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Melih DOĞANCI and Sadiye VELIOĞLU

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Review Article

Identification of H_2/CO_2 Separation Performance of Inorganic Porous Adsorbents via Molecular Simulations

Melih Doğancı , Sadiye Velioğlu*

Gebze Technical University, Institute of Nanotechnology, Gebze, 41400, Kocaeli, TURKEY

* Corresponding author: Sadiye Velioğlu
E-mail: sadiyevelioglu@gtu.edu.tr

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Abstract

The H_2/CO_2 gas separation is extremely emerging both for the production of H_2 which is useful as an energy source/fuel due to high energy content per unit of weight and capturing the CO_2 emissions that cause global warming and climate change. The adsorption method has come to the fore because it requires less energy for the separation process than other technologies and has a reduced environmental impact. In order to determine the promising adsorbent, it is really time-consuming and cost-intensive to carry out experimental studies for each adsorbent material. Since the capability and efficiency of molecular simulation methods are too high, recently they are emerged to reveal the adsorption performance of existing adsorbent materials. In this review study, we aimed to identify the performance of inorganic porous adsorbents that were defined by molecular simulation approaches. For this scope, we considered three metrics for adsorbents such as CO_2 adsorption capacity, CO_2/H_2 adsorption selectivity, and isotherm obtained depending on pressure. Accordingly, it was proposed from the literature survey that HP adsorbent for pure CO_2 adsorption, PAF-1 for CO_2/H_2 adsorption selectivity and diamondyne for CO_2/H_2 adsorption selectivity at high pressures attracted attention. As a result, we aimed to guide the experiments in choosing the adsorbent material from the data collected and proposed from simulation studies.

Keywords: Inorganic nanomaterials, H_2 purification, CO_2 capture, molecular simulations.

Introduction

Hydrogen (H_2) has a high energetic efficiency and zero carbon emission and is produced from a wide range of resources. Therefore, it received considerable attention and caused rapid intensification of scientific and industrial studies. However, in order to be used as an efficient energy carrier, H_2 must be purified and produced without CO_2 emissions. Because CO_2 emission is also one of the biggest sources for global warming and climate change, which are the main environmental problems experienced (Ülker et al., 2018-2021). Therefore, it is very important to use CO_2 capture technology, which can efficiently reduce CO_2 emissions and separate CO_2 from other gases. In addition, it is crucial to separate H_2 from CO_2 used in processes such as oil refining, methanol, and ammonia productions (Zito et al., 2018). H_2 can mainly be produced via syngas, but this process cannot meet the long-term demand. Another method is the coal gasification which uses the HyPr-RING method. This method attracts more attention due to the abundance of coal resources (Lin et al., 2002; Lin et al., 2004). Similarly, CO_2 again produces from these processes and needs to be separated. Additionally, reducing CO_2 emissions from sources such as coal-fired power plants, which are very common, will play an important role in slowing global warming and climate change. For H_2 purification and CO_2 capture, common separation processes such as amine-based chemical absorptions and cryogenic distillation have been used considerably. However, since these methods require high energy and cost and are limited to some specific applications, alternative separation technologies have been sought. Adsorption technology, which is an alternative method for the separation process, has been promising for CO_2 capture and H_2 sequestration. Additionally, it is widely used for the separation of aromatic isomers and volatile organic chemicals from the air.

Leading gas adsorption processes in industry are Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA), and Temperature Swing Adsorption (TSA) (Mason et al., 2011; Ben-Mansour et al., 2018; Kamotoki et al., 2014). Gas separation is governed by the adsorption and desorption amounts measured using different parameters pressures or temperatures. The relationship between the amount of substance adsorbed by the adsorbent at constant temperature and the equilibrium pressure or concentration is known as the adsorption isotherm. Adsorption isotherms can be defined for any interface: solid-liquid, liquid-gas, or solid-gas. Particularly at the solid-gas interface, isotherms can be classified into six types. The most common adsorption isotherm type is that the amount of adsorbed gas approaches a limiting value due to the saturation of an external surface area of adsorbents. This type of adsorption isotherm is usually modeled by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models (Okumuş and Doğan, 2019).

