emerges as a promising candidate, offering a clean and efficient alternative to traditional fossil fuels.<sup>1–3</sup> In comparison to gasoline, which has an energy density of 44 MJ/kg, hydrogen boasts a significantly higher energy density of 120 MJ/kg.<sup>4</sup> However, despite this advantage in mass-based energy density, hydrogen encounters challenges in volumetric energy density, posing difficulties for storing large quantities in vehicle applications. The primary obstacle is devising a storage solution that allows for a driving range exceeding 500 km on a single fill, comparable to the current fossil fuel-based vehicles. This challenge must be addressed while considering factors such as safety, weight, volume, efficiency, and  $\cot 5^{-9}$  The present on-board hydrogen storage methods involve compression under pressures of up to 700 bars, entailing high costs and safety concerns. In pursuit of achieving hydrogen fuel cell powered vehicles with the mentioned autonomy of 500 km, the US Department of Energy (DOE) outlined short-term objectives for 2025. These goals encompass achieving a gravimetric storage capacity of 5.5 wt. % and a volumetric capacity of 0.04 kg/l at ambient temperature and under moderate pressures.

While hydrogen is developed as an efficient technology, methane stands as a crucial intermediary between conventional fossil fuels and the hydrogen economy. Methane is a cleaner-burning alternative to traditional gasoline and diesel fuels. It is readily available and can be used in existing internal combustion engines with minimal modifications. In addition, the existing infrastructure



for natural gas can be utilized for methane-based transportation. Methane shows a higher ability to store energy by weight when compared to gasoline. The Advanced Research Projects Agency–Energy (ARPA-E) under the Department of Energy has set clear goals for efficient methane storage: a volumetric capacity of 0.250 kg of methane per liter and a gravimetric capacity of 33.33 wt.% at room temperature and under moderate pressures.<sup>10–14</sup> However, the ultimate goal is often seen as transitioning to hydrogen since it is considered a promising long-term solution for sustainable and zero-emission transportation.<sup>15–17</sup>

There are three main storage techniques for both methane and hydrogen:<sup>18,19</sup> compression, liquefaction, and physical adsorption. The first two methods entail high costs and maintenance efforts. On the other hand, physisorption storage is an emerging process. In this technology, hydrogen molecules are lightly adsorbed on the surface of the material through London dispersion forces.<sup>20,21</sup> Physical adsorption is the most competitive in terms of price, as the hydrogen molecules are stored at room temperature and under low-to-moderate pressures. Typically, materials employed for physisorption are characterized by their porosity, possessing a significant specific surface area. These materials offer advantages such as lightweight nature, high storage density, excellent reversibility, and stability across cycles, as well as rapid charging and discharging speed.

Solid porous materials with well-defined pores, including zeolites,<sup>22-26</sup> covalent organic frameworks (COFs),<sup>27-33</sup> various carbon-based structures (such as fullerenes, nanotubes, and graphene),<sup>34-48</sup> and metal-organic frameworks (MOFs),<sup>49-56</sup> have been extensively explored for their potential in physisorption-based storage systems for both hydrogen and methane. MOFs are distinguished by their exceptional porosity and structural versatility, manifesting in both 2D and 3D formations.<sup>57,58</sup> They are crafted from metal ions as well as organic ligands, offering a vast array of possible combinations due to the diverse selection of organic ligands and metal ions available. This diversity enables the synthesis of numerous MOFs with unique and adjustable properties. Particularly noteworthy is their immense potential to revolutionize the landscape of gas storage.<sup>59-67</sup>

The gas adsorption capabilities of  $MOFs^{68}$  have been the subject of extensive exploration, with a particular focus on their potential to store hydrogen and methane. Numerous experimental studies<sup>63,69–78</sup> and simulations<sup>49–51,79–91</sup> have been conducted over the past decades to unravel their adsorption properties. These investigations often employ the widely utilized Grand Canonical Monte Carlo (GCMC) method for hydrogen and methane.<sup>46–51,91–98</sup>

Recently, a novel Br-based material, with the CCDC<sup>99</sup> database identifier, SIGSUA,<sup>100</sup> was synthesized by Yufit at Durham University. This study aims to analyze and predict the usable storage capacities for both hydrogen and methane of this promising MOF at room temperature. Grand Canonical Monte Carlo (GCMC) simulations were employed to assess the usable storage capacities across the different sets of MOFs. The first set comprises MOFs based on Br and share a comparable C/Br ratio with SIGSUA, the Br-selected set. The second set comprises MOFs based on halogens, Cl, and F, with a C/halogen ratio similar to the C/Br ratio of SIGSUA, the halogensselected set, while the third set involves MOFs possessing a similar density and average pore radius as SIGSUA, the  $\rho - R_{ave}$ -selected set. The fourth set consists of well-known classical MOFs. Furthermore, the study explores the correlation between the usable storage capacities and structural properties, such as porosity, density, and pore size, for all the simulated MOFs. This detailed understanding of the complex interplay between the adsorbed molecules and MOFs is crucial for deciphering the origins of storage capacities and contributes significantly to the strategic design of novel metal–organic frameworks.

# **II. METHODOLOGY**

### A. Details and settings for the GCMC simulations

The simulation methodology employed in this paper involves the application of the Grand Canonical Monte Carlo method. This method utilizes the grand canonical ensemble to change the number of molecules involved in the simulation calculations.

GCMC simulations were employed to obtain the volumetric and gravimetric storage isotherms of hydrogen and methane of SIGSUA.<sup>100</sup> These simulations were executed at room temperature, 298.15 K, and across a pressure spectrum ranging from 0.5 to 35 MPa. A total of ten million iterations were conducted for each GCMC simulation. The first five million iterations were dedicated to reaching equilibrium. The remaining iterations were employed to determine both gravimetric and volumetric storage capacities for hydrogen and methane.

The Metropolis algorithm<sup>101</sup> was employed in each iteration. Simulations were conducted using a custom in-house code named mcmgs. Possible changes or movements (insertion, deletion, and translation of a molecule) were taken into account following the same percentages as employed by Granja-DelRío and Cabria in Ref. 50.

In each iteration, three categories of possible changes or movements were taken into account. Nearly 20% of the tests involved the movement of a molecule, 40% focused on molecule deletion, and the remaining 40% implied molecule insertion. These percentages were chosen after several tests to ensure accurate system representation.

