Materials Research Express

PAPER

Impact of ammonia treatment and platinum group or nickel metal decoration on the activated carbon storage of carbon dioxide and methane

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Keywords: activated carbon, adsorption, carbon dioxide and methane storages, metal decoration

Abstract

Greenhouse gases, chiefly carbon dioxide (CO2) and methane (CH4), emission is responsible for the global warming and heat waves which strike the world causing floods and droughts everywhere with more CO2 attributions. The adsorption and desorption capacities of CO2 and CH4 at room temperature and up to 5.0 and 100 bar, respectively, were investigated for the untreated and ammonia-treated activated carbons (ACs), metal-anchored (metal: Ru, Rh, Pd, Ir or Ni) samples. We merged ammonia treatment and metal decoration to discover their influences on the CO2 and CH4 storage capability of ACs and the potential use of such modified ACs for capturing greenhouse gases and purifying natural gas from CO2. The CO2 storage capacities ranged between 25.2 and 27.7 wt% at 5.0 bar with complete regeneration upon desorption, while the uptakes for CH4 were in the range of 9.6 − 12.6 wt% at 35 bar with hysteresis behavior of the adsorbed gas. The highest adsorption capacities were achieved for the pristine samples, showing that metal decoration reduced slightly the adsorption. Ammonia-treated samples showed minor enhancing effect on the CH4 adsorption in comparison to the CO2 adsorption. The higher adsorption capacities of CO2 than those of CH4 could be employed for upgrading the natural gas, while the 9.6 wt% (2.2 mmol g−1) CO2 storage capacity would allow for its removal from the flue gases at ambient temperature and pressure. The higher adsorption capacity and preferentiality of CO2 over CH4 could be attributed mainly to its higher quadrupole moment and its higher clustering above the AC surfaces, while a minor effect, if any, would be attributed to the modifications of the ACs, implying that physiosorption mechanism acted significantly in the adsorption process in comparison to chemisorption mechanism at the studied conditions.

Introduction

The increase in the concentrations of greenhouse gases [carbon dioxide (CO2), methane (CH4) and nitrous oxide (N2O)] is the main reason for global warming as they trap the Sun’s radiation within atmosphere [1, 2]. Their concentrations were increased dramatically in 2020 in comparison to the pre-industrial levels in 1750 by 149% for CO2, to reach 413.2 ppm, while the increase was by 262% for CH4 and 123% for N2O [3]. Although the global warming decreased from 3.5 °C in 2009 to 2.7 °C in 2015 and to 2.6 °C in 2020, but it is still higher than its target of 2.1 °C [1].

In Paris summit in 2015 [4], the participating governments agreed on the target of net zero emission for reducing the global warming to 1.5 °C. For achieving this target, many countries announced different green
 iniciatives through a multidimensional approaches such as: increasing renewable energy capacities, implementing energy efficiency programs, and developing carbon capture technologies, but regrettably the implemented polices have not fulfilled the optimistic net zero emission target, warming trajectory is still higher than the target, and the present pledges would only bound the overall warming to about 2.4 °C. Recently, the USA have announced a plan to spend 2.0 trillion dollars for controlling the global warming and climate change [3]. In addition, many countries gathered in the UN climate change conference in Glasgow [6] and ended with an enthusiastic goal of stopping the global warming at 1.5 °C through reducing the CO2 emissions. On the other hand, regarding methane, which may be responsible for around quarter of global warming, the countries agreed on a volunteer pledge to reduce its emissions by 30% by 2050 [7].

CO2 is the most significant greenhouse because it is responsible for 80% of the warming effect [3] and it comes from two sources: natural such as bio-decomposition, ocean release, respiration, and its natural presence with natural gas, oil and coal reservoirs; and anthropogenic activities such as burning of fossil fuel for different applications, especially from power generation plants [8]. Unfortunately, the long life of carbon dioxide due to its high thermodynamic stability [9] preserves its high concentrations within atmosphere even after keeping its emission low.

