Design of carbon dioxide sorbents in the context of the potential energy landscape

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Abstract: This article explores a modern approach to the design of carbon dioxide (CO_2) sorbents based on the concept of the potential energy landscape (PEL). The authors analyze the relationship between PEL characteristics and CO_2 sorption efficiency. The article demonstrates how the manipulation of PEL parameters enables the development of optimized materials with desired sorption properties. The article examines the influence of the depth and distribution of energy minima on the selectivity, capacity, and kinetics of CO_2 sorption. Various strategies for modifying the PEL, including surface functionalization and the targeted introduction of defects, to achieve the desired sorption characteristics are highlighted. Examples of different types of sorbents, such as MOFs, zeolites, and activated carbons, designed within the framework of the PEL concept are presented. Potential applications of the developed sorbents in carbon capture and storage technologies, as well as the synthesis of chemically valuable products have been considered. This review will be of interest to materials science and energy specialists involved in the development of new sorption materials.

Keywords: carbon dioxide; molecular modeling; sorption; quantum chemistry; potential energy landscape.

Проектирование сорбентов диоксида углерода в рамках концепции ландшафта потенциальной энергии

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Аннотация: Рассмотрен современный подход к проектированию сорбентов диоксида углерода (CO_2) на основе концепции ландшафта потенциальной энергии (ЛПЭ). Приведен анализ взаимосвязи между характеристиками ЛПЭ и эффективностью сорбции CO_2. Показано, как изменение параметров ЛПЭ позволяет разрабатывать оптимизированные материалы с требуемыми сорбционными свойствами. Исследовано влияние глубины и распределения энергетических минимумов на селективность, емкость и кинетику сорбции CO_2. Обсуждаются различные стратегии изменения ЛПЭ, включая функционализацию поверхности, целенаправленное введение дефектов для достижения желаемых сорбционных характеристик. Приведены примеры различных типов сорбентов, таких как MOF, цеолиты, активированные угли, проектирование которых осуществлялось в рамках концепции ЛПЭ. Рассмотрены потенциальные применения разработанных сорбентов в технологиях улавливания, хранения углерода, а также синтез химически ценных продуктов. Обзор представляет интерес для специалистов в области материаловедения и энергетики, занимающихся разработкой новых сорбционных материалов.

1. Introduction

With the ever increasing concentration of carbon dioxide (CO_2) in the atmosphere and the associated alarming climatic changes – global warming and suppression of certain ecological systems – the development of effective methods for CO_2 capture is becoming an increasingly urgent task [1]. The chemical and physicochemical properties of this sorbate make the problem of CO_2 fixation complex. It should be noted that CO_2 has an extremely low-energy chemical structure, which determines its phenomenal thermodynamic stability. It cannot be efficiently decomposed into its simple constituents, solid carbon and molecular oxygen. CO_2 does not react chemically with other low-energy substances [1]. For example, even the most energetically successful chemical interactions of CO_2 (with water and amines) are reversible. The enthalpic increase of the Gibbs free energy only partially compensates for the entropic prohibition against reducing the conformational freedom of the sorbed gas molecules [2].

Plants and some bacteria use CO_2 to produce glucose, which is further converted to cellulose for cell walls, starch as a form of chemical energy storage, and proteins and lipids for the daily functioning of living things. The thermodynamic potential of CO_2 physisorption is also estimated to be mediocre. Because of the lack of dipole moment of this gas molecule, its electrostatic attraction to the particles of potential sorbents (Lewis bases or nanometer pore walls) is not strong enough. While effective binding of CO_2 is in principle hardly possible, many materials show a reasonably satisfactory sorption capacity [2, 3].

Currently, promising approaches include CO_2 adsorption by solid sorbents and absorption by liquid sorbents [4]. In particular, porous materials [5] stand out due to their ability to utilize their high surface area. In order to obtain the maximum practical benefit from this group of materials, it is necessary to optimize the diameters of the available pores as well as their volumes [5, 6]. In turn, liquid sorbents can be competitive in terms of their performance as they have similar intermolecular interaction energies in sorbent-sorbent and sorbent-sorbate pairs. The resulting favorable enthalpic factor should numerically exceed the unfavorable entropic factor. The latter is always unfavorable in gas sorption applications due to the increase in the order of the system, i.e. the suppression of the degrees of freedom of the bound sorbate [7]. In this case, the absolute efficiency and rating of any test sorbent is determined by its ability to selectively bind CO_2 and by the kinetics of sorption and desorption.

The aim of this review was to consider the basic principles of rational design of CO_2 sorbents on the basis of the potential energy landscape (PEL) concept. The review provides examples of satisfactory theoretical realizations of this approach to obtain more functional materials. The PEL describes the dependence of the potential energy of a system on its internal coordinates, where the system under study consists of a certain number of atoms or molecules that define fundamentally important properties of the material.

