Enhanced ammonia adsorption on functionalized nanoporous carbons

Ali Qajar [a], Maryam Peer [a], Mohammad Reza Andalibi [a], Ramakrishnan Rajagopalan [b], Henry C. Foley [a, b, c, *]

[a] Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA
[b] Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA
[c] Department of Chemical Engineering, University of Missouri System, Columbia, MO 65211, USA

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ABSTRACT

Nanoporous carbons were synthesized and treated with nitric acid after which the change in their propensities for ammonia adsorption was determined. The adsorbents had mean pore sizes ranging from 0.5 to 12 nm and they included polyfurfuryl alcohol (PFA)-derived carbons, commercial activated carbons, and both soft and hard-templated mesoporous carbons. The carbons were treated with concentrated nitric acid at elevated temperatures (e.g. 90 °C) and for time spans between 15 and 240 min. The textural properties of carbons, before and after nitric acid treatment, were determined using CO_2 adsorption at 0 °C. Ammonia adsorption uptakes were measured at 25 °C and at pressures up to 9.5 bar. The highest total uptake of ammonia on the native carbons, that is prior to nitric acid treatment, was ~10 mmol/g at 1 bar and 25 °C; this was obtained on a microporous carbon derived from the pyrolysis of polyfurfuryl alcohol and polyethylene glycol blends followed by CO_2 oxidation. Nitric acid treatment of this carbon significantly increased its total uptake of ammonia to 17 mmol/g. This sample provided a reversible uptake of 14 mmol/g after it was outgassed at 160 °C and 10^{-5} bar under dynamic vacuum. This is 2 mmol/g higher than state-of-the-art ammonia adsorbents such as COF-10. An x-ray photoelectron spectrum (XPS) showed that the oxygen content of the carbon increased from 3 at.% to 16.4 at.% after the nitric acid treatment. Heats of adsorption profiles, calculated from adsorption isotherms, started from 165 kJ/mol and quickly dropped to 40 kJ/mol with ammonia loading. This showed that the isosteric heat of adsorption on the remaining surface was still higher than the native carbon sample resulting in high reversible adsorption uptake, even after excluding the irreversible adsorption on the very high energy sites.

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1. Introduction

Ammonia is an important source of hydrogen for fuel cell applications. Since it is efficiently condensed to liquid for storage, and because it can be readily reformed into hydrogen. However, it is toxic, corrosive and environmentally hazardous. Thus it requires careful handling, especially as a liquid. For that reason, adsorption on a carrier has been considered as a safe alternative to liquefaction for ammonia storage and transportation [1].

Ammonia adsorption uptakes ranging from 5 to 11 mmol/g at 1 bar and 25 °C have been reported for conventional organic and inorganic adsorbents including activated carbons, zeolites and porous polymers [2]. In most of the earlier studies, the materials were compared based on their total ammonia uptake rather than their actual reversible and deliverable ammonia adsorption. The reversible extent of adsorption is indicative of the working capacities of the carrier and this capacity is very important from the perspective of engineering and system design. The activated carbons showed notable reversible adsorption uptakes, whereas for many other adsorbents there is a large gap between the initial equilibrium extent of adsorption and that which is reversibly adsorbed.

In recent years, there has been significant interest in developing novel adsorbents for enhanced ammonia adsorption with much higher working capacities. Much of the research effort has been aimed at the synthesis of metal oxide adsorbents with ammonia adsorption enhanced by acid–base interactions, especially those between the Lewis acid sites and ammonia [3,4]. In another

approach, the adsorption of ammonia was enhanced by functionalizing the surfaces of adsorbents using various acidic reagents [5–7]. With molecular modeling, Kim et al. examined the effect that various metal ions and organic functional groups would have on total reversible ammonia adsorption, both in the presence and absence of co-adsorbed water [5]. Those simulations indicated that carboxylic acid and hydroxyl groups were the most effective for reversible ammonia adsorption under dry conditions [5]. Although, in the presence of water, none of the functional groups were satisfactorily effective.

Recently, graphene oxide composites and organic frameworks also have been examined as potential adsorbents for ammonia storage. Yaghi and coworkers studied adsorption of ammonia on metal organic frameworks (MOFs) and showed that they could control the affinity of the adsorbent for ammonia by manipulating the metal centers [8]. Bandosz and coworkers synthesized composites from graphene oxide (GO) and MOFs and achieved further enhancements with ammonia equilibrium uptake of 12.5 mmol/g. However, because of the strong bonding between the adsorbed ammonia molecules and the active sites of the MOFs, the adsorption of ammonia was not reversible because these frameworks were quite prone to collapse during desorption [9,10]. Later, Doonan et al. showed that framework collapse did not occur with COF-10 (covalent organic framework) and that it adsorbed ammonia reversibly with working capacity of 12 mmol/g at 25 °C and 1 bar. They attributed the enhanced ammonia adsorption to acid–base interactions between ammonia molecules and the boron atoms in the adsorbent framework [11].

