Current Research on Gaseous Ammonia Detecting and Capture Technologies

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Abstract

Ammonia is currently widely used for fertilizers, and it continues to grow as a potential clean fuel source or hydrogen carrier, which may result in growing trace amounts in the atmosphere. Increasing anthropogenic ammonia emissions raises concerns such as disrupting the global nitrogen cycle and negating the greenhouse gas reduction. This review article outlines and compiles recent studies on gaseous ammonia sensing and absorption/adsorption, which could alert or reduce rogue emissions, i.e., unintended anthropogenic releases of ammonia. Different sensors and their characteristics are outlined with a focus on the more popular chemoresistive technologies. Several absorption/adsorption methods from metal-organic frameworks (MOFs) and deep eutectic solvents (DESs) are described and highlighted.

Highlights

- Several chemoresistive style gas sensors show <1 ppm LOD and fast response times (< 1 min)
- New class of DES V show promising absorption capabilities for ammonia

- Computational screening allows the wide field of potential absorbents/adsorbents to be narrowed down to higher potential value options

Keywords

Ammonia; Gas sensor; Metal-Organic Frameworks (MOFs); Deep Eutectic Solvents (DES); Adsorption capacity; Absorption;

Background

Ammonia has been applied in the agriculture sector as a binding site for atmospheric nitrogen to supply nitrogen to crops, and more recently, is proposed for uses as a carbon-free fuel, a hydrogen carrier, and an energy vector [1]. However, ammonia is disruptive to ecosystems being toxic to organisms and causing eutrophication in surface water [2]. Ammonia, when it is released and stay in the atmosphere, can react to create toxic ammonium, nitrous oxides (N_2O) and nitrate. N_2O is a potent greenhouse gas that may offset the reduction in greenhouse gas (GHG) emissions of fuel switching from fossil fuels to clean ammonia [3]. Additionally, particulate matter 2.5 (PM 2.5) are fine particles less than 2.5 microns wide, in which nitrates make up a large portion of this classification. Since ammonia is a large contributor to the formation of nitrate, the rapidly increasing production of gaseous ammonia increases the amount of PM 2.5 in the air [4]. As the ammonia industry continues to grow with its variety of uses and decarbonization potential, the mitigation and remediation strategies for atmospheric ammonia must grow as well [3]. A variety of technologies have been developed to detect, separate and capture ammonia from leakage, rogue or fugitive emissions, combustion flue gas, and even directly from the atmosphere. This work focuses on recent studies regarding gaseous ammonia detection and capture to cope with the potential increase of ammonia emissions when it is widely used as a clean fuel or energy carrier. Readers are recommended to visit highlighted reviews that are more comprehensive and cover a further depth of history [5]–[7].

Gases Ammonia Sensing

Ammonia is found to be pungent and noticeable by human smell at about 20 ppm and an occupational hazard at 25 ppm [8]. It quickly becomes impairing at 400 ppm and increasingly fatal beyond 3000 ppm. Ammonia sensing devices are used in many different fields with several intended for indoor use for health and safety [9]. The automotive industry tests vehicles for emission regulation and the health industry uses sensors for breath analysis [7]. As production of ammonia grows, the need to detect rogue emissions from production, storage, distribution, and utilization sites grows concurrently.

Rogue emissions are unintended releases of gaseous pollutants through undetected leaks in the system or pipe failures. They can be environmentally detrimental based on two major characteristics. Firstly, rogue emissions can be very low in concentration, but constantly emitted for an extended period, resulting in a large total loading into the atmosphere. Secondly, a large amount can escape from a site unknowingly as ammonia is colourless and only perceptible to humans by odour [10]. Therefore, it is critical to have low limit of detection (LOD) sensors assisting in the first case and quick responding sensors in the second case. Response time is heavily affected by the concentration of the target gas being detected, relative humidity and other environmental factors [11]. Sensors should be tested in similar conditions to where they will be employed for optimal results. In Table 1, many recently studied sensors with their response time and LOD are summarized, and we only highlight a few examples in the following sections.

