Review

Materials Design for N_2O Capture: Separation in Gas Mixtures

Daniel Ballesteros-Plata [ID], Juan Antonio Cecilia [ID], Isabel Barroso-Martín [ID], José Jiménez-Jiménez, Antonia Infantes-Molina [ID] and Enrique Rodríguez-Castellón *[ID]

Department of Inorganic Chemistry, Crystallography, and Mineralogy (Unidad Asociada al ICP-CSIC), Faculty of Sciences, University of Málaga, Campus de Teatinos, 29071 Málaga, Spain
* Correspondence: castellon@uma.es

Abstract: The adsorption of greenhouse gases (GHG) as a method to reduce their emissions into the atmosphere is an alternative that is easier to implement industrially and cheaper than other existing technologies, such as chemical capture, cryogenic separation, or membrane separation. The vast majority of works found in the literature have focused their efforts on capturing CO_2 as it is the largest GHG. However, although N_2O emissions are not as large as CO_2, the impact that N_2O has on the stratosphere and climate is much larger in proportion, despite which there is not much research on N_2O capture. Since both gases are usually emitted into the atmosphere together (along with other gases), it is necessary to design selective adsorbents capable of capturing and separating these gases from each other and from other gases, to mitigate the effects of climate change. This review aims to compile the existing information to date on porous adsorbents, the characteristics of the N_2O adsorption processes and, above all, aims to focus the reader's gaze on the importance of designing selective adsorbents for greenhouse gas mixtures.

Keywords: N_2O adsorption; N_2O/CO_2 selectivity; porous materials; MOFs; zeolites; activated carbons

1. Introduction

The energy production industry accounts for approximately two-thirds of global greenhouse gas (GHG) emissions, followed by agriculture and other non-energy-related industrial processes [1]. The main anthropogenic greenhouse gases emitted into the atmosphere are CO_2 (80%) mainly from the burning of fossil fuels, CH_4 (10%) and N_2O (7%) [2].

The increasing concentration of these GHG in the atmosphere (in 2022, ~417 ppm CO_2 [3], ~1908 ppb CH_4 [4], and ~335 ppb N_2O [5]) is the main cause of global warming and therefore climate change. For this reason, and given the current global climate situation, it is essential to reduce the global emissions of pollutants to avoid irreversible global warming. For this, different strategies must be considered, such as the electrification of transport, the integration of renewable energies, the capture, storage, and use of GHG as raw material for the synthesis of fuels and chemical products and the sustainable production of H_2 as well as the integration of the energy system incorporating new technologies efficiently.

CO_2 is the most abundant anthropogenic GHG in the atmosphere and great efforts are being performed for its capture, storage, and utilization, which play a very important role in the decarbonization of the energy sector and in the transition from our current linear economy based on fossil fuels to a circular carbon economy powered by renewable energies and with zero net CO_2 emissions. However, the global warming potential of N_2O is 310 times that of CO_2 and the lifetime of N_2O in the atmosphere is around 116 years (this is ~9.5 times longer than the lifetime of CH_4). In addition, N_2O is the main element that depletes the stratospheric ozone layer [6,7], behaving similarly to chlorofluorocarbons (CFCs).

N_2O emissions have grown strongly in the last 50 years, mainly due to the combustion of fuels, waste management, the use of synthetic nitrogen fertilizers, and the manufacture of adipic acid and nitric acid [8], so its concentration in the atmosphere is expected to

continue to increase in the coming decades [6]. Much of the N_2O emissions from the use of agricultural fertilizers are unavoidable. In this case, the reduction in N_2O involves improving the formulation of the fertilizers as well as using the appropriate dose at the best time for the crop. Where action can and must be taken is in the reduction in N_2O emissions from the production of adipic acid and nitric acid. Adipic acid is obtained using nitric acid oxidation of cyclohexanone and cyclohexanol, processes from which gaseous effluents composed of CO, CO_2, and N_2O, among other products, are generated, which are passed through adsorption columns, although the reduction in N_2O in the gas stream is negligible. For its part, obtaining nitric acid, either by oxidation or dehydration methods, generates NO_x where more than 20% is N_2O (5.3 kg N_2O/ton nitric acid produced). According to these facts, the elimination of N_2O must be the priority to avoid erratic climate changes in the not-too-distant future. Therefore, it is necessary to design processes to reduce, remove, or capture these gases.

Technologies to mitigate the N_2O concentration through emission reduction or gas removal include thermal decomposition, catalytic reduction, or photo-electrocatalytic decomposition of N_2O [9]. The capture and storage of gases such as CO_2 and N_2O has emerged as a potential strategy to reduce their emissions, mainly for stationary sources. Among the solutions proposed to replace traditional absorption technologies, which are inefficient, the N_2O capture through porous materials appears to be the most sustainable. Porous materials with a narrow pore size distribution and small pores could have enough potential for N_2O capture by acting as a molecular sieve through solid–gas interactions by an adsorption process.

Since industrial gaseous effluents are mixtures of various gases [10], the synthesis of suitable adsorbents for the selective capture of N_2O, CO, CO_2, etc. and optimization of the adsorption process, is crucial. In gas adsorption, porous materials have proven to be effective and easy to use, as well as being economically accessible [11,12]. The main drawback is the difficulty in separating N_2O and CO_2, since both gases have very similar physical and electronic properties [13]. For this reason, the design of effective adsorbent materials capable of selectively capturing one of the two gases is a very complicated challenge facing the research community. In this sense, efforts should focus on the design of selective CO_2/N_2O adsorbents from waste to mitigate the effects of both GHG and waste pollution. This manuscript aims to review the literature on adsorbents used for the selective capture of N_2O.

