Ammonia Sorbent Development for On-Board H₂ Purification

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Abstract

The application of chemical hydrides (e.g. ammonia borane) and amide-based hydrogen storage materials would benefit from an effective means to remove ammonia, which is an impurity that is detrimental to the performance of a PEM fuel cell. One option is to adsorb ammonia on a sorbent with high capacity that would also be regenerable. Such a sorbent was developed by impregnating super activated carbon with metal chlorides (MgCl₂, ZnCl₂, MnCl₂). The sorbent was characterized through static and dynamic adsorption experiments. It was shown to have a good cyclic stability. The filter weight, volume and pressure drop appears reasonable for an onboard vehicle application when it would be replaced/regenerated every 1800 miles, similar to an oil change.

1. Introduction

On-board materials-based hydrogen storage systems for light-duty vehicles need to meet stringent targets in order to be able to compete with physical storage systems. A comprehensive set of such targets has been developed by U.S.DRIVE, a government-industry partnership between the U.S. Department of Energy (DOE), U.S. automobile manufacturers, and energy and utility companies [1]. This set of targets serves as the technical targets of the DOE-funded Hydrogen Storage Engineering Center of Excellence (HSECoE). The HSECoE focuses on materials-based hydrogen storage systems that use on-board reversible metal hydrides, off-board regenerable chemical hydrogen storage materials and cryo-adsorbents. All three DOE supported materials-based hydrogen storage centers of excellence [2-4] have suggested promising materials to the HSECoE.

This paper focuses on the development of ammonia (NH₃) adsorbents for a chemical hydrogen storage material system that is based on ammonia borane [5]. The adsorbent is also applicable to some reversible metal hydride materials, such as in the Li-Mg-N-H system [6,7,29]. The ammonia impurity in hydrogen that is released from these

storage materials needs to be removed in order to protect the fuel cell system from degradation [8,9]. The SAE J2719 Hydrogen Purity guideline [10] specifies an upper ammonia limit of 0.1 ppm, in order to achieve that goal. NH_3 is not the only impurity in hydrogen that is released during the thermolysis of ammonia borane and a different separation needs to be performed in order to remove the other impurities as well. Hydrogen from these storage systems tends to be anhydrous, which needs to be taken into account when selecting adsorbent materials with a high gravimetric and volumetric capacity.

Activated carbon plays an important role as an adsorbent to protect people from ammonia exposure [11,12] and to purify process streams [13,14]. Adsorbents are an important stepping block for the development of on-board H_2 purification for a chemical hydrogen storage material system. Commercially available adsorbents have been reported [11] to have a limited gravimetric capacity (1-5 wt.%), especially under dry conditions. Recent sorbent development work [15-17] has focused on the increase of acidic surface oxides through activation with mineral acids. The resulting combination of physisorption and chemisorption yielded adsorbents with high gravimetric capacity (4-14 wt.%). Their capacity exceeds the capacity of activated carbons that have not been impregnated with mineral acids.

Metal-organic frameworks (MOF's) have been proposed by Brit et al. [18] as high capacity and selective adsorbents for removing harmful gases. They reported high capacity MOF's for NH_3 adsorption (8.7–10.5 wt.% in 9900 ppm NH_3 in N_2). The results show sharp breakthrough curves, indicating an efficient mass transfer and high rate of adsorption. UTRC's measurements confirmed the high sorption capacity of MOF-199 (HKUST-1 or Cu-BTC) but the sorbent could not be regenerated, which was also reported by Petit et al. [19]. MOF-5 and MOF-177 frameworks also get destroyed upon ammonia exposure according to Saha and Deng [20]. Glover et al. [21] reported ammonia adsorption by MOF-74 up to 12.9 wt.% by having coordinatively unsaturated (open) metal sites but they do not report whether this MOF can be regenerated. Ammonia adsorption by MOF-199 creates a distinct color change, which can be used as a visual indicator for NH_3 breakthrough when deployed downstream of a main ammonia scrubber. This is similar to the visual indicator that has been reported by J. Wilkes [30], Long et al. [31] and Schmidt [32].