Porous adsorbents with a high surface area, adjustable pore sizes, and mechanical strength, thermal and chemical stability are expected to offer high gas separation performance for the application of interest. With the development of reticular chemistry, novel porous nanomaterials have been developed to be used as adsorbents. Chief among these are metallic organic frameworks (MOFs), covalent organic frameworks (COFs), and zeolitic imidazolate frameworks (ZIFs) (Janiak and Vieth, 2010). Besides these materials, carbon-based porous materials such as activated carbons (ACs), carbon nanotubes (CNTs), graphene (GR), and graphene oxides (GOs) are proposed as promising adsorbents for gas separation (Saridari et al., 2005; Pellarano et al., 2009; Bhatia et al., 2004; Amadou, and Arouna 2022).

There is a strict requirement for compilation of all existing experimental gas adsorption measurements of these novel adsorbents in order to understand the adsorption mechanism and propose the best one to the industry for specific application. Moreover, it is necessary to carry out adsorption measurements for the rest of novel adsorbents. However, it is not time- and cost-effective approach. In this context, molecular simulation approaches are emerged increasingly to define the promising adsorbent materials for specific industrial separation applications. In this way, complex materials can be easily modeled, and their separation performance can be compared from those of other adsorbents. Recently, it was proved that simulated adsorption performances of many adsorbent materials were very close to experimental results. There are two highly preferred molecular simulation methods such as Monte Carlo (MC) and Molecular Dynamics (MD) approaches (Frenkel et al., 2002; Yiannourakou et al. 2013).

In this review study, we aim to compile the adsorption-based CO_2/H_2 separation performances of porous materials computed using molecular simulations in the literature. Accordingly, we target to reveal the promising materials considering the CO_2/H_2 adsorption selectivity and CO_2 adsorption performances of porous nanomaterials tested under the similar conditions. On top of that, the literature mainly focuses on CO_2 capture by altering the adsorption conditions, especially increasing the pressure. Therefore, gas adsorption isotherms of inorganic porous adsorbents are also reviewed and compared with each other. Collectively, by syncretizing the data proposed from computational studies, this review study will provide a perspective regarding the situation of inorganic porous materials in the adsorption-based CO_2/H_2 separation.

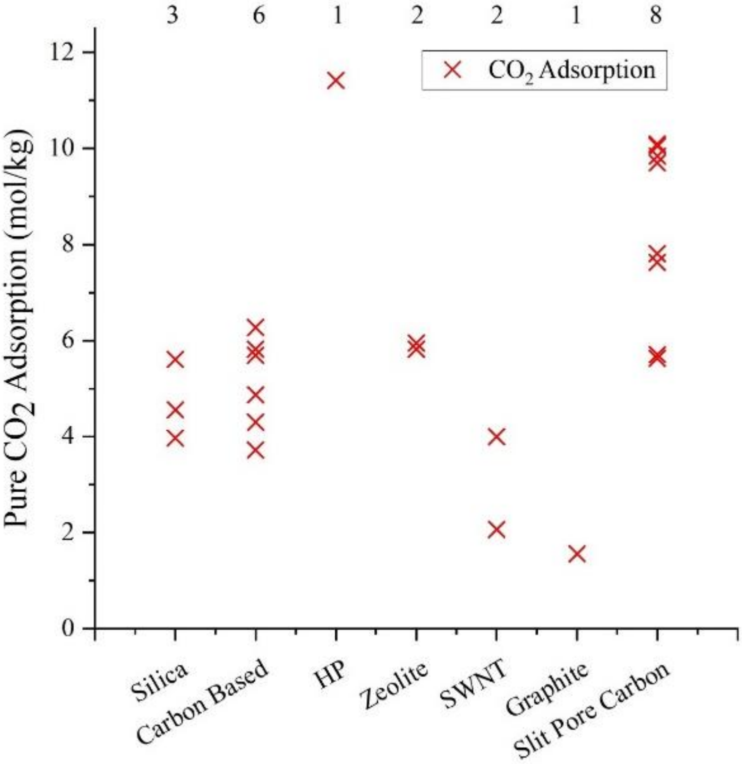

Fig. 1. Pure CO_2 adsorption amounts of different materials adsorbent

Pure CO_2 adsorption capacities of inorganic porous adsorbents

Due to the simplicity, it is preferred to carry out single gas adsorption simulations using MC approaches. More than 20 different studies, pure CO_2 adsorption capacities of seven different adsorbents calculated under almost same temperature and pressure are compiled and given in Figure 1. The numbers at the top of the graph represent the total number of inorganic porous adsorbent examined. For instance, there are 8 pure CO_2 adsorption data of slit pore carbon. As a result of the material classification, carbon-based adsorbents were highly investigated in the literature. This is due to their ease of synthesis, availability, selectivity, and unprecedented stability to the temperature and humidity. However, the best pure CO_2 adsorption performance belongs to the Hex-star phosphorene (HP) studied by Lei et al. (2021), with CO_2 adsorption capacity of 11.42 mol/kg. HP was modeled as a hexagonal lattice by Lei et al. (2021) and proposed as an effective adsorbent for CO_2 adsorption due to its large surface area and the strong interaction with CO_2.