2. The concept of potential energy landscape

The concept of PEL provides a powerful tool for rational design of sorbents with given properties [8–12]. Within the PEL concept, all possible values of the potential energy of a system (or other suitable thermodynamic potential) are unified by a single mathematical function depending on a set of internal coordinates of the system (Fig. 1).
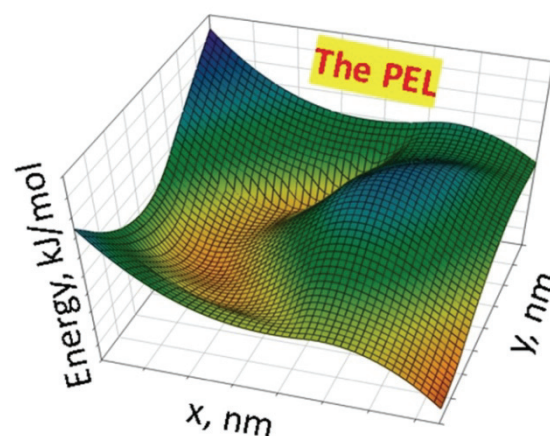

Fig. 1. Model PEL calculated for a small area of an arbitrary CO_2 sorbent: *x, y* are arbitrarily chosen linear directions on a multidimensional surface; "Energy" is the total potential energy of the system; "The PEL" is the potential energy landscape

The concept of PEL is close in meaning to the concept of phase space, with the difference that PEL does not operate with instantaneous values of atomic momentum when a point within the space is given. Both PEL and phase space are mathematical models and have no material analogs. The multidimensionality of the PEL does not allow one to visualize all its surfaces simultaneously, but suggests mechanisms for analyzing the PEL by means of differential analysis for multidimensional functions.

The PEL concept is applied to analyze systems having many possible states with different stability. In the context of molecular modeling, the PEL makes it possible to:

– *Determine the geometry of molecules*: Minima on the PEL correspond to the most stable conformations of molecules;

– *Study mechanisms of chemical reactions*: A reaction pathway on the PEL corresponds to a transition from one minimum (reactants) to another (products) through a saddle point (transition state). The height of the barrier between minima determines the activation energy of the reaction;

– *Analyze molecular dynamics*: PEL allows to simulate the movement of atoms in a molecule and to study transitions between different conformations.

Theoretical methods for studying the PEL of a material or working system include any mathematical algorithm that supports the physically relevant evolution of the system geometry, i.e. the change of its internal variables in the direction of a systematic decrease of the total energy of the z-matrix. These include classical and ab initio molecular dynamics, Monte Carlo Metropolis, iterative algorithms for minimizing the forces acting on each atom in the system, and algorithms for finding the global minimum of energy with a stochastic component, such as the periodic kinetic energy injection method [13–16]. The most valuable information provided by the latter is the list of low-energy stationary points. The obtained minima of the potential energy of the system are uniquely characterized in terms of total energy and geometrical parameters (z-matrix of the structure). The total energy depends on the Hamiltonian applied to the model system. It is useful to express this quantity in terms of the detected global minimum belonging to the PEL. Among the most relevant groups of model Hamiltonians, we would like to highlight the following three, which are characterized below.

First, we deal with the molecular-mechanical Hamiltonians. In standard applications they represent the integral potential energy by the sum of independent equations for the interatomic Coulomb ($\sim R^{-12}$) and London ($\sim R^{-6}$) forces and the interelectronic repulsion forces ($\sim R^{-12}$). If covalent bonds are present in the system, bond, valence plane angle and valence dihedral angle equations must be defined [17–19]. These equations specify a harmonic or more complex dependence of the energy of the system on its actual deviation from the initially given equilibrium value. Such interaction potentials do not imply the breaking and forming of covalent bonds, but adequately reproduce the thermal motion of atoms at sufficiently high temperatures and pressures [20–23]. Molecular mechanical potentials are still actively used in biophysical and materials science research projects [24], including the design of sorption materials for CO_2.

Second, Density Functional Theory (DFT) provides the optimal balance between the accuracy of capturing the electronic structure of the material and the cost of the computational cycle. DFT is ubiquitously used in materials science problems, including the analysis of possibilities for improvement of previously known sorbents [14, 25–28]. The screening of possible directions for improving the properties of the base material is performed by testing the PEL for each structural modification option in terms of thermodynamic potentials. In particular, PEL scans are often performed along the assumed coordinates of the chemisorption reaction and physisorption process to identify activation barriers and preferred sorption centers in the case of functionalized materials.

