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Review

Natural gas treating by selective adsorption: Material science and chemical engineering interplay

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ABSTRACT

The paper addresses current needs in Natural Gas (NG) treating. Basic principles of Pressure Swing Adsorption (PSA) separation processes are described. A state of the art of microporous adsorbents in the frame of NG treating is given. It includes reference and advanced zeolites, carbon based materials and Metal-Organic Frameworks (MOFs). The pros and cons of each material category are discussed. Guidelines to develop on-purpose materials are given from thermodynamics and material state of the art. Finally, PSA applicability to inert (nitrogen and carbon dioxide) rejection from NG is discussed.

1. Scope of the review

Gas treating technologies can be roughly divided into two main categories [1,2]: (i) *separation*, with contaminant concentration of about 10 wt.% or higher in feed; (ii) *purification*, with contaminant concentration less than about 3 wt.% in feed. Pressure Swing Adsorption (PSA) represents a state of the art technology both in separation and purification of gaseous mixtures [3–9]. As in all adsorption technologies, the nature of feed and products drives the choice of the most adequate adsorbing material and process design. For this reason, a strong integration between process engineering and material science is requested in PSA development and optimisation.

The paper addresses current needs in *Natural Gas* (NG) treating. Basic principles of adsorption processes including adsorbent–adsorbate interactions and current PSA technologies are described. A state of the art of microporous adsorbents in the frame of NG treating is given. It includes reference and advanced *zeolites*, *carbon-based materials* and *Metal-Organic Frameworks* (MOFs). Finally, PSA applicability to inert (nitrogen and carbon dioxide) rejection from NG is discussed.

2. Natural gas: from the reservoir to the marketplace

2.1. Resources and specifications

The progress of the international energy demand shows a 1.7% average annual growth in the 2005–2020 period. This growth concerns all energy sources, although fossil fuels will still rule the energy scene for the next fifteen years.

NG demand will account for the highest growth rate and in 2020 it will exceed that of coal, that will be penalised by the increasing restrictions in pollutant emissions (especially in Europe).

Novel transport technologies, the remarkable reserves found, the lower overall costs and the environmental sustainability all point to NG (less polluting than oil and coal and now used in more efficient plants) as the primary energy source in the near future [10,11].

Reservoirs are frequently far from final markets (Table 1): as a consequence, NG has to be transported either by pipelines as gaseous mixture containing at least 75 vol.% of methane or by tankers as *Liquified Natural Gas* (LNG), containing at least 85 vol.%

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Table 1
2007 world gas reserves (referred to world gas reserves = 1.82×10^{14} m^3) compared to 2005 world gas production (referred to world gas production = 2.84×10^{12} m^3) and 2005 world gas consumption (referred to world consumption = 2.82×10^{12} m^3) [11].

Area	Reserves [%]	Production [%]	Consumption [%]
Western Europe	3.0	10.4	17.6
Industrialised Asia and Pacific	1.6	1.8	6.0
North America	4.2	24.4	24.7
Central Europe	0.3	0.8	2.7
Eastern Europe	27.0	22.4	18.5
Central Asia	4.6	5.3	3.6
Middle East	40.3	10.3	8.9
Africa	7.9	6.5	3.0
Developing Asia and Pacific	7.2	11.7	8.9
Latin America	4.0	6.4	6.2

of methane [12]. The choice between the two transportation technologies depends mainly on the distance and on the volume of gas to be transported. According to an Eni on-shore case-study, LNG could be considered the preferred choice in case of relatively small fields (less than 1 Tcf y^{-1} = 2.83×10^{11} m^3 y^{-1}) and long distance (more than 3000 miles = 4800 km). NG is frequently identified according with its origin and/or chemical composition. Classification by origin provides three main categories: (i) *non-associated gas* which is not in contact with oil; (ii) *gas-cap associated gas* overlying the oil phase in the reservoir; (iii) *associated gas* dissolved in the oil at the reservoir conditions (*solution gas*).

As produced from gas fields, NG generally contains variable amounts of several contaminants such as water, light paraffins, aromatics, carbon dioxide, nitrogen and sulphur compounds. Minor amounts of helium (less than 1 vol.%) and mercury (generally 5–300 μg Nm^{-3}, in few cases more than 1000 μg Nm^{-3}) can be also present. Furthermore, enhanced hydrocarbon recovery operations by nitrogen and/or carbon dioxide injection into reservoirs modify the chemical composition of produced gas. NG can be also classified into *dry* or *wet* depending on the amount of C_{2+} hydrocarbons (wet gas for C_{2+} content higher than 10 vol.%) and into *sweet* or *sour* depending on the amount of acid gas (sour gas for hydrogen sulphide content higher than 1 vol.% and/or carbon dioxide content higher than 2 vol.%). Chemical composition determines the operations requested to meet specifications requested for NG transportation and final processing (Table 2).

Unconventional hydrocarbon sources such as *CoalBed Methane* (CBM) and *LandFill Gas* (LFG) have recently drawn energy companies' attention. The gaseous mixtures entrapped in coal beds are mainly composed by methane (up to 80–99 vol.%) and minor amounts of carbon dioxide, nitrogen, hydrogen sulphide and sulphur dioxide [14]. The gas produced by waste decomposition in landfills is a complex gaseous mixture containing carbon dioxide as the main contaminant [15]. In general, before supplying to processing plants and downstream customers *gas conditioning* operations are requested [12,13,16–18]. Water content has to be reduced to levels that prevent corrosion, hydrate formation and freezing in cryogenic equipments. Indeed, the formation of hydrates from water and hydrocarbons is considered the primary cause of plugging of transmission lines. Until today, the most applied water separation technology remains scrubbing with TriEthyleneGlycol (TEG), followed by scavenging on solid adsorbents (zeolite, silica, silica–alumina, alumina pure or mixed together, activated carbons) [19]. After dehydration, TEG is regenerated at high temperature (about 473 K) and recycled to scrubbers. Hydrocarbons heavier than methane contribute to NG heating value. On the other hand, C_{3+} hydrocarbons can cause problems: either pressure or temperature variations can cause their fall out of the gas phase. C_{3+} hydrocarbons can also cause plugging of downstream valves and pipes or fouling of other equipments (*i.e.* gas separation membranes). Their content is generally adjusted by gas chilling and/or scrubbing with liquid hydrocarbons and successive scavenging on the same solid adsorbents used for dehydration.

Table 2
Typical compositional specifications on feed to LNG plant and on pipeline gas (Total Sulfur refers to H_2S + carbonyl sulphide, COS + organic sulphur) [12,13].

Impurity	Feed to LNG Plant	Pipeline Gas
H_2O	<0.1 ppmv	150 ppmv
H_2S	<4 ppmv	5.7–22.9 mg Sm^{-3}
CO_2	<50 ppmv	3–4 vol.%
Total Sulfur	<20 ppmv	115–419 mg·Sm^{-3}
N_2	<1 vol.%	3 vol.%
Hg	<0.01 mg/Nm^3	–
C_4	<2 vol.%	–
C_{5+}	<0.1 vol.%	–
Aromatics	<2 ppmv	–

The removal of inert gases (mainly nitrogen but also helium) and acid gases (such as carbon dioxide and hydrogen sulphide) is of considerable importance inasmuch as they can be present to a significant extent. NG containing hydrogen sulphide in proportions higher than 10 vol.% are not very common and many gases contain practically no hydrogen sulphide. Conversely, nitrogen and carbon dioxide are common NG contaminants, with average proportions in the range 0.5–5.0 vol.% for nitrogen (with peaks of over 25 vol.%) and 0.5–10 vol.% for carbon dioxide (with peaks up to 70 vol.%). When sulphur compounds and carbon dioxide levels are too high, they need to be reduced in order to avoid formation of solids in cryogenic units and steel pipes corrosion. Furthermore, both nitrogen and carbon dioxide can be considered *inert gases* with no heating value: for this reason, they must be removed to low levels (Table 2) before distribution to final users. Nitrogen and helium rejection from NG are usually operated by cryogenic fractional distillation. Cryogenic *Nitrogen Rejection Units* (NRUs) are considered economically acceptable for gas flows exceeding 15 MMscf d^{-1} = 4.25×10^5 Sm^3 d^{-1} [20], although higher flow ranges are recommended (50 MMscf d^{-1} = 1.42×10^6 Sm^3 d^{-1}) [18]. Acid gas bulk removal (*gas sweetening*) is mainly performed either by aqueous amine or organic solvent scrubbing. The acid gas saturated (*rich*) fluid is regenerated by high temperature stripping (less than about 400 K, in case of amine) or by pressure reduction (in case of solvents) and then recycled to scrubbers. These treatments have to be run carefully, in order to reduce risks deriving from dangerous chemical handling and toxic waste production.