2. N_2O Capture

Although some studies have addressed the adsorption of N_2O and CO_2 using ionic liquids [14,15], adsorption seems a potentially more viable process for capturing N_2O/CO_2 given its low operating cost. That is why the study and understanding of an adsorbent material is essential when designing efficient adsorption processes. Although there is not much work in the literature about N_2O capture with porous materials, some works based on silica [16], MOFs [17], activated carbons, or zeolites [18] can be found. Table 1 briefs some characteristics of these material.

Table 1. Some advantages of silica gel, activated carbons (AC), zeolites, and Metal Organic Frameworks (MOFs) as sorbents.

Material	Features
Silica gel	Possible to modulate the dimensions and morphologies of the pore, possible to functionalize, good surface area, and low cost [19–22]
AC	Hydrophobic, high surface area and micropore volume, and low cost [8,23]
Zeolites	High-volume pores and surface area, capacity to be modified by ion exchange [24]
MOFs	High specific surface high ordering and narrow microporosity, crystalline nature, possibility of modification of the pore network and functionalization, and high-cost synthesis [25].

Silica gel is an amorphous and hydrophilic material whose surface is negatively charged, which makes it capable of adsorbing species with an electron deficit [19,22]. Given its electronic characteristics, textural properties, and low cost, it has been used as an adsorbent in many processes [19–21]. Although silica-based materials have been widely studied in CO_2, N_2, and O_2 adsorption processes [26–29], not much information is found on the use of silica as an N_2O adsorbent. D. Park et al. [16] evaluated the adsorption of N_2O on commercial silica gel with different particle sizes, from 0.2 mm to higher than 4 mm, at temperatures between 293 and 323 K and pressures up to 1000 kPa, finding that the diffusion of N_2O through the adsorbent is greater as the adsorbent particle size increases. The adsorption capacity improves at room temperature and with increasing pressure (4.02 mmol g^{-1} at 1008 kPa and 1.01 mmol g^{-1} at 102 kPa). So, pressure and temperature play an important role and this is confirmed by all the N_2O adsorption studies with porous materials (as will be seen throughout the review), where it is systematically observed that the adsorption capacity improves markedly at low temperatures (ambient or lower) and to a lesser extent with increasing pressure. However, silica gel is a better CO_2 adsorbent than N_2O [16].

Continuing with the study of silica as a sorbent and the influence of the surface area, G. Cornelissen et al. [18] compared the N_2O adsorption capacity of two commercial silicas with quite different surface areas, 205 and 598 $m^2 \, g^{-1}$, verifying that the increase in surface area contributes to the better N_2O adsorption capacity of the SiO_2-598 sample. Some N_2O adsorption data on siliceous materials are shown in Table 2, where the limited capacity of silica-based materials in the N_2O adsorption can be verified.

Table 2. N_2O adsorption in silica-based materials.

Adsorbent	T (K)	P (kPa)	BET ($m^2 \, g^{-1}$)	V_p ($cm^3 \, g^{-1}$)		q (mmol g^{-1})	Ref.
				Micro	Meso/ Macro		
Silica gel	293	102	775	0.350	0.103	1.01	[16]
SiO_2-205	293	100	205	-	-	0.38	[18]
SiO_2-598	293	100	598	-	-	1.53	[18]
Silica gel	298	100	759	0.485		0.79	[30]

BET: Brunauer–Emmett–Teller surface area ($m^2 \, g^{-1}$). V_p: Pore volume ($cm^3 \, g^{-1}$). q: Maximum sorption capacity (mmol g^{-1}).

2.1. Kinetic and Thermodynamic Considerations

Since silica-based adsorbent materials do not have much N_2O adsorption capacity, activated carbons, zeolites, and MOFs have been more extensively studied in N_2O adsorption processes. These materials usually have large surface areas and high microporosity content as well as the advantage of being able to modify the pore network and even functionalize them with ligands capable of improving selectivity in CO_2–N_2O separation processes. In any case, all of these materials behave in the same way against pressure and temperature; the higher the pressure and the lower the temperature, the greater the adsorption [31,32]. In general, the influence of the temperature is greater than that of the pressure. However, it is important to know the mechanism of N_2O adsorption is not entirely clear. For instance, it is known that the greater the surface area and pore volume, the greater the adsorption capacity, as shown in the study carried out by D. Park et al. [8]. In these cases, the diffusion through the micropores dominates the adsorption kinetics over the diffusion of the meso and/or macropores. At low pressures, the interaction between N_2O and the surface of the micropores is stronger and, therefore, the adsorption kinetic increases, however, at high pressures the interaction of the N_2O molecules with the surface in larger pores is favored [8]. Y. Peng et al. [31] studied the behavior of various activated carbons with different pore sizes in the N_2O adsorption and found that in carbons with a higher content of micropores (Kureha [14.7 mmol g^{-1}] and Ovcls [12.1 mmol g^{-1}]) the adsorbent–adsorbate interactions were stronger; however, in carbons with a higher content of total pore volume (micro and

mesopores) (Vruf [19.2 mmol g^{-1}]) the highest adsorption capacity was achieved at 193 K, that is, materials with a higher adsorption capacity will be those containing a greater total pore volume and materials with a greater micropore volume, the adsorption kinetics will be faster.