The chemical potential employed in the GCMC simulations was extracted from the Soave–Redlich–Kwong (SRK) equation of state.<sup>102</sup> The dimensionless acentric factor ( $\omega$ ), critical pressure ( $P_c$ ), and critical temperature ( $T_c$ ) values for hydrogen and methane were sourced from Zhou and Zhou<sup>103</sup> and Xu *et al.*,<sup>104</sup> as presented in Table I.

Lennard-Jones (LJ) interaction potentials<sup>105</sup> were employed to model the interactions between the atoms of the MOFs and gas molecules, as well as the interactions between the gas molecules themselves (H<sub>2</sub> or CH<sub>4</sub>). This potential energy approach encapsulates both attractive and repulsive forces, providing a comprehensive mathematical framework for describing intermolecular interactions within the system. This potential is defined by the well-known Lennard-Jones equation, which represents both attractive and repulsive aspects of the interactions between the gas molecules and the

**TABLE I.** Parameters of the SRK equation of state of hydrogen and methane:  $\omega$ , P<sub>c</sub> in MPa, and T<sub>c</sub> in K.

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Gas	ω	P <sub>c</sub>	T <sub>c</sub>	Source
H2 CH4	-0.216 0.011 42	1.28 4.5992	33.2 190.56	Zhu and Zhu <sup>103</sup> Xu <i>et al</i> . <sup>104</sup>

TABLE II. Lennard-Jones	coefficients	$\sigma$ (in Å)	and	ε (in e	eV) of	the	molecules	and
atoms of the MOFs studied	d in the prese	ent GCM	C sim	ulation	ns.			

Atom or molecule	σ	ε	Source
Al	2.574	0.507 220	Filippova <i>et al.</i> <sup>107</sup>
Br	3.519	0.016 043	Mayo <i>et al.</i> <sup>108</sup>
$CH_4$	3.730	0.012748	Jorgensen <i>et al.</i> <sup>109</sup>
Cu	2.297	0.520 310	Filippova <i>et al.</i> <sup>107</sup>
$H_2$	2.970	0.002 870	Rzepka <i>et al.</i> <sup>110</sup>
Н	2.846	0.000 659	Mayo <i>et al.</i> <sup>108</sup>
Ν	3.310	0.003 214	Cheung and Powles <sup>111</sup>
0	3.033	0.004 150	Mayo <i>et al.</i> <sup>108</sup>
S	3.590	0.014 916	Mayo <i>et al</i> . <sup>108</sup>
Zn	0.998	0.008 291	Soper <sup>112</sup>
Zr	2.910	0.735 981	Beyer and Hoheisel <sup>113</sup>
C-H <sub>2</sub>	3.190	0.002 628	Rzepka <i>et al.</i> <sup>110</sup>

atoms of the MOFs. The Lennard-Jones equation is expressed as follows:

$$V = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right],\tag{1}$$

where  $\varepsilon > 0$  represents the minimum value of the Lennard-Jones interaction potential energy,  $\sigma$  denotes the distance at which the potential energy function between two particles is zero, and r denotes the distance between the two particles. The values for the  $\varepsilon$  and  $\sigma$  coefficients are particle-dependent and are implemented as in the work by Granja-DelRío and Cabria.<sup>50</sup> Table II presents the  $\varepsilon$  and  $\sigma$  coefficients for the atoms and molecules involved in the current GCMC simulations. The established cutoff distances governing the LJ interaction potential have been thoroughly elucidated in earlier investigations.<sup>46,51</sup> The quantum effects in the interaction potential were included through the Feynman–Hibbs correction,<sup>106</sup> applied to all the GCMC simulations.

### **B.** Calculation of porosity

Porosity is the proportion between the accessible volume and the total volume of the simulation cell of a MOF. The accessible available volume for a gas molecule is calculated as the difference between the simulation cell volume (V) and the volume occupied by the atoms of the MOF ( $V_{occ}$ ). The porosities obtained in the simulations were determined using the methodology described by Granja-DelRío and Cabria in Ref. 50.

### 1. Calculation of pore radius

An algorithm was applied to pinpoint pores within the MOFs, focusing on those with a radius of 3 Å or larger. This choice was made due to the inadequacy of pores with smaller radii in accommodating hydrogen and methane molecules. The algorithm process is explained in Ref. 50. The algorithm computes a set of pore radii and determines the average pore radius,  $R_{av}$ . The initial pore radius obtained through this algorithm corresponds to the largest pore radius,  $R_l$ , within the MOF. The spherical pores generated by this algorithm do not protrude.

### C. Calculation of the isosteric heat

The isosteric heat of adsorption,  $Q_{st}$ , is the heat at the constant specific volume, or equivalently, at constant volumetric density. The isosteric heat is given by  $Q_{st} = -q + RT$ , where q is the average energy of adsorption, which is calculated in the GCMC simulations as

$$q = (\langle EN \rangle - \langle N \rangle \langle E \rangle) / \operatorname{Var}(N), \qquad (2)$$

where *E* is the energy of the system, *N* is the number of molecules,  $\langle EN \rangle$  is the average of the product *E* by *N*,  $\langle N \rangle$  is the average of the number of molecules,  $\langle E \rangle$  is the average of the energy, and Var(N) is the variance of the number of molecules, given by  $Var(N) = \langle N^2 \rangle - \langle N \rangle \langle N \rangle$ . In addition,  $\langle N^2 \rangle$  is the average of the square of the number of molecules.

### D. Definitions of the storage capacities

GCMC simulations have been employed to model the total gravimetric and volumetric storage capacities for both hydrogen and methane. In the present simulations, the formal definition of the total volumetric storage capacity  $v_c$ , often termed as the density of stored gas, at pressure *P* and temperature *T* is as follows:

$$v_c = \frac{M_g(P,T)}{V}.$$
(3)

The total gravimetric storage capacity,  $g_c$ , of the stored gas is formally expressed as

$$g_{c} = \frac{100M_{g}(P,T)}{M_{g}(P,T) + M_{ads}}.$$
 (4)

As a result, the units of  $v_c$  are expressed as kilograms of H<sub>2</sub> per liter or kilograms of CH<sub>4</sub> per liter. The units for the total gravimetric capacity are calculated in weight percentage units, wt. %. More information about these definitions is given in Ref. 50.

In a fully loaded gas tank, the gas is delivered to the fuel cell or the engine till the tank pressure reaches the so-called depletion pressure, also called minimum, back pressure, or backpressure. There should be enough differential pressure between the tank and the fuel cell or the engine to drive the gas flow from the solid porous adsorbent material to the fuel cell or engine. Hence, not all the stored gas is used and this leads to the usable, also called delivery, deliverable, or working, storage capacities.