2.2. Opportunities from PSA technologies for natural gas treating

So far, the exploitation of highly contaminated gas streams (*poor gases* or *low-Btu gases*) has not been considered economically attractive because of high capital and operative costs of current gas treating technologies. As a consequence, these gaseous mixtures are frequently not converted into energy [21]. In this context, among the emerging gas treating technologies, PSA processes have drawn market attention because of their intrinsic eco-compatibility and flexibility:

- PSA technology is based on the use of regenerable solid adsorbents. According to that, it does not require the management of chemicals (*e.g.* amine, solvents), thus providing considerable environmental benefits;
- adsorbent regeneration does not require heating. Consequently, PSA process energy intensity is low;
- PSA units can be easily downsized to skid-mounted modules suitable for the exploitation of small gas reservoirs.

3. PSA general features

PSA basic concepts are described in two patents granted in the late 1950s [22,23] and since then, R&D effort in this field has been continuous [4,7]. Sizes of commercial PSA units range from small devices (about 300 scf d^{-1} = 8.50 $Sm^3\ d^{-1}$) for the production of 90 vol.% oxygen from air for medical use, to large refinery plants (about 100 MMscf d^{-1} = $2.83 \times 10^6\ Sm^3\ d^{-1}$) for the production of high purity hydrogen from *Steam Methane Reforming* (SMR).

Like all adsorption separation processes, PSA involve two basic steps:

- during *adsorption step*, certain components of a gaseous mixture are selectively adsorbed on a porous solid. This operation, performed at relatively high pressure by contacting the gaseous mixture with the adsorbent in a packed column, produces a gas stream enriched in the less strongly adsorbed component of the feed mixture (the *raffinate*). After a given time of operation, the adsorbing bed approach saturation and regeneration is requested;
- during *regeneration* or *desorption* step the adsorbed components are released from the solid by lowering their gas phase partial pressures inside the column. After this operation, the adsorbent is ready to be employed in a further cycle. The gaseous mixture obtained from regeneration (the *extract*) is enriched in the more strongly adsorbed components of the feed.

In practice, several columns are operated in a swing-mode to make the process continuous and additional steps are added to the basic cycle, in order to maximise productivity and energy saving.

It is common practice to include a low pressure purge step in the cycle in order to promote adsorbent regeneration. Purge is generally operated by recycling part of raffinate (*purge gas* or *sweep gas*). According to that, raffinate is obtained at about the same pressure of feed, in a pure form while the extract is discharged as secondary product, in impure form and at pressure lower than feed. The whole cycle last minutes or even seconds and is operated under approximately isothermal conditions. The *working capacity* is the difference in loading between the points corresponding to adsorption and regeneration pressures on the same adsorption isotherm. It has to be noticed that in cases of strongly adsorbed species heating at high temperature (*e.g.* around 573 K for release of water from zeolites in NG dehydration processes) is the only regeneration option. This strategy is referred as *Temperature Swing Adsorption* (TSA).

NG is often available at wellhead at high pressure. At least in principle, by using adsorbents able to capture contaminants, PSA processes can produce pure methane at high pressure as raffinate, thus reducing further compression work before transmission to downstream customers.

4. Adsorption fundamentals

The essential requirement of adsorption separation processes is an adsorbent that preferentially adsorbs a family of related components from a mixed feed. Adsorbent selectivity may depend on difference in adsorption at equilibrium (*equilibrium selectivity* or *thermodynamic selectivity*) or on a difference in adsorption rates (*kinetic selectivity*). Kinetic selectivity is possible when a great difference among adsorption/desorption rates of different components exists. This is due to sterically hindered diffusion through pores characterised by pore mouth diameter comparable with molecular size of fed species. Difference in rates may be so great that the slower diffusing species are almost excluded from the adsorbent (*size-selective sieving*). Currently, nitrogen separation from air by using small pore zeolites or carbon molecular sieves is the only commercial PSA process based on kinetic selectivity. Therefore, both solid–fluid phase interactions and diffusion through adsorbent pores must be considered during material selection and tailoring [3,6,24,25].

Table 3

Physico-chemical properties of some molecular species present in NG (hydrogen and carbon monoxide are reported for comparison): σ: *kinetic diameter*, α: *polarisability*, μ: *dipole moment*, Θ: *quadrupole moment*, T_c: *critical temperature*. Quadrupole moment indicative values have been computed by *Density Functional Theory* (DFT) method.

Molecule	σ [Å]	α [Å^3]	μ [D]	Θ [D·Å]	T_c [K]
CH_4	3.80	2.448	0.000	0.02	190
N_2	3.64	1.710	0.000	1.54	126
CO_2	3.30	2.507	0.000	4.30	304
H_2O	2.65	1.501	1.850	2.30	647
H_2S	3.60	3.630	0.970	3.74	373
He	2.60	0.208	0.000	0.00	5
H_2	2.89	0.787	0.000	0.43	39
CO	3.76	1.953	0.112	2.04	133
Reference	[26]	[27]	[27]	[27]	[28]

4.1. Gas–solid interactions

Adsorption (*physisorption*) is based on attraction forces among the solid phase and the species constituting the gas phase, with relatively low adsorption heat. Usually, $q_{ads} < 2q_{vap}$, where q_{ads} and q_{vap} represent, respectively, adsorbate heat of adsorption and vaporisation. Adsorption forces can be categorised into two main groups: (i) *van der Waals forces*, directly correlated with adsorbate molecular polarisability and (ii) *electrostatic forces* such as polarisation forces, surface field–molecular dipole interactions and surface field gradient–molecular quadrupole interactions. Adsorption is usually promoted by synergies among these different kinds of interactions. Key physico-chemical properties of common NG components are reported in Table 3. Carbon dioxide and nitrogen adsorption on polar surfaces (*e.g.* zeolites) is mainly promoted by surface field gradient–molecular quadrupole interactions. Conversely, adsorption of large non-polar molecules (*e.g.* hydrocarbons) is essentially due to their molecular polarisability.

Adsorbents able to promote electrostatic interactions (as well as hydrogen bonding) are generally referred as *hydrophilic*. In general, they are able to adsorb small polar molecules (like water) much more strongly than would be expected simply from van der Waals forces alone. Common hydrophilic adsorbents are zeolites, silica and alumina. Conversely, adsorbents operating exclusively by van der Waals forces (*e.g.* most activated carbons) are referred as *hydrophobic*. According with the gas–solid interactions described above, thermodynamic selectivity can be optimised by tailoring adsorbent physico-chemical characteristics. Zeolite polarity can be tuned at the synthesis step (*e.g.* by choosing the Si/Al molar ratio and counter cations) or by post-synthesis treatments [29]. Besides, polar groups such as carboxylic species can be introduced on activated carbons by oxidation treatments [30].

4.2. Adsorbent porous texture

Adsorbent–adsorbate interactions play an important role for the very first adsorption layers. However, adsorption mechanism and hence separation performances are essentially determined by the porous texture of adsorbent. IUPAC classification categorises pores into micro-, meso- and macropores according to their *pore size* (*d*, *i.e.* diameters of cylindrical pores or distance between the sides of slit-shaped pores). This classification corresponds to different adsorption mechanisms, although the ratio adsorbate molecule size *vs.* pore size is the effective discriminating factor. Adsorption in *micropores* ($d \leq 20$ Å) takes place by *micropore filling* [31,32]. In this

Table 4
Isosteric heat of adsorption extrapolated at zero coverage (q_{st}) of some NG components on commercial activated carbons and zeolites at about 303 K.

Adsorbent	q_{st} [kJ mol^{-1}]			Reference
	CH_4	CO_2	N_2	
Norit Extra	20.60	22.00	–	[37]
Calgon BPL	16.10	25.70	–	[37]
Kensai Maxsorb	16.60	16.20	–	[37]
A'dall A10	16.20	21.60	–	[37]
Osaka Gas A	18.30	17.80	–	[37]
Silicalite	20.90	27.20	17.60	[38]
NaZSM-5	26.50	50.00	24.10	[39]
NaX	19.20	49.00	19.90	[39]

Table 5
Average heat of adsorption (q) of some NG components on various adsorbents at about 303 K.