Three well-developed combustion technologies, with different CO2 capture and storage (CCS) techniques, are being used nowadays in the thermo-electrical power generation plants which emit huge amounts of CO2: (1) pre-combustion, (2) oxy-fuel combustion, and (3) post-combustion [10, 11]. In pre-combustion technology, coal gasification treatment is performed before the ambient air combustion step, then steam is reacted with the syngas to form a mixture of (H2/CO2), and finally CO2 is separated parting H2, as a clean source of energy [12]. In oxy-fuel combustion, pure oxygen instead of air, after removing its nitrogen, is used for complete burning of the fossil fuel, resulting in high concentration of CO2 in the flue gas, which is recirculated to further increase its concentration, and is finally captured [13]. In post combustion, the most well-established technology, a separate unit system is installed to remove ashes and CO2 from the flue gases after the combustion process, which is easy fitted and is attached to the pre-existing power plants [14]. The CCS techniques are mature for reducing CO2 concentrations within atmosphere and can be categorized as follows [15]: (1) absorption technology, where amine solutions such as mono/diethanolamine [16] or piperazine [17] are used to chemically absorb CO2 gas. This technology suffers from several drawbacks such as equipment corrosion, generation of toxic volatile chemicals due to solution degradation, and regeneration of CO2 at elevated temperatures [18], (2) chemical adsorption as hydrate compounds, where the flue of the exhausted gas is exposed to stream of water to react with the CO2 gas under high pressure to form hydrated compounds [19]. Usage of chemicals such as tetrahydrofuran (THF) to improve the thermodynamics of the hydrates formation and to overcome the difficulties of the regeneration of CO2 from hydrates make this process costly and keep it in its R&D phase [20], (3) chemical looping combustion (CLC) is based on the use of metal oxides such as NiO and Mn2O3, as an oxygen source, during combustion process instead of pure oxygen [21]. In the CLC process, the carbon dioxide separation and the energy conversion are integrated, but special attention should be directed to avoid material poisoning for highly efficient CO2 separation process [21–24], (4) and the cryogenic distillation is also used for the CO2 separation, based on performing the distillation process under low temperature (−100 °C to −135 °C) and high pressure to form dry ice [25, 26]. The energy requirements for the low temperature cooling of the flue gas make this process very expensive in comparison to the other CCS techniques [27]. Regarding methane storage, it is usually accomplished through high energy consuming methods such as low-temperature liquefaction technique or compression under high pressure [28]. The latter process is performed under high pressure up to ~2000 bar, requiring multi-stage compression facilities and special mandatory safety necessities for the storage tanks [29, 30]. Chemical adsorption as methane hydrates is another storage option, but the problems associated with the sluggish adsorption kinetics and the difficulties in releasing methane back in the desorption process make this technique inadequate [31]. Physical adsorption process allows the spontaneously physical attraction of gas molecules to the surface of the porous materials due to van der Waals attraction forces [32, 33]. These forces are nonspecific interactions, but when polar molecules are involved in the adsorption with polar or ionic surfaces, these interactions are specific and would remain as physisorption state as long as no chemical bonding or electronic perturbation of the adsorbed molecules [34, 35]. These forces include interactions between permanent dipoles, named Keesom forces, between induced dipoles, named London dispersion forces, or between induced and permanent dipoles, named Debye forces [36, 37]. The simplicity of physisorption and the availability of many porous materials have attracted great attention [38]. The physically adsorbed gas molecules can be simply regenerated back through pressure or temperature swing adsorption (PSA or TSA) process of the adsorbents, making the storage process costly effective in both capture and regeneration method [39, 40].

Different varieties of porous materials [41] such as activated carbons (ACs) [33], zeolite [42], and metal–organic frameworks (MOFs) [43] can be used as good adsorbents for the adsorption process of different adsorbates such as gases and liquids. ACs are excellent adsorbents in comparison to the others due to their high surface, low cost, high thermal and chemical stability, and resistance to wet conditions [44, 45]. Their textural properties can be
controlled through chemically or physically activated high carbon contents precursors such as petroleum coke [46], coal [47], agricultural waste materials of rice husk [48], peanut shell [49], fruit stones and seeds [50, 51] and industrial wastes of used tires [52] and polymers [53]. In addition, they can be synthesized from unconventional materials such as sewage sludge, which have positive impact on environment in many aspects as waste disposal and greenhouse gases adsorbents [54].

The ACs are composed of flat hexagonal array of aromatic carbon rings, forming the basal plane sheets (graphene layers) which are broken in different locations to form pores with different shapes and are arranged in a three-dimensional crystalline or mostly amorphous structure [55]. The graphene layers have high electron density regions [56] due to the un-hybridized 2p orbitals, which participate in the π-bonding, providing the AC with its Lewis base character [57]. ACs could be synthesized and modified to enhance their adsorption capacity [58] by doping with heteroatoms such as nitrogen, sulfur, and oxygen, etc, or changing their surface acidity or basicity by attaching acidic functional groups such as carboxylic acid groups through oxidation reactions or basic functional groups of nitrogen moieties such as amine groups through reduction reactions [59, 60].

Furthermore, decorating the ACs surfaces with metal particles may introduce additional active adsorption sites for gas molecules [61, 62]. The CO2 fixations or adductions with transition metals were reported for the CO2 gas molecules, where the CO2 molecule was inserted within the structure to form metal carbon complexes (M-CO2) [63–67]. These interactions were reported for the platinum group metals such as rhodium (Rh) [61, 68], ruthenium (Ru) [69], iridium (Ir) [70], and palladium (Pd) [71, 72] as well as nickel (Ni) [73–75]. They all showed good interactions with CO2, but their interactions could be considered as electron acceptor-donor interactions [76], where the CO2 carbon atom was susceptible to nucleophilic attack [67]. On the basis of the above literature, we combined ammonia treatment and metal decoration and to explore their effects on the carbon dioxide and methane storage capacity of activated carbon and the potential use of such modified activated carbon for capturing greenhouse gases and upgrading natural gas by the selective removal of carbon dioxide.

Experimental section

The preparation and characterization of all adsorbents were published in our previous article papers [32, 33] and were investigated for hydrogen adsorption and desorption measurements at both room and cryogenic temperatures [32]. In brief, the commercially available Norit AC was doped by 2.0 wt% nitrogen via heat treatment under ammonia flow at 850°C. A platinum group metal (Ru, Rh, Pd, Ir) or Ni was loaded as 5.0 wt% on either untreated or ammonia-treated ACs by wet impregnation, followed by reduction under hydrogen atmosphere at 350°C. They were characterized by using a JEOL X-ray fluorescence (XRF; JSSX-3202M), Japan. Nitrogen isotherms were generated by using a Micromeritics Gemini VII, 2390 analyzer, USA. X-ray powder diffraction (XRPD) was recorded on a Rigaku MiniFlex 600, Japan. Elemental analysis (CHNS) was accomplished by using a PerkinElmer 2400 Series instrument, USA. Morphology was studied by using a JSM-7600F Schottky Field Emission Scanning Electron Microscope (FE-SEM), Japan, equipped with INCAx-al chemical energy-dispersive x-ray (EDX) spectroscopy, Oxford instrument, England. The storage capacity measurements were evaluated with high-pressure volumetric analyzer HPVAl (Micromeritics), USA. The CO2 and CH4 storage uptakes were assessed by measuring the pressure-composition-isotherms (PCI) at RT and up to 5.0 bar for CO2 and 100 bar for CH4. The PCI curves were measured 5 times for validity and repeatability of the results, where the details of characterizations were elucidated in [32, 33].