Surprisingly, little work has been reported about the use of metal chlorides as active phase of an ammonia sorbent material [22-25], despite the abundant data on the thermodynamic stability of metal chlorides in their ammoniate forms [26, 27] and ease of impregnation. Sharonov et al. [22] reported the ammonia capacity of alumina impregnated with alkaline-earth metal chlorides (BaCl_2 , CaCl_2 and MgCl_2). Badosz and Petit [23] reported that a coal based activated carbon reached a dynamic sorption capacity of 6-7 wt.% at an ammonia inlet concentration of 1000 ppm in air after impregnation with either zinc chloride or copper chloride. Fortier et al.[24] and Furtado et al. [25] reported a high capacity ammonia sorbent that was prepared by impregnating ZnCl_2 in either activated carbon or in a siliceous material (MCM-41).

This paper focuses on the selection of metal chlorides for chemisorption of ammonia, the impregnation in super activated carbon (IRH-33 from the Institut de recherche sur l'hydrogène, Université of Québec à Trois-Rivières) and the

characterization of the resulting composite material as a regenerable ammonia sorbent for onboard fuel cell vehicle applications.

2. Experimental

2.1 Materials

Helium (5.0 UHP grade) and Nitrogen (5.0 UHP grade) were purchased from Praxair (U.S.A). Anhydrous pure ammonia (Ammonia > 99.9992 %, Carbon Dioxide < 1 ppm, Carbon Monoxide < 0.1 ppm, Methane < 0.1 ppm, Nitrogen < 2 ppm, Oxygen < 1 ppm, Water < 2 ppm), ammonia nitrogen gas mixture (10,200 ppm NH₃ in N₂) were purchased from Matheson. Anhydrous magnesium(II) chloride (MgCl₂), anhydrous zinc(II) chloride (ZnCl₂) and anhydrous manganese(II) chloride (MnCl₂) were purchased from Sigma Aldrich. Ammonasorb II (<20 wt.% phosphoric acid in activated carbon (Calgon Carbon)), Kuraraycoal T-B (27 wt.% phosphoric acid in activated carbon (Kuraray Chemical Co., LTD)), Selexsorb CD (BASF), Chemsorb (Molecular Products), Basolite C 300 (Sigma Aldrich), Vermiculite, and activated carbon SG6 (Cameron carbon) were kindly provided as samples by the vendors.

2.2 Synthesis

2.2.1 IRH-33 Preparation

Raw material is a commercial activated carbon named CNS-201 (AC-Carbon company) and the pilot oven (Pyradia) for activation is a 100 liters rotary kiln externally heated with electrical resistances (36 kW). CNS-201 has a bulk density of 0.45 g/ml and a BET surface area of 1400 m²/g. Activation agent is CO₂ and activation temperature is fixed to 900 °C. This is a batch production with an initial mass of 10 – 11 kg of raw material and the CO₂ flow rate is fixed to around 4.0 liter STP / min. To reach a bulk density of 0.20 g/ml, activation duration is around 80 hours. Final production is between 4 and 5 kg. The super-activated carbon IRH 33 was used in a granular form. The weight fraction of + 20 mesh was 71.4%, the weight fraction from -20 mesh to +35 mesh was 26.2% and the weight fraction from -35 mesh to +70 mesh was 2.4%. No change was observed in the sorbent granularity before and after MnCl₂ impregnation and drying and before and after NH₃ adsorption, indicating that the IRH33 material could handle the volumetric expansion of the MnCl₂ upon NH₃ adsorption.

2.2.2 Impregnated IRH-33 Preparation

Sorbents were prepared in batches of 36 g. The desired amount of metal chloride salt was transferred into a 200ml of ethanol filled two-neck round bottom flask placed over a heating mantle. The solvent was refluxed and the solution was stirred continuously under nitrogen environment for about 20 minutes at 90 °C until all the salts dissolved in the solvent. The desired amount of IRH-33 was loaded into the round bottom flask and refluxed for about 4 hrs. The solvent was removed by rotary evaporation using a BUCHI Rotovapor R-205. The sample was dried in a vacuum oven at 200 °C under vacuum overnight. Table 1 summarizes the samples prepared using this technique. As verification, MnCl₂ that had been impregnated in IRH-33 was dissolved in ethanol in a soxhlet apparatus. The weight loss of the sorbent was consistent with the intended

amount of MnCl_2 . The loading of the IRH-33 with impregnates is high as that yielded the highest dynamic sorption capacity.

Table 1, Composition of impregnates in the sample studied in this work

Sample description	Wt% metal
MgCl_2 on IRH-33	50
ZnCl_2 on IRH-33	50
MnCl_2 on IRH-33	30, 40, 50, 60, 70

2.3 Characterization

2.3.1 SEM Measurements

A scanning electron microscope (JEOL Model 6335F) with a Thermo Fisher EDS system was used to image the samples.