Third, semiempirical Hamiltonians – both derived from Hartree-Fock theory and based on simplified Density Functional Theory – provide a rather comfortable balance between the size of the system and the duration of the numerical calculation [29–32]. It seems possible to improve the computational performance by more than three orders of magnitude compared to Hartree-Fock and most DFT methods. Unfortunately, none of the semi-empirical methods solve the problem of increasing the computational cost by three orders of magnitude while increasing the problem size by only a factor of two [30]. Because of the relatively low computational cost, semiempirical Hamiltonians are particularly important for the study of PEL, which requires extensive initial scans to qualitatively understand the shape of the landscape [30, 33–35].

Certain PEL properties can be obtained or verified by experimental physical methods [36–40], such as structural analysis (XRD, AFM), spectroscopy (FTIR, Raman, NMR) and, to a large

extent, modern electron microscopy (REM, SEM, TEM). The measurement of the heat of adsorption by chemical calorimetry techniques allows determining the binding energy of CO_2 to the sorbent. On the other hand, by measuring adsorption isotherms, adsorption capacity and adsorption kinetics can be determined to better parameterize and confirm the main patterns on the PEL. A combination of theoretical and experimental methods is the most relevant philosophy of modern materials science. In this case, the more resource-intensive part is delegated to molecular modeling methods.

3. Results and Discussion

The development of more efficient materials for primary CO_2 sorption is being actively pursued worldwide. While some technologies have already been implemented in industry, e.g. amine scrubbing [40], many still need to be improved and made more competitive [38–41]. However, the largest group of methods is of purely academic interest [21, 24, 42–45]. The main reason for this situation is the excessive cost of the proposed materials. Systematic research on the PEL characteristics of economically inefficient materials can pave the way for their cheaper production.

Let us consider some currently used and promising carbon dioxide sorbents to which the concept of potential energy landscape has been applied.

3.1. Using inorganic compounds

According to the principle of chemistry of inorganic compounds, the reactions of carbonate formation can be a basic solution. For example, strong bases – hydroxides of calcium, sodium, potassium, lithium – have good CO_2 sorption parameters. Calcium and iron oxides are also worth mentioning [1, 46]. A PEL study using a combination of global minimum search and molecular dynamics simulations for an alkaline earth metal salt with a weakly coordinating anion showed that calcium tetrakis (pentafluorophenyl)-borate traps 5.5 CO_2 molecules per calcium atom, while barium tetrakis (pentafluorophenyl)-borate traps 3.6 CO_2 molecules per calcium atom [46]. Iron oxide reacts with CO_2 and moisture to form iron carbonate, effectively removing CO_2 from the environment. This is widely used as an absorber in food packaging and industrial applications.

3.2. Using organic compounds

Among the organic sorbents, ionic liquids should be mentioned [7]. This term covers a large group of solvents with a very wide temperature range of the liquid state. Due to the liquid aggregate state of the sorbent, gas absorption occurs with its entire volume (Fig. 2). Many ionic liquids form hydrogen bonds of varying strength with one of the oxygen atoms of CO_2. Thus, the sorbent and the sorbate develop an affinity between them [23, 47–50]. Lanyun Wang et al. performed molecular dynamics calculations for hybrid systems containing ionic liquids, metal cations and CO_2, which showed that in [Bmim][BF$_4$]–MBF$_4$, the Na^+ ion has the least tendency to aggregate and form an M^+ layer, making it difficult for CO_2 to contact the anion. In addition, Na^+ has the strongest attraction to the [BF$_4$]$^-$ anion, which favours the expansion of the [Bmim][BF$_4$] space and consequently an increase in the number of CO_2 molecules absorbed. This is in agreement with the experimental data. On the other hand, the addition of other metal cations weakens the ability of the [Ac]$^-$ anion to chemically bind to CO_2, which is the main reason for the decrease in the absorption capacity of the system [23].
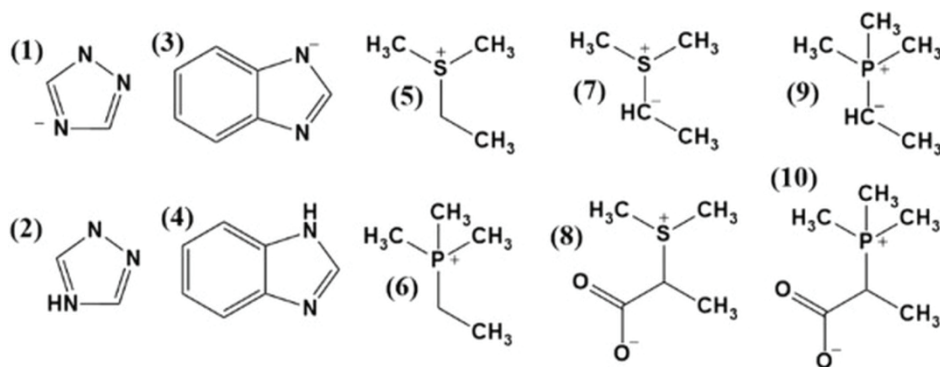

Fig. 2. Phosphonium and sulfonium ionic liquids with aprotonic heterocyclic anions for CO_2 chemisorption. Reproduced from the author's open-access source [51]

The authors of this article have investigated the mechanism of carbon dioxide sorption by sulfonium and phosphonium ionic liquids (Fig. 2) through the formation of intermediate products – ylides. To evaluate the efficiency of sorbents, electronic properties were calculated, charge transfer was studied, and geometrical parameters of compounds were estimated [51].

