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Microporous and Mesoporous Materials 114 (2008) 137–147

MICROPOROUS AND MESOPOROUS MATERIALS

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Activated carbons modified with aluminium–zirconium polycations as adsorbents for ammonia

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Received 29 August 2007; received in revised form 13 November 2007; accepted 21 December 2007
Available online 2 January 2008

Abstract

Microporous/mesoporous wood-based activated carbon was modified by impregnation with aluminium–zirconium oxycations and calcined at 300 °C, and then used as an adsorbent of ammonia. Water was present either on the carbon or in the gas phase. The initial (before ammonia adsorption) and exhausted materials were characterized using adsorption of nitrogen, potentiometric titration, XRD, FTIR and thermal analysis. Aluminium–zirconium polycations improve ammonia uptake by providing new Brønsted acidic centers that form strong interactions with the adsorbed gas in its protonated form. When calcined, the capacity of the impregnated carbon is reduced in dry air stream but increased in wet air stream. Indeed, for this sample, when exposed to dry gas stream, only Lewis acidic centers (associated with the presence of alumina and zirconia formed during the calcination process) are involved, and they lead to weaker interactions with ammonia. On the contrary, under wet gas stream, Brønsted acidic centers are also present and provide stronger interactions with ammonia. It was also evidenced that impregnation with polycations has a "screening" effect on the carbon surface by protecting it from the oxidative effect of hot air when the sample is calcined.

Keywords: Activated carbon; Aluminium–zirconium oxycations; Ammonia adsorption; Surface acidity; Porosity

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1. Introduction

Ammonia is an air pollutant which contributes to particulate matter formation [1] and it is also toxic for human beings owing to its high water solubility and basicity [2]. As a strong base, ammonium affects respiratory system and skin via an exothermic reaction leading to severe burning. Despite all of this, ammonia is one of the major gases used in industry to produce fertilizer, polymers or resins. That is why, there is still a continuous search for effective ammonia adsorbents.

To remove toxic gases from the atmosphere or reduce their noxious potential, personal protection equipment such as gas masks and air filters in HVAC systems are used [3]. In them various sorbents such as zeolites, alumina and activated carbons work as adsorbents [4–16]. In the case of ammonia removal, owing to its small molecular size and basic properties, the adsorbents should have very small pores along with an acidic surface.

So far, the surface area and pore volume [17] of activated carbons have been considered as the most useful features for the removal of pollutants. In the case of ammonia uptake, the hydrophobic surface of carbon becomes a paramount importance. Unlike zeolites whose high capacity is significantly reduced in moist/ambient air, activated carbons do not face this problem kind of problem. Gas pollutants removal becomes effective when the pore size is similar to the size of the molecule to be removed and when dispersive forces are the main mechanism of the adsorption process. In the case of ammonia, the physical adsorption forces at ambient conditions are very weak. Its size, about (3 Å) [18], suggests that only very small pores can be involved in adsorption. All of this causes that ammonia is very easily desorbed from the carbon surface [19].

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1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.12.029

Therefore, to remove ammonia effectively, specific adsorption forces such as hydrogen bonding, acid-base interactions or surface chemical reactions such as complexation, precipitation, oxidation, etc. should be employed. These processes can only occur on the carbon surface after it is modified extensively via for instance, oxidation [12,14,15] or impregnation with metal oxides [13] or metal chlorides [5,19].

Oxidation represents one of the most common ways to introduce surface acidic groups [20,21] that enhance ammonia adsorption via formation of strong hydrogen bonding interactions [12,14,15]. Presence of water in the reaction system was also found beneficial for ammonia removal since it promotes acid–base interactions via formation of ammonium ions [12]. Indeed, water enables dissociation of carboxylic groups present on the carbon's surface and thus ammonium salts can be formed. Nevertheless, these adsorption forces are still too weak to prevent ammonia desorption when only air purging is applied [19].

