



Evaluation of metal oxide nanoparticles for adsorption of gas phase ammonia



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ABSTRACT

MgO, ZnO, CuO, and TiO₂ nanoparticles along with activated charcoal (AC) were evaluated for ammonia adsorption. Adsorption experiments were conducted under atmospheric pressure in a packed bed column. Among the tested adsorbents, TiO₂ had the highest equilibrium adsorption capacity of 6.87 mg NH₃ g⁻¹ followed by AC, ZnO, MgO, and CuO. Increasing gas flowrate negatively impacted TiO₂ breakthrough adsorption capacity by lowering residence time of ammonia in the bed. Using Wheeler-Jonas expression, total mass transfer coefficient for ammonia adsorption on TiO₂ was estimated as 1061 min⁻¹. Adsorption isotherms for 50 to 500 ppmv ammonia at temperatures in the range of 5–280 °C revealed that TiO₂ equilibrium adsorption capacity decreased as temperature increased. Among the evaluated isotherms Langmuir-Freundlich best described the equilibrium adsorption data. Examination of exposed TiO₂ by CNHS, TGA, and FT-IR revealed that molecular ammonia was the most abundant surface feature at room temperature, while for temperatures in the range of 70–280 °C formation of amido (NH₂) and imido (NH) species through hydrogen abstraction from ammonia was evident. Using the characterization data a mechanism scheme for adsorption of ammonia on TiO₂ nanoparticles was proposed.

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1. Introduction

Ammonia is an odorous air pollutant with adverse effects on humans, animals, and environment. It can cause nose and throat irritation, nausea, and respiratory tract problems upon inhalation. Emission of ammonia also contributes indirectly to the formation of ground level ozone and fine ammonium nitrate particulates [1,2]. Deposition of these particulates, molecular ammonia, and ammonium ions could damage the soil and plants, and led to eutrophication of water bodies. Agriculture sector through application of fertilizers and operation of livestock facilities contributes significantly to emission of ammonia, with the extent of these emissions is anticipated to double by 2050. As a result development of novel and feasible technologies for mitigating the emission of ammonia is necessary [3,4].

Technologies such as thermal incineration, selective catalytic oxidation, condensation, scrubbing, membrane separation, bio-filtration, and adsorption have been used for the removal of

ammonia from gaseous streams [2,5]. Incineration is an effective approach but it is highly energy-intensive and could result in NO_x emission. Selective catalytic oxidation of ammonia by noble metal catalysts reduces the reaction temperature and promotes higher N₂ selectivity. However, the complex reactor design required for the catalytic oxidation, cost of the catalyst, and catalyst poisoning make the process less attractive when compared to other options. Separation by membrane and scrubbing are both effective in removal of ammonia but suffer from high capital and operating costs. Bio-filtration and condensation are efficient in elimination of ammonia at low and high concentrations, respectively. However, their applicability is dictated by the level of ammonia in the gas phase [2,5]. Adsorption is one of the most commonly used approaches for the removal of ammonia due to simplicity of implementation, low operating cost, and effectiveness over a wide range of ammonia concentrations and gas phase compositions.

Three categories of adsorbents have been used for the removal of gaseous ammonia. The first category consists of porous adsorbents such as activated carbon, graphene, carbon nanotubes, zeolites, and aluminium oxides [6–12]. Activated carbon is commonly used for the removal of ammonia due to its availability and low cost [7,11]. The second category includes porous materials

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impregnated with metallic nanoparticles [13–18]. Deposited metallic ions are mainly in chloride form and include ZnCl_2 , CaCl_2 , MgCl_2 , FeCl_2 , and CuCl_2 [13,15–18]. The impregnated metal chlorides are usually in the nanometer range which provides high particle dispersion for ammonia adsorption. The third category consists of pure nanoparticles in oxide phase (i.e. nanoparticles without any support) [19–23]. TiO_2 , MgO , and ZnO are among the metal oxide nanoparticles which have been used for the removal of ammonia [19,22,23]. Adsorptive characteristics of these nanoparticles such as surface area and surface acidity or basicity could be tailored to improve their effectiveness in the abatement of target gases. Compared with conventional sorbents such as activated carbon, the unsupported nanoparticles also demonstrate higher durability during the high temperature adsorption-desorption cycles.