3.3. Using liquid membranes

CO_2 is separated from other gases by liquid membranes, which are thin layers of liquid. Liquid membranes selectively allow CO_2 to pass through while retaining other gases due to the different binding strengths of different gases. The liquid layer can be sandwiched between two gas-permeable membranes or deposited on a porous substrate [52–54]. Hao Dong et al. investigated the CO_2/H_2 sorption selectivity of graphene oxide based membranes with different ionic liquids. PEL calculation by density functional theory method and binding energy determination explained the preferential permeation of CO_2 over H_2 and the anomalously high values for graphene oxide with C_4mimBF_4 ionic liquid [52]. Compared to traditional gas separation methods such as cryogenic distillation, liquid membranes require less energy. In addition, membrane systems are generally more compact than other gas separation technologies. In a supported liquid membrane, the liquid phase is retained in the pores of the porous substrate. In an emulsion membrane, the liquid phase is dispersed as an emulsion in another liquid. This technology is used in natural gas purification, CO_2 capture from flue gas waste and separation of gases such as CO_2, H_2S and N_2 in the petrochemical industry [42, 55–58]. Guangyao Yu et al. studied the reduction reaction of carbon dioxide on graphene substrate doped with magnesium, nickel and nitrogen. The PEL calculation and the resulting charges, electronic state densities and Gibbs energies confirmed the assumption that both magnesium and nickel centres are jointly involved in the reaction [55]. The study of the PEL of a sorbent in direct contact with the pollutant gas is the most obvious application of the PEL concept. The same applies without reservation to the solution of competitive absorption problems. The knowledge of the parameters of the corresponding PEL dramatically changes the speed of the design of a new material, although it requires experimental verification.

3.4. Development of polymeric membranes

PEL can be of great support for the synthesis of polymeric membranes in which the most successful structural patterns are purposefully combined to accelerate CO_2 absorption kinetics and increase sorbent capacity. Understanding the activation barriers of the process and the specificity of steric factors makes it possible to design the most promising new sorbents.

3.5. CO_2 capture using biological systems

Microalgae such as chlorella and spirulina are capable of absorbing CO_2 during photosynthesis [59]. This is an environmentally friendly and sustainable way to capture CO_2, which can be used to produce biofuels and other valuable products. Some enzymes, such as carboanhydrase, can catalyze the hydration reaction of CO_2, converting it into bicarbonate. This approach can be used to create biological CO_2 capture systems [59].

3.6. PEL study to evaluate the efficiency of CO_2 sorption

In the context of gas sorption by a solid or liquid material, the PEL determines the interaction of a CO_2 molecule with the sorbent surface [60–63]. In cases where CO_2 is fixed by the entire volume of the sorbent, the difficulty of PEL analysis increases significantly because of the number of landscape dimensions involved. For example, the minima on the PEL correspond to stable states of the sorbed molecule, and the depth of the minimum characterizes the energy of its binding to the sorbate. A sorbent can have different types of active centers with different CO_2 binding energies. This is shown on the PEL as multiple minima of different depths. The barriers on the PEL determine the kinetics of sorption and desorption and indicate the relative simplicity or complexity of activation of these processes. A comparison of the activation barriers present on the PELs allows the researcher to understand the microscopic scenario in which the physical and chemical processes induced in the system will unfold [15, 27, 28, 64, 65]. Note that each PEL contains information about a large number of behavioral scenarios, but only the lowest energy scenarios are projected in the real world. In systems confined at high temperatures and pressures, the probabilities of high-energy and low-energy scenarios are balanced as the limiting role of activation barriers on PELs is offset [66–68].