In relation to the adsorption mechanism, it is also important to take into account the kinetic diameter (to design a suitable pore structure), which refers to the free path of a molecule and indicates the size of the molecule [33]. Therefore, the smaller the kinetic diameter of the gas molecule (note that for N_2O and CO_2 it is the same [3.3 Å]), the easier it enters the pore, as long as the pore is larger than the kinetic diameter. However, there are some discrepancies in the literature. For instance, D. Park et al. [8] found that although N_2O has a smaller kinetic diameter than other molecules such as O_2 (3.46 Å) or N_2 (3.64 Å), it is expected that it enters the pores of activated carbon and carbon molecular sieves in an easier way. However, the adsorption rate of N_2O was lower than that O_2, suggesting that factors other than the kinetic diameter influence the adsorption mechanism. So, the adsorption capacity also depends on other factors [30,31,34], which cause the mechanism of N_2O adsorption to be not as clear as expected considering the kinetic diameter and textural properties. Therefore, apart from these properties, it is important to take into account the thermodynamics of the process, that is, the affinity between adsorbent and adsorbate. The parameters such as diffusivity, adsorption enthalpy ($-\Delta H_0$), or Henry constant (K_H) help to highlight the interaction between adsorbate and adsorbent and other parameters such as gate-opening pressure (or threshold pressure) can help to establish the optimal adsorption pressure in the adsorption process of a gas, alone or in a mixture of gases.

The adsorption enthalpy ($-\Delta H_0$) helps to understand the interactions established between the adsorbate and the adsorbent on the surface of the latter, providing useful information to design a more efficient adsorption process. At the beginning of the adsorption process, N_2O will be adsorbed on the sites of the adsorbent with the highest energy level (microporous), interacting with the walls of the adsorbent and causing the release of energy in the form of heat as a consequence of the adsorbent–adsorbate interaction, and faster adsorption kinetics. After the higher energy sites are occupied, the occupation of the lower energetic sites begins (greater porous) and then the amount of adsorbed N_2O begins to increase at the same time that the adsorption enthalpy decreases [8,31,34]. However, diffusivity studies indicate that the diffusion time constant decreases considerably at high pressures in N_2O adsorption, due to partial blockage of the pores [35,36], which leads to slower adsorption kinetics. This fact is even more accentuated in those materials that have a narrower pore size distribution such as zeolite 4A [34] and zeolite 5A [35]. In contrast, it is interesting to note, in view of the selective separation of N_2O and CO_2 that although N_2O and CO_2 have very similar characteristics [37], something completely different happens during CO_2 adsorption. At high pressure, the CO_2 concentration on the surface of the adsorbent increases and surface diffusion (slip) of CO_2 molecules across the surface of the adsorbent occurs, increasing the amount of CO_2 adsorbed [35] without producing the pore blockage.

Henry's constant (K_H) can be applied to quantify the degree of adsorption of a given material if working at low pressures (<100 kPa) [17]. It is a value that is a function of the properties of the adsorption process and of the adsorbent. Thus, K_H decreases with increasing temperature. This was highlighted by J.C. Groen et al. [38] when studying the adsorption capacity of N_2O in the silicalite-1 zeolite. It was determined that the K_H value changed substantially with a slight change in adsorption temperature, from 273 K (q = 2.4 mmol g^{-1}) to 298 K (q = 1.7 mmol g^{-1}), K_H was 13.09 and 5.03 mol kg^{-1} kPa^{-1}, respectively. Therefore, a higher adsorption capacity implies a higher K_H value.

Tables 3 and 4 show some materials based on activated carbon and zeolites, respectively, used in the adsorption of N_2O under similar pressure and temperature conditions, in order to be able to compare them. It should be noted with respect to activated carbons, that in the best of cases up to 3.6 mmol g^{-1} (100 kPa, 293 K) of adsorption capacity are reached [8,31]. A slight increase in the adsorption capacities (at 298 K and

100 kPa) has been observed for zeolite 13X (q = 4.01 mmol g^{-1}) [30] and for zeolite 5A (q = 4.10 mmol g^{-1}) [35,37]. Some natural zeolites have also been investigated [34] but have not shown high N_2O adsorption capacities (1.5–2 mmol g^{-1}) [32].

Table 3. Carbon-based materials in N_2O adsorption studies.

Adsorbent	T (K)	P (kPa)	BET (m^2 g^{-1})	V_P (cm^3 g^{-1})		q (mmol g^{-1})	Ref.
				Micro	Meso/Macro		
AC-775	293	100	775	-	-	3.24	[18]
AC-569	293	100	569	-	-	3.21	[18]
AC	298	100	904	0.502	-	2.39	[30]
Porous carbon	298	106	798	-	0.87	2.40	[36]
AC	293	100	1306	0.370	-	3.70	[8]
CMS	293	100	641	0.241	0.236	2.50	[8]
Kureha	293	101	1300	0.560	-	3.10	[31]
Ovcls	293	101	1055	0.397	0.104	3.60	[31]
Vruf	293	101	1330	0.040	0.770	2.10	[31]

AC: Activated carbon; CMS: Carbon molecular sieve. BET: Brunauer–Emmett–Teller surface area (m^2 g^{-1}). V_P: Pore volume (cm^3 g^{-1}). q: Maximum sorption capacity (mmol g^{-1}).

Table 4. Zeolites based materials in N_2O adsorption studies.