Results and discussion

Carbon dioxide uptake

Figures 1–5 show the PCI adsorption-desorption isotherms at 298 K, before and after ammonia treatment, for CO2 adsorption and desorption isotherms of the Ru-, Rh-, Pd-, Ir- and Ni-anchored ACs, respectively. Table 1 summarizes the excess CO2 storage capacities for all of the samples at both 1.0 and 5.0 bar. All the PCI isotherms were type-I of IUPAC classification [77, 78], where the storage capacities increased gradually with pressure, without the observation of saturation limit up to 5 bar, indicating higher achievable storage capacities at higher pressures. The shape of the isotherms could represent the shape of the empirical Freundlich isotherm model [79, 80], supported by Freundlich data fitting for CO2 adsorption, reported by Singh et al [81]. Total reversibility, without hysteresis, was achieved after removing the pressure during the desorbing cycle, indicating complete regeneration of CO2.

At ∼5.0 bar, the CO2 storage capacities of our various ACs were within the range of 25.2 to 27.7 wt% (an average of ∼26.5 wt%), equivalent to 5.7–6.3 mmol g−1 (an average of ∼6.0 mmol g−1). Our reported CO2 storage values were within the cited literature for different ACs with different textural properties, much higher
than the values of (2.4, 3.1 and 3.19) mmol g\(^{-1}\) [82–84], little above the values of (5, 5.2, 5.5 and 5.7) mmol g\(^{-1}\) [85–88], comparable to the values of 6.0 mmol g\(^{-1}\) [89–92], and within the values of 15 – 30 wt% reported for some other ACs [93], but little lower than the storage value of 8.5 mmol g\(^{-1}\), reported for 3250 m\(^2\) g\(^{-1}\) Maxsorb AC [94]. At ~1.0 bar, the CO\(_2\) storage capacities of our various ACs were ~9.6 wt% (2.2 mmol g\(^{-1}\)), higher than the required value for good capture of 1.0 mmol g\(^{-1}\) at ambient conditions [95]. This storage capacity was higher than the 7.6 wt% or 7.88 wt%, reported for the untreated or NH\(_3\)-treated ACs [96, 97] and within the reported storage of 2.1–3.9 mmol g\(^{-1}\) values for different nitrogen-doped ACs [98–100], but much lower than the 5.39 mmol g\(^{-1}\), reported for the highly nitrogen-doped (22.3 wt%) ACs [101].

Ammonia treatment, which eliminated the surface impurities and amorphous carbon species from the carbonaceous structure [102–104], showed minor improvement of carbon dioxide uptake with very slight difference from one sample to another. Anchoring the transition metals on the ACs skeleton did not improve their CO\(_2\) uptake, but uptake reduction was observed, which could be attributed to the counter-effect of metal pore-blocking and the higher density of the metal-anchored ACs than the pristine ones [40, 105]. The high strength of the double bonds in CO\(_2\) molecule of 803.75 kJmol\(^{-1}\) [9] would prevent its cleavage over the

![Figure 1. CO\(_2\) adsorption and desorption isotherms (PCI) at 25 °C for untreated and NH\(_3\)− treated ACs, decorated with Ru.](image)

![Figure 2. CO\(_2\) adsorption and desorption isotherms (PCI) at 25 °C for untreated and NH\(_3\)− treated ACs, decorated with Rh.](image)
transition metals surfaces, at the studied conditions, which supported the presence of CO₂ configuration as un-activated flat geometry onto the porous materials without being modified [106]. Even though, our metal-anchored samples showed superior CO₂ storage capacity in comparison to 0.856 mmol g⁻¹ storage capacity for some metal oxides–decorated ACs [107].

**Methane uptake**

Figure 6—10 show the PCI adsorption–desorption isotherms at 298 K, before and after ammonia treatment, for CH₄ adsorption and desorption of the Ru-, Rh-, Pd-, Ir- and Ni-anchored ACs, respectively. The excess CH₄ storage capacities at 5, 35 bar, and at saturation plateau are briefed in table 2. All the PCI isotherms were of type-I of IUPAC classification [77, 78], where the storage capacities increased with pressure until the adsorption plateaus started at ~50 bar.
The hysteresis phenomenon, with no tangential trajectories between the adsorption and desorption, could be attributed to the meta-stability of CH$_4$ gas molecules within the pore network [77]. Retaining of some CH$_4$ gas upon pressure removal could be attributed to some chemical interactions as cushion gases with AC's surfaces [29]. At 35 bar, the CH$_4$ storage capacities of our various ACs ranged between 9.6 to 12.6 wt% (an average of ∼11.1 wt%), which were equivalent to 6.0–7.9 mmol g$^{-1}$ (an average of ∼6.9 mmol g$^{-1}$). Our reported CH$_4$ storage values were superior as 7 folds as of the storage capacities of ACs, reported by Kumar et al [108]. They were in consistence with the reported values of different ACs [29, 92, 94, 109–111]. In addition, they showed better storage capacities values than the 8.9 wt% storage capacity value, reported for MOFs [112]. Our values were lower than the storage capacities values of 8.3 and 9.0 mmol g$^{-1}$, reported for the higher surface area Maxsorbs ACs samples [91, 94]. Ammonia treatment showed a little bit enhancement, above 20 bar, for almost all the samples, which could be accredited to its erosion effect on the AC surface [102–104]. Anchoring the transition metals on the ACs decreased the CH$_4$ uptake, attributed to the counter-effect of metal pore-blocking and the higher density of the metal—anchored ACs in comparison to the pristine ones [40, 105]. The high bond strength for CH$_4$ molecule, with a value of 429 kJmol$^{-1}$ [113], would result in high thermodynamic stability of the CH$_4$ bonds to be dissociated by the transition metals, as it was supported by the difficulty of its dissociation.
on nickel surfaces [114]. Furthermore, the high tetrahedral symmetry of the CH₄ gas molecules may prevent the formation of polar interactions on the surface of the transition metals [115].