2.3.2 Tap Density

Tap densities were measured manually by measuring the mass and volume of the tapped sorbent loaded in a 10 ml graduated cylinder. The results are reported in Table 6.

2.3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) were acquired with a Physical Electronics VersaProbe XPS System equipped with a monochromatic Al K (α) X-ray source ($E = 1486.6$ eV). Spectra were collected with survey scan settings of 117.4eV pass energy, 20ms dwell time, 1.0 eV/step and high-resolution settings of 29eV pass energy, 50ms dwell time and 0.1 eV/step. Both argon ion and electron neutralization were utilized to mitigate the effects of sample charging. Sample powders were sprinkled onto carbon tape, placed into the sample introduction chamber which was evacuated with a turbomolecular pump for 1 hour prior to introduction to the main chamber and analysis. The data was analyzed using a software package called CasaXPS Version 2.3.15 Dev 36. Survey spectra were utilized to confirm elemental composition. High Resolution scans of the main elemental peaks were fit with a Shirley background, height averaged over three data points at each end of the region. Peaks data was deconvoluted using Gaussian-Lorentzian (30) artificial peaks using a fixed full-width at half height for each set of element peaks, allowing the CasaXPS software to iterate peak area (intensity) and position to optimize the fit to the raw data.

2.3.4 Nitrogen and Ammonia Adsorption Equilibrium Measurements

A Micrometrics volumetric adsorption instrument (ASAP 2020) was used to measure the nitrogen adsorption equilibrium isotherm at 77 K. Prior to nitrogen gas adsorption experiments, the sample was degassed at 90 °C for 15 minutes and then heated to 200 °C overnight under vacuum. Helium gas was used to measure the free space volume of the sample holder. Typically about 40 mg of sample was loaded in the glass sample holder used for this instrument. No difference was observed between tests with 40 mg or 100 mg of sample, but the measurement time was shorter for the 40 mg sample in the small dose mode of the instrument. The specific surface areas were estimated from

the nitrogen adsorption equilibrium data using the BET model within the P/P_0 range from 0 to 0.03. Pore size distribution was calculated by using the density functional theory (DFT).

Few modifications were made on the low-pressure volumetric gas adsorption apparatus (Micromeritics) for performing anhydrous ammonia gas adsorption equilibrium measurements. The standard liquid N_2 dewar (4L), for the sample tube bath, was replaced with a dewar (1L) containing a copper coil through which a 50 % propylene glycol/water thermal fluid (temp. range -30°C to $+105^{\circ}\text{C}$) was pumped from a Julabo FP50 refrigerating circulator. An ammonia gas detection system (Draeger Polytron) and safety controls were put in place in order to reduce the risks of working with anhydrous ammonia. Ammonia adsorption equilibrium isotherm measurements were performed at -20, 0, 20, 50, and 77°C .

2.3.5 Dynamic Adsorption Breakthrough Experiment

A process flow diagram of the experimental set up for dynamic adsorption breakthrough experiments is depicted in Figure 1. Nitrogen was used as a surrogate in these experiments for hydrogen in order to minimize risk. A gas mixture containing 10,200 ppm ammonia in nitrogen and in-house nitrogen were used for dynamic breakthrough experiments. The sample was loaded in a 11.5 cm long and 1.12 cm inner diameter stainless steel sample column with glass wool at the bottom and the top to hold the sample. Typically 4 – 9 g of sorbent was filled in the sample column, depending on the tap density of the sorbent. A K-type thermocouple was positioned at the center on the outer surface of the column. Experiments with the thermocouple in the stated position revealed a peak temperature rise of 3 to 7°C , which was followed by a gradually decline back to the starting temperature. Inserting the thermocouple inside the small diameter sorbent bed (ID=1.12 cm) could have caused channeling of the impurity through the bed, which the authors wanted to avoid. The gas flow rates were controlled by mass flow controllers (Brooks, USA). Rotameters (Matheson, USA) were used as flow indicators. Ammonia pressure relief valves and safety controls were put in place to reduce the risk of working with anhydrous ammonia. Back pressure regulators were used to maintain a constant pressure. At the column outlet, the ammonia and water vapor concentration in the effluent gas stream were monitored by flowing the effluent gas stream through a 1412 Innova photo-acoustic field gas monitor (Air Tech Instruments). Prior to testing, the photo-acoustic field gas monitor was calibrated over a range of concentrations in order to correct for non-linearity at higher concentrations. In order to meet the flow rate requirement of the analyzer, the effluent stream was diluted with a N_2 gas stream at a flow rate of 2 SLPM.