Table 1. Relationship between PEL characteristics and CO_2 sorption efficiency

Sorbent	Coordination centers	Distance between adsorption center and CO_2, nm	Enthalpy of the formation, kJ·mol^{-1}	Binding energy, kJ·mol^{-1}	Source
Study of geometrical parameters					
[emim][TfO]	C(CO_2)–O(TfO)	0.235		29.8	[14]
[emim][Tf2N]	O(CO_2)–H(emim)	0.236		23.3	[14]
amino-functionalized graphene (FG)	C(CO_2)–N(FG)	0.137	+9.36		[16]
–CH$_2$–COO$^-$	C(CO_2)–O	0.254		19	[39]
–CH$_2$–NH–CO–CH$_2$–	C(CO_2)–O	0.289		9	[39]
–CH$_2$–N(CO)$_2$–C$_6$H$_3$–	C(CO_2)–O	0.295		8	[39]
–CH$_2$–O–CH$_2$–	C(CO_2)–O	0.275		10	[39]
–C$_6$H$_4$–O–C$_6$H$_4$–	C(CO_2)–O	0.318		4.4	[39]
–CH$_2$–Si–(OCH$_3$)$_3$	C(CO_2)–O	0.293		7.3	[39]
bmim	O(CO_2)–H	0.231		14	[39]
TBA	O(CO_2)–H	0.267		6.7	[39]
TBP	O(CO_2)–H	0.324		3.7	[39]
BMPYRR	O(CO_2)–H	0.262		9.3	[39]
Study of chemical reaction path					
indazolide	C(CO_2)–N		−68		[15]
1,2,4–triazolide	C(CO_2)–N		−46		[15]
benzimidazolide	C(CO_2)–N		−40		[15]
3–trifluoromethyl-pyrazolide	C(CO_2)–N		−6		[15]
[P2224][BENZIM]	C(CO_2)–C(P2224)	0.157	−132		[27]
[P66614][BENZIM]	C(CO_2)–C(P66614)	0.158	−129		[27]
[P2224][2MTBENZIM]	C(CO_2)–C(P2224)	0.159	−71		[27]
[P66614][2MTBENZIM]	C(CO_2)–C(P66614)	0.158	−127		[27]
tetraethylammonium 1,2,3-triazolide	C(CO_2)–N(triazolide)	0.152	−23		[28]
Study of molecular conformations					
Dialkylcarbonates (DAC)	C(CO_2)–O(DAC)	0.246	−11.6 (D8C)		[25]
[Bmim][BF4]					[23]
[Bmim][BF4]–[Li][BF4]					[23]
[Bmim][BF4]–[Na][BF4]					[23]
[Bmim][BF4]–[K][BF4]	anion/ cation/metal– CO_2.	anion – CO_2<cation – CO_2			[23]
[Bmim][Ac]					[23]
[Bmim][Ac][Li][Ac]					[23]
[Bmim][Ac]–[Na][Ac]					[23]
[Bmim][Ac]–[K][Ac]					[23]
[Ca][TFPB]	O(CO_2)–Ca	0.22	−8		[46]
[Ba][TFPB]	O(CO_2)–Ba	0.30	−7.8		[46]
C$_1$mimBF$_4$				1.01	[52]
C$_4$mimBF$_4$				1.32	[52]
C$_8$mimBF$_4$				1.54	[52]
C$_4$mimPF$_6$				1.34	[52]
C$_4$mimOTf				1.44	[52]
C$_4$mimNTf$_2$				1.82	[52]

Table 1 shows the relationships between some parameters characterizing the CO_2 sorption efficiency and the PEL for a number of sorbents studied. Geometric parameters, chemical reaction pathways, and molecular conformation studies were considered as options for applying the PEL concept. The following descriptors were selected for analysis: distance between interacting centers, enthalpy of formation, and binding energy. The distance between interacting centers is an important parameter that reflects the force of attraction between the particles. The bond length determined by this distance indicates the nature of the interaction – electrostatic or covalent – and is inversely proportional to the bond strength: the smaller the distance, the stronger the bond. The distances for the sorbents shown in Table 1 range from 0.137 nm between CO_2 carbon and nitrogen of functionalized graphene, corresponding to a covalent bond, to 0.324 nm between CO_2 oxygen and hydrogen of tetrabutylphosphonium (TBP), corresponding to an electrostatic interaction. The enthalpy of formation, whose negative value indicates the exothermic character of the process, is also an important factor that often favors sorption. For amine-functionalized graphene, the enthalpy of addition of the CO_2 molecule is positive, +9.36 kJ·mol^{-1}. This indicates a lower stability of the obtained compound compared to the starting materials. A negative enthalpy of formation, as in [P2224][BENZIM] –132 kJ·mol^{-1}, [P66614][BENZIM] –129 kJ·mol^{-1} and others, indicates the stability of the formed product. Finally, the binding energy, which characterizes the strength of the interaction between the elements of the system, is directly correlated with the bond strength and corresponds to the depth of the potential well on the PEL.