At 5.0 bar, the storage capacity of CO₂ was as ~6 folds as that of CH₄ and as 530 folds as that of hydrogen at ambient temperature [32], a feature enables the upgrading of natural gas as clean fuel sources after the removal of CO₂ contamination by physical adsorption. While purifying hydrogen from CO₂ impurities is essential, it would be so beneficial for numerous industries such as steam reforming of methane (SRM) [116, 117], water gas shift (WGS) [118, 119], and ammonia synthesis [120, 121].

This high adsorption preference of CO₂ in comparison to CH₄ cannot be justified through the Lewis acid–base interactions between the acid gases and the Lewis base sites of graphene basal planes [57, 122, 123]. The CO₂ has a basicity of 515.8 kJ mol⁻¹ and a proton affinity of 540.5 kJ mol⁻¹ [124, 125], which are little lower than the basicity of CH₄ of 520.6 kJ mol⁻¹ and proton affinity of 543.5 kJ mol⁻¹ [124, 126]. Such small difference in acidity between the two gases would not give CO₂ gas such adsorption superiority over CH₄ gas in this context. Even though, a proportional correlation was reported between the acidity of C–H bond and its electrostatic interactions with the resonating π electrons of the graphene basal plane [127, 128], which would increase upon its coordination with the 3d metal ions [129]. However, in our study, the case did not appear to be the same due
to the absence of any interactions between the anchored metals and the CH₄ molecules. In addition, the high critical temperature \( (T_C) \) of CO₂ gas of 304 K, in comparison to the lower critical temperature of 190 K for CH₄ \[130\], would allow CO₂ molecules to be easily liquefied and to act as a condensed liquid instead of volatile supercritical gas on the AC’s surfaces. Nevertheless, CO₂ did not condense, in our study, because we performed our experiments at pressure much lower than the critical pressure \( (P_C) \) of 64 bar for CO₂ gas at 298 K, where the CO₂ gas molecules existed in their vapor form \[131\].

In spite of the overall non-polarity of both CO₂ and CH₄ molecules due to their molecular symmetry with 0.0 Debye dipole moments \[131, 132\], the large difference between the carbon electronegativity of 2.5 and that of oxygen of 3.5 in comparison to the tiny difference between carbon and that of hydrogen of 2.1 \[133\] would result in high molecular quadrupole moment of 4.3 \( (\text{D.Å}) \) for CO₂ molecule in comparison to 0.02 \( (\text{D.Å}) \) for CH₄ molecule \[62\]. This CO₂ high quadrupole moment may result in the formation of a high CO₂ molecular clustering geometry, where a positively charged pole on the carbon atom of one CO₂ molecule would interact with a negatively charged pole on the oxygen atom of a second CO₂ molecule and so on to form large clusters over the AC surfaces. This high stacking of the linear CO₂ molecules in a flat parallel orientation was simulated over the aromatic carbon ring \[134\] and was reported by Meconi \[135\] by using the classical force-fields theory, where the optimized geometry showed that the flat CO₂ molecules would stack with its carbon atom along the middle half above the two carbons of the aromatic ring, while the two oxygen atoms of the CO₂ molecules were located in the middle empty center above the carbon aromatic ring. This high clustering of CO₂ molecules in comparison to CH₄ molecules may be supported by the high van der Waals forces between CO₂ molecules, as

Table 1. Excess CO₂ uptake (wt%) at 25 °C for pristine, NH₃—treated ACs, and their decoration with Ru, Rh, Pd, Ir, or Ni.

| Sample                        | CO₂ excess uptake (wt%) at R.T. and 1.0 bar | CO₂ excess uptake (wt%) at R.T and 5.0 bar | Incremental in CO₂ excess uptake wt% after NH₃ treatment at 5.0 bar |
|-------------------------------|--------------------------------------------|------------------------------------------|---------------------------------------------------------------|
| AC (Norit) \[33\]             | 9.9 ± 0.1                                  | 26.2 ± 0.1                               | 5.7                                                            |
| NH₃-treated AC \[34\]         | 10.4 ± 0.1                                 | 27.7 ± 0.1                               |                                                                |
| Ru-anchored, AC               | 9.3 ± 0.1                                  | 25.2 ± 0.1                               | 2.4                                                            |
| Ru-anchored, NH₃-treated AC   | 9.3 ± 0.1                                  | 25.8 ± 0.1                               |                                                                |
| Rh-anchored, AC               | 9.3 ± 0.1                                  | 25.3 ± 0.1                               | 1.2                                                            |
| Rh-anchored, NH₃-treated AC   | 9.3 ± 0.1                                  | 25.6 ± 0.1                               |                                                                |
| Pd-anchored, AC               | 9.7 ± 0.1                                  | 26.6 ± 0.1                               | 0.4                                                            |
| Pd-anchored, NH₃-treated AC   | 9.7 ± 0.1                                  | 26.7 ± 0.1                               |                                                                |
| Ir-anchored, AC               | 9.6 ± 0.1                                  | 25.6 ± 0.1                               | 3.1                                                            |
| Ir-anchored, NH₃-treated AC   | 9.6 ± 0.1                                  | 26.4 ± 0.1                               |                                                                |
| Ni-anchored, AC               | 9.6 ± 0.1                                  | 25.5 ± 0.1                               | 5.1                                                            |
| Ni-anchored, NH₃-treated AC   | 9.6 ± 0.1                                  | 26.8 ± 0.1                               |                                                                |