Adsorbent	q [kJ mol^{-1}]					Reference
	CH_4	CO_2	N_2	H_2O	C_2H_6	
NaX	13.81	34.31	16.74	51.46	31.38	[40]
KClinoptilolite	25.10	39.75	25.10	–	29.29	[40]
CaClinoptilolite	15.06	25.10	20.08	–	10.46	[40]
MgClinoptilolite	29.98	–	19.99	–	–	[41]
SrETS-4	14.67	–	21.20	–	–	[41]
γ-Al_2O_3	10.46	33.47	8.37	48.53	17.57	[40]

case, adsorbent–adsorbate interactions are greatly enhanced since gas molecules and pore sizes are comparable and each gas molecule experience the force field generated by pore walls. In addition, molecular sieving can take place if one component is larger than pore opening. Microporous zeolites and carbons commonly used adsorbents as described in Sections 4.1 and 4.2.

Regarding adsorption both in *mesopores* (20 Å < d ≤ 500 Å) and in *macropores* (d > 500 Å), adsorbate molecules are organised by multiple layers according to the proposed mechanistic models (*e.g.* the Brunauer–Emmett–Teller one [33]). Molecules belonging to the layer contacting the solid surface are strongly attracted while molecules in the central region of the pore are essentially free from the force field. Adsorbate partial pressure inside mesopores is higher than outside. As partial pressure exceeds critical value (if adsorption temperature is below the critical value), bulk adsorbate condensation takes place inside the pore. This phenomenon is referred as *capillary condensation*.

Together with surface interactions, capillary condensation causes water and C_{3+} hydrocarbon adsorption on mesoporous absorbents. For this reason, mesoporous silica, alumina and silica–alumina are extensively used in NG dehydration and C_{3+} hydrocarbon removal (Section 1). Besides, M41S materials have been recently proposed for gas treating [34].

Macropores (d > 500 Å) behave in gas adsorption as open surfaces. Thus, their contribution to adsorption capacity is generally negligible and their main role is to facilitate transport within adsorbent particles. According to that, most commercial adsorbents consist of aggregated microporous grains, usually with a binder, to form macroporous hyper-structures. The binder also provides mechanical resistance (*e.g.* to pressure shocks) to adsorbent particles.

4.3. Adsorption equilibrium and heat of adsorption

The concept of adsorption equilibrium is deeply involved in the evaluation of adsorbent specific capacity, selectivity and regenerability (working capacity). Equilibrium *adsorption isotherms* $n_i = f(p_i, T)$ (where n_i is the amount of component i adsorbed at temperature T and at partial pressure p_i) and *heat of adsorption* represent essential input data for PSA process modelling [35].

Heat of adsorption is a measure of the strength of interactions between adsorbate and adsorbent (adsorption is an exothermal phenomenon). For adsorbents characterised by energetically heterogeneous surfaces (*e.g.* most zeolites) heat of adsorption is higher at low loadings, describing interactions on strongest sites. Thus, it is properly referred as *isosteric* (*i.e.* at a definite loading) heat of adsorption, q_{st}. From process engineering point of view, heat of adsorption is a measure of the energy required for adsorbent regeneration and provides an indication of temperature variations that can be expected on the bed during adsorption (and desorption) under adiabatic conditions. Tables 4 and 5 provide representative heat of adsorption values for some NG components referred to common adsorbents. Due to high adsorption heat, variations of about 30 °C are reported on zeolitic materials for carbon dioxide capture from NG [36]. These temperature variations are detrimental for PSA efficiency since temperature rising during adsorption step decreases adsorbate uptake and bed temperature decrease during desorption step reduces adsorbate release.

4.4. Selectivity

Equilibrium selectivity is the key parameter to evaluate adsorbent separation ability. It is based on differences in affinities of the adsorbent for the different species constituting the fluid phase. Given an adsorbent and a gaseous mixture in which N is the more strongly adsorbed component and M the predominant but less strongly adsorbed one, equilibrium selectivity is generally expressed by using the *separation factor* $\alpha_{N,M}$:

$$\alpha_{N,M} = \frac{n_N}{n_M}\frac{p_M}{p_N} \approx \frac{K_N}{K_M} \qquad (1)$$

where n_N, p_N, n_M, p_M are values obtained from pure component isotherms. It may be shown that in many cases $\alpha_{N,M}$ can be computed as the ratio among N and M Henry's constants (K_i) thus often referred as *Henry's selectivity*. For PSA applications, $\alpha_{N,M}$ values comprised between 2 and 104 may be considered acceptable [9]. For the same adsorbent, adsorbed and desorbed amounts can differ significantly from different conditions of pressures and temperatures. Furthermore, kinetic effects have to be considered when relevant. According to that, additional selectivity criteria have been suggested [42–44].

4.5. Selectivity vs. regenerability

An energy intensive regeneration step is the price you have to pay in case of very selective adsorbents. For this reason, adsorbent design main objective should be to find out an optimal trade-off between selectivity and regenerability. Table 6 contains a collection of separation factors referred to different couples of gases on Calgon BPL^{TM} activated carbon and CaNaA zeolite (commercial 5 A molecular sieve) [8].

Table 6
Separation factors $\alpha_{N,M}$ on Calgon BPL^{TM} activated carbon and CaNaA zeolite (commercial 5 A molecular sieve) at 303 K [8].

Mixture N–M	$\alpha_{N,M}$	
	BPL^{TM} Activated Carbon	CaNaA Zeolite
CO_2–CH_4	2.5	195.6
CO_2–CO	7.5	59.1
CO_2–N_2	11.1	330.7
CO_2–H_2	90.8	7400.0
CO–CH_4	0.33	3.3
CO–N_2	1.48	5.6
CO–H_2	12.11	125.0
CH_4–N_2	4.5	1.7
CH_4–H_2	36.6	37.8
N_2–H_2	8.2	22.3

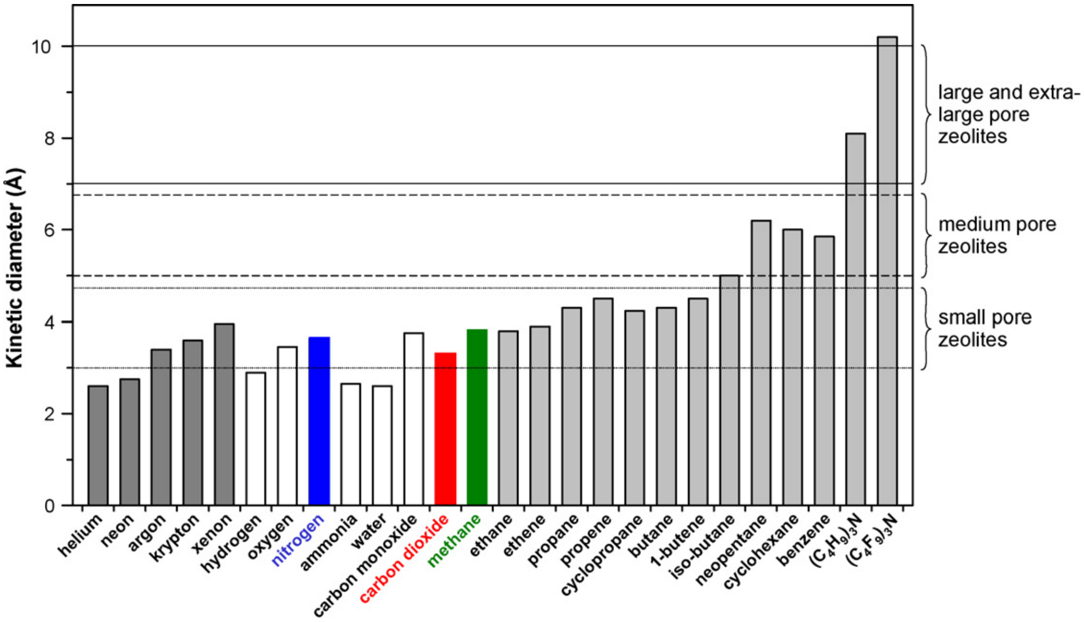

Fig. 1. Kinetic diameter of several molecules (taken from ref. [26]) compared with the pore diameter of different types of zeolites.

Zeolite CaNaA is much more selective than activated carbon in carbon dioxide separation from other gases. On the other hand, the great affinity of CaNaA zeolite for carbon dioxide make extremely difficult carbon dioxide displacement by sweeping with other gases (*e.g.* methane, hydrogen), as requested in typical PSA processes (Section 2). Effective carbon dioxide desorption from CaNaA zeolite can only be obtained by applying more complex or energy intensive strategies like vacuum or high temperature heating (TSA). Regarding nitrogen rejection from NG, it is evident that both Calgon BPL^{TM} activated carbon and CaNaA zeolite show poor selectivities. Although this is merely a case study, it depicts a general behaviour: both methane and nitrogen are able to interact weakly with most adsorbents. Furthermore, their molecules show similar kinetic diameters ($\sigma_{N2} = 3.64$ Å, $\sigma_{CH4} = 3.80$ Å), making molecular sieving extremely difficult. Thus, very few adsorbents are able to selectively adsorb nitrogen from NG (Section 4.1).