The closest performing adsorbent to HP is the slit pore carbon adsorbent studied by Kumar et al. (2015). Kumar et al. (2015) modeled an adsorbent by adding three graphite sheets on both sides of the carbon pores and investigated the nitrogen doping effect of adsorbent. They tested four different pore widths (H=0.8, 1.2, 1.6, and 2.0 nm) for ordered structure and two random orientation for carbon sheets. In these models, CO_2 adsorption capacities of these N-doped structures were computed up to 60 bar. It was proposed that the N-doped structures had no effect on the pressure changes, and the adsorbed amount of the N-doped models was almost the same in ordered structures having different pore widths. The greatest CO_2 adsorption capacity was observed for the structures having pore widths of 1.6 nm and 1.2 nm at 10 bar. The reason for this was explained as the shift of adsorption from the surface regime to the pore volume regime. Thus, the higher the pore volume, the higher the maximum excess adsorption, regardless of the surface chemistry. In conclusion, hexagonal lattice phosphorene and slit pore carbons are promising adsorbents for pure CO_2 adsorption.

CO_2 adsorption capacities of inorganic porous adsorbents from gas mixtures

To propose the actual performance of any adsorbent, of course, it is essential to carry out mix gas simulations rather than single gas calculations. The presence of second gas in the feed stream can alter both gas adsorption capacity and adsorption-based selectivity. Therefore, gas adsorption performances of some porous inorganic materials from gas mixture of CO_2/H_2 is collected and illustrated in Figure 2. It is worth to note that both CO_2 adsorption from gas mixture of CO_2/H_2 and CO_2/H_2 adsorption-based selectivity, which is the ratio of adsorption and molarity of each gas, are the two important parameters that we used to interpret the performance of any adsorbent. In other words, for the separation of the CO_2/H_2 mixture, both the selectivity and CO_2 adsorption should be considered.

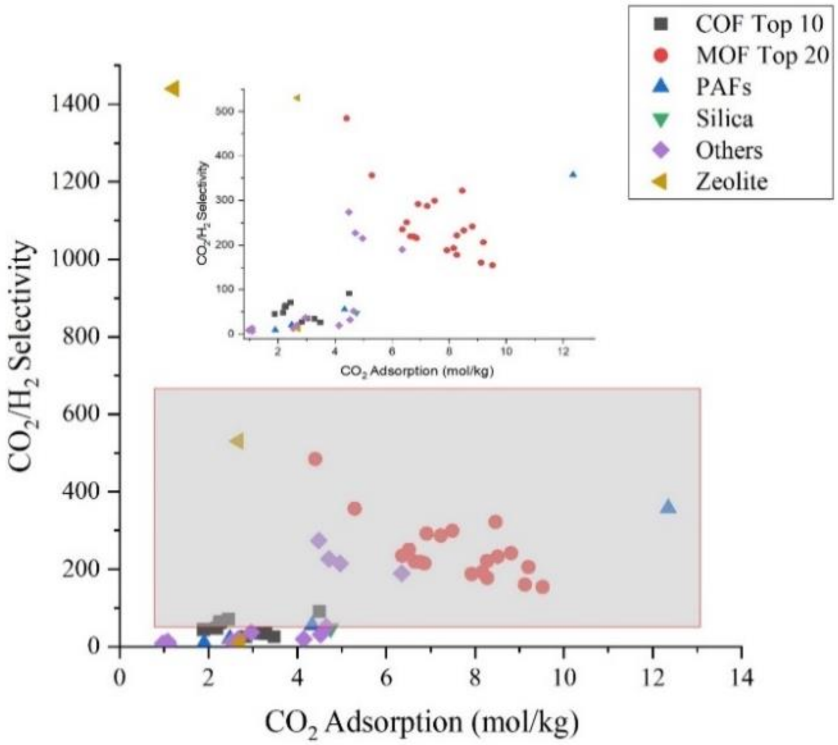

Fig. 2. Mixture CO_2/H_2:15/85 gas selectivity and CO_2 adsorption.