Figure 9. CH₄ adsorption and desorption isotherms (PCI) at 25 °C for untreated and NH₃—treated ACs, decorated with Ir.
reflected by their higher $T_C$ than the lower $T_C$ for CH$_4$ molecules. This clustering state may also be supported by the negative values of the entropy ($\Delta S^\circ$), reported upon CO$_2$ adsorption on activated carbon surfaces, favoring the conversion of randomizations state to ordered state upon adsorption [136]. On the other hand, the stacking of the tetrahedral CH$_4$ gas molecules over the aromatic ring was reported [137] to be located on one of the atoms of the C—C bond in a bidentate or tridentate rather than mono-dentate fashion. The linear flat geometry stacking of CO$_2$ in comparison to the tetrahedral stacking would allow higher assembling and accumulations of the CO$_2$ molecules over the graphene sheets. This favorable CO$_2$ clustering could also explain the steeped adsorption behavior, reported by Krishna et al [138], of the CO$_2$ in comparison with the mild increase of CH$_4$ adsorption and support the higher adsorption energy of $-25.1$ kJ mol$^{-1}$ for CO$_2$ molecules than the lower adsorption energy of $-16.5$ kJ mol$^{-1}$ for CH$_4$ above graphene sheets [135]. Moreover, the smaller kinetic diameter for the CO$_2$ molecule of $3.3$ Å than the $3.8$ Å for CH$_4$ molecule [62] may explain the higher response to pressure on the graphene layers due to the higher diffusivity of the smaller CO$_2$ molecules within the pore structure of the ACs.
Conclusion

High storage capabilities were achieved for both carbon dioxide and methane storages for the ACs before and after their modifications with a mean average value of ~26.5 wt% at 5 bar and 11.1 wt% at 35 bar for CO2 and CH4, respectively. Such high storage would make them appealing materials for the removal of both CO2 and CH4. At 5 bar, the adsorbents showed ~ as much 6 folds as predilection towards carbon dioxide in comparison to methane, a feature working beneficially for natural gas upgrading and decreasing greenhouse gasses. This high adsorption capacity and preferentiality of CO2 over CH4 could be attributed to its physicochemical nature, mainly quadrupole moment, and higher clustering effect.

The dominant adsorption mechanism for CO2 and CH4 is mainly the physical adsorption with little attribute, if any, toward the chemical adsorption. This behavior would have its good economical aspect as no extra costs would be needed for expensive metals decoration of the AC’s surfaces for biased enhancement of the CO2 and CH4 adsorptions under the studied conditions. In addition, their CO2 storage capacities were as 530 folds as of their H2 storage capacities, which would be so beneficial for generating hydrogen with low-carbon contents, as one of the most crucial issues in hydrogen production.

Acknowledgments

This Work was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, grant Number (11-ENE1472-02).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

Dr Mohamed F Aly Aboud conceived and designed the experiments, performed all experiments and all data analysis, and wrote the paper; Both Prof. Zeid A ALOthman and Prof. Abdulaziz A Bagabas participated in the methane and carbon dioxide storage measurements, data analysis, paper writing and corrections. All authors examined and approved the final manuscript.

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References

[1] 2022 Emission database for global atmospheric research (https://edgar.jrc.ec.europa.eu/)
[2] Tollefson J 2018 Clock ticking on climate action Nature 562 172–3 (http://marronnier.ch/wp-content/uploads/2019/05/nature-global-warming-d41386-018-06876-2.pdf)
[3] W. M. O. (WMO) 2022 Greenhouse Gas Bulletin: Another Year Another Record (https://library.wmo.int/index.php?lvl=notice_display&id=21975#Y-Yv5syBReIU)
[4] 2022 The Paris Agreement (https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement)
[5] 2022 Biden Announces $2 Trillion Climate Plan. The New yourk Times (https://nytimes.com/2020/07/14/us/politics/biden-climate-plan.html)
[6] 2022 26th UN Climate Change Conference of the Parties (COP26) (https://ukcop26.org/)
[7] U. e. program. 2022 New global methane pledge aims to tackle climate change (https://unep.org/news-and-stories/story/new-global-methane-pledge-aims-tackle-climate-change)
[8] C. H. E. (CHE) 2022 Main sources of carbon dioxide emissions (https://che-project.eu/news/main-sources-carbon-dioxide-emissions/)
[9] Glöckler G 1958 Carbon–oxygen bond energies and bond distances J. Phys. Chem. 62 1049–54
[10] Feron P and Hendriks C 2005 CO2 capture process principles and costs Oil & Gas Science And Technology 60 451–9
[11] Yang H et al 2008 Progress in carbon dioxide separation and capture: a review J. Environ. Sci. 20 14–27
[12] Gibbins J and Chalmers H 2008 Carbon capture and storage Energy Policy 36 4317–22
[13] Zheng L 2011 Oxy-Fuel Combustion for Power Generation and Carbon Dioxide (CO2) Capture (Netherlands: Elsevier) 1–13
[14] Guo Y, Zhao C, Li C and Lu S 2014 Application of PEI–K2CO3/AC for capturing CO2 from flue gas after combustion Appl. Energy 129 17–24
[15] Metz B, Davidson O, De Coninck H, Loos M and Meyer L 2005 IPCC special report on carbon dioxide capture and storage (Cambridge: Cambridge University Press) (https://ipcc.ch/report/carbon-dioxide-capture-and-storage/)

[16] Hendriks C 1995 Energy conversion: CO2 removal from coal-fired power plant (Netherlands: Kluwer Academic Publishers)

[17] Bougie F and Iluita M C 2011 CO2 Absorption in aqueous piperazine solutions: experimental study and modeling Journal of Chemical & Engineering Data 56 1547–54