5. Adsorbent design and state of the art

Adsorbent development is an essential step in PSA process design, as outlined in previous Sections. Adsorbents suitable to PSA processes have to satisfy several requisites: (i) selectivity; (ii) regenerability by pressure reduction; (iii) specific capacity; (iv) fast interparticle diffusion; (v) chemical and physical stability; (vi) low cost per unit volume; (vii) reasonable packing density to avoid oversized vessels. It is important to stress that adsorbent cost is a key parameter to be considered for industrial application. Common A, X and Y zeolites are extensively employed in gas industry, although the use of more sophisticated structures is frequently proposed in literature as a way to improve separation performances. Zeolite and carbon adsorbents have been successfully used for inert rejection from raw NG streams whereas MOFs are emerging adsorbents that are gathering great attention because of their outstanding pore volumes. These three categories of adsorbents are described in Sections 4.1–4.3.

5.1. Microporous zeolites and aluminophosphates

Zeolites found in nature and synthesised ones are obtained under hydrothermal conditions and can be divided in those having low Si/Al molar ratio (from 1 to 5) and those of high Si/Al molar ratio (from 5 to ∞), being the formers much more hydrophilic materials [26]. Zeolites are tridimensional aluminosilicate frameworks constituted by Si and Al tetrahedra linked through bridging oxygen atoms giving rise to a regular distribution of pores and cavities of molecular dimensions (Fig. 1). In low Si/Al molar ratio zeolites, the negative charge generated by aluminium in the framework is compensated by small cations such as alkali and alkaline-earth metal cations, whereas the use of large organic molecules allows obtaining higher Si/Al molar ratio zeolites. By means of a great variety of organic molecules based on quaternary ammonium cations as *Structure Directing Agents* (SDAs), several existing zeolites have been obtained with higher Si/Al molar ratios and interestingly, a large number of new zeolitic materials have been synthesised. Up to now, 191 different zeolitic materials with known structure exist [45] and this number is even larger since zeolites in which the structure has not been solved are reported in the open and patent literature. Aluminophosphates (AlPOs) are related materials with similar structures than zeolites constituted by Al and P tetrahedra.

Discovery of zeolitic microporous adsorbents has represented one of the major breakthroughs in the field of adsorption and separation of gas mixtures. The great availability of zeolite structures with different pore size and topology, together with the possibility of preparing them in a wide range of chemical compositions make zeolites very useful adsorbents for gas separations, getting chances for the selection of the most appropriated material for a given separation process. As a consequence of their well defined crystalline structures, these materials have uniform pore sizes in the range of molecular dimensions (3–10 Å) achieving microporosity volumes up to 0.35 $\text{cm}^3\,\text{g}^{-1}$. Furthermore, the benefit of the high thermal, hydrothermal and chemical stability, allows their use as adsorbents and catalysts in many processes [46,47].

Zeolites can be classified according to different criteria. The most commonly used is the one referring to the *dimensions of the pore apertures*. According to that, zeolites can be divided in the following groups:

- *small pore zeolites*: constituted by channels delimited by 8 *Member Rings* (8 MR) with pore diameters around 4 Å. In this group, zeolitic materials such as zeolite A (LTA) and chabasite (CHA) are the most common;

- *medium pore zeolites*: constituted by channels delimited by 10 MR and pore apertures around 5–6 Å. Zeolites ZSM-5 (MFI) and ferrierite (FER) belong to this group;
- *large pore zeolites*: constituted by channels delimited by 12 MR with pore diameters around 7 Å. Faujasite (FAU) type of zeotites (X and Y) and beta (BEA) are large pore ones;
- *extra-large pore zeolites*: constituted by channels delimited by rings of more than 12 MR and pore apertures larger than 7 Å. These zeolitic materials have been obtained in the latest years and examples of them are CIT-5 (CFI) and ITQ-33 zeolites.

The *shape of the pores* is another important factor, since there are zeolites with pore apertures delimited by the same number of tetrahedra but with different shapes, making them to behave quite differently when adsorbing molecules. For instance, zeolite A (LTA) and analcime (ANA) are both small pore zeolites, being the former comprised by circular pores of 4.1 Å and the latter consisting of elliptical pores with a smaller dimension of 1.6 Å that makes it useless for adsorption of molecules.

Other criterion for classifying zeolitic materials is the *dimensionality of their channels*. Thus, zeolite structures comprised by one-dimensional, two-dimensional and three-dimensional pore systems exist, depending on the arrangement of the channels in one, two or the three directions of the space. Examples can be found in the medium pore size zeolitic materials theta-1 (TON), ZSM-5 (MFI) and ITQ-13 (ITH) consisting of one-, two- and three-dimensional pore systems, respectively. Dimensionality of the channels is a quite important parameter for separation processes in terms of diffusion of the molecules along the porous structure. Indeed, a one-dimensional zeolite usually results a less open structure with lower micropore volume and limitations by diffusion may take place since the molecules must diffuse along one straight channel. As an example, the micropore volume of the small pore one-dimensional zeolite MCM-35 (MTF) is $0.07\,cm^3\,g^{-1}$ whereas that of the small pore three-dimensional chabasite (CHA) is $0.30\,cm^3\,g^{-1}$.

Finally, the *channel connection* is another way of differentiating these materials and zeolites with interconnected pores, independent ones and those forming cages can be found. Examples of zeolites with interconnected pores are beta (BEA) and ZSM-5 (MFI), zeolite MCM-22 (MWW) contains independent channels and examples of zeolitic structures with cages are zeolite A (LTA) and faujasite (FAU). The presence of interconnected pores is relevant in adsorption processes since diffusion of the molecules along the channels is favoured in this type of materials. Also the presence of large cages in the structure is an important point for adsorption as these zeolites usually are characterized by very large micropore volume available for adsorption of the molecules.

The earliest reports on the use of zeolitic materials as gas adsorbents are dated on the 1950s and 1960s. Use of zeolites as adsorbents for gas chromatography able to separate gases such as hydrogen, oxygen, carbon dioxide, nitrogen, methane and carbon monoxide was reported [48]. Later, different zeolites have been described as useful adsorbents in gas mixtures containing carbon dioxide, nitrogen and methane, such as ion exchanged mordenite [49], where it is stated that the separation ability increases with increasing electrostatic field in the zeolite cavities. Also, faujasite-type zeolites (X and Y) while ion exchanged with alkali or alkaline-earth ions, NaA, CaA, silicalite, ZSM-5 and other microporous molecular sieves (*e.g.* the silicoaluminophosphate SAPO-5 and SAPO-11) have been described as adsorbents. On the other hand, natural occurring zeolites have been also used in different gas separation processes. Indeed, zeolites such as erionite, mordenite, chabasite and clinoptilolite have been widely employed as adsorbents in air separation and purification, NG purification, hydrocarbon separation, oxygen/argon and hydrogen purifications, among others [50]. A comparison on the use of three different natural zeolites (erionite, mordenite and clinoptilolite) as adsorbents for purification of methane mixed with carbon dioxide shows that clinoptilolite is the best adsorbent for purifying NG [51]. Several reports on the use of clinoptilolite exchanged with different cations as adsorbents for removing carbon dioxide and in separation of methane/nitrogen mixtures have been also reported [52,53]. It has been described that when using clinoptilolite for the separation of methane/nitrogen mixtures, separation efficiency can be controlled by the cationic surface population [54].

The low cost of natural zeolites is often cited as a major incentive for their use. It has been demonstrated that although the raw material cost is relatively low, processing and shipping operations could make these adsorbents even more expensive than the synthetic ones. According to that, also in the case of natural zeolites a wise evaluation of adsorbent separation performances and cost is recommended [50].

Regarding to the use of zeolites in PSA, several processes have been reported in where adsorbents such as zeolites A, X, silicalite or mordenite are employed [55–57] and comparison with other adsorbents such as activated carbon can be also found [58]. The Petlyuk^{TM} PSA process has been proposed for the separation of ternary gas mixtures, such as carbon dioxide/methane/nitrogen. It consists of two pairs of adsorption columns employing three kinds of adsorbents: activated carbon, zeolite 13X and carbon molecular sieves [59].