Prior to all measurements, the sample was dried at 200°C under 2 SLPM nitrogen flow overnight. First N_2 was allowed to pass through the column at 2 SLPM and it was pressurized up to the desired pressure with the backpressure regulator (BPR1) while the mixed gas stream in the bypass of the column was set with the second backpressure regulator (BPR2) to the same pressure with the NH_3/N_2 mixture at gas flow rate of 2 SLPM. After obtaining a good baseline for NH_3 and water vapor concentrations, the N_2 stream was switched to the NH_3/N_2 mixture and the NH_3 concentration was monitored versus time well beyond the actual breakthrough time.

The breakthrough time was defined as the time at which the NH_3 concentration started to exceed 0.1 ppm which is the upper limit according to the SAE J2719 APR2008

H₂ purity guideline [10]. The dynamic sorption capacity was calculated from the breakthrough time, impurity concentration, flow rate and sorbent amount. The sample in the column was subjected to several cycles to test the stability of the sorbent material. Between each cycle, regeneration of the column was performed at 200 °C under N₂ flow with a flow rate of 2 SLPM.

Figure 1, Diagram of the experimental setup for dynamic ammonia adsorption experiments. TC = thermocouple, MFC = mass flow controller, 3WV = 3 way valve, 4WV = 4 way valve, NV = needle valve, V = ball valve, PRV = pressure relief valve, BPR = back pressure regulator, DAQ = data acquisition, P = pressure gauge, B&K = 1412 Innova photo-acoustic NH₃ analyzer.

2.3.6 Nitrogen Permeability Measurements

The same experimental apparatus used for dynamic adsorption breakthrough experiments was used to conduct the permeability experiments with NH₃ adsorbents (MnCl₂ supported on IRH-33) using nitrogen gas at 20°C. The inlet pressure was measured by a pressure gauge and the pressure drop across the bed was measured by a differential pressure gauge. The permeability measurements were performed with N₂ gas at a flow rate in the range of 1 to 10 SLPM using the mass flow controller (Brooks, USA). Taking into account the inlet pressure, pressure drop and the mass flow rate measurements, the permeability of nitrogen gas in the sorbent bed was calculated using the expression obtained from the Darcy equation for compressible fluids.

$$P_1^2 - P_2^2 = 2 \cdot Z \cdot \frac{R_g T}{M} \left(\frac{\mu \cdot Q}{K \cdot A} \right) \quad (1)$$

where K is the permeability (m²), μ is the dynamic viscosity of nitrogen gas (kg/m.s), Q is the mass flow rate (kg/s), T is the operating temperature (K), M is the molecular weight

of N_2 , Z is the length of the sorbent bed (m), R_g is the ideal gas constant (J/mol/K), P_1 and P_2 are the upstream and downstream pressure across the sorbent bed (Pa).

3. Theory

3.1 Metal Chlorides Selection

Selection of composite adsorbents for this application required the selection of a metal chloride salt and a porous support. Metal chlorides (MCl_2) can be used to reversibly adsorb NH_3 according to the following exothermic chemical reaction:

The heat released in this reaction is $y\Delta H_r$, where ΔH_r the reaction enthalpy on a per mole NH_3 basis (J/mol NH_3). The equilibrium is monovariant, which means that by specifying the temperature, the equilibrium NH_3 partial pressure will be fixed. The basic thermodynamic properties [26] of some working pairs are shown in Figure 2. $MgCl_2$, $ZnCl_2$ and $MnCl_2$ were selected as they enable an NH_3 equilibrium concentration below 0.1 ppm up to an operating temperature of 60°C and because they can be regenerated by heating the adsorbent to modest temperatures (180-200°C). Among these three metal chlorides, $ZnCl_2$ has been widely used as impregnant in porous materials (MCM-41, activated carbons) for ammonia removal applications in the literature [23-28] as it exhibits high ammonia adsorption capacities and binds ammonia strongly over a wide range of temperatures even at low partial pressures.

Figure 2, Equilibrium NH_3 partial pressure for various ammoniate forming metal chlorides as a function of temperature. The designator y-x behind each metal chloride (e.g. $MnCl_2$ 2-1, y=2, x=1) indicates the number of NH_3 molecules before (x) and after

(y) NH_3 adsorption as each equilibrium reaction has its own equilibrium partial pressure [26], as calculated from $-\text{RgTln}(\text{PNH}_3/\text{Pa}) = \Delta\text{H}_i - \text{T}\Delta\text{S}_i$, using literature values of Table 5.