The PEL of a sorbent is determined by its chemical composition and surface structure. The key factors affecting the PEL are as follows. The *chemical nature of the adsorption centers* determines the intermolecular interactions between the sorbent and the sorbate. The *introduction of functional groups* capable of interacting specifically with CO_2 can increase the binding energy and selectivity of adsorption (Fig. 3). For example, amine, hydroxyl, and carboxyl groups exhibit relatively strong electrostatic interaction with the bound gas molecules [69–71]. This increases the enthalpic gain in absorption and adsorption applications by liquid and solid porous materials. The *porosity and specific surface area of the sorbent* have a positive effect on its CO_2 sorption capacity. At the same time, such
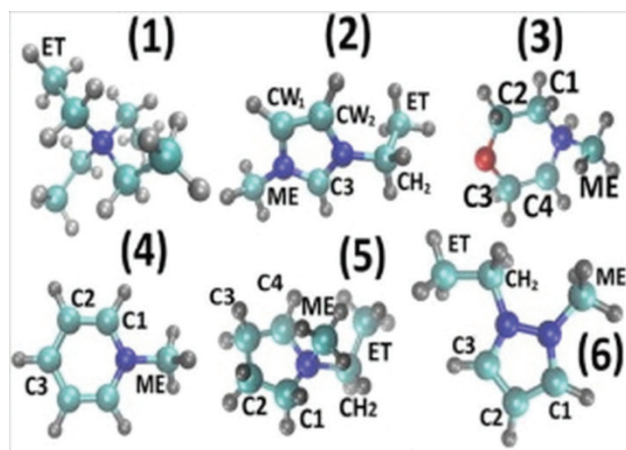

Fig. 3. The use of aminated cations representing different families of ionic liquids for CO_2 chemisorption. Thermodynamic modeling based on the PEL concept. Reproduced from the author's source [76] with permission from Elsevier. CopyrightElsevier 2024

sorbent characteristics can worsen the sorption and desorption kinetics. The manifestation of this effect should be expected in case of the presence of "pockets" in the porous sorbent sample, which are difficult to access for sorbate particles. The correct design of hierarchical porous structures is the primary task in the application of the PEL concept. A developed porous structure with a large specific surface area provides a large number of sorption centers and, consequently, a high sorption capacity of the material [5, 71–75].

Achieving a perfect match between the pore diameter of the synthesized material and the effective diameter of the CO_2 molecule is considered a challenge for current chemical nanotechnology. Visible success in the controlled production of pores with a strictly required diameter could fundamentally change the situation with the adsorption of greenhouse gases. These gases are (in order of their negative impact on the planet's atmosphere) water vapor, CO_2, methane, ozone, and nitrous oxide. It is not difficult to see the similarity in the size of the molecules of the most harmful greenhouse gases. Having a cheap way to synthesize a material of random chemical composition with a significant number of pores with an effective diameter of about 0.5 nm could take the current state of this field of research to a new level. Even if such a nanomaterial does not provide the desired selectivity towards dinitrogen and dioxygen, it would easily capture harmful emissions from industries.

Currently, it is believed that efficient adsorption of CO_2 requires micropores (less than 2 nm), which provide a sufficiently strong interaction with CO_2.

In turn, mesopores, 2–50 nm, satisfy the requirement for rapid transport of CO_2 molecules to the adsorption centers. Surface morphology, such as defects and roughness, can influence the availability of adsorption centers and adsorption kinetics [77–80].

3.7. Development of sorbents by functional groupsgrafting

The introduction of functional groups into the sorbent surface is one of the most effective ways to modify the PEL towards its affinity for CO_2. As Lewis bases, amines form chemical bonds with CO_2, resulting in significant chemisorption energy. Nevertheless, the reaction of amine-functionalized material with CO_2 is reversible [16]. In the development of new sorbents, it is important to consider the sorption energy, as CO_2 desorption and sorbent regeneration are still required [81–84].

Hydroxyl groups only form hydrogen bonds with CO_2. This ensures moderate gas adsorption energy and consequently cheaper desorption. Carboxyl groups, on the other hand, are also capable of forming hydrogen bonds with CO_2 and can participate in ionic interactions that are sufficiently strong by the standards of physisorption processes. The PEL directly reflects these non-covalent interactions and makes the search for optimal structural parameters more rational. Further grafting of the sorbent has minor effects to the PEL.

3.8. The use of porous materials

It should be reiterated that, in addition to the presence of molecular fragments with the properties of Lewis bases in the sorbent composition [16], the hierarchical porous structure should be considered as an independent factor stimulating the sorption capacity. When located in a very narrow pore, the CO_2 molecule is attracted by the London forces simultaneously to all its walls. Because of this, the enthalpy of adsorption more than doubles compared to the above mentioned two-nanometer pores. The developed porous structure with high specific surface area is an important factor for efficient CO_2 adsorption.