Adsorbent	T (K)	P (kPa)	BET (m^2 g^{-1})	V_P (cm^3 g^{-1})		q (mmol g^{-1})	Ref.
				Micro	Meso/Macro		
Silicalite-1	298	100	372	0.179	-	1.74	[38]
5A	298	100	580	-	0.257	3.72	[30]
13X	298	100	529	0.425	-	4.01	[30]
ZSM-5	298	100	241	0.258	-	1.34	[30]
4A	298	108	-	x	-	3.49	[34]
13X	298	108	-	x	-	0.84	[34]
5A	298	106	-	x	-	4.10	[35]
Erionite	293	100	426	0.188	0.032	2.10	[32]
Clinoptilolite	293	100	23	0.108	0.082	1.75	[32]
Mordenite	293	100	266	0.119	0.055	1.50	[32]

x: The research article does not provide pore volume data but notes that the pores are microporous. BET: Brunauer–Emmett–Teller surface area (m^2 g^{-1}). V_P: Pore volume (cm^3 g^{-1}). q: Maximum sorption capacity (mmol g^{-1}).

MOFs have been studied most extensively in N_2O capture processes. They have shown a high potential for capturing N_2O and for gas separation, due to their high ordering and narrow microporosity. The main drawback lies on the high cost of their synthesis, which could cause it to be difficult to use on a large scale. Nonetheless, much of the research on N_2O capture and separation has focused on adsorbents based on Metallic Organic Frameworks, given their adaptability to certain processes [39]. Table 5 shows some MOFs used in N_2O adsorption.

The first studies based on MOFs in N_2O adsorption were zinc-based MOFs materials (MOF-5 and MOF-177), which are considered good adsorbents for H_2 [43,44], given their high surface areas (900 and >3500 m^2 g^{-1}, respectively) and size porosity around 1 nm. However, they have not proven to be such good N_2O adsorbents, showing adsorption capacities of less than 1 mmol g^{-1} in the best case (MOF-5). Contrary, they proved to have more affinity for gases such as CO_2 and CH_4 working at high pressures (1000 kPa, 298 K) [35].

Table 5. MOFs based materials in N_2O adsorption studies.

Adsorbent	T (K)	P (kPa)	BET ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$) Micro	Meso/ Macro	q (mmol g^{-1})	Ref.
MIL-100Cr-150	298	100	1764	-	-	1.95	[40]
MIL-100Cr-250	298	100	2118	-	-	5.78	[40]
MIL-100Cr-250	273	100	2118	-	-	8.25	[40]
MIL-100Cr	298	100	1574	0.81	-	5.77	[37]
ED *-MIL-100Cr-0.2	298	100	1050	0.39	-	2.14	[37]
ED *-MIL-100Cr-0.4	298	100	952	0.34	-	2.00	[37]
ED *-MIL-100Cr-0.6	298	100	981	0.34	-	1.99	[37]
MOF-5	298	106	900	-	-	0.90	[35]
MOF-177	298	106	3500	1.60	-	0.07	[35]
Ni-MOF	298	100	447	0.094	-	2.81	[11]
HKUST-1	298	100	-	-	-	3.91	[37]
ZIF-7	298	100	-	x	-	2.50	[12]
ZIF-8	298	100	-	-	-	1.39	[37]
UiO-66	298	100	-	-	-	4.32	[37]
MIL-100Fe-300	298	100	-	x	x	4.70	[41]
MIL-101(Cr)-NO$_2$	298	100	3255	1.14	0.76	2.38	[13]
MIL-101(Cr)-Br	298	100	1626	0.65	0.33	2.58	[13]
MIL-101(Cr)-NH$_2$	298	100	3768	1.42	0.82	5.08	[13]
MIL-101(Cr)-H	298	100	4156	2.03	0.31	5.44	[13]
MIL-53Al	298	100	-	-	-	2.70	[42]
CuBTC	297	122.8	-	-	-	5.38	[17]

* ED: ethylenediamine-functionalized; x: The research article does not provide pore volume data, but notes that the sample contains micro and/or mesoporous. BET: Brunauer–Emmett–Teller surface area ($m^2 g^{-1}$). V_p: Pore volume ($cm^3 g^{-1}$). q: Maximum sorption capacity (mmol g^{-1}).

2.2. Separation Efficiency

The potential adsorption capacity of MOFs is related to their ability to modify internal structural stresses, which allows MOFs to modify the "opening" of their pores as a function of the temperature. This is known as threshold pressure or gate-opening pressure. Thus, in theory, the lower the gas pressure threshold, the greater the preference for being adsorbed [12,42]. Previous investigations on nickel-based MOFs [45,46] reveal that the incorporation of nickel allows a structural change of the material that leads to an increase in adsorption capacity. Based on this fact, K. L. Kauffmann et al. [47] studied a nickel-based MOF (NiDBM-Bpy) against a gas mixture (N_2, O_2, CH_4, N_2O, and CO_2) as a function of threshold pressure. Above the threshold pressure it is known that the adsorption of a gas increases rapidly. However, in this regard, there are two currents of thought: (a) the one that thinks that the threshold pressure would serve to selectively adsorb one gas over another and (b) the one that thinks that there is a cooperation between the gases so that everyone can access to the adsorption sites. In any case, both CO_2 and N_2O compete strongly (given their similar physical properties) for the adsorption sites, so the thermodynamic conditions of adsorption are a determining factor in achieving the effective separation of both gases. The study on the gate-opening pressure of some MOFs against CO_2 and N_2O mixtures has been carried out, and varies depending on the MOF and the adsorption temperature and pressure used, as deduced, for example, from the investigations carried out by D.L. Chen et al. [12] with the MOF ZIF-7 (zeolitic imidazolate framework) and by L. Wang et al. [42] with the MOFs ELM-11, ELM-12, and MIL-53Al. Based on the gate-opening pressure at 298 K, ZIF-7 shows a lower pressure for N_2O (0.35 bar^{-1}) than for CO_2 (0.50 bar^{-1}), that is, for N_2O it will be easier to interact with the adsorbent inside the pores. With ELM-11 (N_2O: 1.0 bar^{-1}, CO_2: 0.8 bar^{-1}) and ELM-12 (N_2O: 6.0 bar^{-1}, CO_2: 4.0 bar^{-1}) the opposite occurs. Therefore, the greater the gate-opening pressure difference between gases, the greater the selectivity toward the gas with lower pressure is expected when the applied adsorption pressure is between the minimum and maximum gate-opening pressures. For example, for

