Adsorption of ammonia using mesoporous alumina prepared by a templating method

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ABSTRACT

Ammonia, NH_3 , is a key chemical widely used in chemical industries and a toxic pollutant that impacts human health. Thus, there is a need for the development of effective adsorbents with high uptake capacities to adsorb NH_3 . An adsorbent with a high surface area and a small pore size is generally preferred in order to have a high capacity for the removal of NH_3 . The use inorganic nanoporous materials as gas adsorbents has increased substantially and emerged as an alternative to zeolite and activated carbon. Herein, mesoporous alumina (MA) was prepared and used as an NH_3 adsorbent. MA showed good pore properties such as a uniform pore size and interlinked pore system, when compared to commercial adsorbents (activated carbon, zeolite, and silica powder). MA has free hydroxyl groups, serving as useful adsorption sites for NH_3 . In an adsorption isotherm test, MA exhibited 4.7-6.5 times higher uptake capacities for NH_3 than commercial adsorbents. Although the larger surface areas of adsorbents are important features of ideal adsorbents, a regular and interlinked adsorbent pore system was found to be a more crucial factor to adsorb NH_3 .

Keywords: Adsorbents, Ammonia, Mesoporous alumina, Nanopore, Toxic gases

1. Introduction

Ammonia (NH_3) is a valuable chemical resource for use in industry as a fertilizer, refrigerant, and to refine petroleum [1]. However, NH_3 is also a toxic gas that has a pungent odor and it has potentially harmful effects on the public [2]. When the NH_3 content in the atmosphere exceeds 35 ppm, it impacts the health of humans and animals [3]. In addition, an aerodynamic study of particulate matter (PM) in the presence of NH_3 found that it played a vital role in the formation of the fine fraction of the aerosol ($\text{PM}_{2.5}$) [4]. Hence, NH_3 adsorption is of great importance for human health.

Ideal adsorbents with high surface areas and small pore sizes are preferred for high capacities to remove contaminants. Research into such porous materials has gradually addressed these applications with respect to NH_3 adsorption or filtration [5-7]. The traditional inorganic adsorbents, including activated carbon, alumina, silica gel, and 13X zeolite, have low adsorption capacities in the range from 2.3 to 12.0 mol/kg (37 to 192 mg/g) [7]. In recent years, the number of available nanoporous materials, such as mesoporous silica (MS) has increased substantially and emerged

as a gas adsorbent alternative to zeolite and activated carbon. The highly regular pore structure and internal surface area of ordered MS make these particles attractive substrates that can be tailored for NH_3 adsorption [8]. For example, MS particles showed very high uptake capacities and selectivities for CH_4 [9], CO_2 [10], H_2S [11], NH_3 [12], and volatile organic vapors [13]. Few studies on the removal of hazardous gases by adsorption using MA are reported, even though MA and MS share similar pore properties and high thermal stabilities, as seen in comparison to reports about MS in the literature [14, 15].

Therefore, herein, MA prepared by a templating method was used as an NH_3 adsorbent. In previous studies [16, 17], MA showed a high adsorption capacity for metal ions (Hg^{2+} , Pb^{2+} , and As^{3+}) from the aqueous phase. We found that the surface area provided by different adsorbents did not significantly affect the adsorption capacity, and in fact, the key factor was a uniform pore size and an interlinked pore system. Since those particle properties of MA enhanced the adsorption capacity of the substrate for the removal of metal ions, MA might also be helpful to use as gas-adsorbent. Because zeolite, activated carbon and silica nanoparticles were used as commercial gas adsorbents in re-

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al-world applications, we also evaluated these materials for their NH_3 -adsorption capacities.