3.2 Ammonia isotherm models

3.2.1 Activated Carbon

The Dubinin-Ashtakov (DA) model was used to model NH_3 isotherm for IRH-33, as shown in Equation 2 [33-36].

$$q_{AC}(p) = x_o \exp \left[- \left(\frac{A}{E} \right)^m \right] \quad (2)$$

$$\text{where } A = -\Delta G = \text{RTln} \left(\frac{P_s}{P} \right) \quad (3)$$

$$\text{and } P_s = \left(\frac{T}{T_c} \right)^r P_c \quad (4)$$

where $q_{AC}(p)$ is the measured gravimetric adsorption amount (g NH_3 /g adsorbent), x_o is the maximum amount adsorbed (g NH_3 /g adsorbent), A is the adsorption potential (J/mol NH_3), E is the characteristic energy of adsorption (J/mol NH_3), m is the structural heterogeneity parameter, P_s is the virtual saturation vapor pressure of the adsorbate (Pa), r is a constant, T_c and P_c are critical temperature (K) and pressure (Pa) of the adsorbate. UTRC evaluated several adsorption isotherm models (Toth, Langmuir, Langmuir Freundlich, DR, and DA) and the DA isotherm model resulted in the lowest sum of squares of errors in the studied range of NH_3 partial pressure and temperature.

3.2.2 Impregnated Activated Carbon

The enthalpy of ammoniate formation for each of the three reactions in Table 5 was assumed to have a Gaussian distribution. This causes a log-normal distribution of the NH_3 equilibrium pressure (Figure 3), which gave a better fit between the model and the experimental results.

Figure 3. Probability density function and cumulative distribution function as a function of ammonia equilibrium pressure for different MnCl_2 ammoniates.

The mean value of the NH_3 equilibrium pressure for each of the three reactions in Table 5 can be calculated from the enthalpy and entropy of ammoniate formation, as shown in Equation 5. The contribution to the total ammonia uptake by each of the three reactions can be calculated with Equation 6.

$$\mu_i = \log \left[\exp \left(\frac{(\Delta H_i - T\Delta S_i)}{RT} \right) * 10^{-5} \right] \quad (5)$$

$$q_i(p) = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{(\log p - \mu_i)}{\sqrt{2\sigma_i^2}} \right) \right] h_i \quad (6)$$

$$Total = q_1(p) + q_2(p) + q_3(p) + q_{AC}(p) \quad (7)$$

Where q_i is the ammonia uptake at a specific ammonia pressure p (bar) for reaction i , ΔH_i , ΔS_i is the enthalpy and entropy of ammoniate formation for reaction i , μ_i and σ_i is the mean and standard deviation of the log-normal distribution for reaction i , h_i is the maximum uptake of the manganese chloride ammoniate for reaction i . The adsorption isotherm at -20C indicated the presence of a separate step that can be associated with a hypothetical $\text{MnCl}_2 \cdot 4\text{NH}_3$ phase and the estimated thermodynamic properties were added to Table 5 for clarity.

A constraint that has been applied is that the maximum uptake of MnCl_2 to form $\text{MnCl}_2 \cdot 1\text{NH}_3$ is equal to that of the maximum uptake of $\text{MnCl}_2 \cdot 1\text{NH}_3$ to form $\text{MnCl}_2 \cdot 2\text{NH}_3$ and the maximum uptake of $\text{MnCl}_2 \cdot 2\text{NH}_3$ to form $\text{MnCl}_2 \cdot 6\text{NH}_3$ is four times the maximum uptake of MnCl_2 or $\text{MnCl}_2 \cdot 1\text{NH}_3$, due to the stoichiometry of the reactions. The sum of the contributions represents the full model, given by Equation 7.