The usable mass of gas  $M_{ug}(P, T)$  represents the effective amount of either hydrogen or methane at a given pressure P and temperature T. The usable mass is computed by the difference between the total mass of gas stored at P and T and the total mass of gas stored at the depletion pressure  $P_{dep}$  and at the same temperature T,<sup>4,48,50,96,114</sup>

$$M_{ug}(P, T; P_{dep}) = M_g(P, T) - M_g(P_{dep}, T).$$
(5)

The effective capacity of these materials is notably restricted by the back pressure. The equations used to calculate the usable or deliverable volumetric and gravimetric capacities for either hydrogen or methane involve Eqs. (3) and (4), respectively. The definitions and equations of these magnitudes are developed by Granja-DelRío and Cabria in Ref. 50.

The usable volumetric capacity at *P* and *T* is the difference between the gas (hydrogen or methane) stored per volume in a deposit at *P* and the gas that remains in the deposit at the depletion pressure  $P_{dep}$ . The usable gravimetric capacity at *P* and *T* is more complicated than the difference between the two amounts.

The usable capacities share the same units as the total capacities. The depletion pressure  $P_{dep}$  of 0.5 MPa is employed in this paper. Hydrogen fuel cells can operate, in general, at backpressures between 0.1 and 0.5 MPa.<sup>115</sup> ARPA-E set a depletion pressure of 0.58 MPa<sup>13,116,117</sup> in order to have enough differential pressure to drive the methane gas flow from the solid porous adsorbent material to the engine. Throughout this work, only the usable storage capacity will be utilized, unless explicitly mentioned otherwise.

The excess storage capacities are defined using  $M_{ex}(P, T)$  and the available volume instead of  $M_g(P, T)$  and V in Eqs. (3) and (4), respectively. The available volume is the difference between the volume of the simulation cell, V, and the volume occupied by the atoms or skeleton volume.

# E. Simulation cells and MOF sets

To enable a comprehensive comparison of storage capacities, the GCMC simulations were executed for four sets of MOFs. Among the CCDC database, only five Br-selected MOFs were found with similar C/Br ratios as the SIGSUA, 2.67. The CCDC database identifiers of the five Br-based MOFs are VUSJUP (3.0), VUSKIE (3.0), VUSKEA (2.0), VUSKAW (2.0), and XANMUX08 (3.3). Those MOFs form the Br-selected set. The halogens-selected set is composed of four Cl and F-based MOFs. The MOFs in the  $\rho - R_{ave}$ selected set were chosen from the CCDC database, specifically including MOFs with density that differs by 5% from the SIGSUA density and an average pore radius differing by 10% from that of SIGSUA. These selections generated the  $\rho - R_{ave}$ -selected set. The CCDC database identifiers of those MOFs are JEDVIA, QUSSAB, ROTNUM01, and ROTNUM. The set of 21 classical MOFs, the fourth set, includes IRMOF-1 to IRMOF-20 (excluding 10, 13, 17, and 19), along with HKUST-1, MOF-177, NU-111, NU-125, and ZIF-8 (IRMOF: isoreticular metal–organic frameworks).

The simulation cells for all the aforementioned MOFs were extracted from their Crystallographic Information File (CIF) format files obtained from the Crystallographic Database Center (CCDC) database.<sup>99</sup> The simulation cells of the sets of MOFs were obtained from the MOF CCDC subset.<sup>118</sup> The simulation cell of SIGSUA was obtained from the general CCDC database and is shown in Fig. 1,



FIG. 1. Simulation cell of the SIGSUA. Oxygen, carbon, hydrogen, and bromine atoms are represented by the blue, gray, yellow, and red balls, respectively.

**TABLE III.** Hydrogen storage capacities of some classical MOFs at different temperatures and pressures from experiments and GCMC simulations performed with the mcmgs code in the present and previously published studies. Pressure P is in MPa, temperature T in K, gravimetric capacity  $g_c$  in wt. %, and  $v_c$  in kg/l. Type means the type of capacity.

MOF	Gas	Р	Т	Technique	g <sub>c</sub>	vc	Туре	Source
IRMOF-1	$H_2$	3.5	77	Expt.	5.75		Excess	Zhou <i>et al.</i> <sup>78</sup>
IRMOF-1	$H_2$	3.5	77	mcmgs	5.34		Excess	Present
IRMOF-1	$H_2$	4.8	77	Expt.	5.2		Total	Collins and Zhou <sup>121</sup>
IRMOF-1	$H_2$	4.8	77	mcmgs	6.7		Total	Present
IRMOF-1	$H_2$	6	77	Expt.	5.6		Excess	Zhou <i>et al.</i> <sup>78</sup>
IRMOF-1	$H_2$	6	77	mcmgs	5.7		Excess	Present
IRMOF-1	$H_2$	6	298	Expt.	0.45		Total	Collins and Zhou <sup>121</sup>
IRMOF-1	$H_2$	6	298	mcmgs	0.72		Total	Present
IRMOF-1	$H_2$	6	300	Expt.	0.3		Excess	Zhou <i>et al.</i> <sup>78</sup>
IRMOF-1	$H_2$	6	300	mcmgs	0.37		Excess	Present
ZIF-8	$H_2$	3	77	Expt.	3.3		Excess	Zhou <i>et al.</i> <sup>78</sup>
ZIF-8	$H_2$	3	77	mcmgs	2.74		Excess	Present
ZIF-8	$H_2$	5	77	Expt.	3.2		Excess	Zhou <i>et al.</i> <sup>78</sup>
ZIF-8	$H_2$	5	77	mcmgs	2.86		Excess	Present
ZIF-8	$H_2$	5	300	Expt.	0.1		Excess	Zhou <i>et al</i> . <sup>78</sup>
ZIF-8	$H_2$	5	300	mcmgs	0.18	•••	Excess	Present

TABLE IV. Methane storage capacities of some classical MOFs at different temperatures and pressures from the experiments and GCMC simulations performed with the mcmgs code in the present and previously published studies. Pressure P is in MPa, temperature T in K, gravimetric capacity  $g_c$  in wt. %, and  $v_c$  in kg/l. Type means the type of capacity.