Among compiled CO_2/H_2 selectivity – CO_2 adsorption (mol/kg) data given in Figure 2, adsorption conditions such as pressure (10 bar), temperature (298 K), gas concentration (CO_2/H_2:15/85) were almost same. There are more than 100,000 different MOF structures and 1,000 different COF structures that have been synthesized. However, only tens of them have been examined as an adsorbent and did not display promising adsorption performances. Therefore, high throughput computational screening studies have been carried out to find the promising or best ones from these thousands of different structures. Rather than collecting MOF and COF data from separate studies, we aimed to utilize from these computational screening studies and provide the ones with highest adsorption performances. Therefore, the best 20 MOF structures from the study of Avcı et al. (2018) (Figure 2, red circles), and the best 10 COF structures from the study of Aksu et al. (2020) (Figure 2, black square) are included. In these studies, 3,846 MOFs and 286 COFs were examined for CO_2/H_2 separation. Promising MOF and COF structures were defined based on rejenerability (R%) and adsorbent performance score (APS) metrics. Structures having R% greater than 85% were ranked based on APS and the ones having highest APS values were defined as the promising structures.

Considering Figure 2, highest adsorption selectivity of 1257 belongs to zeolite NaX (Krishna and Van Baten, 2011). However, CO_2 adsorption capacity of NaX is too low. To find the best adsorbent, we need an adsorbent having the adsorption performance at the upper right corner of Figure 2. MOFs attract attention due to both their high adsorption selectivity and CO_2 adsorption capacity. The ones predicted from the study of Avcı et al. (2018) reveal the most promising adsorbent structures. More specifically, DABWUA MOF is the most suitable one for CO_2/H_2 separation with greater than 8 mol/kg CO_2 uptake and 300 CO_2/H_2 selectivity. The high gas adsorption performance of the MOF adsorbent was explained by the narrow pore geometry which increases the accessibility of gases through the adsorption sites available on the frame surface. Another type of adsorbent, PAF, attracts attention due to almost same adsorption selectivity with DABWUA and much greater CO_2 uptake of 12.35 mol/kg. Moreover, PAF studied by Babarao et al. (2009), has approximately 32% higher adsorption than the MOF structure having highest CO_2 adsorption uptake. Babarao et al. (2009) theoretically designed three different PAF structures by functionalizing different groups ($-NH_2$, $-OCH_3$, $-CH_2OCH_2$). The one with highest CO2 uptake was functionalized with $-CH_2OCH_2$. These functional groups provided an increase in the interaction energy with CO_2. Moreover, from an experimental point of view, PAFs have very high surface areas, high thermal and hydrothermal stability. As a result, when both adsorbent performance parameters are considered, PAFs and MOFs become prominent. Therefore, they are highly recommended for the experimentalists to further investigate in the future gas separation processes.

CO_2 adsorption isotherms of inorganic porous adsorbents

Gas separation using adsorption processes in the industry generally takes place at high pressure depending on the conditions of output stream that comes from the reaction media. To provide the industrial-base performance of adsorbents, adsorption measurements are carried out at different pressures ranging from low to high pressures, which lead to observe an adsorption isotherm for each adsorbent. Adsorption isotherm is the collection of gas uptake at each pressure and generally expressed as the equilibrium state between the amount of adsorbed gas on to the adsorbent at constant temperature and the remaining gas in the gas mixture. Novel and hypothetical adsorbents are proposed in the literature and to provide their industrial performance, their CO_2 and H_2 adsorption isotherms were computed up to high pressures. Since adsorption selectivity is an unitless metric, it is more desired to use it in the simulation studies in order to provide a comparison within adsorbents. Figure 3 depicts the CO_2/H_2 adsorption selectivity isotherms of 11 different adsorbents. The adsorption selectivities of adsorbents are collected at 1, 10, 20, and 30 bar and at similar temperatures (~298 K).

