



Moisture insensitive adsorption of ammonia on resorcinol-formaldehyde resins



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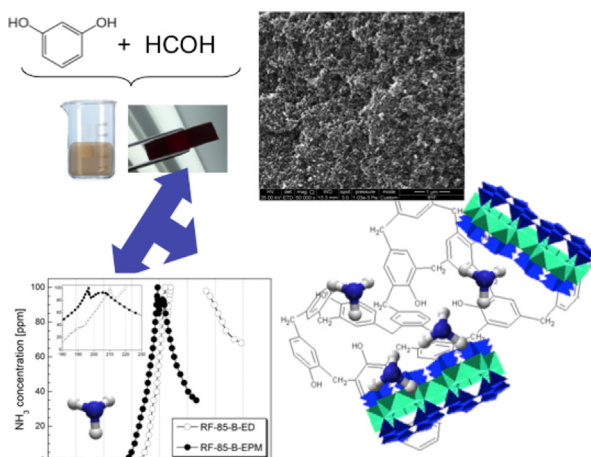
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HIGHLIGHTS

- Ammonia adsorption on RF resin/bentonite was strong and not sensitive to moisture.
- Bentonite boosted the surface acidity of RF resins due to partial exfoliation.
- Clay/RF hybrids show both weak and strong NH₃ adsorption centres.
- Addition of bentonite drastically changed the porosity of the RF resins.

GRAPHICAL ABSTRACT



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ABSTRACT

Phenolic-formaldehyde resins aged at 85, 90 and 95 °C were used as ammonia adsorbents at dynamic conditions in dry and moist air. To avoid pressure drops 10% bentonite was added as a binder. The initial and hybrid materials (before and after ammonia adsorption) were extensively characterized from the point of view of their porosity and surface chemistry. The results showed that the addition of the binder had various effects on materials' properties depending on the chemistry of their surface groups. When the phenolic acidic groups were predominant, the largest increase in surface acidity upon the addition of the binder was found. It was linked to the exfoliation of bentonite by polar moieties of the resins, which made acidic groups from aluminosilicate layers available for ammonia adsorption. On this sample, a relatively high amount of ammonia was strongly adsorbed in dry conditions. Insensitivity to moisture is a significant asset of ammonia adsorbents.

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1. Introduction

Ammonia, besides being a highly toxic gas, affects the formation of a particulate matter in the atmosphere and thus the state of the pollution in the atmosphere. It can have its origin either in natural

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or anthropogenic sources. To decrease ammonia emissions and/or to protect against its toxicity adsorption on various solid media is used [1–9]. Since ammonia is a small molecule gas, its physical adsorption on the surface of porous materials is rather weak [2]. This directed the attention of scientists to design adsorbents on which ammonia could be retained employing specific forces such as polar or acid–base interactions.

One of the methods often used is the acidification of an adsorbent surface. This method was successfully applied to activated carbons where an introduction of acidic groups increased the adsorption of ammonia of about 46 mg/g [10]. On another group of carbonaceous materials, graphite oxides (GO), high adsorption of ammonia (90 mg/g) was linked to its direct reactions with surface groups leading to not only ammonium salt formation but also to amines and amides [11]. Polar surfaces promoted the interactions of ammonia between the graphene oxide layers of otherwise nonporous graphite oxide.

Chemical reactions also increased the adsorption of ammonia on transition metal modified activated carbons where the complexation was indicated as the main mechanism [4,12]. Complexation was also found important for adsorption of ammonia on metal organic frameworks, MOF, or on their composites with GO [7]. For instance, on Cu-BTC or on MOF-5 the adsorption capacities of ammonia in dry conditions reached 115 mg/g [13] and 6 mg/g [14], and on their composites with GO—149 mg/g [13] and 82 mg/g [14], respectively. The chemical complexation reactions lead to the collapse of MOF and thus prevents the large scale industrial application of MOF or their composites as ammonia adsorbents. The mechanism and the extent of ammonia adsorption was also found important for the development of sensing devices based on ZnO/SiO₂ [15], Ag-doped γ -Fe₂O₃/SiO₂ [16], graphene [17] and S- and N-co-doped nanoporous carbons [18].

Generally, the presence of moisture in air from which ammonia has to be removed was found as beneficial for the separation process. Water, when adsorbed in the pores of rich surface chemistry, promotes the dissociation of acidic groups and protonation of ammonia, thus enhancing its reactivity with the surface [2]. Moreover, owing to the high solubility of ammonia in water, it can be also removed in the dissolved state [2,4,7]. Nevertheless, the latter process leads to the fast removal of ammonia from the pore system when the adsorbent is exposed to air (drying). This weak adsorption is a big disadvantage of the separation process, which can result to the secondary air pollution/exposure to hazardous conditions.