Chemoresistive Sensors

Chemoresistive sensors work on the principle that semiconductors have varying resistances, and thus conductivity, when the target gas adsorbs onto them. At the initial state, oxygen is adsorbed onto the sensor; when the target gas (e.g., ammonia) comes into contact, adsorbed oxygen is replaced by the target gas molecules, resulting in a change in resistance that can be used to detect the target gas [9]. Chemoresistive sensors depend on adsorption, and metals, organic materials, and metal-organic frameworks (MOFs) are all studied. Doping is a common technique to increase the performance of chemoresistive sensors by

creating impurities which increases the amount of adsorption sites, resulting in a higher detection of the target gas [9]. In addition, nanostructures such as carbon nanotubes are used to increase the adsorption area [12].

Metal oxide semiconductor (MOS) gas sensors are widely used due to their ease of production, good reliability, and fast response times. MOS gas sensors work most optimally in high operating temperatures up to 600 °C making them ideal in ammonia production facilities [7], [13]. Boomashri et al. worked on a 2% antimony doped tin oxide sensor, which was able to detect ammonia concentrations down to 50 ppm with a response time of 42 seconds [14]. Thomas et al. studied a nanostructure of ZnO with a lower detection range of 5-100 ppm and a response time of 36 seconds at 5 ppm [15].

Organic semiconductor (OSC) gas sensors work similarly to MOS sensors. Their interactions with gas molecules cause a shift of electrons affecting the concentration of carriers in the sensor [16]. They tend to be cheaper compared to their metal oxide counterparts as well as performing well at room temperatures [17].

As discussed earlier, the relative humidity of the environment may affect the sensor performances, and resistance to humidity is critical especially for outdoor applications. A ZIF-8 MOF/ carbon nanotubes (ZIF-8/CNT) chemoresistive gas sensor was developed with a strong resistance to humidity: ammonia response only begun to falter at 90% relative humidity [11].

Field-Effect Transistor Sensors

Field-Effect Transistor (FET) sensors can be composed of metal, organic or polymer variants. They operate by having a sensing material as a gate and lowering the threshold voltage when the target gas adsorbs onto the material [18]. Their excellent stability and low power consumption make them suitable in many fields such as medical diagnostics and industrial safety [6], [18]. Verma et al. designed an OSC ammonia sensor using P3HT (Poly(3-hexylthiophene-2,5-diyl))/GO (Graphene Oxide) for use in the poultry industry. The

sensor was found to respond to very dilute concentrations down to 0.278 ppm with a response time of 44 seconds [17].

Quartz Crystal Microbalance Sensors

Quartz Crystal Microbalance (QCM) sensors operate based on the piezoelectric effect of quartz crystals [13]. For example, Zhang et al. [13] compare the Ti_3C_2Tx QCM sensor to other chemoresistive sensors with the same alloy and found tremendous success in the lower-level detection limit at 0.01ppm with the QCM sensor.

Optical Sensors

Optical sensors work on the principle that the adsorbed gas changes the optical properties of the sensing layer such as the refractive index or light absorbance [19]. This change in property is measured and used to determine the amount of gas adsorbed.

Table 1. Recently studied sensors for gaseous ammonia.

Name	Type of Sensor	Tested Detection Range (ppm)	Limit of Detection (ppm)	Response Time (secs)	Source
SnO_2: 2% Sb dope	Chemoresistive	50-250	--	42 @ 250ppm	[14]
Thin film ZnO	Chemoresistive	10-70	10	112 @ 30ppm	[20]
ZnO nanostructure	Chemoresistive	5-100	5	36 @ 5ppm 29 @ 100ppm	[15]
WO_3	Chemoresistive	0.5-100	0.04955	52 @ 30ppm	[21]
ZIF-CNT[1]	Chemoresistive	25-250	0.208	120 @ 25-250ppm	[11]
PAPYP[2]	Chemoresistive	0 – 20	0.05	136 @ 1ppm	[22]