4. Results and Discussion

4.1 Rationale for Selection of IRH-33 as a Porous Support

The impregnated metal chloride expands substantially upon ammoniate formation. This requires a strong support material in order to prevent the formation of fines that reduce the permeability of the packed bed. Cameron activated carbon and Vermiculite were not strong enough supports as cycle tests had to be stopped prematurely as the pressure drop across the packed bed became very high (30 psid). This effect is similar to what has been reported by J. Wilkes [30], Long et al. [31] and Schmidt [32]. On the other hand, the Super Activated Carbon (SAC) IRH-33 yielded after impregnation with metal chlorides not only a sorbent with a superior capacity but also a packed bed with a pressure drop that stayed constant at about 11 psi during seven cycles (50 wt% loading of MgCl_2 on IRH-33), as shown in Figure 4. Therefore IRH-33 was selected as porous support for the other metal chlorides that were tested (ZnCl_2 , MnCl_2). Actual strength measurements of the sorbent granules have not been performed as part of this study.

Figure 4, Comparison of the dynamic sorption capacity of three regenerable NH_3 adsorbent materials: 1) 50 wt.% MgCl_2 on IRH-33 (light blue), 2) 50 wt.% MgCl_2 on Cameron activated carbon (dark blue), 3) 50 wt.% MnCl_2 on Vermiculite (red). The measurements were performed with 2 SLPM of 10,200 ppm NH_3 in N_2 gas mixture at 5 bar absolute pressure and room temperature.

4.2 Nitrogen Adsorption-Desorption Equilibrium Measurements

The dispersion of the metal chlorides for a high ammonia adsorption rate and capacity requires a porous support with a high specific surface area and pore volume, which were measured by nitrogen adsorption/desorption equilibrium measurements at 77K (see section 2.3.4). Those measurements were performed on four samples (Table 2): 1) pristine IRH-33, 2) 40 wt% MnCl_2 loaded on IRH-33 before NH_3 exposure, 3) IRH-33 prepared by dissolving 40 wt% MnCl_2 loaded on IRH-33 in ethanol and filtering ethanol solution from the super activated carbon in a soxhlet apparatus, 4) 40 wt% MnCl_2 loaded on IRH-33 that had been exposed to 12 ammonia adsorption-desorption cycles in a dynamic adsorption breakthrough column.

Figures 3 and 4 show the experimental nitrogen adsorption-desorption isotherms at 77 K and DFT pore size distribution for all four samples. The BET surface areas and DFT total pore volumes derived from the nitrogen isotherms for these samples are given in Table 2.

Table 2, BET surface areas and DFT pore volume of super activated carbon and its different modified versions.

Sample no	Sample description	BET SA (m^2/g)	DFT total pore volume (cm^3/g)
1	Pristine IRH-33	2157	1.296
2	40 wt% MnCl_2 on IRH-33 before NH_3 exposure	903	0.59
3	IRH-33 after MnCl_2 dissolution	2001	1.209
4	40 wt% MnCl_2 on IRH-33 after NH_3 exposure	862	0.539

All the isotherms in Figure 5 show Type I behavior. A small hysteresis is seen for these samples with the desorption isotherms due to the capillary condensation of nitrogen in the few mesopores (between 20 and 500 Å). Figure 5 shows the pore size distribution of the samples. Pore size for all these samples varies between 5 and 50 Å. The pore size distribution has a maximum in the range from 20 – 50 Å, well above the size of the ammonia molecule (3 Å).

Upon impregnation of the salt into the pores of super activated carbon, the BET surface areas dropped from 2157 to 903 m²/g and the pore volume dropped down from 1.296 cm³/g to 0.59 cm³/g. The loading of MnCl₂ did not cause any damage to the microstructure of super activated carbon. This is evident from the N₂ adsorption isotherm of sample 3 as there is no significant change in surface area and DFT pore volume between sample 1 and sample 3, e.g. after dissolving the MnCl₂. Ammonia adsorption and regeneration only causes a slight reduction in the surface area and pore volume, as indicated by the results for sample 4 in comparison to sample 2.

Figure 5, Nitrogen adsorption-desorption isotherms of different samples at 77 K.

Figure 6, Pore size distribution of different samples.

4.3 NH₃ Adsorption Isotherms on IRH-33

Figure 7 shows the experimental NH₃ adsorption isotherms at super activated carbon IRH-33. Several adsorption isotherm models (Langmuir, Freundlich, DR and DA) were evaluated and the DA model was found to be the best fit in the lowest sum of squares of errors in the studied range of temperature. DA fit parameters of super activated carbon IRH-33 are listed in Table 3. The model fits well to the experimental data with a slight deviation at 20 °C.

Table 3, DA fit parameters of super activated carbon.

Parameter	Value
x_0 (gNH ₃ /g adsorbent)	2.616
r	8.914
E (J/mol)	509.697
m	0.622
P_c (bar)	112.9
T_c (K)	405.5