2. Materials and Methods

2.1. Materials

As described in our previous reports [16-18], stearic acid and aluminum sec-butoxide were used as the anionic surfactant, and an aluminum precursor was used to prepare MA. The aluminum precursor and stearic acid were dissolved separately in sec-butyl alcohol, and then the two solutions were mixed. A small amount of water was slowly added dropwise to the mixture, generating a white precipitate. After further stirring for 24 h, the resulting materials were calcined for 3 h at 500°C. The molar ratio of this reaction mixture was 1 $\text{Al}(\text{sec-BuO})_3$: 0.2 $\text{C}_{17}\text{H}_{35}\text{COOH}$: 0.04 NaOH : 5 sec-BuOH : 4 H_2O . Zeolite (Ze, < 45 μm , CAS#1318-02-1), activated carbon (AC, 100 mesh), and silica (Si, 12 nm) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further treatment as commercial adsorbents. The porosities of the adsorbents were analyzed by transmission electron microscopy (TEM, JEM-2010, Jeol, Japan). N_2 adsorption/desorption experiments were carried out using a BELSORP-mini volumetric adsorption measurement instrument (BEL, Japan), and pore size distributions were calculated using the Barret-Joyner-Halenda (BJH) pore size and volume analytical model on the desorption branch.

2.2. Adsorption of NH_3

Helium (99.999%) and NH_3 (99.999%) were used as carrier and target gas molecules, respectively. As shown in Fig. 1, the experimental setup for measuring the isotherm consisted of a stainless-steel column (18 cm length and 2.54 cm inner diameter) with 5 g of packed adsorbent sample, a mass flow controller (max. 5 L/min), a pressure controller (max. 5 bar), and a continuous gas analyzer (AR8500, Smart Sensor, USA). The gas hourly space velocity was fixed as 28 min^{-1} . The desorption of NH_3 adsorbed on MA was carried out at 400°C at 5 L/min He for 2 h. After regeneration, three recycling tests were carried out at a given pressure. In addition, to define the Gibbs free energy for the adsorption of NH_3 on MA, the temperature of the reactor was changed from 25 to 5°C.

Fig. 1. Experimental system for the adsorption of NH_3 .

3. Results and Discussion

3.1. Characterizations of Adsorbents

As shown in Fig. 2 and Fig. 3, MA showed a pore diameter of 3.4 nm with a narrow and uniform pore size distribution ($D_{\text{FWHM}} \sim 2$ nm). In the N_2 adsorption/desorption isotherm of MA, a typical type of IV isotherm of mesoporous porosity and a hysteresis loop in the range 0.4-0.8 P/P_0 was observed, showing both the framework and textural porosity of the substrate. The framework porosity was in the range 0.4-0.7 P/P_0 , indicating that the porosity was contained within the uniform channels of the templated framework, whereas the textural porosity in the range 0.8-1 P/P_0 was indicative of the porosity arising from the non-crystalline intra-aggregate voids and spaces formed by interparticle contacts [16]. The TEM images (Fig. 3(a)) of MA showed a sponge-like porous appearance and an interlinked pore system, consistent with the analysis for the N_2 adsorption/desorption result of MA. An interconnected pore structure has an advantage of a reduced diffusion limitation and an enhanced molecular accessibility to the inner surface.

However, other adsorbents (AC, Ze, and Si samples) showed irregular and broad pore size distributions, as shown in Fig. 2. The AC sample had a small pore at the inner surface and a large surface area (1,024.2 m^2/g), but both the non-uniform pore structure and very broad pore distribution in the range 1-25 nm did not match with the physical properties of ideal adsorbents. A molecular sieve such as the Ze sample generally has a very small pore (2-10 Å), which is too small to be able to adsorb NH_3 into the inner surface of Ze. The Si sample consisted of single particle with a size of 12 nm and aggregates of these particles are depicted in Fig. 2(d). Because the void fraction originated from aggregation between the primary particles, it acted as pores in the N_2 adsorption/desorption test. The pore properties of all the adsorbents are listed in Table 1. Therefore, NH_3 might be adsorbed on the outer surface of Ze and Si samples, but on both inner and outer surface of MA and AC samples.

Fig. 2. N_2 adsorption/desorption curves for MA, AC, Ze, Si samples. Inset is pore size distribution of 4 adsorbents, calculated by the BJH model of the desorption branch of the N_2 adsorption/desorption test.