MOF	Gas	Р	Т	Technique	<i>g</i> <sub>c</sub>	vc	Туре	Source
IRMOF-1	$CH_4$	6	300	Expt.	16.7		Excess	Zhou <i>et al.</i> <sup>78</sup>
IRMOF-1	$CH_4$	6	300	mcmgs	15.6		Excess	Present
IRMOF-1	$CH_4$	3.6	300	Expt.	13.5	0.0787	Total	Zhou <i>et al</i> . <sup>78</sup>
IRMOF-1	$CH_4$	3.6	300	mcmgs	12.3	0.0837	Total	Granja-DelRío and Cabria <sup>50</sup>
ZIF-8	$CH_4$	5	300	Expt.	7.7		Excess	Zhou <i>et al</i> . <sup>78</sup>
ZIF-8	$CH_4$	5	300	mcmgs	7.54		Excess	Present
MOF-177	$CH_4$	10	298	Expt.	22.0		Total	Saha and Deng <sup>77</sup>
MOF-177	$CH_4$	10	298	mcmgs	26.6		Total	Granja-DelRío and Cabria <sup>50</sup>
HKUST-1	$CH_4$	6.5	298	Expt.	17.8	0.1910	Total	Peng et al. <sup>76</sup>
HKUST-1	$CH_4$	6.5	298	mcmgs	15.4	0.1724	Total	Granja-DelRío and Cabria <sup>50</sup>
NU-125	$CH_4$	6.5	298	Expt.	22.3	0.1659	Total	Peng et al. <sup>76</sup>
NU-125	$CH_4$	6.5	298	mcmgs	20.5	0.1570	Total	Granja-DelRío and Cabria <sup>50</sup>
Al-nia-MOF-1	$CH_4$	8	258	Expt.	28.6	0.1880	Total	Alezi <i>et al</i> . <sup>122</sup>
Al-nia-MOF-1	$CH_4$	8	258	mcmgs	29.1	0.2010	Total	Granja-DelRío and Cabria <sup>49</sup>
Al-nia-MOF-1	$CH_4$	8	273	Expt.	24.5	0.1660	Total	Alezi <i>et al</i> . <sup>122</sup>
Al-nia-MOF-1	$CH_4$	8	273	mcmgs	27.6	0.1870	Total	Granja-DelRío and Cabria <sup>49</sup>
Al-nia-MOF-1	$CH_4$	8	298	Expt.	23.1	0.1420	Total	Alezi <i>et al</i> . <sup>122</sup>
Al-nia-MOF-1	$CH_4$	8	298	mcmgs	24.8	0.1610	Total	Granja-DelRío and Cabria <sup>49</sup>
Al-nia-MOF-1	$CH_4$	8	298	Expt.	21.3	0.1230	Usable	Alezi <i>et al.</i> <sup>122</sup>
Al-nia-MOF-1	$CH_4$	8	298	mcmgs	22.1	0.1390	Usable	Granja-DelRío and Cabria <sup>49</sup>

using the XCrySDen code.<sup>119,120</sup> The GCMC simulations were carried out for all MOFs in the sets and for SIGSUA under the same temperature, pressures, and conditions as detailed earlier. This process facilitates a meaningful evaluation and comparison of their respective usable storage capacities.

# F. Comparison of hydrogen and methane storage capacities with experimental results

The hydrogen and methane storage capacities of classical MOFs, obtained at 77, 258, 273, 298, and 300 K, in experiments and in the simulations with the mcmgs code are presented in Tables III and IV. The differences between the experimental and the GCMC gravimetric capacities are within the interval of 3%–20%, except for the gravimetric capacities with low values. The differences between the experimental and the GCMC volumetric capacities are about 10%–13%.

# **III. HYDROGEN STORAGE CAPACITIES**

# A. Hydrogen storage capacities' dependence on porosity, density, and pore size

The usable capacities of SIGSUA, the Br-selected, the halogensselected, the  $\rho - R_{ave}$ -selected, and the 21 classical MOFs, obtained from GCMC simulations at 298.15 K and 25 MPa, are shown in Figs. 2 and 3. The labels on these and other figures indicate the CCDC database identifier of the MOF, each corresponding to the one with the best hydrogen usable gravimetric or volumetric storage capacity. These figures illustrate the relationship between usable capacities and the density, porosity, and pore size (both the largest and the average pore sizes). The usable capacities exhibit a decrease with increasing density of the material and an increase as the porosity of the material increases, as shown in Fig. 2. While this trend holds for most MOFs, there are exceptions. The trend of volumetric capacity for Br-selected MOFs as a function of density exhibits a slight deviation from the expected pattern. However, this discrepancy is not observed in the gravimetric capacity.

It is noteworthy that in Fig. 2, the gravimetric and volumetric capacities of SIGSUA aligns closely with the general trend formed by the gravimetric and volumetric capacities of classical and selected  $\rho - R_{ave}$  MOFs as a function of density or porosity. SIGSUA exhibits a slightly higher volumetric capacity compared to classical and  $\rho - R_{ave}$  MOFs at similar densities. Conversely, the gravimetric capacity of SIGSUA is a bit different from that of classical and  $\rho - R_{ave}$  MOFs at comparable densities.

In relation to porosity, the volumetric capacity exhibits an ascending trend until it attains a certain threshold, beyond which the values fluctuate. Notably, the volumetric capacity of SIGSUA surpasses that of classical MOFs with equivalent porosities. However, the gravimetric capacity follows a linear pattern. Specifically, the gravimetric capacity of SIGSUA is marginally lower than that of classical MOFs with comparable porosities. This suggests the potential to predict the usable gravimetric and volumetric capacity of SIGSUA based on either its density or porosity. The values for these magnitudes are presented in Tables V and VI.

The correlation between usable hydrogen storage capacities and both the largest pore radius and the average pore radius is shown in



FIG. 2. Usable hydrogen gravimetric and volumetric capacity at 298.15 K and 25 MPa vs density and porosity for SIGSUA, the Br-selected, the halogens-selected, the  $\rho - R_{ave}$ -selected, and the classical MOFs.

Fig. 3. In terms of usable hydrogen volumetric capacity, an increment in the pore radius enhances the volumetric capacity. However, beyond a certain threshold, the saturation effect becomes apparent, leading the volumetric capacity to stabilize at a constant value as the pore radius increases. The usable volumetric capacity can be estimated using a function of the form a - b/R, where *R* means either the largest  $R_l$  or the average pore radius  $R_{av}$ .

For the usable hydrogen gravimetric capacity, a linear trend is observed with fluctuations: as both the largest and average pore radii increase, the gravimetric capacity also increases. In general, the expansion of the pore radius is associated with a decrease in density, leading to an increase in the gravimetric capacity. It is important to note that this is an approximation. The values for these parameters are presented in Tables V and VI.

In regards to the dependence of the hydrogen storage capacities in the halogen-based sets with the density, porosity and pore radius, it can be noticed in Figs. 2 and 3 that is similar to the dependence of the other sets of MOFs studied.