More advanced acid–base interactions as a way to increase ammonia adsorption were studied on carbons impregnated with metal salts [19] or oxypolycations [22]. In the former, besides a metal working as a Lewis acidic center, complexation occured between ammonia and metals [19]. In the case of oxypolycations, which examples are Keggin Al_{13} species, the strong Brønsted and Lewis interactions were involved with aluminium oxides [22]. Similar observations were found by Yin and coworkers in their study of ammonia interactions with vanadium oxides [9]. In addition, they showed that even though on the surface V_2O_5 both Brønsted and Lewis sites are important for ammonia adsorption, the former ones are much more energetically favorable for hydrogen bonding interactions. In the case of V_2O_5, ammonia is adsorbed at hydroxyl groups containing the vanadyl oxygen.

The objective of this paper is to evaluate the changes in the carbon surface as a result of introduction of aluminium–zirconium oxycations and their effects on the amount and strength of ammonia adsorption. This kind of oxycation was used to improve the catalytic properties of smectites via introduction of new Brønsted and Lewis centers [23]. The latter are formed when the materials are calcined at elevated temperatures (about 300 °C). The effects of changes in acidity and porosity of carbons on ammonia retention are discussed. The purpose of the modification applied is application of carbons for ammonia retention in personal protection such as masks, in HVAC systems or in industrial installations.

2. Experimental

2.1. Materials

Two carbon samples containing hydroxylaluminium–zirconium species were prepared by impregnation of BAX 1500 carbon (MeadWestvaco, apparent density: 0.296 g/cm^3, mean particle diameter: 2.23 mm, pellet strength: 69.5%) with a 10 wt% solution of aged (for 6 months) Rezal® supplied by Reheis Chemical Company. Rezal® is the trade name of a solution of hydroxylaluminium–zirconium polycations of the following formula: $Al_{1.2}Zr_{0.3}Cl\ 5H_2O$. Upon aging, aluminium–zirconium polycations are expected to be formed [23], which should increase carbon's surface acidity and thus, their adsorption capacity.

The treatment applied was based on incipient impregnation by adding to the carbon the volume of Rezal® solution equal to its pore volume. The sample was dried overnight at 120 °C and then calcined at 300 °C for 3 h in air atmosphere. The dry sample is referred to as a BAX-R and the calcined one – as BAX-R300.

Another carbon sample, namely BAX-300, was prepared by calcination of the initial BAX 1500 carbon at 300 °C for 3 h, in order to better assess the role of aluminium–zirconium polycations in BAX-R 300 sample.

2.2. Methods

2.2.1. Ammonia breakthrough capacity

Adsorption capacity for removal of ammonia was assessed by carrying out dynamic tests at room temperature. In this process, a flow of ammonia diluted in air went through a fixed bed of a carbon sample. The total flow rate of the inlet gas was 450 mL/min with an ammonia concentration of 1000 ppm. Those conditions were chosen to accelerate the test and to shorten the exposure of the sensor (limited lifetime). Carbon samples were previously crushed and sieved (1–2 mm) and then packed into a glass column. The size of the bed was 80 mm (high) × 10 mm (diameter). The ammonia concentration in the outlet gas was measured using an electrochemical sensor in a Multi-Gas Monitor ITX system. The adsorption capacity of each sample was then calculated in mg per g of sorbent, as the difference between the inlet and outlet concentrations multiplied by the inlet flow rate, the breakthrough time and the ammonia molar mass in the experimental conditions. To evaluate the influence of water, the experiments for all carbon samples were performed with a flow of ammonia gas diluted either in dry air (ED) or in moist air (70% humidity) (EM). Moreover, the experiments were run with and without a 2-h prehumidification (70% humidity). On all samples, the desorption of ammonia was evaluated when exposed to 360 mL/min of dry air only. If ammonia concentration exceeded 100 ppm during the desorption, no curve was plotted since 100 ppm represents our sensor's limit for detection.

The combination of all these experimental parameters led to four different experiments for each carbon sample. In two experiments, carbon samples were exposed to a flow of ammonia diluted in dry air with, or without, prehumidification. In these cases, the references of the exhausted samples are, respectively: -EPD and -ED (D – dry, P – prehumidification). For the two other experiments, ammonia gas was diluted in moist air with or without prehumidifica-