MIL-53Al, the gate opening pressures for N_2O and CO_2 are 2.7 and 5.0 bar^{-1}, respectively. Then, with adsorption pressure (2.7 < p < 5.0), the adsorbed amount of N_2O is maximum (8 mmol g^{-1}) and that of CO_2 minimum (3 mmol g^{-1}). With p < 2.7 bar and p > 5.0 bar, the adsorbed quantities of N_2O and CO_2 are equal, 3 and 8 mmol g^{-1}, respectively [42].

More recently and continuing with the research on nickel-based MOFs, X. Zhang et al. [11] have developed the solvothermal synthesis of a nickel acetate functionalized MOF (Ni-MOF) to obtain a polar microporous (Ø 1 nm) structure. After activation of Ni-MOF (323 K/12 h under vacuum), the material is capable of separating CO_2 (q = 3.24 mmol g^{-1}, 100 kPa, 298 K) and N_2O (q = 2.81 mmol g^{-1}, 100 kPa, 298 K) of other gases such as CH_4, N_2, O_2, mainly due to the fact that N_2O, and CO_2 have a smaller kinetic diameter and both molecules strongly interact with the pore surface. Strong competition for adsorption sites is observed, which prevents the selective separation of both gases (CO_2, N_2O).

Delving into the study of the adsorption mechanism and the competition for the adsorption sites of a gaseous mixture (CO_2, N_2O, CH_4, and N_2), F.A. Kloutse et al. [17] carried out monocomponent and multicomponent adsorption studies on an MOF functionalized with Cu (CuBTC). This adsorbent is non-polar, has unsaturated Cu sites, and two interconnected pore sizes (0.9 and 0.5 nm) that result in the creation of two preferential adsorption sites. The monocomponent data revealed a high adsorption capacity for N_2O and CO_2 on CuBTC at the unsaturated copper sites (direct interaction with the adsorbent surface), which increased considerably with pressure (q(N_2O) = 5.4 and 10.9 mmol g^{-1}; q(CO_2) = 4.5 and 10.2 mmol g^{-1}, at 120 and 900 kPa, respectively). As can be seen, CuBTC is capable of capturing very similar amounts of CO_2 and N_2O, under the same pressure and temperature conditions, and the small difference between N_2O and CO_2 capacity could be due to the small permanent dipole moment of N_2O and its polarizability. Additionally, the smaller kinetic diameters of CO_2 and N_2O could be the main cause of the greater adsorption capacity of both gases compared to CH_4 and N_2 (with a larger kinetic diameter). Unfortunately, the multicomponent study reveals that the adsorption capacity of each gas decreases considerably (q(N_2O) = 3.7 mmol g^{-1} and q(CO_2) = 3.1 mmol g^{-1}, at 112 kPa and 297 K) because molecular competition between CO_2 and N_2O for adsorption sites. CO_2 and N_2O begin to dominate the adsorption to the detriment of CH_4 and N_2 at pressures above 250 kPa, however, CuBTC is not capable of selectively separating CO_2 and N_2O.

One of the drawbacks of MOFs is that they need to be activated, usually under conditions of temperature and vacuum, to remove the solvent from the material structure. The control of the activation temperature is essential to remove the maximum amount of solvent from the structure without collapsing and to maximize the surface area, in addition to allowing more metallic active sites to be exposed to bind to the adsorbate molecules during the adsorption process, as shown by J. Yang et al. [40] when investigating the influence of activation temperature (using high vacuum, 10^{-10} bar) in the metal–organic-framework MIL-100Cr in the adsorption/separation of N_2O and N_2 process. This study reveals the preference of unsaturated Cr^{3+} metal sites for N_2O versus N_2 and that the adsorption of N_2O is maximum when the adsorbent is activated at 523 K (1.95 mmol g^{-1} activation at 423 K; 5.78 mmol g^{-1} activation at 523 K). At 523 K, and for this material, the solvent molecules more strongly anchored to the Cr^{3+} sites are removed, so the surface area increases considerably and more Cr^{3+} sites remain free to preferentially bind N_2O, improving adsorption capacity and separation of N_2. At more than 523 K, the structure collapses.

Following the MIL-100 metal–organic framework, L. Wang et al. [41] replaced Cr with Fe, thus generating two different adsorption sites: on the one hand Fe^{3+} sites that interact with CO_2 ($-\Delta H_0$ = 12 kJ mol^{-1}) and on the other hand unsaturated Fe^{2+} sites that interact with N_2O ($-\Delta H_0$ = 36 kJ mol^{-1}). During the activation of the adsorbent at 573 K the presence of Fe^{2+} sites predominate, so a small difference is observed in the adsorbed amounts of CO_2 and N_2O.