Activated carbons possess the high specific surface area and relatively adjustable porous structure desired by researchers. Such carbon materials are highly reactive, i.e., they can be easily functionalized with carboxyl, hydroxyl, or amine groups [85, 86]. For example, the previously well-studied oxidized graphite and graphene samples, which also

preferentially contain sp^2-hybridized carbon atoms, can be applied [86]. Activated carbon definitely represents a suitable starting platform for the improvement of CO_2 sorbents. The PEL concept assists in comparing the thermodynamic effect in the case of different types of grafting of the initial carbon material.

3.9. The use of zeolites

Zeolites are crystalline aluminosilicates that also have a fairly ordered porous structure [87–90]. The pore size and chemical composition of zeolites can be varied to a certain extent by chemical methods to optimize the adsorption properties [89, 90]. The thermodynamic stability of this group of sorption materials promotes their large-scale application in environmental technologies [91–93].

3.10. Metal-organic frameworks

Similarly, metal-organic frameworks (MOFs) represent a new class of porous materials with high specific surface area and tunable structure [71]. The research interest in MOFs in the context of CO_2 sorption is primarily due to their structural diversity and suitable pore sizes [94–97]. More importantly, it seems uncomplicated to use MOF active centers to intercalate additional sorption active centers. A full-fledged study of the PEL of MOFs has still not been carried out, despite many localized problems in this field solved using DFT [98, 99]. PEL is crucial to understand the limiting capacities of MOF structures with respect to greenhouse gases. The practical difficulty in analyzing the PEL for different MOF structures is that the unit cell size of these periodic structures is too large [71] to allow a full PEL sampling by DFT methods with a plane-wave basis set.

3.11. Composite materials

The design of composite materials combining the properties of different components with individual adsorption properties can achieve synergetic effects and improve the adsorption performance of the new product [16, 76, 100–102]. Carbon-based composites have attracted paramount attention in this context because carbon chemistry is extremely diverse and the techniques for its realization are not badly documented as of today. The incorporation of metal oxide nanoparticles into the carbon matrix allows to increase the binding energy of the thus obtained new sorbent material with CO_2. Improved MOF-based composite materials can

be obtained in a similar manner [71, 103, 104]. Combinations of MOFs with polymers show improved mechanical properties and thermodynamic stability of the sorbent. The flexible polymer chains are able to partially penetrate the MOF pores because of the matching size. Thus, more perfect atom packing variants are achieved. At the same time, the polymer contains groups important for CO_2 sorption, and the obtained material can be considered for gas binding. The combined effect of the combination of micropores and functional groups can be quite large in the context of practical applications of the composite material.

3.12. Nanotubes and zeolites

By combining carbon nanotubes with various substances, sorbents with high adsorption capacities and good regenerability can be created [60, 66]. In turn, zeolites allow to achieve high selectivity for CO_2, but only under the condition of proper selection of the pore hierarchy, which thermodynamically favor the retention of this gas. Note that the size of pores and the variation of their diameters in materials based on silicon compounds, in most cases is significantly larger compared to carbon materials. In turn, the preparation of zeolites for adsorption tasks is often cheaper and can be a more relevant solution for large industrial applications.

3.13. Electrochemical adsorption of carbon dioxide

A recent workable method of electrochemical CO_2 capture, in which a charged carbon cathode is the adsorbent, has been proven by the authors of this review using molecular modeling [105] (Fig. 4).
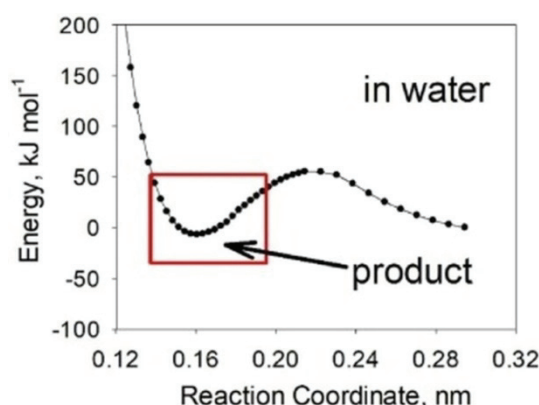

Fig. 4. One of the measurements of the PEL, the linear distance between the CO_2 carbon atom and the carbon atom of the positively charged graphite layer, characterizing the electrochemical chemisorption of CO_2 on the graphite cathode. Reproduced from the author's source [105] with permission from Elsevier. Copyright Elsevier 2024

The point is that when voltage is applied to the cathode, the carbon structure constituting it receives additional π-filled orbitals. Due to this, the carbon partially acquires the chemical properties of nitrogen. A nucleophilic addition reaction occurs with the formation of a covalent bond carbon (sorbent)-carbon (CO_2) [106].