Recently, zeolite and other molecular sieve membranes have also shown potential for application in separation processes. Small-, medium-, and large-pore zeolites have been used to prepare membranes able to separate carbon dioxide from methane, as is the case of SAPO-34 [60], silicalite-1 [61] and zeolite Y [62], respectively. Because both carbon dioxide ($\sigma_{CO_2} = 3.3\,Å$) and methane ($\sigma_{CO_2} = 3.80\,Å$) molecules are much smaller than the pores of large pore and medium pore zeolites, separation with these membranes was mainly based on competitive adsorption. In contrast, it is reported that membranes based on small pore zeolites and molecular sieves such as zeolite DDR [63] and SAPO-34 [64], having pores similar in size to methane but larger than carbon dioxide, allow the separation of these molecules by differences in size. A recent review on carbon dioxide separation by zeolite membranes can be found elsewhere [65]. However, it is worth to mention that the up-scaling of high quality zeolite membranes is still a major issue for commercialisation purposes. Finally, it shall be pointed out that the very recent great availability of different zeolitic materials in their pure silica composition has opened a new application field for hydrocarbon separation processes involving olefins separations. Indeed, the use of pure silica microporous materials instead of charged silicoaluminate zeolites is preferred, since the former will not suffer any pore blocking due to the oligomerization of the adsorbed olefins. In this line, non-charged zeolites with pore openings formed by 8MR, such as chabasite [66], ITQ-32 [67] and AlPO materials [68], among others, have shown excellent olefin/paraffin separation properties, suggesting separation procedures alternative to energy intensive cryogenic distillations, currently used for that purpose.

Separation of molecules by using zeolites as adsorbents can be taken place by molecular sieve effect or by selective adsorption. Regarding separation by molecular sieving and, taking into account the kinetic diameter of the molecules involved ($\sigma_{CO_2} = 3.30\,Å$, $\sigma_{N_2} = 3.64\,Å$, $\sigma_{CH_4} = 3.80\,Å$), zeolites with pore diameters smaller than 3.80 Å would be required. In the database of the *International Zeolite Association* (IZA) [45], 62 small pore (8MR) zeolites appear, but only four of them have pore sizes smaller than

Table 7
Small pore (8 MR) zeolites with pore size smaller than 3.8 Å.

IZA Code	Name	Dimensionality	Pore Size [Å^2]
ACO	ACP-1	3	2.8 × 3.5 3.5 × 3.5
AFX	SAPO-56 SSZ-16	3	3.4 × 3.6
PAU	Paulingite ECR-18	3	3.6 × 3.6
RHO	Rho	3	3.6 × 3.6

3.80 Å (Table 7) that would be adequate for separation of carbon dioxide and nitrogen from methane.

On the other side, the interaction of the adsorbent with the adsorbate molecules is a key factor for separation processes. Indeed, as the interaction is stronger the desorption step becomes harder and the regenerability of the adsorbent decreases. Taking into account the differences in polarity of the molecules ($CO_2 \gg N_2 \approx CH_4$), it is expected a very strong interaction of carbon dioxide with polar zeolite adsorbents making more difficult their regenerability as, indeed, has been observed in some zeolites such as CaNaA (Section 3.5). For this reason, high silica and pure silica zeolites being much less polar materials would be more desirable for this separation process provided that these adsorbents exhibit a satisfactory adsorption capacity. Among the existing small pore zeolites, those that can be synthesized in pure silica form are listed in Table 8 and could be in principle the most adequate adsorbents for this purpose.

Regarding to the availability for preparing and using these materials, in the case of those selected for the separation based on molecular sieve effects (Table 7), ACP-1 is a cobalt-phosphate that is unstable, paulingite is a mineral and the possible candidates would be SAPO-56, SSZ-16, ECR-18 and zeolite rho. In the case of the small pore pure silica zeolites (Table 8), most of them can be prepared and among them, it is expected that good adsorbents could be found for their use in these separation processes.

The titanosilicate ETS-4 is a small pore member of the *Engelhard TitanoSilicate* (ETS) family [69,70]. The ETS-4 structure consists of an interconnected octahedral–tetrahedral framework with narrow 8 MR pore openings. The ETS-4 structure involves corner sharing SiO_4 tetahedra and TiO_6 octahedra units as well as TiO_5 units. Although larger openings are present in its structure, faulting ensures that access to the crystal interior of ETS-4 occurs through the relatively narrow 8 MR, analogous to what is seen in small-pore zeolites. The size of the 8 MR pore can be tuned by exchanging cations from sodium to strontium and by dehydration using a controlled thermal treatment (between 373 K–573 K). The progressive contraction of the effective pore size of the 8 MR pore openings profoundly affects the adsorption properties. When the material is calcined at 463 K, methane is readily adsorbed while larger molecules are essentially excluded. Methane adsorption declines with further pore contraction and once the material has been dehydrated at 543 K, substantial methane exclusion occurs whereas smaller molecules (like nitrogen or carbon dioxide) are readily adsorbed. Due to these peculiar properties, an adsorbent based on ETS-4, referred as *Contracted TitanoSilicate-1* (CTS-1), has been implemented in the Molecular Gate^{TM} technology for nitrogen rejection from NG (Section 5.1) [71,72].

Table 8
Small pore (8 MR) pure silica zeolites.

IZA Code	Name	Dimensionality	Pore Size [Å]
CHA	Chabasite	3	3.8 × 3.8
DDR	Deca-dodecasil 3R	2	3.6 × 4.4
IHW	ITQ-32	2	3.5 × 4.3
ITE	ITQ-3	2	3.8 × 4.3 2.7 × 5.8
ITW	ITQ-12	2	2.4 × 5.4 3.9 × 4.2
LTA	ITQ-29	3	4.1 × 4.1
MTF	MCM-35	1	3.6 × 3.9
NSI	Nu-6(2)	2	4.5 × 2.6 4.8 × 2.4
RTE	RUB-3	1	3.7 × 4.4
RTH	RUB-13	2	3.8 × 4.1 2.5 × 5.6
RWR	RUB-24	1	5.0 × 2.8

5.2. *Carbon adsorbents*

Carbon adsorbents are widely employed because of their peculiar properties, mainly due to their low polarity [73]: (i) they are able to perform separation and purification without requiring prior stringent moisture removal (in contrast to most zeolites); (ii) they adsorb more non-polar and weakly polar organic molecules than other adsorbents do; (iii) they exhibit low heat of adsorption, resulting in low energy intensive regeneration operations. Carbon adsorbents can be roughly divided into four categories:

- Activated Carbons (ACs);
- Carbon Molecular Sieves (CMS);
- Activated Carbon Fibers (ACFs);
- carbon-based nanomaterials (e.g. Single Wall Carbon Nanotubes, SWNTs).

Among them, ACs and CMS are the most employed materials in industrial gas separations.

AC source raw materials are carbonaceous matters such as wood, peat, coals, petroleum coke, bone, coconut shell, fruit nuts. AC preparative route is largely empirical although a general understanding of the related phenomena has been reported [74]. It essentially involves a low temperature (about 773 K) carbonisation followed by activation at high temperature (about 1273 K). During carbonisation, condensation of polynuclear aromatic compounds, breakage of sidechain groups together with cross-linking reactions occur. In particular, cross-linking avoids the development of graphitic structures that are virtually nonporous, thus not suitable for adsorption applications. Starting with the initial pores present in the raw material, additional pores with the desired pore size distribution can be created by activation processes. Flushing with mild oxidising gases (*e.g.* carbon dioxide, steam) or treatments with inorganic chemicals (*e.g.* potassium hydroxide, zinc chloride, phosphoric acid) are usual procedures. Both oxygenate groups and inorganic cations introduced during the activation step determine the polarity of the final product. By proper choice of precursor, carbonisation and activation steps it is possible to obtain ACs characterised by the desired pore size distribution and polarity. *Iodine number* is the most common empirical descriptor for AC adsorption capacity. It is defined as the milligrams of iodine adsorbed by one gram of carbon. Iodine number values are directly correlated with specific surface area ones.

Presently, main AC applications in the NG industry are [75]: (i) purification of recycled amines and glycols in gas sweetening and dehydration facilities; (ii) NG contaminants (*e.g.* sulfur, mercury) scavenging; (iii) equipment and catalyst protection. ACs impregnated with chemicals are frequently used. In this case, due to absorption phenomena, regeneration can be laborious and often promoted by high temperature heating (*e.g.* gas sweeping at till

723 K for alkali-impregnated ACs for sulphur scavenging from Claus reactor tail gas). Additional *ex situ* treatments can be requested.