Given the similarities between CO_2 and N_2O that cause their separation to be notably difficult, it seems that taking advantage of the acidic properties of both gases (CO_2 is acidic and N_2O is not) could help achieve this. The functionalization of MOFs with alkaline

or acid molecules seems to have sufficient potential to achieve a higher selectivity of MOF-based adsorbents, as has been shown, for example, with the functionalization of the MIL-100Cr MOF with ethylenediamine [37], in order to generate alkaline holes in the structure capable of selectively adsorbing CO_2 (acid). The amount of N_2O adsorbed after modifying the MOF with ethylenediamine is greatly reduced relative to the unmodified MOF. However, the yield of adsorbed CO_2 also decreases considerably because after incorporating ethylenediamine, the volume of pores decreases greatly. The porosity control after functionalization is, therefore, a fundamental aspect to take into account in the adsorbents design, in order to improve adsorption performance.

Table 6 shows the separation capacity in N_2O-CO_2 mixtures of recently investigated materials, most of them MOFs. Unfortunately, as far as we know, zeolites and activated carbon have hardly been investigated in the adsorption processes of N_2O–CO_2 mixtures.

Table 6. Adsorbed amount of N_2O and CO_2 in separation processes.

Adsorbent	T (K)	P (kPa)	q (mmol g^{-1})		Ref.
			N$_2$O	CO$_2$	
Porous carbon	298	106	2.40	1.49	[36]
Ni-MOF	298	100	2.81	3.24	[11]
ZIF-7	298	100	2.50	2.29	[12]
CuBTC	297	112	3.70	3.10	[17]
MOF-5	298	106	0.90	0.77	[35]
ZIF-8	298	100	1.39	1.03	[37]
UiO-66	298	100	4.32	1.03	[37]
HKUST-1	298	100	3.91	3.66	[37]
MIL-100Cr	298	100	5.77	5.80	[37]
ED *-MIL-100Cr-0.4	298	100	2.00	4.10	[37]
MIL-100Fe-300	298	100	4.70	3.86	[41]
MIL-101(Cr)-NO$_2$	298	100	2.38	2.34	[13]
MIL-101(Cr)-Br	298	100	2.58	2.35	[13]
MIL-101(Cr)-NH$_2$	298	100	5.08	4.54	[13]
MIL-101(Cr)-H	298	100	5.44	5.38	[13]
ELM-11	298	100	0.06	2.5	[42]
ELM-12	298	100	0.86	0.75	[42]
MIL-53Al	298	100	2.70	2.71	[42]

* ED: Ethylenediamine-functionalized. q: Maximum sorption capacity (mmol g^{-1}).

3. Conclusions

Although there is a wide variety of adsorbent materials, especially for CO_2 capture, there are not many materials applied to N_2O capture. Most GHG adsorption studies have focused on the adsorption capacity of various adsorbents, zeolites, activated carbons, or MOFs, against individual gases, i.e., CH_4, CO_2, or N_2O alone. In these studies, good adsorption capacities are frequently achieved, especially with zeolites and MOFs. However, the biggest problem is that industrial effluents contain mixtures of all these gases, which must be selectively separated in order to use them as raw material in industrial processes for the production of high value-added chemicals. As a result of the fact that CO_2 and N_2O have very similar physical and electronic properties, their separation by means of selective adsorbents is complicated. Despite the efforts made in many of the investigations on the adsorption of CO_2 and N_2O, the main focus should be on the separation of these two gases using selective adsorbents. In this sense, MOFs have especially been studied in greater depth than activated carbon, due to their porous moldability and possible functionalization with heteroatoms or molecules that could cause these materials to be more selective toward CO_2 or N_2O. It would be necessary to achieve greater differences in the gate opening pressures, as well as to optimize porosity, control acidity, etc. for more efficient separation.

Given the difficulty, especially economic, that industrializing a selective adsorption process through the use of MOFs can entail, a cheaper alternative could be found in natural zeolites, which they have hardly been studied.