[18] Hinkov I, Lamari F, Langlois P, Dicko M, Chilev C and Pentchev I 2016 Carbon dioxide capture by adsorption Journal of Chemical Technology and Metallurgy (JCTM) 51 609–26

[19] Sun D and Englellos P 2014 Storage of CO2 in a partially water saturated porous medium at gas hydrate formation conditions Int. J. Greenhouse Gas Control 1 1–8

[20] Zhang Y, Yang M, Song Y, Jiang L, Li Y and Cheng C 2014 Hydrate phase equilibrium measurements for (THF + SDS + CO2 + N2) aqueous solution systems in porous media Fluid Phase Equilib. 370 12–8

[21] Lyngfelt A and Mattisson T 2011 Materials for chemical-looping combustion Efficient Carbon Capture for Coal Power Plants 63 475–504

[22] Younas M, Sohal M, Leong L, Bashir M J and Sumathi S 2016 Feasibility of CO2 adsorption by solid adsorbents: a review on low-temperature systems Int. J. Environ. Sci. Technol. 13 1839–60

[23] Fang H, Haibin L and Zengli Z 2009 Advancements in development of chemical-looping combustion: a review International Journal of Chemical Engineering 2009 710515

[24] Hossain M M and de Lasa H I 2008 Chemical-looping combustion (CLC) for inherent CO2 separations—a review Chem. Eng. Sci. 63 4433–51

[25] Tuinier M J, van Sint Annaland M, Kramer G J and Kuipers J A M 2010 Cryogenic CO2 capture using dynamically operated packed beds Chem. Eng. Sci. 65 114–9

[26] Font-Palma C, Cann D and Udemu C 2021 Review of cryogenic carbon capture innovations and their potential applications Journal of Carbon Research 7 1–18

[27] Song C, Liu Q, Deng S, Li H and Kitamura Y 2019 Cryogenic-based CO2 capture technologies: State-of-the-art developments and current challenges Renew. Sustain. Energy Rev. 101 265–78

[28] Ghai K and Ben-Fares F-Z 2018 Power-to-Methane: A state-of-the-art review Renew. Sustain. Energy Rev. 81 433–46

[29] Quinn D F, MacDonald J A and Socin K 1994 Microporous carbons as adsorbents for methane storage, presented at the Microporous Carbons as Adsorbents for Methane Storage Conference. 208. American Chemical Society (ACS) national meeting (Washington, DC, United States, 21-26 Aug 1994)

[30] Menon V C and Komarneni S 1998 Porous adsorbents for vehicular natural gas storage: a review J. Porous Mater. 5 43–58

[31] Zhou Y, Wang Y, Chen H and Zhou L 2005 Methane storage in wet activated carbon: studies on the charging/discharging process, Carbon 43 2087–12

[32] Aboud M F A, ALothman Z A and Bagabas A A 2021 Hydrogen storage in untreated/ammonia-treated and transition metal-decorated (Pt, Pd, Ni, Rh, Ir and Ru) activated carbons Applied Sciences 11 6604

[33] Aboud M F A, ALothman Z A and Bagabas A A 2021 Storage and separation of methane and carbon dioxide using platinum-dioxide-decorated activated carbons treated with ammonia Mater. Res. Express 8

[34] Thommes M 2010 Physical adsorption characterization of nanoporous materials Chem. Eng. Tech. 82 1059–73

[35] Thommes M and Cychoz K A 2014 Physical adsorption characterization of nanoporous materials: progress and challenges Adsorption 20 233–50

[36] Kanai H, Inoue Y, Yuzawa L, Goo R and Wakatsuki H 2005 Importance of Debye and Keesom interactions in separating m-xylene and p-xylene in GC-MS analysis utilizing PEG stationary phase (in eng), J Chromatogr Sci 43 57–62

[37] Gooch J W (ed) 2007 London dispersion forces (London forces) In Encyclopedic Dictionary of Polyomers (New York: Springer) 582

[38] Morris R and Wheelley P 2008 Gas storage in nanoporous materials Angewandte Chemie (International ed. in English) 47 9496–81

[39] Leung D Y C, Caramanna G and Maroto-Valer M M 2014 An overview of current status of carbon dioxide capture and storage technologies Renew. Sustain. Energy Rev. 39 426–43

[40] Aboud M F A, ALothman Z A, Habila M A, Zlotocka C, Latroche M and Cuevas F 2015 Hydrogen storage in pristine and d10-block metal-anchored activated carbon made from local wastes Energies 8 3578–90

[41] Sai Bhargava Reddy M, Ponnamma D, Sadasivuni K K, Kumar B and Abdullah A M 2021 Carbon dioxide adsorption based on porous materials RSC Adv. 11 12658–81

[42] Dong J, Wang X, Xu H, Zhao Q and Li J 2007 Hydrogen storage in several microporous zeolites Int. J. Hydrogen Energy 32 4998–5004

[43] Uzun A and Keskin S 2014 Site characteristics in metal organic frameworks for gas adsorption Prog. Surf. Sci. 89 56–79

[44] Sircar S, Golden T and Rao M 1996 Activated carbon for gas separation and storage Carbon 34 1–12

[45] Bottani E J and Tascón J M 2008 Adsorption by Carbons 1st edn (Netherlands: Elsevier)

[46] Zhu X, Fu Y, Hu G, Shen Y, Dai W and Hu X 2012 CO2 Capture with activated carbons prepared by petroleum coke and KOH at low pressure Water Air Soil Pollut. 224 14387

[47] Wazir A H, Haq I u, Manan A and Khan A 2020 Preparation and characterization of activated carbon from coal by chemical activation with KOH International Journal of Coal Preparation and Utilization 42 1477–88