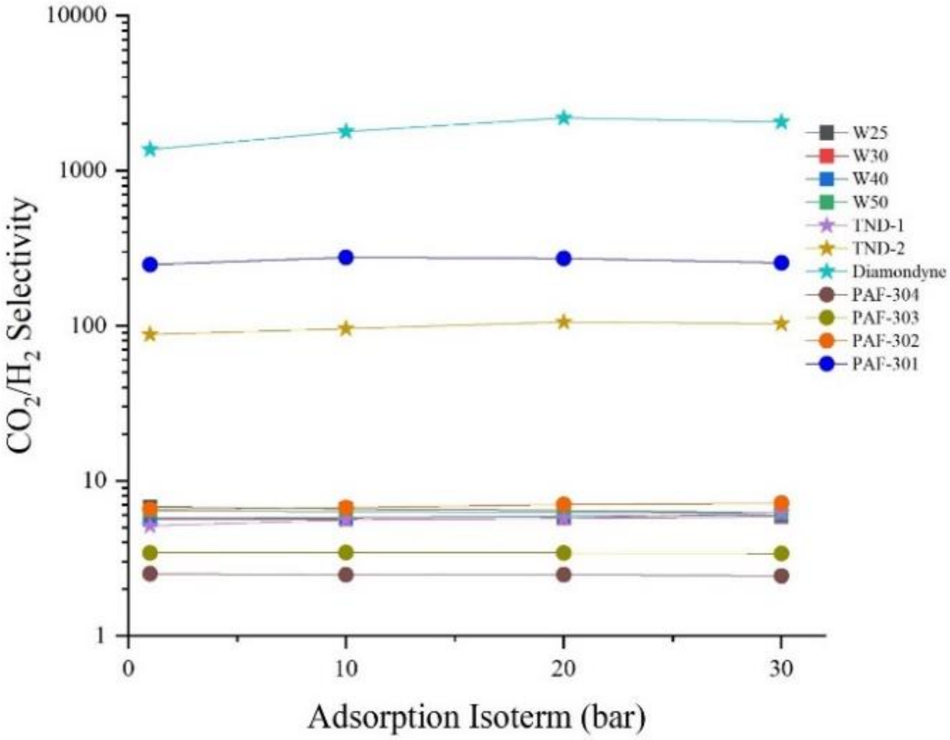

Fig. 3. Adsorption isotherms of selectivity for CO_2/H_2 mixture.

Considering Figure 3, the performance of diamondyne studied by Wang et al. (2015) stands out with its high adsorption selectivity performance at each pressure. With a CO_2/H_2 adsorption electivity of 1,790, it offers about 6 times greater selectivity than the other adsorbent identified in Figure 3. Its adsorption selectivity increases with pressure and reaches to 2,188 at 20 bar. This was attributed to the specific surface area and geometric structure of diamondyne. However, with the further increase adsorption selectivity decreases to 2,062 at 30 bar. Wang et al. [20] also computed the performance of four porous adsorbents. By changing all C−C bonds in a diamond to −C≡C− linkers, they observed a new diamond-like carbon framework (diamondyne). And further replacing the diamond's carbon nodes with acetylenic linkage (C−C≡C−C) tetrahedron node, they designed two new tetrahedral nodes of diamond (TND) frameworks (TND-1 and TND-2) and finally the porous aromatic framework (PAF-301), which was experimentally synthesized. However, rather than diamondyne, all three adsorbents provided comparable adsorption selectivities. On the other hand, the closest structure to the performance of Dimondyne is PAF-1 adsorbent with a CO_2/H_2 adsorption selectivity of 276 at 10 bar studied by Yang et al. (2013). The modeled PAF structures were constructed by replacing the C-C bonds in diamonds with a different number of phenyl rings and finally porous 3D structure were observed with ranging of number of phenyl rings. The lowest phenyl ring concentration led to the greatest CO_2/H_2 selectivity within four PAFs. This is attributed to the low concentration of phenyl ring which yield in a very small pore size of 5.2 Å.

Conclusion

In this review study, the CO_2/H_2 separation performance of several adsorbents computed by molecular simulation approaches was examined and compared considering specific adsorbent metrics. Attention is drawn to the nanomaterials that stand out with best performance in each metric. In this review, it is aimed to guide the adsorption-based CO_2/H_2 separation applications and reveal the promising adsorbents proposed from theoretical studies. As a result of the literature research, three different metrics for the CO_2/H_2 gas separation were noted; pure CO_2 adsorption, CO_2/H_2 selectivity for gas mixture and adsorption isotherm considering CO_2/H_2 selectivity. The adsorbent with the highest pure CO_2 adsorption capacity was reported as Hex-star phosphorene (HP) due to its large surface area and hexagonal pore structure. On the other hand, for CO_2/H_2 gas mixture separation, PAF structure gave the best performance. Finally, diamondyne shined out again in for CO_2/H_2 gas mixture separation but also at high pressures. Collectively, all research were aimed to design imaginary structures including specific sites to accelerate the adsorption selectivity and either increase surface area or alter geometric structure to promote adsorption capacity.

Declaration of interest statement

The authors report there are no competing interests to declare.

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