Author Contributions: D.B.-P.: Investigation, writing—original draft. J.A.C.: Investigation and writing—review. I.B.-M.: Investigation and review. A.I.-M. and J.J.-J.: Supervision and review. E.R.-C.: Conceptualization, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kamkeng, A.D.N.; Wang, M.; Hu, J.; Du, W.; Qian, F. Transformation Technologies for CO_2 Utilisation: Current Status, Challenges and Future Prospects. *Chem. Eng. J.* **2021**, *409*, 128138. [CrossRef]
2. Available online: https://Www.Epa.Gov/Ghgemissions/Overview-Greenhouse-Gases#CO2-References (accessed on 8 September 2022).
3. Monthly Average Mauna Loa CO_2. Available online: https://gml.noaa.gov/ccgg/trends/ (accessed on 8 September 2022).
4. Available online: https://Gml.Noaa.Gov/Ccgg/Trends_ch4/. (accessed on 9 September 2022).
5. Available online: https://Gml.Noaa.Gov/Ccgg/Trends_n2o/ (accessed on 9 September 2022).
6. Hanqin, T.; Rongting, X.; Canadell, J.G.; Thompson, R.L.; Winiwarter, W.; Suntharalingam, P.; Davidson, E.A.; Ciais, P.; Jackson, R.B.; Janssens-Maenhout, G.; et al. A Comprehensive Quantification of Global Nitrous Oxide Sources and Sinks. *Nature* **2020**, *586*, 248–256. [CrossRef]
7. Ravishankara, A.R.; Daniel, J.S.; Portmann, R.W. Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century. *Science* **2009**, *326*, 123–125. [CrossRef] [PubMed]
8. Park, D.; Ju, Y.; Kim, J.H.; Ahn, H.; Lee, C.H. Equilibrium and Kinetics of Nitrous Oxide, Oxygen and Nitrogen Adsorption on Activated Carbon and Carbon Molecular Sieve. *Sep. Purif. Technol.* **2019**, *223*, 63–80. [CrossRef]
9. Ko, B.H.; Hasa, B.; Shin, H.; Zhao, Y.; Jiao, F. Electrochemical Reduction of Gaseous Nitrogen Oxides on Transition Metals at Ambient Conditions. *J. Am. Chem. Soc.* **2022**, *144*, 1258–1266. [CrossRef] [PubMed]
10. Shimizu, A.; Tanaka, K.; Fujimori, M. Abatement Technologies for N_2O Emissions in the Adipic Acid Industry. *Chemosphere—Glob. Chang. Sci.* **2000**, *2*, 425–434. [CrossRef]
11. Zhang, X.; Chen, W.; Shi, W.; Cheng, P. Highly Selective Sorption of CO_2 and N_2O and Strong Gas-Framework Interactions in a Nickel(II) Organic Material. *J. Mater. Chem. A* **2016**, *4*, 16198–16204. [CrossRef]
12. Chen, D.L.; Wang, N.; Wang, F.F.; Xie, J.; Zhong, Y.; Zhu, W.; Johnson, J.K.; Krishna, R. Utilizing the Gate-Opening Mechanism in ZIF-7 for Adsorption Discrimination between N_2O and CO_2. *J. Phys. Chem. C* **2014**, *118*, 17831–17837. [CrossRef]
13. Ma, L.; Zhang, F.; Li, K.; Zhang, Y.; Song, Z.; Wang, L.; Yang, J.; Li, J. Improved N_2O Capture Performance of Chromium Terephthalate MIL-101 via Substituent Engineering. *J. Solid State Chem.* **2022**, *309*, 122951. [CrossRef]
14. Shiflett, M.B.; Elliott, B.A.; Niehaus, A.M.S.; Yokozeki, A. Separation of N_2O and CO_2 Using Room-Temperature Ionic Liquid [Bmim][Ac]. *Sep. Sci. Technol.* **2012**, *47*, 411–421. [CrossRef]
15. Pereira, L.M.C.; Oliveira, M.B.; Llovell, F.; Vega, L.F.; Coutinho, J.A.P. Assessing the N_2O/CO_2 High Pressure Separation Using Ionic Liquids with the Soft-SAFT EoS. *J. Supercrit. Fluids* **2014**, *92*, 231–241. [CrossRef]
16. Park, D.; Hong, S.H.; Kim, K.M.; Lee, C.H. Adsorption Equilibria and Kinetics of Silica Gel for N_2O, O_2, N_2, and CO_2. *Sep. Purif. Technol.* **2020**, *251*, 117326. [CrossRef]
17. Kloutse, F.A.; Gauthier, W.; Hourri, A.; Natarajan, S.; Benard, P.; Chahine, R. Study of Competitive Adsorption of the N_2O-CO_2-CH_4-N_2 Quaternary Mixture on CuBTC. *Sep. Purif. Technol.* **2020**, *235*, 116211. [CrossRef]
18. Cornelissen, G.; Rutherford, D.W.; Arp, H.P.H.; Dörsch, P.; Kelly, C.N.; Rostad, C.E. Sorption of Pure N_2O to Biochars and Other Organic and Inorganic Materials under Anhydrous Conditions. *Environ. Sci. Technol.* **2013**, *47*, 7704–7712. [CrossRef] [PubMed]
19. Parida, S.K.; Dash, S.; Patel, S.; Mishra, B.K. Adsorption of Organic Molecules on Silica Surface. *Adv. Colloid Interface Sci.* **2006**, *121*, 77–110. [CrossRef] [PubMed]
20. Yan, K.L.; Wang, Q. Adsorption Characteristics of the Silica Gels as Adsorbent for Gasoline Vapors Removal. *IOP Conf. Ser. Earth Environ. Sci* **2018**, *153*, 022010. [CrossRef]
21. Wahshi, F.S.; Alqahtani, M.D.; Abdulla, M.; Ramachandran, T.; Hamed, F.; Thiemann, T. Adsorption of Model Dyes on Recycled Silica Gel. *Proceedings* **2020**, *48*, 10. [CrossRef]
22. Chapter 9 Physical Methods of Gas Analysis. *Compr. Anal. Chem.* **1991**, *28*, 123–221. [CrossRef]

23. Xia, K.; Gao, Q.; Wu, C.; Song, S.; Ruan, M. Activation, Characterization and Hydrogen Storage Properties of the Mesoporous Carbon CMK-3. *Carbon* **2007**, *45*, 1989–1996. [CrossRef]

24. Centi, G.; Generali, P.; Dall'olio, L.; Perathoner, S.; Rak, Z. Removal of N_2O from Industrial Gaseous Streams by Selective Adsorption over Metal-Exchanged Zeolites. *Ind. Eng. Chem. Res.* **2000**, *39*, 131–137. [CrossRef]

25. Mueller, U.; Schubert, M.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastré, J. Metal-Organic Frameworks—Prospective Industrial Applications. *J. Mater. Chem.* **2006**, *16*, 626–636. [CrossRef]

26. Loganathan, S.; Tikmani, M.; Edubilli, S.; Mishra, A.; Ghoshal, A.K. CO_2 Adsorption Kinetics on Mesoporous Silica under Wide Range of Pressure and Temperature. *Chem. Eng. J.* **2014**, *256*, 1–8. [CrossRef]

27. Liu, X.; Li, J.; Zhou, L.; Huang, D.; Zhou, Y. Adsorption of CO_2, CH_4 and N_2 on Ordered Mesoporous Silica Molecular Sieve. *Chem. Phys. Lett.* **2005**, *415*, 198–201. [CrossRef]