The preparation of CMS is broadly similar but often includes additional treatments with organic species that are cracked or polymerised on the carbonised matter [76]. CMS for large scale applications are obtained from coals. A very narrow pore size distribution, in general centered on 5 Å, is obtained by accurate control of synthesis conditions. Due to precise pore size tuning, CMS are discriminated from ACs on the basis of the separation mechanism exploited. ACs separate molecules exploiting differences in their adsorption equilibrium constants. Conversely, CMS provide molecular separation on the basis of rates of adsorption. Currently, CMS are mainly employed in PSA processes for hydrogen and helium purification (which can also be done by ACs) and nitrogen production from air [77,78]. Carbon dioxide separation from natural gas by CMS-based PSA systems has been extensively studied [79,80,81,82,83] and commercial units (suitable also for nitrogen rejection) are available (Sections 5.1 and 5.2).

ACFs are produced from polymeric and pitch fibers [84]. Besides their fibrous form, they have the following peculiar properties with respect to ACs: (i) narrow and uniform pore size distribution (8–10 Å) which enhance interaction with adsorbates; (ii) small and uniform fiber diameter (hence fast adsorption–desorption diffusion); (iii) electrically conductive and heat resistant allowing desorption by electrical heating; (iv) high strength and elasticity.

Despite of these favourable properties, their high cost limits the use to small units, mainly in environmental applications (*e.g.* air or water treatment). On the other hand, manufacture of ACF thin membranes appear promising for high purity hydrogen production from refinery gases [8,85].

Finally, SWNTs consist in seamless cylinders wrapped by a graphite sheet (or graphene sheet). The hexagonal honeycomb lattice of the graphene sheet can be oriented in many possible directions relative to the axis of the tube, determining the metallic or semiconducting nature of these materials. They are prepared mainly by hydrocarbon or carbon monoxide decomposition at high temperature. SWNT main characteristics are: (i) high thermal and electrical conductivities; (ii) high strengths; (iii) high stiffness. According to that, they hold potential application in high technology fields (*e.g.* microelectronics). As adsorbent, they have provided promising results for hydrogen storage, although careful validation of published data is recommended [86,87]. Presently, neither industrial production processes nor commercial applications of these materials are reported.

5.3. *Metal-organic frameworks*

In contrast to zeolites, for which a relatively limited number of structures exists (Section 4.1), the versatility of coordination and organic chemistry allow to design an almost infinite variety of MOF structures [88–91].

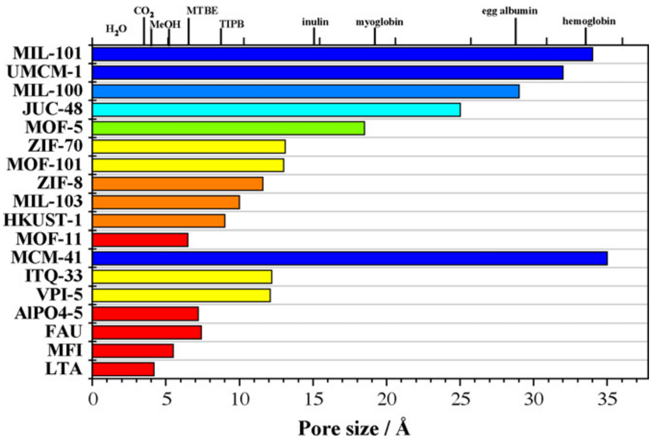

Fig. 2. Cavity size of porous MOFs (Å) compared with standard aluminosilicates and aluminophosphates. Porous materials are selected arbitrarily; pore sizes are approximate due to the variety of pore shapes involved.

MOF materials actually bridge the pore size gap between zeolite and mesostructured silica such as M41S materials, as shown in the arbitrary selection in Fig. 2. Aside from pore size and when pore topology is considered, one can find analogies between zeolites and MOFs. For instance, the pore structure can be one-dimensional with straight channels such as found for rod-like materials (MIL-53, MIL-68 and MOF-69), while IRMOF structures show three-dimensional cubic channel arrangements. In addition, as for zeolites, complex porous architecture with large cavities, reduced pore aperture and side pockets can be observed. A striking example is the HKUST-1 structure consisting of two types of “cages” and two types of “windows” separating these cages [92,93]. Large cages (13.2 and 11.1 Å in diameter) are interconnected by 9 Å windows of square cross-section. The large cages are also connected to tetrahedral-shaped side pockets of roughly 6 Å through triangular-shaped windows of about 4.6 Å. Typical zeolite topologies are also found in imidazolate based MOFs (also called ZIFs) such as SOD, LTA, RHO [94]. As a consequence, beta (9.6 Å) and alpha (16.4 Å) cages can be found in *sod*- and *rho*-ZMOF, respectively [95]. In terms of adsorption properties, MOF materials exhibit two major differences with respect to classical adsorbents:

- Framework flexibility upon adsorption–desorption [96,97]. In contrast with the permanent porosity typical of classical “rigid” adsorbents (carbons, zeolites), adsorption on MOF may evolve dynamically depending on the nature and quantity of host molecules [98–100]. In many examples, it is observed that the adsorption process can take place stepwise at different pressures depending on the adsorbed gas leading to adsorption–desorption isotherms with hysteresis phenomena. This phenomenon, usually named *gate opening* arises mainly from the flexibility of the networks. For instance, carbon dioxide and methane adsorptions on MIL-53 are strongly affected by the presence of water which causes drastic changes in the pore shapes [101,102].
- Very high adsorption capacities per mass unit due to very large micro-, mesoporous volumes. This is specially the case when considering high pressure domains ($P > 25$ bar). For example, CO_2 adsorption capacities at 50 bar are twice and three time larger for MOF-177 and MIL-101 with respect to NaX [103]. These outstanding capacities can be advantageous for gas storage applications [104–106,88].

For comparison purposes, carbon dioxide adsorption isotherms of various carboxylate based MOFs and reference carbon materials and zeolites are plotted in Fig. 3. The stability of carboxylate based MOFs upon water adsorption is usually pointed out as a major drawback for their applications [116,117]. In contrast, imidazolate based MOFs (also called ZIFs) are much more chemically stable and have been recently proposed as candidates for carbon dioxide capture [94,118,119]. Similarly to high silica zeolites and carbon adsorbents, the observed linear trend of carbon dioxide isotherms on MOFs (at low pressure) is a general feature. The adsorption mainly proceeds by van der Walls and quadrupole interactions. As a result, MOF exhibits lower heats of carbon dioxide adsorption which can be taken as a decisive advantage for PSA process (Table 9). Indeed, it shall allow desorbing much more carbon dioxide at the regeneration step, thus increasing the working capacity. However, it is at the expenses of lower selectivity values which directly penalize the rate of methane recovery and which may not be sufficient to fulfil raffinate specifications (Table 2).

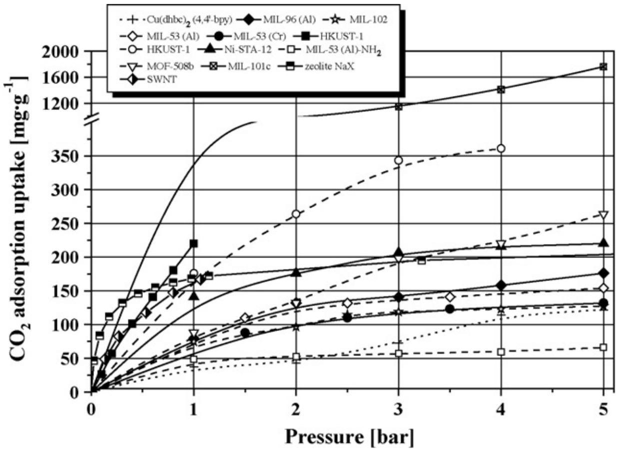

Fig. 3. Carbon dioxide adsorption isotherms measured at about 300 K for various MOFs and reference materials: Cu(dhbc)$_2$(4,4′-bpy) [107], MIL-96 (Al) [108], MIL-102 [109], MIL-53 (Al) [98], MIL-53 (Cr) [101], HKUST-1 [110], HKUST-1 [111], Ni-STA-12 [99], MIL-53 (Al)-NH$_2$ [112], MOF-508b [113], MIL-101c [114] and SWNTs [115].