[48] Alam M M et al 2020 The potentiality of rice husk-derived activated carbon: from synthesis to application Processes 8 203

[49] Arjunan A and Viswanathan B 2018 Porous activated carbon material derived from sustainable bio-resource of peanutshel for H2 and CO2 storage applications Indian J. Chem. Technol. 25 140–9

[50] Martinez M L, Torres M M, Guzmán C A and Maestri D M 2006 Preparation and characteristics of activated carbon from olive stones and walnut shells Ind. Crops Prod. 23 23–8

[51] Mopounj S, Moomsi P, Palas W and Khumpai S 2015 Characterization and properties of activated carbon prepared from tamarind seeds by KOH activation and for Fe(II) adsorption from aqueous solution The Scientific World Journal 2015 415961

[52] Arysadejwarachich W, Tantrapapanichakoon W, Nakagawa K, Muki S R and Tanom M 2003 Preparation and characterization of mesoporous activated carbon from waste tires Carbon 41 157–64

[53] Evans M J B, Halliop E and MacDonald J A F 1999 The production of chemically-activated carbon Carbon 37 269–74

[54] Miricioiu M G et al 2021 Sewage sludge derived materials for CO2 adsorption Applied Sciences 11 7139

[55] Moseley P T, Rand D A, Davidson A and Monahov B 2018 Understanding the functions of carbon in the negative active-mass of the lead–acid battery: A review of progress Journal of Energy Storage 19 272–90