28. Serna-Guerrero, R.; Sayari, A. Modeling Adsorption of CO_2 on Amine-Functionalized Mesoporous Silica. 2: Kinetics and Breakthrough Curves. *Chem. Eng. J.* **2010**, *161*, 182–190. [CrossRef]

29. Serna-Guerrero, R.; Belmabkhout, Y.; Sayari, A. Modeling CO_2 Adsorption on Amine-Functionalized Mesoporous Silica: 1. A Semi-Empirical Equilibrium Model. *Chem. Eng. J.* **2010**, *161*, 173–181. [CrossRef]

30. Wu, T.; Shen, Y.; Feng, L.; Tang, Z.; Zhang, D. Adsorption Properties of N_2O on Zeolite 5A, 13X, Activated Carbon, ZSM-5, and Silica Gel. *J. Chem. Eng. Data* **2019**, *64*, 3473–3482. [CrossRef]

31. Peng, Y.; Zhang, F.; Xu, C.; Xiao, Q.; Zhong, Y.; Zhu, W. Adsorption of Nitrous Oxide on Activated Carbons. *J. Chem. Eng. Data* **2009**, *54*, 3079–3081. [CrossRef]

32. Hernández Huesca, R.; Pérez Arcos, J.; Vargas Hernández, D.; Pérez Cruz, M.A. Adsorption Kinetics of N_2O on Natural Zeolites. *Int. J. Environ. Pollut.* **2016**, *32*, 237–242. [CrossRef]

33. Jahandar Lashaki, M.; Fayaz, M.; Niknaddaf, S.; Hashisho, Z. Effect of the Adsorbate Kinetic Diameter on the Accuracy of the Dubinin-Radushkevich Equation for Modeling Adsorption of Organic Vapors on Activated Carbon. *J. Hazard. Mater.* **2012**, *241–242*, 154–163. [CrossRef]

34. Saha, D.; Deng, S. Adsorption Equilibrium, Kinetics, and Enthalpy of N_2O on Zeolite 4A and 13X. *J. Chem. Eng. Data* **2010**, *55*, 3312–3317. [CrossRef]

35. Saha, D.; Bao, Z.; Jia, F.; Deng, S. Adsorption of CO_2, CH_4, N_2O, and N_2 on MOF-5, MOF-177, and Zeolite 5A. *Environ. Sci. Technol.* **2010**, *44*, 1820–1826. [CrossRef]

36. Saha, D.; Deng, S. Adsorption Equilibrium and Kinetics of CO_2, CH_4, N_2O, and NH_3 on Ordered Mesoporous Carbon. *J. Colloid Interface Sci.* **2010**, *345*, 402–409. [CrossRef]

37. Wang, L.; Zhang, F.; Wang, C.; Li, Y.; Yang, J.; Li, L.; Li, J. Ethylenediamine-Functionalized Metal Organic Frameworks MIL-100(Cr) for Efficient CO_2/N_2O Separation. *Sep. Purif. Technol.* **2020**, *235*, 116219. [CrossRef]

38. Groen, J.C.; Pérez-Ramírez, J.; Zhu, W. Adsorption of Nitrous Oxide on Silicalite-1. *J. Chem. Eng. Data* **2002**, *47*, 587–589. [CrossRef]

39. Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R.A. Flexible Metal-Organic Frameworks. *Chem. Soc. Rev.* **2014**, *43*, 6062–6096. [CrossRef] [PubMed]

40. Yang, J.; Du, B.; Liu, J.; Krishna, R.; Zhang, F.; Zhou, W.; Wang, Y.; Li, J.; Chen, B. MIL-100Cr with Open Cr Sites for a Record N_2O Capture. *Chem. Commun.* **2018**, *54*, 14061–14064. [CrossRef] [PubMed]

41. Wang, L.; Zhang, F.; Yang, J.; Li, L.; Li, J. The Efficient Separation of N_2O/CO_2 using Unsaturated Fe^{2+} sites in MIL-100Fe. *Chem. Commun.* **2021**, *57*, 6636–6639. [CrossRef]

42. Wang, L.; Li, Y.; Wang, Y.; Yang, J.; Li, L.; Li, J. Research on CO_2-N_2O Separation Using Flexible Metal Organic Frameworks. *Sep. Purif. Technol.* **2020**, *251*, 117311. [CrossRef]

43. Saha, D.; Deng, S.; Yang, Z. Hydrogen Adsorption on Metal-Organic Framework (MOF-5) Synthesized by DMF Approach. *J. Porous Mater.* **2009**, *16*, 141–149. [CrossRef]

44. Li, Y.; Yang, R.T. Gas Adsorption and Storage in Metal-Organic Framework MOF-177. *Langmuir* **2007**, *23*, 12937–12944. [CrossRef]

45. Culp, J.T.; Smith, M.R.; Bittner, E.; Bockrath, B. Hysteresis in the Physisorption of CO_2 and N_2 in a Flexible Pillared Layer Nickel Cyanide. *J. Am. Chem. Soc.* **2008**, *130*, 12427–12434. [CrossRef] [PubMed]

46. Culp, J.T.; Goodman, A.L.; Chirdon, D.; Sankar, S.G.; Matranga, C. Mechanism for the Dynamic Adsorption of CO_2 and CH_4 in a Flexible Linear Chain Coordination Polymer as Determined from in Situ Infrared Spectroscopy. *J. Phys. Chem. C* **2010**, *114*, 2184–2191. [CrossRef]

47. Rowsell, J.L.C.; Yaghi, O.M. Strategies for Hydrogen Storage in Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **2005**, *44*, 4670–4679. [CrossRef] [PubMed]