Therefore, based on the above, the objective of this paper is an analysis of resorcinol/formaldehyde (RF) polymeric resins as adsorbents of ammonia. They are obtained by catalyzed sol–gel polymerization of resorcinol/formaldehyde mixtures in basic conditions, and their surface is rich in polar and reactive oxygen groups. While the porosity and these groups are expected to enhance adsorption, the hydrophobicity of the aromatic chains formed during the cross-linking of the monomers might contribute to water repelling and thus might lead to a decrease in ammonia solubility in the pore system. Moreover, the polymeric nature of resins and the abundance of acidic groups might affect the structure/chemistry of the bentonite used as a binder and thus, by synergy, might affect ammonia adsorption. Additionally, insensitivity of ammonia adsorption on the humidity level is important for their application as separation media.

2. Experimental

2.1. Materials

Nanoporous resorcinol/formaldehyde (RF) polymeric resins were synthesized by the conventional sol–gel polymerization of

resorcinol (R) and formaldehyde (F) in water (W), using sodium carbonate (C) as catalyst. Details of the synthesis have been reported elsewhere [19,20]. Briefly, the precursors (molar ratios R/C 200, R/W 0.06 and R/F 0.5) were mixed under magnetic stirring and immediately heated in airtight sealed glass vessels for gelation/aging at different temperatures (ca. 85, 90, 95 °C) for 4 h in a conventional oven. After completion of the gelation/aging step, the resulting hydrogels were dried at 150 °C for 12 h without solvent removal. The nanoporous RF resins are labeled as RF-*T*, where *T* is the temperature of the gelation/aging step. Thus RF-85, RF-90 and RF-95 are RF resins aged at 85, 90 and 95 °C, respectively.

Owing to the powder nature of the resins they are not suitable for their application in an as-received forms as adsorbents in the dynamic conditions (pressure drop in the adsorbent bed), hence bentonite (Swy-2; the source clay minerals repository, University of Missouri (Columbia, MO); CEC 76.4 meq/100 g [21]) was used as a binder. The resins were mixed in distilled water with 10 wt.% bentonite until a homogeneous paste was formed and dried at 120 °C. After drying, the materials was crushed and sieved to get the resin/binder composites in a pelletized form and controlled particle size. The resin/bentonite composites are labeled as RF-T-B, where-B stands for the bentonite.

2.2. Methods

2.2.1. NH₃ breakthrough dynamic test

Ammonia adsorption capacity was measured at dynamic condition at room temperature [4]. Ammonia diluted in dry or moist air (70% humidity) was passed through a fixed bed of an adsorbent, which contained about 2 cm³ of the adsorbent particles (1–2 mm in diameter). The total flow rate of 1,000 ppm ammonia in air was 225 mL/min. Breakthrough tests were arbitrarily stopped at 100 ppm (sensor limit). Then desorption tests were carried out by purging the adsorbent bed with carrier air. An electrochemical sensor (Multi-Gas Monitor ITX system) was used to measure an ammonia concentration in the outlet gas.

The adsorption capacity was calculated in mg per g of sorbent and in mg per a unit volume of the bed using the difference between the inlet and outlet concentrations, the inlet flow rate, the breakthrough time and the ammonia molar mass. The experiments were performed either in dry (-ED) or in moist conditions after two hours pre-humidification (-EPM) to evaluate the influence of water on the performance of adsorbents. The spent adsorbents were labeled as -ED (exhausted in dry conditions) or -EPM (exhausted in moist conditions).

2.2.2. Potentiometric titration

Potentiometric titration was performed using a DMS Titrand 888 automatic titrator (Metrohm) set at the mode to collect the equilibrium pH. The initial samples and those exposed to ammonia (0.05 g) were dispersed in NaNO₃ (25 mL, 0.01 M) in a container maintained at 25 °C, equilibrated overnight and continuously saturated with N₂. 0.1000 M NaOH was used as a titrant. The experimental pH window was 3–10. The samples were acidified with HCl. The collected data was transformed into a proton binding curve, *Q*, representing the total amount of protonated sites. The following integral equation relates it to the p*K*_a distribution:

$$Q(\text{pH}) = \int_{-\infty}^{\infty} q(\text{pH}, \text{p}K_a) f(\text{p}K_a) d\text{p}K_a \quad (1)$$

SAIEUS numerical procedure [22,23] applying regularization combined with non-negativity constraints was used to solve this equation. The initial pH of the suspension is discussed as a surface pH value.

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