When compared to the newer organic frameworks, carbon adsorbents exhibit excellent mechanical strength, and good physical and chemical stability but lower interaction energetics with ammonia. They also provide high surface area, high packing density and they can be easily decorated with heteroatoms and functional groups. As a result, carbons continue to hold promise for ammonia adsorption and storage [12–15]. Earlier studies showed that decoration of carbon based adsorbents with oxygen heteroatoms could significantly improve their ammonia adsorption affinity [16–18]. Addition of heteropolyacids and metal oxides to porous carbons or direct treatment with acids successfully enhanced ammonia adsorption through both chemisorption and physisorption [17,18]. On these carbons, a calorimetric heat of adsorption of over 150 kJ/mol was reported for low-pressure ammonia adsorption, and this energy was associated with the ammonia adsorbed at the highest energy sites (carbonates and carboxylic acid) on the surface. Therefore it was also observed that as the degree of adsorption increased at higher pressures, the heat of adsorption decreased and fell to values as low as 15 kJ/mol [14].

One advantage of activated carbon materials is their typical high pore volume and tunable pore size distribution ranging from micropores as small as 0.5 nm to meso- and macropores with mean pore sizes over 50 nm [19–22]. Thus, we chose to investigate in some detail how nitric acid treatment of different carbons with different morphologies and textures affects reversible working capacity for ammonia adsorption.

2. Experimental

2.1. Synthesis

Chemical reagents used in this work were obtained from Sigma–Aldrich and were used without further treatment. Different types of carbons were synthesized or obtained as commercial products for this study. Microporous carbons derived from polyfurfuryl alcohol (FA) were synthesized by a method already explained in detail [20]. In a typical experiment, FA was polymerized in a THF solution using p-toluene sulfonic acid (p-TSA) as the initiator, for 2 days at 10 °C to form polyfurfuryl alcohol (PFA). Then the polymer solution was transferred to a quartz boat and was pyrolyzed at 800 °C for 5 h under flowing Ar in a horizontal tube furnace. The pyrolysis yielded a porous carbon with pore volume of ~0.2 cc/g. The carbonization product was crushed and sieved down to 38 micron and then was activated using CO_2. For the CO_2 activation step, the carbon powder was placed in a quartz boat in a tube furnace and was heated under flowing Ar up to 900 °C. Then the gas flow was switched to CO_2 and the carbon powder was activated until 50% of the original mass burned off. The product of activation process was a microporous carbon, named NPC-AC.

Microporous PFA-derived carbon with enhanced mesoporosity was synthesized by adding a mesopore forming agent, polyethylene glycol (PEG) (MW = 8000) [21]. After polymerization, the resultant PFA solution was mixed with PEG at mass ratio of 1:1. The solution was heated to 60 °C for 1 h under stirring to form a uniform blend of PFA and PEG polymers. The polymer blend was pyrolyzed at 800 °C and activated with CO_2 to 75% burn-off. The carbons before and after activation are referred to as NPC-PEG and NPC-PEG-AC, respectively.

Ordered mesoporous carbons were derived from phloroglucinol [22]. In a typical procedure, 1.25 g of phloroglucinol and 1.25 g of Pluronic F-127, an amphiphilic block copolymer surfactant with two hydrophilic tails, were mixed in a solution containing 4.26 g H_2O and 4.76 g EtOH. Once a clear solution was obtained, 5 drops of HCl (37 wt.%) was added to the solution while stirring. After 30 min when the solution turned light pink, 1.3 g formaldehyde was added to the solution. Within 1 h the polymerization was complete. The excess water and ethanol were removed from the polymer and polymer was dried at 100 °C overnight. The native mesoporous carbon was formed by pyrolyzing this polymer at 850 °C. Then, the carbon was activated with CO_2 at 900 °C to achieve 30% burn off of its original mass. The native ordered mesoporous carbon and the activated ordered mesoporous carbon derived from phloroglucinol are referred to as OMC and AC-OMC.

ACS, refers to an activated microporous carbon with mean pore size of 2 nm, and CMK8 is mesoporous carbon, derived from templating Kit-6 silica, both were obtained commercially from ACS Materials.

The treatment of these 4 carbons with nitric acid was performed by suspending them in refluxing in concentrated nitric acid, 68 wt.%, at elevated temperatures. Prior to the nitric acid treatment, the carbon was outgassed under vacuum at 100 °C overnight. Then 500 mg of the carbon was mixed with 50 ml concentrated nitric acid and refluxed for 30 min at 90 °C. After this, the solid was thoroughly washed with cold distilled water until the pH was above 5. Then the solid was dried at 90 °C under dynamic vacuum for 12 h. The samples treated as such are referred to as X–F with X being the name of the carbon substrate.

2.2. Characterization

Both CO_2 and ammonia adsorption data were collected on a custom-made high pressure adsorption instrument. Detailed operation of the instrument was provided earlier [23]. Prior to gas adsorption measurements, each sample was degassed at 160 °C under vacuum of 10^{-5} bar for 12 h. Then the sample was cooled to the target temperature prior to collecting the adsorption data. For each adsorption data point, the pressure data were continuously recorded until the changes in the pressure were below 10^{-3} bar over 30 min; at this point the gas and solid were taken to be at equilibrium. After gas adsorption measurements were completed, low-pressure helium expansion was used to determine free volume