GCMC simulations were conducted at 298.15 K and 25 MPa to assess the  $H_2$  storage capacities of SIGSUA and all the MOFs from each of the sets. MOFs with the highest usable gravimetric and volumetric capacities at 25 MPa from the sets were selected for comparison with the SIGSUA (see Tables V and VI). Within the chosen Br-selected MOFs, the structure with the highest volumetric and gravimetric capacity at 25 MPa, reaching 0.0172 kg/l

and 1.14 wt. %, respectively, is identified with the CCDC database code VUSJUP. Notably, this MOF has been recognized for its significant adsorption capabilities, particularly for gases such as CO2 and H<sub>2</sub>.<sup>123</sup> In the  $\rho - R_{ave}$ -selected set, the CCDC database code ROT-NUM or HUST4<sup>124</sup> corresponds to the MOF exhibiting the highest usable volumetric and gravimetric capacities at 25 MPa and 298.15 K with values of 0.0165 kg/l and 3.24 wt. %, respectively. Within the classical MOF lineup, IRMOF-20125,126 stands out with the highest volumetric capacity (0.019 kg/l), while IRMOF-15<sup>127,128</sup> achieves the highest gravimetric capacity, reaching 4.4 wt. %. When SIGSUA and the best Br-selected MOFs with the same ratio are compared then it can be noticed that the SIGSUA has higher usable gravimetric capacities than those. Tables V and VI present a summary of usable hydrogen storage capacities, densities, porosities, and pore sizes for the various MOFs under consideration. This dataset will serve to analyze and compare the storage capacities in the upcoming subsections.

# B. Hydrogen storage capacities as a function of the isosteric heat of adsorption

The adsorption and storage of gases is also related to the isosteric heat of adsorption, which indicates the intensity of the interaction of a gas molecule with the adsorbent material. Hence, it makes sense to analyze the storage capacities of these materials vs



FIG. 3. Usable hydrogen gravimetric and volumetric capacity at 298.15 K and 25 MPa vs the largest pore radius and the average pore radius for SIGSUA, the Br-selected, the halogens-selected, the  $\rho - R_{ave}$ -selected, and the classical MOFs.

**TABLE V.** Hydrogen volumetric (in kg/l) and gravimetric (in wt. %) usable capacities at 298.15 K and 25 MPa obtained in the present GCMC simulations, density (in kg/l), porosity, and largest and average pore radii (Å) of SIGSUA, the Br-selected and the  $\rho - R_{ave}$ -selected MOFs with the highest storage capacities.

MOF	Ratio C/metal	Vc	$\mathbf{g}_{c}$	Density	Porosity	$R_l$	Rav
SIGSUA	C/Br = 2.67	0.0170	3.25	0.505	0.696	8.20	6.75
VUSJUP	C/Br = 3.00	0.0172	1.14	1.483	0.352	9.11	9.06
VUSKIE	C/Br = 3.00	0.0163	1.08	1.492	0.335	7.46	7.27
VUSKEA	C/Br = 2.00	0.0152	1.12	1.335	0.408	9.08	9.02
VUSKAW	C/Br = 2.00	0.0148	1.09	1.344	0.399	7.95	7.72
XANMUX08	C/Br = 3.33	0.0142	0.93	1.514	0.232	6.12	4.27
ROTNUM	C/Zr = 10.67	0.0165	3.24	0.492	0.543	7.83	7.28
JEDVIA	C/Zn = 9.00	0.0144	2.67	0.524	0.497	7.70	7.42
QUSSAB	C/Cu = 18.00	0.0156	3.03	0.500	0.445	7.45	7.30
ROTNUM01	C/Zr = 10.67	0.0163	3.16	0.501	0.521	7.91	7.36

**TABLE VI.** Hydrogen volumetric (in kg/l) and gravimetric (in wt. %) usable capacities at 298.15 K and 25 MPa obtained in the present GCMC simulations, density (in kg/l), porosity, and largest  $R_l$  and average  $R_{av}$  pore radii (Å) of the classical MOFs.

MOF	Vc	gc	Density	Porosity	$R_l$	R <sub>av</sub>
IRMOF-5	0.0038	0.14	2.731	0.030	3.95	3.42
IRMOF-15	0.0162	4.38	0.354	0.861	12.99	4.76
IRMOF-20	0.0187	2.78	0.655	0.535	10.12	9.95
IRMOF-1	0.0144	2.35	0.598	0.431	9.12	8.24
IRMOF-2	0.0147	0.67	2.191	0.213	8.17	7.73
IRMOF-3	0.0133	1.79	0.731	0.364	9.02	8.76
IRMOF-4	0.0109	0.49	2.189	0.102	7.00	6.04
IRMOF-6	0.0122	1.66	0.724	0.303	8.89	6.12
IRMOF-7	0.0088	0.53	1.665	0.115	5.33	3.82
IRMOF-8	0.0175	2.92	0.582	0.559	10.38	10.20
IRMOF-9	0.0125	1.59	0.771	0.334	6.85	4.16
IRMOF-11	0.0156	3.08	0.491	0.585	11.20	10.50
IRMOF-12	0.0162	3.71	0.420	0.585	11.58	11.31
IRMOF-14	0.0156	3.98	0.376	0.582	11.90	11.57
IRMOF-16	0.0147	3.25	0.437	0.628	11.61	11.61
IRMOF-18	0.0128	1.63	0.770	0.274	8.40	8.28
HKUST-1	0.0157	1.63	0.949	0.229	7.14	6.94
MOF-177	0.0158	3.32	0.462	0.562	9.99	8.47
NU-111	0.0159	3.56	0.430	0.528	12.12	5.99
NU-125	0.0159	2.55	0.607	0.393	11.27	10.76
ZIF-8	0.0099	0.95	1.029	0.206	7.39	4.20

the isosteric heat. The usable storage capacities of SIGSUA and the selected MOFs vs the isosteric heat and the product of the isosteric heat by the porosity obtained in the GCMC simulations are shown in Fig. 4. The isosteric heat of hydrogen adsorption for the porous materials studied at 298.15 K and 25 MPa, as obtained in the present GCMC simulations, range from 0.03 to 0.11 eV. In addition, the values of the product of porosity by isosteric heat fall between 0.003 and 0.034 eV.