According to the calculated PEL plots, this bond is kinetically stable up until the cathode is disconnected from the current source [105]. The developed sorbent can be used in solid state. Thus, a more significant chemisorption energy is added to the physisorption energy due to the London interaction with the pore walls. A reformulation of the method in which the nano-organized carbon (graphene, nanotube, graphite) is dispersed in some suitable solvent that supports exfoliation is probably also possible [16]. Since electrochemical adsorption relies on an electrical energy source rather than a chemical one, as more traditional methods of CO_2 capture, its implementation and scaling appear to be more efficient [105].

The PEL modifications presented in this work are summarized in Table 2.

4. Conclusion

We have reviewed all relevant chemical compounds and materials that can be expected to improve CO_2 sorbents and noted the applicability of the PEL concept to the given objectives. All the discussed promising materials should be categorized into three groups. The first includes amine scrubbing technology related solutions in which the chemisorption centers are the same amino group cleaved to a liquid carrier, for example, an ionic liquid cation [102]. The second group includes solid porous materials with complex hierarchical pore structure based on carbon, silicon or MOF [99, 107]. The third group includes combinations of structural fragments belonging to the first and second groups recombined into a single material. For example, an extensive surface of activated carbon, decorated with amino groups [16], solves the problem of sorbent volatility in the case of classical amine scrubbing [40].

The PEL concept is a powerful tool for the rational design of porous CO_2 sorbents. Further development in this area involves systematizing the design of new materials with specific properties. Using nanotechnologies and composite materials opens up broad opportunities for creating highly efficient CO_2 sorbents. Applying more precise quantum-chemical methods and developing new experimental techniques will allow to more accurately reveal the types of CO_2-sorbent interactions depending on the sorption's specificity and purpose [16].

Table 2. Strategies for changing the potential energy landscape

Type of PEL changing	Source
Modification of the sorbent surface	
Grafting amino groups onto the graphene surface changes the PEL and creates active centers for interaction with sorbate molecules. Quantum-chemical calculations, including calculation of electron density distribution, electrostatic potential and thermodynamic potentials, allow to study the interaction of sorbate with the modified surface	[16], [85]
In order to study the mechanism of sorption during cellulose modification to produce a polyionic liquid, both experimental studies and molecular dynamics calculations were carried out. Modeling allowed to establish the key role of anion in the sorption process and to reveal the peculiarities of interaction of each element in the system	[38]
Functionalization of ionic liquid cations by amino groups for CO_2 sorption. The sorption capacities of the new compounds were determined by calculating thermodynamic potentials	[76], [102]
Modification of fullerene C-60 by grafting amino groups yields a non-volatile compound promising for CO_2 sorption. Quantum chemical calculations including charge distribution, dipole moment and HOMO-LUMO energy analyses, as well as calculation of the Gibbs energy change (ΔG) upon interaction with CO_2 are used to evaluate the sorption capacity of the modified fullerene	[100]
Introduction of defects	
The incorporation of magnesium, nickel and nitrogen into the carbon matrix, as well as the calculation of Gibbs energy, allowed the identification of the centers involved in the electroreduction of CO_2	[55]
Nickel and nitrogen atoms were deposited on a carbon carrier. Thermodynamic potentials were calculated for the modified system. The study shows that Ni plays an important role in CO_2 activation, providing a low energy barrier for Ni−C bond formation and facilitating further CO_2 reduction	[56]
Charge transfer to the sorbent	
Modification of the sorbent surface by introducing additional negative charge changes the PEL. In the case of graphene, the negative charge is responsible for lowering the energy barrier and reducing the thermal effect of the reaction, which contributes to the increase of its sorption properties	[105], [106]

PEL is an important tool for the theoretical and modeling study of substances and materials. Incorporating it into the working program of a materials research group makes it possible to consider potential energy as a physical property at the atomic level. Meanwhile, although experimental research on materials allows for the acquisition of indirect energy descriptors, it cannot compare to the spatial resolution of the microscopic results provided. Even the interpretation of new types of electron microscopy relies to some extent on the PEL modeling. As convincingly demonstrated in this review, the specific features of PELs can be correlated with macroscopic properties of materials or processes.

The PEL concept can be used to develop carbon dioxide sorbents for various industries that emit CO_2 or require CO_2 capture. Currently, fossil fuel-fired thermal power plants, cement and metallurgical plants, oil refineries, and chemical plants are the main producers of carbon dioxide [1–3, 18, 24, 53].

Technological optimization of sorption and desorption process parameters will allow for increased efficiency and cost-effectiveness of the CO_2 capture process in the future. Currently, our expert opinion leans toward microporous silicon and carbon materials, along with MOFs that have the right elemental composition to trigger electrostatic interaction between the sorbent and the sorbate [98, 99]. When discussing competing materials science solutions, it should be understood that the winning technology is almost always the cheapest. Developing commercially successful methods for obtaining narrow pores with small diameter variation should be prioritized.

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7. Conflict of interest

The authors declare no conflict of interest.

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