Polyaniline-Ag	Chemoresistive	1-200	1	100 @ 1ppm 30 @ 100ppm	[23]
Bis-Phenylalanine Naphthalene Diimide	Chemoresistive	2-50	2	15.3 @ 50ppm	[24]
Graphene: 7.5% F dope	Chemoresistive	0.5-10	0.064	380 @ 10ppm	[25]
NiO (spherical sheets)	Chemoresistive	1-20	--	136.5 @ average	[26]
NiO (porous sheets)	Chemoresistive	1-20	--	108.5 @average	[26]
Carbon Nanotubes (AuNPs sputtered)	Chemoresistive	0-10	0.5	12 @ 1ppm	[12]
Carbon Nanotubes (AuNPs chemically impregnated)	Chemoresistive	0-10	--	25 @ 1ppm	[12]
P3HT:GO[3]	FET	0-80	0.278	44 @ 80ppm	[17]
TIPS-pentacene[4]	FET	1	--	26 @ 1ppm	[27]
Polyacrylic Acid:Polyaniline	Optical	0-300	--	100 @ 150ppm	[19]
Ti_3C_2Tx-S	QCM	0.01 – 100	0.01	33 @ 0.1ppm	[13]
PSS/ZIF-C/PANI[5]	QCM	1-50	1	28 @ 10ppm	[28]
1: Zeolitic Imidazolate Framework-8/Carbon Nanotube 2: Poly(aniline-co-pyrrole) on flexible porous polyvinylidene fluoride based sensitive membrane					

3: Poly(3-hexylthiophene-2,5-diyl))/GO (Graphene Oxide)

4: 6,13-Bis(triisopropylsilylethynyl) pentacene

5: PSS: Poly (sodium 4-styrenesulfonate), ZIF-C: ZIF-8 derived porous carbon, PANI: Polyaniline

Gases Ammonia Capture

Gaseous ammonia capture can be separated into two major categories: ammonia absorption into a liquid phase or ammonia adsorption onto a typically acidic surface. Depending on the circumstance, the critical properties of the sorbent may vary. For example, in regions with high humidity, e.g., coastal regions, the selectivity of ammonia over water vapour is critical, while in environmental remediation contexts the need for selectivity of ammonia over other pollutants may be less prioritized. In addition, in ammonia production facilities, ammonia separation techniques are often used to separate and purify the effluent stream allowing for unreacted inputs to be recycled. In this scenario, ammonia desorption should be considered and high thermal stabilities of the capture medium are important.

As this review focuses on the applications of atmospheric capture of gases ammonia, the need for fast adsorption rates is ideal for large rogue emissions. Table 2 highlights several different sorbents with their ammonia capacity from recent literature. The ammonia capture capacity was usually reported, while other figures-of-merit such as adsorption rate, regenerative stability and desorption ability were not. Hence, we only summarized the capture capacities of different sorbent materials in Table 2.

Liquid Absorbents

Ammonia has high solubility in water, so water seem to be an obvious absorbent of choice. However, the high-pressure requirements for absorption and the high heat capacity of water for desorption make it energy intensive, offsetting the potential GHG emission reduction of the captured ammonia [5], [29].

Ionic Liquids

Ionic liquids (ILs) are solvents comprised solely of anions and cations and have been historically considered for gas adsorption [5]. They often show incredible potential for ammonia absorption, but many recent studies report that they are expensive and difficult to synthesize compared to other sorbents [5], [30]–[32].

Sun et al. synthesized triazole cation-functionalized ionic liquids (TCFILs) by introducing protic sites on triazole based ionic liquids [33]. These ionic liquids were able to achieve high ammonia absorption capacities up to 21.4 mmol/g with an absorption duration of approximately an hour. A stability analysis was conducted for 5 absorption/desorption cycles and no decrease in adsorption capacity could be noticed.