Therefore new generation of MOF adsorbents shall be designed to selectively enhance carbon dioxide interactions with the framework while still limiting methane uptake. Two different strategies can be envisaged: (i) a *structural* route aiming at synthesizing MOF adsorbents with micropore size in the range of medium pore zeolites in order to benefit from stronger wall-molecules interactions. This can be achieved by networks interpenetration strategy [120]; (ii) a *functionalisation* route dealing with the enhancement of framework polarity. Simulations were performed on virtual compounds corresponding to the IRMOF topology with virtual organic linkers. It has been concluded that the use of short linkers or linkers highly functionalised with halogen moieties (*e.g.* bromine) would result in an increase of adsorption heats [121]. At IRCELYON, we have investigated the effect of functionalisation with basic amino groups on various carbolylate based MOFs (Fig. 4) [122,123]. Similarly, other authors have investigated ZIF functionalisation (ZIF-68, 78, 69, 82, 90) with polar groups such as -NO$_2$, -Cl, -CN and carboxyl [118,124]. Clearly, higher heats of CO$_2$ adsorption are found for functionalised adsorbents with respects to unpolar ZIF-8 (Table 10). However, it is worth to mention that the enhancement of the framework polarity is usually accompanied with a stronger adsorption of water as revealed by lager uptake at low pressure (Fig. 4).

Although MOF materials are intensely investigated for capture applications, much more insights is required before envisioning any industrial application for gas separation such as the effects of mixture of various gases and vapours (including water), adsorption-desorption kinetics, shaping and poisoning issues.

Table 9
MOFs CO$_2$/CH$_4$ separation performaces (zeolite 13X is reported for comparison): α_{CO_2,CH_4}: Henry's selectivity, S_{CO_2,CH_4}: selectivity estimated as the molar ratio of adsorbed carbon dioxide and methane at 5 bar, Δn: working capacity estimated as the difference between the adsorbed carbon dioxide at 5 bar and the adsorbed carbon dioxide at 1 bar, n_{CO_2}: amount of adsorbed carbon dioxide at 5 bar; q_{st}: carbon dioxide isosteric heat of adsorption, N.A.: not available.

Adsorbent	α_{CO_2,CH_4}	S_{CO_2,CH_4}	Δn [%]	n_{CO_2} [mg g^{-1}]	q_{st} [kJ mol^{-1}]
Cu(dhbc)$_2$(4,4′-bpy)	N.A.	∞	64	122	N.A.
MIL-96 (Al)	N.A.	9.4	56	180	33
MIL-102	N.A.	6.5	41	128	N.A.
MIL-53 (Al)	N.A.	4.4	42	154	40
MIL-53 (Cr)	N.A.	∞	54	132	N.A.
HKUST-1	5.5	11.3	51	361	26
Ni-STA-12	N.A.	12.5	36	220	34
MOF-508b	2.9	8.2	67	264	16
MIL-101c	31	9.2	65	1760	24
NaX	93	1.8	17	208	49

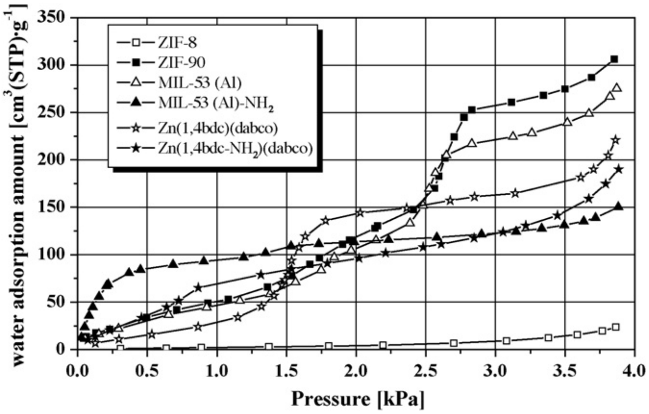

Fig. 4. Effect of MOF functionalisation on water adsorption measured at 313 K.

6. PSA applications

6.1. PSA applications to nitrogen removal from natural gas

The use of CMS as hydrocarbon–selective adsorbents suitable for PSA units for CBM enrichment has been suggested by Bergwerksverband (former Bergbau–Forschung) in a patent assigned in the 1980s [125]. This approach has been implemented by Nitrotec [126–128] for nitrogen rejection. Three gas treating plants (15 MMscf d^{-1} = 4.25 × 10^5 m^3 d^{-1} each) were installed in Texas in the 1990s. Nitrotec process utilises CMS to remove hydrocarbons from the stream containing nitrogen and operates at an optimum pressure of between 2 and 4 bar. The stream flows through the CMS bed with the hydrocarbon being trapped and the nitrogen being vented. Hydrocarbons are recovered by vacuum desorption (recovery of about 95%) and thus, have to be compressed to pipeline delivery pressure.

The Nitrex^{TM} [129,130] process developed by UOP by using the proprietary Polybed^{TM} PSA platform (mainly employed for high purity hydrogen production [8]) appears to be founded on the same principles of Nitrotec one. Hydrocarbon recovery up to 95% is claimed also in this case. One nitrogen rejection unit based on this technology was commissioned in Texas in the early 1990s, with a feed flow rate of about 2.3 MMscf d^{-1} = 6.51 × 10^4 Sm^3 d^{-1}.

On the other hand, very few PSA processes for nitrogen rejection from natural gas based on nitrogen preferential adsorption have been developed. The primary issue is in finding an adsorbent that has selectivity for nitrogen over methane suitable to provide a commercial viable process. In fact, large part of known adsorbents are characterised by equilibrium adsorption selectivity that favour methane over nitrogen (Section 3.5). According to that, processes based on kinetic separation have been suggested. A TSA moving bed process for nitrogen rejection from natural gas, based on fast adsorption/desorption cycles on zeolite 4A, was patented in the 1950s [131]. The apparatus disclosed in this patent

Table 10
ZIFs CO$_2$/CH$_4$ separation performances [118] (see Table 9 for comparison).

Adsorbent	α_{CO_2,CH_4}	S_{CO_2,CH_4}	n_{CO_2} [mg g^{-1}]	q_{st} [kJ mol^{-1}]
ZIF-68	5	3.8	72	20.8
ZIF-78	10	3.7	99	31
ZIF-82	9	4.7	101	23.9
ZIF-8	N.A.	2.8	28	N.A.

Fig. 5. Molecular Gate^{TM} adsorption system for nitrogen and/or carbon dioxide removal (courtesy of Guild Associates, www.moleculargate.com).

appears to be not practical and it does not provide a cost efficient separation method in view of high equipment and maintenance costs and adsorbent degradation by attrition. As a consequence, no plants based on this technology have ever been realised. On the other hand, clinoptilolite (a natural zeolite) is frequently cited in literature as rate selective adsorbent for the separation of nitrogen and methane. In particular, the use of magnesium exchanged clinoptilites has been patented by UOP [132]. Although, UOP patent indicates PSA as the preferred adsorption technology, no technical details are specified.

The Molecular Gate^{TM} PSA process has been developed by Engelhard (now BASF Catalysts) and presently licensed by Guild Associates [18,133–135]. It employs a proprietary adsorbent based on the synthetic titanosilicate ETS-4 (Section 4.1). This adsorbent is referred as Contracted TitanoSilicate 1 (CTS-1). Differently to essentially all known adsorbents, CTS-1 equilibrium adsorption selectivity favours nitrogen over methane. The unique behaviour of CTS-1 adsorbent makes this process suitable for nitrogen rejection from NG by nitrogen selective adsorption. As water adsorption can hydrate and thus change the pore size of CTS-1, it is good practice to remove the water beforehand (*i.e.* by adsorption on silica gel) if present in large amount (Fig. 5).

Feed is introduced into Molecular Gate^{TM} at high pressure. In most cases, optimum operating pressure is around 8 bar. Methane, ethane and about half the propane pass through the bed of adsorbent as raffinate stream, with less than 1 bar pressure drop. The system adsorbs also the residual water, all of the carbon dioxide and all of the C_{3+}. These hydrocarbons do not fit within the pore of the adsorbent. However, they are attracted to the binder used to hold the molecular sieve crystals together and are removed with the other adsorbed components into the tail gas. Adsorbent is regenerated by applying vacuum together with a minimal methane purge. The methane depleted stream (obtained as extract, at atmospheric pressure) is partially recycled to feed. Methane recovery higher than 90% has been declared.

It is interesting to point out that Molecular Gate^{TM} technology has been proposed also for carbon dioxide rejection and successfully tested for the upgrading of biogas (containing 3000 ppmv of H_2S) to pipeline quality NG [136]. Upgrading of landfill gas contaminated by siloxanes has been also claimed [137].