Fig. 3. TEM images of (a) MA, (b) AC, (c) Ze, and (d) Si (1 bar = 50 nm).

Table 1. Pore Properties of the Samples

Samples	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
MA	334.2	3.39	0.759
AC	1,024.2	1 to 25	0.704
Ze	1.9	NA	NA
Si*	365.8	4.92*	1.097*

*Since silica nanoparticles have not porous nanostructure, its pore size and pore volume in the table mean the void fraction originated from agglomeration or aggregation between primary particles.

3.2. Adsorption Equilibrium Study

Applied pressure is the controlling parameter to adjust the gas uptake on adsorbents. When increasing the applied pressure of the NH₃ gas, the uptake capacities of adsorbents generally increased to saturation levels at high pressure. As shown in Fig. 4, the saturation curve for all adsorbents followed a typical

Langmuir isotherm. While the uptake of NH₃ gas on MA increased steadily up to 3 bar, AC, Ze, and Si samples showed rapid saturation after 1.5 bar. NH₃ molecules were first adsorbed on the outer surface of the adsorbent at a relatively low pressure and then gradually penetrated into the inner surface of the adsorbent to adsorb at a relatively high pressure. Since MA has a uniform pore diameter, NH₃ could easily penetrate into the inner surface, leading to an enhancement of the adsorption capacity. Although AC has the largest surface area among the 4 samples, its uptake capacity was smaller than MA and similar to Ze and Si samples. It was noted that the irregular pore structure of AC acted as a bottle-neck for the intrusion of NH₃ molecules into the inner surface, and thus there was a decrease in the uptake of NH₃. Although the Si sample had a similar surface area with MA, induced by the formation of aggregates between single silica nanoparticles, Si also showed a low uptake capacity. These results showed that the surface area of adsorbents did not significantly affect the

Fig. 4. Isotherms of NH_3 on MA, AC, Ze, and Si samples.

Table 2. Parameters of Langmuir Isotherm and Adsorption Density for NH_3 on MA, AC, Ze and Si

Samples	Q_m (mg/g)	$\Gamma_{\max}$ (mg/m ²)
MA	214.8	0.44
AC	45.8	0.11
Ze	43.3	0.10
Si	33.0	0.08

adsorption capacity. A common feature of the AC and Si is their irregular pore size distribution. Namely, ill-defined pore structure reduces the adsorption of NH_3 to adsorbents. Therefore, the surface area of the adsorbent is likely to be large, but the pore structure (i.e., regular interlinked pore system) is the most important factor for the NH_3 adsorption.

The maximum uptake capacities (Q_m , mg/g) for NH_3 was calculated with Langmuir isotherm. As summarized in Table 2, the Q_m values of the NH_3 uptake on MA, AC, Ze, and Si adsorbents was 214.8, 45.8, 43.3, and 33.0 mg/g, respectively. MA had 4.7 times high uptake capacity for NH_3 , compared to AC. It was reported that commercial AC and zeolite have adsorption capacities for NH_3 in the range 37–144 mg/g [7]. Therefore, MA used here is referred as a good gas-adsorbent with a very high adsorption capacity for NH_3 . The adsorption density (Γ , mg/m²) of NH_3 on the active surface of adsorbents was calculated using the well-known equation, $V\Delta C/mS$, where S , m , V , and C are parameters for the surface area, the amount of adsorbent, volume and adsorbed concentration of NH_3 , respectively [16]. The maximum adsorption density ($\Gamma_{\max}$) was obtained from the adsorption isotherm, and a similar trend with the maximum uptake of NH_3 was observed (Table 2).