Deep Eutectic Solvents

Deep Eutectic Solvents (DESs) are an emerging sorbent chemical equivalent to ionic liquids for the adsorption of ammonia [34]. DESs are liquid mixtures that form hydrogen bonds to reduce the melting point of the mixture compared to the ionic bonding the ions would form naturally causing a eutectic solvent [35]. They are often characterized by their hydrogen-bonded donator (HBD) and hydrogen-bonded acceptor (HBA). DESs are heavily desired due to their thermal stability, relative low cost and ease of regeneration through simple processes such as pressure swinging [32].

A recent study by Kazarina et al. [32] investigated using ammonium salt with different ethyl substitutes along with ethylene glycol for ammonia absorption. They found that more hydroxyl groups lowered Henry's law constant (resulting is more solubility of dilute gasses) and vice versa for ether groups [32].

A novel subgroup of DES is recently being investigated deemed Type V DESs [36]. The key difference between Type V and the other four categories of DESs is the detail that Type V do not have ionic components in either substance. The lack of ionic components leads to less viscous solutions with strong deviations from ideality that are easily regeneratable by evaporation [36], [37]. Zhou et al. reports a Type V DES 3-hydroxypyridine/phenol (molar ratio of 1:5) that can absorb 10.00 mmol/g at 1 bar [31]. This is a large improvement compared to other recent DESs in literature.

Solid Adsorbents

Solid state materials such as metal halides, zeolites and metal-organic frameworks (MOFs) can be employed to absorb select atmospheric gasses. They typically operate in a pair of columns, one for adsorption and one for desorption [5]. Metal adsorbents are often introduced to porous materials to increase their adsorption capacities via Lewis acid-base interactions [30]. The large surface area of metal adsorbents incorporated into porous materials allows for high adsorption capacities along with the lack of volatility and viscosity issues make them a prime field to look into for the future of ammonia capture [5]. Zeolites are a traditional adsorbent in separation processes of ammonia production due to their high thermal stability; however metal halides and MOFs have been more recently studied because of their suitability outside of the high temperature and pressure scenarios ammonia production occurs. [38].

Metal Halides

Metal halides are reported to be cheap and easily synthesized compared to other adsorbents, so they have been studied widely [5], [39]. However, the major downside is that pure metal halides have quite slow adsorption rates [5].

A few-layered hexagonal Boron Nitride (h-BN) has been synthesized for the adsorption of ammonia in the Haber-Bosch process [29]. The metal halide was found to have excellent thermal stability and an ammonia adsorption capacity of 8.67 mmol/g at 1 bar, 313.2K. After multiple regenerative cycles, the capacity of adsorption was found to not noticeably change resulting in a very long lasting and stable adsorbent.

Shen et al. investigated the use of chemically impregnating silicon into different chlorides to improve adsorption capacities [40]. The use of silicon kept the adsorption capacity relatively the same or improved. It was also found that $CuCl_2$ had considerable stability in its adsorption capacity thermally.

To speed up the sorbent material discovery, a machine learning tool was developed to design mixed metal halides based on their desorption energies and other thermodynamic properties. The mixed metal halides

$Mg_xCa_{(1-x)}Cl_yBr_{(2-y)}$ where *x*: 0-1 and *y*: 0-2 were investigated; however, future research into other transition metals were also considered [39].

Metal Organic Frameworks

Metal-organic frameworks (MOFs) are popular sorbents with an appropriate combination of an inorganic metal cluster and organic linker to bind with ammonia. There are also some developments on using different nanostructures to increase the surface area of adsorption. Depending on the applications, the presence of certain chemicals can be heavily disadvantageous. For example, MOFs containing chlorine are corrosive to the metal structure of many processing plants and heavy metals are toxic to agricultural systems [41], [42]. The high customizability of MOFs allows researchers to circumvent certain chemicals dependent on their applications.

Two MOFs with zinc as the metal cluster zinc-trimesic acid (ZnTA) and 2-methylimidazole zinc salt (ZIF-8) were explored for its uses of ammonia adsorption in agricultural practices. They were found to have adsorption capacities of 11.37 mmol/g and 1.26 mmol/g respectively at 298K and 1 bar [41]. Another study by the same group investigated Bistrichloromethylcarbonate (BTC, Triphosgene) as a linker to different metal clusters, and ZnBTC, FeBTC and CuBTC exhibited capacities of 11.33, 9.5 and 23.88 mmol/g at 1 bar [43].