The usable storage capacities of these materials decrease as the isosteric heat increases, but they do not decrease monotonously. The capacities of these materials increase as the product of the isosteric heat and the porosity increases. However, the dependence on both variables is not monotonous; there are many oscillations around some average trends. In the case of the volumetric capacity, the dependence on the product  $Q_{st}$  by porosity is more monotonous, almost linear. This implies that increasing the above-mentioned product, it could be possible to find a material with a high volumetric capacity.

## C. Hydrogen storage capacities' dependence on pressure

The MOFs of each set with the highest storage capacities at 25 MPa have been selected to calculate their capacities in a range of pressures between 0.5 and 35 MPa, at 77, 190, and 298.15 K. In Fig. 5, usable hydrogen gravimetric and volumetric storage capacities have been plotted as a function of the pressure at 298.15 K.

The gravimetric capacities vary significantly. They show a gradual and nearly linear increase with pressure across all these MOFs. IRMOF-15 exhibits the highest gravimetric capacity under any pressure and room temperature conditions and reaches the DOE target of 5.5 wt. % at ~35 MPa and 298.15 K. The SIGSUA material shows a consistent upward trend in usable hydrogen gravimetric capacity with increasing pressure, reaching its maximum at 35 MPa with a gravimetric capacity of ~4.2 wt. %, which falls about 36% below the DOE gravimetric target.<sup>4</sup> The ROTNUM MOF demonstrated usable gravimetric capacities that were nearly identical to those of SIGSUA at all pressure levels, as shown in the right panel of Fig. 5. In contrast, VUSJUP showcased notably reduced usable gravimetric capacities, roughly 67% less than those of SIGSUA, despite both MOFs being composed of Br and having similar C/Br ratios.

The variations in usable gravimetric capacities can be attributed to the differences or similarities in density. Specifically, SIGSUA and ROTNUM exhibit closely matched densities, while VUSJUP has a density approximately three times larger (see Tables V and VI). Consequently, the usable gravimetric capacities of VUSJUP are ~67% lower, despite sharing a similar C/Br ratio with SIGSUA. Notably, IRMOF-15 displays the highest gravimetric capacity among the considered MOFs, attributed to its superior porosity and lower density. These findings underscore the direct impact of significantly different or similar density and porosity on the gravimetric storage capacity.

The volumetric capacities exhibit remarkable similarities. IRMOF-20 demonstrates the highest usable volumetric capacity within the pressure range of 0.5–35 MPa. The SIGSUA, while showing values closely resembling those of IRMOF-20, exhibits an approximately 18% reduction in comparison. Moreover, the volumetric capacities of ROTNUM and VUSJUP closely align with those of SIGSUA. The highest value for each one is reached at 35 MPa and is about 0.022 kg/l. This value is about one half of the DOE volumetric target, 0.04 kg/l.<sup>4,114</sup>

The usable volumetric hydrogen isotherms of ROTNUM, IRMOF-20, and SIGSUA appear comparable due to their shared characteristics in terms of porosity, density, radius, and ratio (see Tables V and VI). Surprisingly, despite VUSJUP and SIGSUA having distinct values for these structural properties, the volumetric capacity remains relatively unaffected. This suggests that whether the metal, ratio, or structural properties are consistent or divergent, their impact on the volumetric capacity might be minimal.

The total hydrogen gravimetric and volumetric capacities of SIGSUA and the selected MOFs at low temperatures, 77 and 190 K, are shown in Fig. 6 as a function of the pressure. The ROTNUM MOF and SIGSUA have very similar total gravimetric and volumetric storage capacities at both temperatures and at any pressure. Both materials have similar densities and average pore radii. The total gravimetric capacities of SIGSUA at 77 and 190 K are larger than those of the best Br-based MOF, VUSJUP, and smaller than the capacities of IRMOF-15. In regards to the total volumetric capacities, SIGSUA has larger total volumetric capacities than VUSJUP at 77 K and smaller at 190 K for most of the pressures studied. The volumetric capacities of IRMOF-20. These trends closely resemble those obtained for 298.15 K and 25 MPa, regarding both usable volumetric and gravimetric capacities.



FIG. 4. Usable hydrogen gravimetric and volumetric capacities at 298.15 K and 25 MPa vs isosteric heat and the product of isosteric heat and porosity for SIGSUA, Br-selected, halogens-selected,  $\rho - R_{ave}$ -selected, and classical MOFs.



FIG. 5. Usable hydrogen volumetric and gravimetric capacities of SIGSUA, the best Br-selected MOF with the same C/Br ratio as SIGSUA (VUSJUP), the best  $\rho - R_{ave-}$  selected MOF with similar density and average pore radius as SIGSUA (ROTNUM), and the best classical MOFs (IRMOF-15 and IRMOF-20), as a function of the pressure at room temperature.

# **IV. METHANE STORAGE CAPACITIES**

# A. Methane storage capacities' dependence on porosity, density, and pore size

The usable storage capacities of methane of these MOFs were also examined. The plots shown in Figs. 7 and 8 depict how the usable methane storage capacities at 298.15 K and 25 MPa correlate with the density, porosity, and pore size of the MOFs. The trends observed in the usable methane capacities concerning porosity and density exhibit resemblances to the patterns observed for hydrogen, as shown in Fig. 7.

The usable methane storage capacities of SIGSUA either exceed or are comparable to the pattern observed in classical MOFs, as well as in the Br-selected, the halogens-selected, and  $\rho - R_{ave}$ -



FIG. 6. Total hydrogen gravimetric and volumetric capacity at 77 and 190 K vs pressure for SIGSUA, Br-selected,  $\rho - R_{ave}$ -selected, and classical MOFs.



FIG. 7. Usable methane gravimetric and volumetric capacity at 298.15 K and 25 MPa vs density and porosity for SIGSUA, the Br-selected, the halogens-selected, the  $\rho - R_{ave}$ -selected, and the classical MOFs.



FIG. 8. Usable methane gravimetric and volumetric capacities at 298.15 K and 25 MPa vs the largest and the average pore radii for SIGSUA, the Br-selected, the halogens-selected, the  $\rho - R_{ave}$ -selected, and the classical MOFs.

selected MOFs sets, when plotted against density. This implies that the densities of SIGSUA might be used to predict its gravimetric capacity. Regarding porosity, SIGSUA, as well as Br-selected, halogens-selected,  $\rho - R_{ave}$ -selected, and classical MOFs, consistently exhibit an upturn in usable methane storage capacities with increasing porosity, aligning with the trends observed for hydrogen storage.