Despite the promising properties of metal oxide nanoparticles, there exists a lack of concerted effort in evaluating the performance of these adsorbents in mitigation of hazardous emissions. To be more specific, studies aiming to assess and compare the effectiveness of various metal oxide nanoparticles with regard to adsorption of ammonia are limited. Moreover, the majority of earlier works have been conducted over a narrow range of operating conditions, specially with regard to temperature and ammonia concentration. Therefore, in the present work a number of metal oxide nanoparticles namely CuO , ZnO , MgO , and TiO_2 were evaluated for their ability in adsorption of ammonia from the gaseous streams. Following the identification of the most suitable adsorbent, effects of various operating conditions such as ammonia concentration, gas flowrate, temperature, and adsorbent quantity on performance of the identified adsorbent were investigated over a broad range. Using the generated data, a suitable isotherm describing the adsorption of ammonia was identified and the associated parameters were determined. Finally thermogravimetric analysis (TGA), Fourier transform infra-red (FT-IR) spectroscopy, and CNHS analysis were used to understand the nature of adsorbed species and the mechanism of ammonia adsorption by the best adsorbent.

2. Materials and methods

2.1. Chemicals and gases

Nanoparticles of CuO (99%), MgO (99%), ZnO (99%), and TiO_2 (anatase, 99.5%) were obtained from US Research Nanomaterials Inc, USA. The average particle size of CuO , MgO , and TiO_2 were 40 nm, while ZnO had a particle size in the range of 35–45 nm. Activated charcoal (Darco G-60) with 100 mesh size (149 μm) was obtained from Sigma-Aldrich, Canada. Activated charcoal (AC) was included to compare the effectiveness of a carbon based material with the metal oxide nanoparticles. A premixed gas containing 1000 ppmv ammonia balanced with helium was obtained from Air Liquide Inc, Canada. Industrial grade helium (99.99%) was obtained from Praxair, Canada and used to prepare gas mixtures with desired ammonia concentrations.

2.2. Experimental set-up

Experiments were conducted in a packed bed column located inside a walk-in fume hood. The schematic of the experimental set-up is shown in Fig. 1. The premixed gas (1000 ppmv NH_3 - balanced He) was diluted with helium to achieve desired ammonia concentrations in the range 50–500 ppmv (corresponding partial pressures: 0.005–0.051 kPa). The mixed gas with the desired concentration then passed through an adsorption column packed with the designated adsorbent (0.1–0.5 g) to generate breakthrough curves. The column outlet was directed to an online gas chromatograph (GC) to measure the concentration of ammonia in real time. A bleed line was devised at the outlet of the column to prevent choking of the flow during GC injections. The outlets from the GC and the bleed line were passed through water to capture any residual ammonia. Flowrates of ammonia and helium were adjusted to desired levels using two mass flow controllers (Aalborg Instruments and Controls, GFC17, USA). Flowrates were reported in standard conditions (101.3 kPa and 21.1 $^\circ\text{C}$). The accuracy of the mass flow controllers was $\pm 1.5\%$ of the full scale. The adsorption column was a Pyrex glass tube with an O.D. = 1.27 cm (1/2 in) and a length (L) of 29.5 cm. The column temperature was maintained at

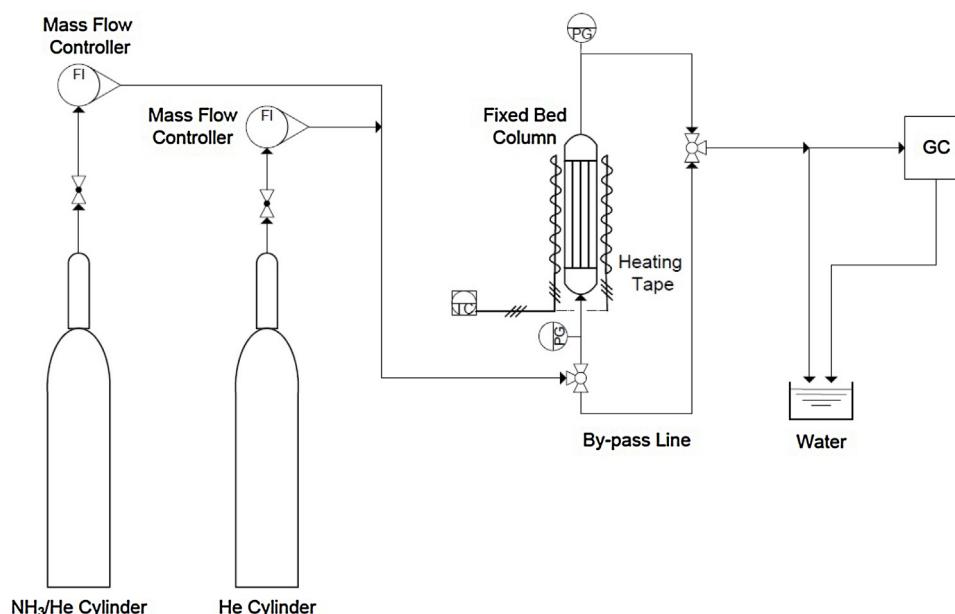


Fig. 1. Schematic of the experimental set-up. FI: flow indicator, TC and TI: temperature controller and indicator, PG: pressure gauge, GC: gas chromatograph.

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