Computational screening of MOFs has been completed via Grand Canonical Monte Carlo (GCMC) simulations. Using GCMC, Zhu et al. identified several candidates for further research based on adsorption capacity and selectivity, and some of the top candidates with high adsorption capacities are shown in Table 2 [44].

Other adsorbents

Xerogels are the solid result of unconstrained shrinkage by evaporation of a gel [45]. Hu et al. [46] synthesized SO_3H-modified silica xerogel using different volume ratios (X) of Mercaptopropyl trimethoxy silane (labelled as MPTS-X) and tested their performances for the capture of atmospheric ammonia. The

MPTS-X showed excellent adsorption capacity because the -SO_3H acidic sites create stronger bonds than the hydrogen bonding process of the unmodified Si-OH in MPTS-0; but as more MPTS was added, the shrinkage of the xerogel increased, resulting in smaller pores. MPTS-1 had a breakthrough point at 10 hours in 50ppm, 298K conditions with a 95% saturation capacity of 1.4 mmol/g. After 5 regenerative cycles, MPTS-1 kept at about 80% of the saturation capacity. In a field test with 2 ppm ammonia, MPTS-1 was able to reduce the initial concentration to 55% in approximately 110 mins [46].

Table 2. Recently studied materials for adsorption and absorption of ammonia.					
Name	Capture Mechanic	Testing Conditions		Capacity (mmol/g)	Ref.
Liquid Absorbents					
[Li-TEG][Tf2N][1]	IL	T = 313.2K, P = 102.5 kPa	Bubbled pure NH_3 with magnetic stirrer	7.685[2]	[47]
[1, 2, 3-TrizH_2] $[NO_3]_2$[3]	TCFIL	T = 303K, P = 1 bar	3g of TCFIL was place in a bottle controlled by thermostatic water bath with pure NH_3 gas bubbling at 150ml/min	21.4	[33]
[1, 2, 4-TrizH_2] $[NO_3]_2$[3]				21.2	[33]
[1, 2, 3-TrizH_2] $[CF_3SO_3]_2$[3]				17.6	[33]
[1, 2, 4-TrizH_2] $[CF_3SO_3]_2$[3]				16.7	[33]
$MgCl_2$/Res/EG (0.1:1:2)[4]	DES	T = 313.2K, P = 1 bar	8g of DES was bubbled with NH_3-N_2 mixed gas at 60 cm^3/min	12.12	[30]
3,4-DHBA/EG (1:3)[5]	DES	T = 298.2K, P = 1 bar	Test was complete in stainless steel tank with magnetic stirrer and pure NH_3	11.69	[35]
DES 1[6]	DES	T = 313.2 K, P = 101 kPa	A high-pressure equilibrium cell was used to determine Henry's Law Constant and other thermodynamic properties	3.640	[32]
DES 2[6]				4.295	[32]
DES 3[6]				2.861	[32]
DES 4[6]				3.081	[32]
3-hydroxypyridine/phenol	DES V	P = 1 bar	NH_3 was bubbled at 60 cm^3/min	10.00	[31]

Solid Adsorbents					
h-BN[7]	Metal Halide	T = 313.2K, P = 1 bar	Adsorption isotherms were measured using a NH_3 stream. Mixed gas samples were found to have little impact on the adsorption capacity.	8.67	[29]
$CuCl_2$	Metal Halide	T = 298K, P = 1 bar	A fixed bed reactor was used with a 100ml/min pure NH_3 stream at varying temperatures.	39.3[8]	[40]
$CuCl_2$: Silicon				37.6[8]	[40]
$MnCl_2$		T = 308K, P = 1 bar		24.7[8]	[40]
$MnCl_2$: Silicon				31.7[8]	[40]
$CaCl_2$		T = 298K, P = 1 bar		22.3[8]	[40]
$CaCl_2$: Silicon				25.2[8]	[40]
$MgCl_2$		T = 303K, P = 1 bar		22.4[8]	[40]
$MgCl_2$: Silicon				27.6[8]	[40]
CuCyhdc	MOF	T = 298K, P = 1 bar	Adsorption isotherms collected by a gas adsorption analyzer	17.5	[42]
Zinc-Trimesic Acid	MOF	T = 298K, P = 1 bar	Adsorption was measured with a 4:1 (v:v) mix of NH_3 and H_2O	11.37	[41]
ZIF-8				1.26	[41]