[56] Haydar S, Ferro-Garcia M, Rivera-Utrilla J and Joly J 2003 Adsorption of p-nitrophenol on an activated carbon with different oxidations Carbon 41 387–95
[57] Rehman A, Park M and Park S-J 2019 Current progress on the surface chemical modification of carbonaceous materials Coatings 9 103
[58] Gao X, Yang S, Hu L, Cai S, Wu L and Kawi S 2022 Carbonaceous materials as adsorbents for CO2 capture: synthesis and modification Carbon Capture Science & Technology 3 100039
[59] Arrigo R et al 2010 Tuning the acid/base properties of nanocarbons by functionalization via amination JACS 132 9616–30
[60] Shafereyn M S, Daud W M A W, Houshmand A and Shamiria A 2010 A review on surface modification of activated carbon for carbon dioxide adsorption J. Anal. Appl. Pyrolysis 89 143–51
[61] Kim J et al 2020 How RH surface breaks CO2 molecules under ambient pressure Nat. Commun. 11 5649
[62] Ries R et al 2013 Studies on the adsorption behavior of CO2-CH4 mixtures using activated carbon Braz. J. Chem. Eng. 30 939–51
[63] Scheuermann M L, Semproni S P, Pappas I and Chirik P J 2014 Carbon dioxide hydrosilylation promoted by cobalt pincer complexes Inorg. Chem. 53 9463–5
[64] Lundquist E G, Huffman J C and Caulton K G 1986 Formation of a heterometallic carbon dioxide complex with concurrent reduction of carbon dioxide JACS 108 8309–10
[65] Brookes N J, Ariefard A, Stranger R and Yates B F 2011 Tuning the Laplaza-Cummins 3-coordinate Mn(R)Rh3 catalyst to activate and cleave CO2 Dalton Trans. 40 5599–78
[66] Guy J and Sheldrick G M 1978 Bis(triethylphosphine)iminium [m+]hydrido-decarbonyltriosmium-[m]carboxylato-heptadecacarbonylhexaosmate, [Ph3P2N]3+[(HO3hCO)10.02C.Os17] Acta Crystallographica B 34 1718–22
[67] Appel A M et al 2013 Frontiers, opportunities, and challenges in biochemically and chemical catalysis of CO2 fixation (in eng) Chem. Rev. 113 6621–58
[68] Calabrese J C, Herskovitz T and Kinney J B 1983 Carbon dioxide coordination chemistry. 5. The preparation and structure of the carbon dioxide adsorption ternary mixtures on activated carbon 5649
[69] Lundqvist E G, Huffman J C and Caulton K G 1986 Formation of a heterometallic carbon dioxide complex with concurrent reduction of carbon dioxide JACS 108 8309–10
[70] Brookes N J, Ariefard A, Stranger R and Yates B F 2011 Tuning the Laplaza-Cummins 3-coordinate Mn(R)Rh3 catalyst to activate and cleave CO2 Dalton Trans. 40 5599–78
[71] Guy J and Sheldrick G M 1978 Bis(triethylphosphine)iminium [m+]hydrido-decarbonyltriosmium-[m]carboxylato-heptadecacarbonylhexaosmate, [Ph3P2N]3+[(HO3hCO)10.02C.Os17] Acta Crystallographica B 34 1718–22
[72] Appel A M et al 2013 Frontiers, opportunities, and challenges in biochemically and chemical catalysis of CO2 fixation (in eng) Chem. Rev. 113 6621–58
[73] Calabrese J C, Herskovitz T and Kinney J B 1983 Carbon dioxide coordination chemistry. 5. The preparation and structure of the rhodium complex Rh(eta1-CO2)(CO)(diars)2 JACS 105 5914–5
[74] Tanaka H, Nago H, Peng S M and Tanaka K 1992 Crystal structure of cis-(carbonyl)eta1-carbonylbis(2,2’-bipyridyl) ruthenium, an active species in catalytic carbon dioxide reduction affording carbon monoxide and HCOO Organometallics 11 1450–1
[75] Truscott B J, Nelson D J, Slawin A M Z and Nolan S P 2014 CO2 fixation employing an iridium(0)-hydrido complex Chem. Commun. 50 286–8
[76] Dubois D L 1997 Development of metal phosphine complexes as electrocatalysts for CO2 and CO reduction Comments Inorg. Chem. 19 307–25
[77] DuBois D L, Miedaner A and Halliwanger R C 1991 Electrochemical reduction of carbon dioxide catalyzed by [Pd (triphenphine) (solvent)](BF4)2 complexes: synthetic and mechanistic studies JACS 113 8753–64
[78] Aresta M and Nobile C F 1977 Carbon dioxide-bis(triethylphosphine)nicket complexes J. Chem. Soc., Dalton Trans. 7 708–11
[79] Kim Y-E, Kim I and Lee Y 2014 Formation of a nickel carbon dioxide adduct and its transformation mediated by a Lewis acid Chemical Communications, 10.1039/C4CC04080H 50 11438–61
[80] Aresta M, Nobile C F, Albano V G, Forini E and Manassero M 1975 New nickel–carbon dioxide complex: synthesis, properties, and crystallographic characterization of (carbon dioxide)bis(tricyclohexylphosphine)nicket J. Chem. Soc., Chem. Commun. 15 636–7
[81] 2012 Lewis Concept of Acids and Bases [https://chem.libretexts.org/Go/page/1282]
[82] Matthias T et al 2015 Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report Pure Appl. Chem. 87 1051–69
[83] Sing KS 1985 Reporting physiobsisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984) Pure Appl. Chem. 57 603–19
[84] Ayasew N, Ebelgi A N and Wankasi D 2017 Modelling and interpretation of adsorption isotherms Journal of Chemistry 2017 3039817
[85] Proctor A and Toro-Vazquez J F 1996 The freundlich isotherm in studying adsorption in oil processing Journal of the American Oil Chemists’ Society 73 1627–33
[86] Singh I, Basu S and Bhunia H 2019 Dynamic CO2 adsorption on activated carbon adsorbents synthesized from polycrylonitrile (PAN) kinetic and isotherm studies Microporous Mesoporous Mater. 280 357–66
[87] Zhang Z et al 2012 Sustainable and hierarchical porous enteromorpha prolifera based carbon for CO2 capture J. Hazard. Mater. 229 183–91
[88] Vargas D, Giraldol L, Erto A and Moreno-Piraján J 2013 Chemical modification of activated carbon monoliths for CO2 adsorption J. Therm. Anal. Calorim. 114 1099–47
[89] Blanco Lopez M C, Martinez–Alonso A and Tascón J M D 2000 N2 and CO2 adsorption on activated carbon monoliths for CO2 capture Energy & Fuels 14 647–53
[90] Parshetti G K, Chowdhury S and Balasubramanian R 2013 Biomass derived low-cost microporous adsorbents for efficient CO2 capture Fuel 148 246–54
[91] Wang J, Heerwig A, Lohe M R, Oschatz M, Borchardt L and Kaskel S 2012 Fungi–based porous carbons for CO2 adsorption and separation J. Mater. Chem. 22 13911–3
[92] Vargas D P, Giraldo L and Moreno-Piraján J C 2012 CO2 adsorption on granular and monolith carbonaceous materials J. Anal. Appl. Pyrolysis 96 146–52
[93] Wang R, Wang P, Yan X, Lang J, Peng C and Xue Q 2012 Promising porous carbon derived from celtuce leaves with outstanding supercapacitance and CO2 capture performance ACS Appl. Mater. Interfaces 4 5800–6
[94] Pino D and Bessières D 2017 CH4/CO2 mixture adsorption on a characterized activated carbon Journal of Chemical & Engineering Data 62 1475–80
[95] Grande C A, Blom R, Möller A and Möllmer J 2013 High-pressure separation of CH4/CO2 using activated carbon Chem. Eng. Sci. 89 10–20
[96] Dreisbach F, Staudt L and Keller J 1999 High pressure adsorption data of methane, nitrogen, carbon dioxide and their binary and ternary mixtures on activated carbon Adsorption 5 215–27
[97] Meng L-Y and Park S-J 2012 Investigation of narrow pore size distribution on carbon dioxide capture of nanoporous carbons Bull. Korean Chem. Soc. 33 3749–54
[98] Himeno S, Komatsu T and Fujita S 2005 High-pressure adsorption equilibria of methane and carbon dioxide on several activated carbons Journal of Chemical & Engineering Data 50 369–76
[99] Khatri R A, Chuang S S, Soong Y and Gray M 2006 Thermal and chemical stability of regenerable solid amine sorbent for CO2 capture Energy & Fuels 20 1514–20
[133] Polar Covalent Bonds - Electronegativity 2022 (https://chem.libretexts.org/Courses/Athabasca_University/Chemistry_350%3A_Organic_Chemistry_I/02%3A_Polar_Covalent_Bonds_Acids_and_Bases/2.01%3A_Polar_Covalent_Bonds--Electronegativity)

[134] Liu X-Q et al 2016 Molecular simulation of CH₄, CO₂, H₂O and N₂ molecules adsorption on heterogeneous surface models of coal Appl. Surf. Sci. 389 894–905

[135] Meconi G M and Zangi R 2020 Adsorption-induced clustering of CO₂ on graphene Phys. Chem. Chem. Phys. 22 21031–41

[136] Hesham M A A-M and Ibrahim G 2020 Experimental study of adsorption on activated carbon for CO₂ capture CHAP IntechOpen

[137] Tsuzuki S and Fujii A 2008 Nature and physical origin of CH/π interaction: significant difference from conventional hydrogen bonds Phys. Chem. Chem. Phys. 10 2384–94

[138] Krishna R and van Baten J M 2010 Investigating cluster formation in adsorption of CO₂, CH₄, and Ar in zeolites and metal organic frameworks at subcritical temperatures Langmuir 26 3981–92