Because the adsorption of gas is strongly affected by temperature, the Gibbs energy and the uptake capacity for MA adsorbent were evaluated at different temperatures (25, 30, and 50°C). As shown in Fig. 5, the adsorption curve at high temperature was located below that of the room temperature. The maximum capacities of NH_3 at 30 and 50°C were 174.5 and 132.6 mg/g, respectively, which were lower than those obtained at 25°C. With increasing

Fig. 5. Isotherms of NH_3 on the MA at a different temperature.

temperature, $-\Delta G$ was slightly decreased from 12.0 to 11.7 kJ/mol, decreasing the interaction between NH_3 and supports. Therefore, the adsorption system under high temperature poses a negative impact on the adsorption capacity, decreasing the amount of adsorbed gas.

Chemisorption and physisorption of NH_3 on oxide material have been studied [12]. In the past literatures, it is reported that NH_3 was chemisorbed on silica surface forming the $\text{NH}_3\text{-O-Si}$ [19] or $\text{NH}_2\text{-Si}$ [20] with a siloxane bond (Si-O-Si). For physisorption of NH_3 , the hydroxyl group was the preferred site to bond NH_3 ($\text{NH}_3\text{-OH-Si}$) [21]. Although the walls of calcined oxide (MS and MA) are made of multiple oxide bridges (Si-O-Si or Al-O-Al bonds), the pore surfaces contain free hydroxyl groups. These free polar groups serve as useful sites for adsorption of polar gas, such as NH_3 [22]. In addition, the additional hydroxyl groups formed by hydrothermal conditioning with water increase the acidity of oxide materials, which results in an increase in NH_3 capacity [5]. Therefore, similar to the investigation of NH_3 adsorption on the silica surface, alumina (MA) has free hydroxyl groups, serving as a useful adsorption site for NH_3 . As calculated in our previous work [16], the moles of total surface sites per gram of solid were estimated to be 2.5 mol/kg for MA, assuming 5 hydroxyls/nm² [23]. The maximum capacity of MA was higher than the total moles of hydroxyl sites (as described in isotherm results), and thus, NH_3 adsorbed on the inner and outer surface of MA via both physisorption and chemisorption using hydroxyl groups and oxo-bridge.

In field applications of NH_3 adsorbents, maintaining the initial uptake capacity after regeneration is also an important factor for ideal adsorbents. After the regeneration, the feasibility of the adsorption-desorption cyclic operation was examined to investigate the reproducibility of MA performance, as shown in Fig. 6. The amount of adsorbed NH_3 decreased slightly with repeated use of adsorbent (214.8 to 204.2 mg/g after 3 times recycling). While > 95% of the initial uptake capacity of NH_3 was maintained after three cycles of operations, notably MA could undergo repeated adsorption-desorption cycles without any loss of activity.

Fig. 6. Isotherms of NH_3 on the MA with recycling numbers.

4. Conclusions

MA was prepared by a post-hydrolysis method to use as the gas adsorbent for NH_3 . The MA adsorbent showed pore properties of ideal gas-adsorbents, such as uniform pore size, regular pore size distribution, interlinked sponge-like pore system, and large surface area. The NH_3 adsorption performance of MA was compared to commercial gas-adsorbents (activated carbon, zeolite, and silica nanoparticle). This study on the isotherm adsorption represented a typical pressure-dependence as Langmuir isotherm. The maximum uptake capacity of NH_3 for MA was 4.7-6.5 times larger than the same parameter for commercial adsorbents. There was no correlation between the uptake capacity and pore properties of adsorbents. Namely, the adsorption performance was not good, even if the surface area was large, as in the case of AC. A uniform pore structure with well-defined channels has been shown to more advantageous over a disordered pore network in terms of access to guest species to the binding sites [23]. Consequently, a regular pore structure (prefer to interlinked pore system) was found to be the most critical factor for the removal of NH_3 using MA. In addition, because the adsorption energies of the toxic gases and common adsorbates followed the trend $\text{NH}_3 > \text{PH}_3 > \text{H}_2\text{S} > \text{SO}_2 > \text{CO}$ (Barea et al., 2014), it was possible to apply as-prepared MA readily as conventional gas-adsorbents for H_2S , PH_3 , and NH_3 .

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