The influence of the largest and the average pore radii on usable methane storage capacities is visually shown in Fig. 8. These storage capacities maintain a similar relationship with both the largest and the average pore radii, echoing the observed patterns in hydrogen storage capacities. This alignment implies that, similar to hydrogen, an expansion in pore radius corresponds to a decrease in density, resulting in an increase in the usable gravimetric capacity and indicating a tendency to adopt a lineal behavior with respect to the pore radius. The volumetric capacity increases with the pore radius, but not linearly. As the pore radius increases, it reaches, approximately, a constant or asymptotic value.

Following the approach used for the hydrogen case, MOFs with the highest usable methane gravimetric and volumetric capacities at 25 MPa and room temperature were selected from the classical, Br-selected, halogens-selected, and  $\rho - R_{ave}$ -selected sets for comparison with SIGSUA. The results of these GCMC simulations of the usable methane storage capacities, the C/Br ratios,

the densities, the porosities, and the pore radii of the MOFs at 298.15 K and 25 MPa, are presented in Tables VII and VIII. For the methane investigation, the chosen MOFs from the sets are identical to those selected for the hydrogen study, except for the inclusion of VUSKEA, which replaces VUSJUP. The VUSKEA MOF exhibits the highest usable methane storage capacities among all the Br-selected MOFs.

When examining the usable methane storage capacities at 298.15 K and 25 MPa, SIGSUA demonstrates notably high capacities, surpassing those of Br-selected MOFs and the remaining comparable to the capacities of  $\rho - R_{ave}$ -selected MOFs and the best classical MOFs, IRMOF-20 and IRMOF-15, as presented in Tables VII and VIII The usable methane gravimetric and volumetric capacities of SIGSUA stand at 30.1 wt. % and 0.22 kg/l, respectively, very close to the DOE methane targets.

# B. Methane storage capacities as a function of the isosteric heat of adsorption

The methane isosteric heat of adsorption has also been calculated in the GCMC simulations and compared to the storage capacities to explore any potential relationship between them. The usable storage capacities of SIGSUA and the selected MOFs vs the isosteric heat and the product of the isosteric heat and porosity

**TABLE VII.** Usable methane volumetric (in kg/l) and gravimetric (in wt. %) capacities at 298.15 K and 25 MPa obtained in the present GCMC simulations, density  $\rho$  (in kg/l), porosity, and largest R<sub>I</sub> and average R<sub>av</sub> pore radii (in Å) of the SIGSUA, the Br-selected, the halogens-selected, and the  $\rho - R_{ave}$ -selected MOFs with the highest storage capacities.

MOF	Ratio C/metal	Vc	gc	Density	Porosity	R <sub>l</sub>	R <sub>av</sub>
SIGSUA	C/Br = 2.67	0.218	30.1	0.505	0.644	8.20	6.75
VUSJUP	C/Br = 3.00	0.126	7.8	1.483	0.280	9.11	9.06
VUSKIE	C/Br = 3.00	0.124	7.7	1.492	0.264	7.46	7.27
VUSKEA	C/Br = 2.00	0.153	10.3	1.335	0.339	9.08	9.02
VUSKAW	C/Br = 2.00	0.149	10.0	1.344	0.330	7.95	7.72
XANMUX08	C/Br = 3.33	0.086	5.4	1.514	0.176	6.12	4.27
ROTNUM	C/Zr = 10.67	0.210	29.9	0.492	0.478	7.83	7.28
JEDVIA	C/Zn = 9.00	0.191	26.7	0.524	0.419	7.70	7.42
QUSSAB	C/Cu = 18.00	0.187	27.2	0.500	0.363	7.45	7.30
ROTNUM01	C/Zr = 10.67	0.202	28.8	0.501	0.453	7.91	7.36

**TABLE VIII.** Methane volumetric (in kg/l) and gravimetric (in wt. %) usable capacities at 298.15 K and 25 MPa obtained in the present GCMC simulations, density (in kg/l), porosity, and largest  $R_l$  and average  $R_{av}$  pore radii (in Å) of the classical MOFs.

MOF	Vc	gc	Density	Porosity	$R_l$	R <sub>av</sub>
IRMOF-5	0.013	0.5	2.731	0.015	3.95	3.42
IRMOF-15	0.209	37.1	0.354	0.841	12.99	4.76
IRMOF-20	0.230	26.0	0.655	0.456	10.12	9.95
IRMOF-1	0.194	24.5	0.598	0.349	9.12	8.24
IRMOF-2	0.116	5.0	2.191	0.154	8.17	7.73
IRMOF-3	0.162	18.2	0.731	0.291	9.02	8.76
IRMOF-4	0.040	1.8	2.189	0.070	7.00	6.04
IRMOF-6	0.148	17.0	0.724	0.240	8.89	6.12
IRMOF-7	0.056	3.2	1.665	0.075	5.33	3.82
IRMOF-8	0.223	27.7	0.582	0.491	10.38	10.20
IRMOF-9	0.157	16.9	0.771	0.263	6.85	4.16
IRMOF-11	0.202	29.1	0.491	0.526	11.20	10.50
IRMOF-12	0.213	33.6	0.420	0.516	11.58	11.31
IRMOF-14	0.206	35.4	0.376	0.514	11.90	11.57
IRMOF-16	0.216	33.1	0.437	0.582	11.61	11.61
IRMOF-18	0.151	16.4	0.770	0.217	8.40	8.28
HKUST-1	0.121	11.3	0.949	0.152	7.14	6.94
MOF-177	0.210	31.2	0.462	0.494	9.99	8.47
NU-111	0.185	30.1	0.430	0.456	12.12	5.99
NU-125	0.175	22.4	0.607	0.312	11.27	10.76
ZIF-8	0.110	9.6	1.029	0.154	7.39	4.20

at 298.15 K and 25 MPa are shown in Fig. 9. The isosteric heat of methane adsorption ranges from 0.12 to 0.24 eV. In addition, the values of the product of porosity by isosteric heat fall between 0.01 and 0.11 eV.

Similar to hydrogen, the usable methane storage capacities of these materials tend to decrease as the isosteric heat increases, although not consistently. An exception is observed for Cl-selected materials, where the usable volumetric capacities increase with the isosteric heat. The capacities of these materials tend to increase as the product of the isosteric heat by the porosity increases. The increase

J. Chem. Phys. **160**, 154712 (2024); doi: 10.1063/5.0193291 Published under an exclusive license by AIP Publishing is not monotonic, showing oscillations around an average trend. Specifically, in the case of the volumetric capacity, the dependence on the product of the isosteric heat by the porosity is more consistently monotonic, approaching linearity. According to the present GCMC simulations, an MOF with a product  $Q_{st}$  by porosity equal or larger than 0.13 eV could reach the volumetric DOE target, 0.25 kg/l.