ZnBTC	MOF	T = 323K, P = 1 bar	Adsorption was measured with pure NH3 and selectivity with 4:1 (v:v) mix of NH_3 and H_2O	11.37	[43]
FeBTC				9.5	[43]
CuBTC				23.88	[43]
$CaH_4(C_2O)_4$	MOF	T = 298K, P = 1 bar	Simulated with 1% mol NH and varying amounts of N_2 and H_2.	18.33	[44]
$MgH_4(C_4O_3)_2$				16.49	[44]
$SrH_4(C_2O)_4$				15.60	[44]
MPTS-0[9]	Xerogel	T = 298K, P = 1 bar	Static adsorption tests were completed with pure NH_3. A $3m^3$ field test was also conducted.	3.19	[46]
MPTS-0.5[9]				6.79	[46]
MPTS-1.0[9]				7.00	[46]
MPTS-1.5[9]				6.99	[46]
MPTS-2.0[9]				6.14	[46]
MPTS-3.0[9]				6.25	[46]
Polyaniline (PANI)	Organic Polymer	Not Noted	A fixed bed reactor with 0.5g of adsorbent with a 100L/min pure NH_3 stream at concentrations (35-150ppm) was used.	3.602	[48]
PANI-Clay	Organic Polymer	Not Noted		4.323	[48]

1: Lithium-TriEthylene Glycol + bis(trifluoromethanesulphonyl)imide

2: Converted from mol/mol basis

3: Triz: Triazole

4: Res: Resorcinol, EG: Ethylene Glycol. (0.1:1:2 molar ratio)

5: DHBA: Dihydroxybenzoic Acid

6: These are all N-substituted ammonium salts with ethylene glycol. See paper for specific structure.

7: Hexagonal Boron Nitride

8: Converted from g/g basis

9: Silica based xerogel with varying volume ratios of Mercaptopropyl Trimethoxy Silan

Concluding Remarks

Ammonia's vast uses highlight it as a one of the most important chemicals, and its significance will grow in the future as a clean fuel or an energy carrier. However, the human toxicity and environmental distress that ammonia applies instigate a more diligent environmental regulation system. In this review article, we focus on the detection and capture of gaseous ammonia to reduce the potential environmental impacts associated with rogue emissions when scaling up ammonia applications.

A majority of ammonia gas sensors are chemoresistive style sensors. Research is primarily based on different doping techniques, coating mechanisms and nanostructures to increase surface area without compromising structural integrity and thermal stability. Many chemoresistive sensors are capable of detecting ammonia concentrations below 1 ppm with high selectivity towards ammonia compared to other gases. Many sensors summarized in Table 1 have response times less than 1 minute; however, many environmental factors such as the tested concentrations impact this response. Machin et al. developed a fast reacting sensor in low concentrations using carbon nanotubes and gold particles which is ideal in rogue emission response scenarios [12].

For capturing gaseous ammonia, metal halides and ionic liquids both have high adsorption capacities that are appealing but the slow adsorption rates do not make them ideal for rogue emission capture. The high design dimensions of MOFs and DES have made them popular ammonia sorbents, and focus is mostly on functional group substitutions in MOFs and DES. In addition, computational screening methods have gained some traction to determine where research should be focused. Other sorbents, such as sulphur-based silica xerogel, have shown impressive field results for the capture of trace ammonia from air.

Declaration of interests

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