Molecular Gate^{TM} units able to treat 10 MMscf d^{-1} = 2.83 × 10^5 Sm^3 d^{-1} of NG, downsizeable till 0.5 MMscf d^{-1} = 1.41 10^4 Sm^3 d^{-1} are commercially available.

6.2. Applications to carbon dioxide removal from natural gas

Differently to nitrogen, carbon dioxide shows great affinity for several commercial adsorbents. As a consequence, the patent literature on carbon dioxide rejection from NG by PSA is extremely rich and mainly focused on processes rather than on adsorbents.

One of the earlier patents in this field (assigned to Union Carbide, now UOP) describes a PSA system based on a zeolite able to selectively adsorb carbon dioxide from low quality NG [138]. This system exploits displacement with carbon dioxide (*rinse*) to remove adsorbed methane from zeolite bed and to purge methane from column void space. The high purity of the obtained carbon dioxide is a benefit derived by the addition of this additional step.

A similar strategy is described in a group of patents assigned to Air Products & Chemical [139–141] in which PSA processes for carbon dioxide separation from methane (and/or hydrogen) are described. Carbon-based porous materials (ACs, CMS) are in this case the preferred adsorbents.

After desorption step, high pressure purge with carbon dioxide is followed by rinse at an intermediate pressure with an extraneous gas such as air or carbon dioxide itself. The column is then subjected to vacuum to remove the extraneous gas or any remaining carbon dioxide.

A process for methane recovery from LFG, combining a TSA and PSA units is described in a further patent assigned to Air Products & Chemicals. Specifically, the TSA unit removes water and minor impurities from the gas, which then goes to a PSA system devoted to carbon dioxide rejection [142]. The addition of a further PSA unit aimed to nitrogen rejection has been suggested to improve obtained methane quality [9].

The use of clinoptilolites for carbon dioxide rejection from poor gases is disclosed in a patent assigned to Gas Separation Technology [143]. The adsorbent has such a strong attraction to carbon dioxide that little desorption occurs even at very low pressure. According to that, regeneration by exposure to dry air is suggested.

Engelhard has successfully applied the Molecular Gate^{TM} technology to carbon dioxide rejection from NG (Section 5.1).

Nitrotec commercialises PSA units suitable for carbon dioxide rejection from natural gas. These units operate adsorption at a pressure between 3 and 17 bar. Carbon dioxide is desorbed from the

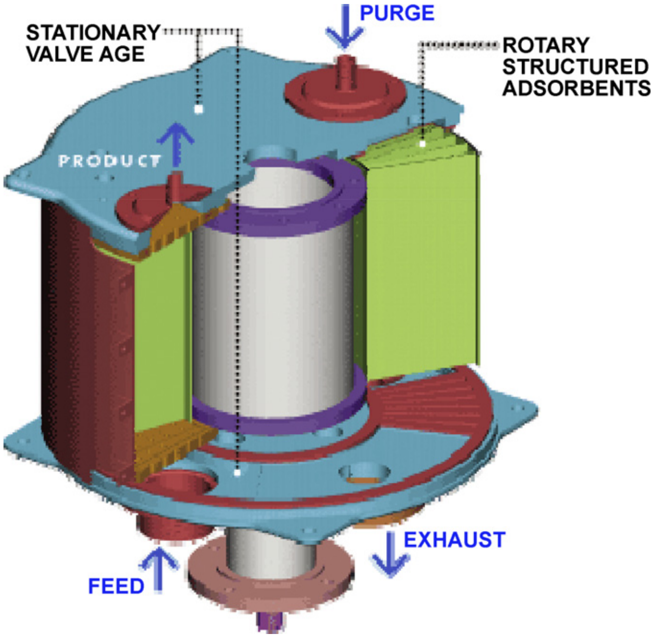

Fig. 6. RCPSA^{TM} module scheme (courtesy of Xebec, www.xebecinc.com).

Fig. 7. Refinery application of RCPSA^{TM} technology (courtesy of Xebec, www.xebecinc.com).

bed by vacuum [144]. In this case, the nature of the adsorbent is not specified.

BOC (now part of Linde) has presented a PSA process (based on an unspecified zeolite) for the production of fuel and carbon dioxide from LFG. According with the proposed scheme, the methane rich stream is partially used as fuel and partially converted into electricity. The carbon dioxide rich stream can be commercialised, due to its high purity. Also in this case, LFG pretreatment is suggested in order to maximise efficiency and avoid damages to the PSA unit.

The effectiveness of the BOC process is discussed as case study based on a 5 MMscf d^{-1} = 1.41 × 10^5 Sm^3 d^{-1}, feed flow [145].

Bergwerksverband (former Bergbau–Forschung) has demonstrated the effectiveness of CMS in carbon dioxide rejection from pretreated LFG. Operations have been performed during the 1980s on two pilot plants located, respectively, in Germany (850 scf d^{-1} = 2.41 · 10 Sm^3 d^{-1}, feed flow) and Holland (25 Mscf d^{-1} = 7.08 × 10^2 Sm^3 d^{-1}, feed flow). Unlike the process developed by the same company for nitrogen rejection by CMS (see Section 5.1), the inert rich stream is recovered as extract and the methane rich stream (up to 97 vol. %) as raffinate stream [146].

Osaka Gas has presented an integrated system for the exploitation of biogas: it comprises a PSA unit (for the separation of carbon dioxide from methane) and a methane adsorptive storage system. The technology (based on ACs) has been validated through a pilot plant able to treat 425 scf d^{-1} = 1.21 × 10 Sm^3 d^{-1} of biogas. Methane with the purity of 98 vol. % or higher was produced with a recovery of 90–95%. The PSA process was stable over one year [147].

7. Conclusions and perspectives

Although many adsorbents are commercially available, there are still demand for robust (high chemical stability against other contaminants, high mechanical stability against attrition), cheap (low synthesis cost since adsorbent cost represents a significant part of the investment cost) and *energy efficient* materials (*e.g.* with appropriate selectivity in order to limit the number of separation steps, large working capacity to reduce the cycle frequency, high regenerability to avoid use of external heat). Nevertheless, breakthrough processes can be anticipated if new materials can be design. Among others, a challenge in the materials development is the design of adsorbents which are less moisture sensitive due to the high cost of intensive drying. On the other hand, all kind of adsorbents which could process nitrogen rejection by molecular sieving shall lead to very valuable alternative processes.

Considering process engineering, *Rapid Cycle PSA* approach (RCPSA^{TM}) is a significant improvement. Xebec (former QuestAir Technologies) offers compact PSA units (0.01–9 MMscf d^{-1} = 2.83 × 10^2 to 2.54 × 10^5 Sm^3 d^{-1} of purified NG), based on proprietary rotary valves [148,149] and state of the art adsorbents (mainly for carbon dioxide and water removal). Xebec plans to build larger capacity PSA systems for NG processing based on the rapid cycle RCPSA^{TM} system jointly developed with ExxonMobil Research and Engineering [150,151]. RCPSA exploits both proprietary valves and structured adsorbents. Structured adsorbents overcome fluidisation limitations of beaded adsorbents, allowing higher cycle speeds (up to 50 cycles per minute) than conventional systems. The result is a significant size reduction of separation units (till 1/20 of state of the art PSA plants of the same productivity). Furthermore, the rotary valve technology replaces the bulky network of piping and valves used in conventional PSA systems with two compact, integrated valves. Structured adsorbent and rotary valve are packaged into modules as depicted in Fig. 6. Modular designs are being developed with total capacities up to 80 MMScf d^{-1} = 2.27 × 10^6 Sm^3 d^{-1} [152]. A prototype has been operated at an ExxonMobil refinery for the production of high purity hydrogen (Fig. 7).

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Appendix A.

Although the use of metric units is strongly encouraged by the scientific community, imperial units are currently employed in the gas industry. Thus, gas volume is frequently reported as *standard cubic feets* (scf or frequently SCF) *i.e.* measured at 60 °F = 289 K and 14.70 psi = 1.01 bar. SCFD is another common acronym for daily flows expressed as standard cubic feet.

In metric units, volume is given as either *normal cubic meters*, Nm^3 (where normal conditions are T = 273 K, P = 1 bar) or *standard cubic meters*, Sm^3 (where standard conditions are T = 288 K, P = 1 bar.

Prefix M represents 10^3 while MM, B, T represent 10^6, 10^9 and 10^{12}, respectively.

In this review imperial units are reported in order to give a realistic picture of the natural gas world, although conversion into metric units is provided too.

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