# C. Methane storage capacities' dependence on pressure

GCMC simulations were employed to assess the usable methane storage capacities of SIGSUA, alongside the best Br-selected,  $\rho - R_{ave}$ -selected, and classical MOFs. The simulations were carried out at 298.15 K, covering pressures ranging from 0.5 to 35 MPa. The results of these simulations are shown in Fig. 10. Only the MOFs with the highest storage capacities from each set (Br-selected, classical, and  $\rho - R_{ave}$ ) are compared in that Fig. 10.

Among all the sets, IRMOF-20 emerges with the highest volumetric capacity at 35 MPa, 0.24 kg/l. However, both ROTNUM and SIGSUA exhibit volumetric capacity isotherms resembling that of IRMOF-20, reaching 0.22 and 0.235 kg/l at 35 MPa, respectively. Significantly, these three values closely approach the methane DOE target of 0.25 kg CH<sub>4</sub>/L,<sup>10-14</sup> experiencing only a marginal 6% reduction. The methane isotherms for SIGSUA and VUSKEA display a significant divergence. VUSKEA consistently exhibits lower usable methane volumetric capacity values compared to SIGSUA. This difference may be attributed to the fact that VUSKEA has higher density and lower porosity compared to SIGSUA, leading to reduced volumetric capacities, despite the similar C/Br ratio. This is in contrast with the hydrogen case, where the volumetric capacity of VUSJUP was unaffected by the structural properties.

The methane gravimetric storage capacities of all MOFs exhibit a rapid increase at low pressures and start to saturate around 10 MPa. IRMOF-15 stands out with the highest usable methane gravimetric capacity values within this pressure range. From all the MOFs studied in this paper, only IRMOF-15 meets the DOE target of 33.3 wt.  $\%^{10-14}$  at 298.15 K and 15 MPa. SIGSUA displays a comparable increasing pattern in usable methane gravimetric capacity with



FIG. 9. Usable methane gravimetric and volumetric capacity at 298.15 K and 25 MPa vs isosteric heat and the product of isosteric heat and porosity for SIGSUA, the Br-selected, the  $\rho - R_{ave}$ -selected, and the classical MOFs.



FIG. 10. Usable methane volumetric and gravimetric capacities of SIGSUA, the best Br-selected MOF with the same C/Br ratio as SIGSUA (VUSKEA), the best  $\rho - R_{ave-selected}$  MOF with a similar density and average pore radius as SIGSUA (ROTNUM) and the best classical MOFs (IRMOF-15 and IRMOF-20), as a function of the pressure at room temperature.

rising pressure, reaching its maximum at 35 MPa with a gravimetric capacity of 32 wt. %, which corresponds to around 96% of the DOE target. Similarly to the hydrogen case, the usable methane gravimetric capacities of ROTNUM match those of SIGSUA at all pressure levels, as shown in the right panel of Fig. 10. VUSKEA exhibited

significantly lower usable gravimetric capacities,  $\sim$ 66% less than those of SIGSUA, even though both MOFs are composed of Br and share similar C/Br ratios.

SIGSUA and ROTNUM share similar densities, while VUSKEA has a significantly higher density (see Tables VII and VIII). These

findings suggest that the usable gravimetric capacity might be more influenced by factors such as density and porosity rather than the type of metal. Consequently, the slight variations in methane volumetric values between SIGSUA and ROTNUM could be attributed to their minor differences in porosity, density, pore radii, and distinct metal compositions (see Tables VII and VIII). The structural attributes of VUSKEA and SIGSUA diverge, except for a similar C/Br ratio. These differences yield significantly different gravimetric storage capacities. In summary, SIGSUA and ROTNUM, having similar densities and porosities, exhibit analogous gravimetric capacities, while VUSKEA, with higher density and lower porosity, shows lower gravimetric capacities. As expected, variations in porosity and density contribute to notable differences in methane gravimetric storage capacities.

### V. CONCLUSIONS AND FUTURE SIGHTS

The GCMC results provided herein offer predictions for the usable storage capacities of hydrogen and methane at pressures spanning from 0.5 to 35 MPa, at room temperature of SIGSUA, which was very recently synthesized by Yufit at Durham University.<sup>100</sup> Based on the GCMC simulations conducted, the newly developed SIGSUA demonstrates notably usable hydrogen and methane storage capacities at room temperature and pressures ranging from 25 to 35 MPa. These capacities are comparable to the best classical MOFs and the top-performing  $\rho - R_{ave}$ -selected MOFs, surpassing those of the Br-selected MOFs. While the best classical MOFs exhibit slightly larger usable hydrogen and methane volumetric and gravimetric capacities than SIGSUA, the differences are marginal. The usable hydrogen gravimetric and volumetric storage capacities of SIGSUA at 298.15 K and 35 MPa are 4.15 wt. % and 0.022 kg/l, respectively. It is worth highlighting that SIGSUA nearly achieves the usable hydrogen volumetric capacity DOE target, 0.025 kg/l,<sup>4,114</sup> at 35 MPa and room temperature. The usable methane storage capacities of SIGSUA at room temperature and 35 MPa are 31.8 wt. % and 0.235 kg/l, respectively. These values closely approach the methane DOE targets of 33.3 wt. % and  $0.25 \text{ kg/l},^{10}$ <sup>14</sup> respectively.

The influence of porosity, density, and pore radius on the usable volumetric and gravimetric storage capacities has been investigated for various MOFs, including classical, Br-selected,  $\rho - R_{ave}$ -selected, and, the recently synthesized, SIGSUA. The outcomes indicate a consistent trend where capacities tend to be inversely proportional to density and directly proportional to porosity. Moreover, both usable gravimetric and volumetric capacities generally show a direct proportion with pore radius. Importantly, these results suggest a prevailing pattern where these capacities exhibit independence from the type of metal atom.

The notable storage capacities observed in the newly developed SIGSUA can be attributed to its significant porosity, low density, and relatively spacious pores. It is essential to highlight that these results serve as predictions for the storage capacities of the real material, SIGSUA, offering valuable insights for experimental researchers. Furthermore, increasing porosity and reducing density could potentially lead to improvements in storage capacities, regardless of the metal type.

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### AUTHOR DECLARATIONS

#### **Conflict of Interest**

The authors have no conflicts to disclose.

### **Author Contributions**

**A. Granja-DelRío**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Resources (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **I. Cabria**: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal); Writing – original draft (equal); Writing – review & editing (equal); Writing – review & editing (equal).

### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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