Journal of Hazardous Materials 305 (2016) 96-104

<http://dx.doi.org/10.1016/j.jhazmat.2015.11.022>

Moisture insensitive adsorption of ammonia on resorcinol-formaldehyde resins

Mykola Seredych¹, Conchi Ania^{2*}, and Teresa J. Bandosz^{1*}

¹*Department of Chemistry, The City College of New York
160 Convent Avenue, New York, NY 10031, USA*

²*Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain*

TOC

*

Corresponding author. Tel: +1 212 650 6017; Fax: +1 212 650 6107. E-mail address: tbandosz@ccny.cuny.edu (T.J. Bandosz); conchi.ania@incar.csic.es (C. Ania)

16

17 **ABSTRACT**

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

30

31 *Keywords:* Resorcinol-formaldehyde resins; Porosity; Surface chemistry; NH₃ reactive
32 adsorption

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 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 in 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 lead 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 lead 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 hours 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/100g [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 paste 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. NH_3 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 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 dry conditions) or -EPM (exhausted moist conditions).

2.2.3. Potentiometric titration

Potentiometric titration was performed using a DMS Titrando 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 pK_a distribution:

$$Q(pH) = \int_{-\infty}^{\infty} q(pH, pK_a) f(pK_a) dpK_a \quad (1)$$

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.

2.2.4. Evaluation of porosity

Nitrogen adsorption isotherms were measured at -196 °C on ASAP 2020 (Micromeritics). Prior to measurements the samples (about 0.1 g) were heated at 120 °C and out-gassed until 10^{-4} Torr was reached. The BET surface area, total pore volumes, V_t , (from the last point of isotherm at relative pressure equal to 0.99) and micropore volume, V_{mic} (from DR equation) were calculated from the isotherms.

2.2.5. Elemental Analysis

The content of carbon, hydrogen and nitrogen was measured on LECO CHNS-932 and the content of oxygen on LECO VTF-900.

2.2.6. Infrared Spectroscopy

FTIR analyses were carried out on the initial and exposed to ammonia samples on a Nicolet Magna-IR 830 spectrometer with the attenuated total reflectance method (ATR) on the powdered samples (without KBr addition).

2.2.7. X-ray Diffraction (XRD)

XRD measurements were conducted on a Phillips X'Pert X-ray diffractometer. The samples were ground with methanol in an agate mortar and then the mixture were smear-mounted and analyzed using $\text{Cu}_{K\alpha}$ radiation (tension -40 kV and current -40 mA).

3. Results and Discussion

The direct results of the breakthrough tests are presented in Figure 1. We have to mention here that on bentonite, at the same experimental conditions the negligible breakthrough capacities (3.3 and 5.1 mg/g of ammonia in dry and moist conditions, respectively) were measured [24]. As mentioned in the experimental part, the powder nature of resins did not allow for their direct evaluation as ammonia adsorbents in dynamic adsorption tests due to pressure constraints in the adsorbent bed; the addition of a binder to form pellets was the only way of their utilization in this process. The gaps between the adsorption and desorption branches of the breakthrough curves -arbitrary stopped at 100 ppm- are related to the weak adsorption of ammonia. The larger gap, the weaker is the adsorption of ammonia on the surface. The results show the weak adsorption on all samples in all conditions but on RF-85-B measured in the moist conditions. For this sample after the stop of the ammonia flow a decrease in its concentration was measured. Then a small increase followed by a steep decrease is noticed (inset Figure 1). Similar trends but with a much larger increase in ammonia concentration can be seen for RF-90-B run either dry or moist conditions. Moreover, for RF-85-B and RF-90-B the adsorption of ammonia in dry condition seems to be stronger than that in moist conditions, which is an opposite behavior to that of activated carbons [2, 4] or MOFs [7, 13, 14]. That specific shape of the desorption curve suggests the complexity of the adsorption mechanism.

Figure 1. Ammonia breakthrough curves measured in dry and moist conditions (inset: magnification of desorption branches for RF-85-B and RF-90-B at different scale).

The calculated breakthrough capacities along with the amount of water preadsorbed and the changes in surface pH are listed in Table 1. While the capacities for RF-85-B in the moist and dry conditions are almost the same, RF-90-B and RF-95-B reveal 25% and 46% increases in the amount of ammonia adsorbed in the moist conditions, respectively. Interestingly, the affinity for water adsorption on RF-85-B and RF-90-B are similar and only on RF-95-B about 40% more water than on the other two samples is adsorbed (Table 1).

Table 1. The NH₃ breakthrough capacities, water adsorbed and the pH values for the samples run in dry and moist conditions.

Sample	NH ₃ Breakthrough capacity		H ₂ O adsorbed (mg/g of ads.)	pH	
	(mg/g of ads.)	(mg/cm ³ of ads.)		Initial	Exhausted
RF-85-B-ED	33.2	11.7	---	4.22	7.54
RF-85-B-EPM	31.0	10.5	148.6	4.22	7.75
RF-90-B-ED	30.5	10.0	---	3.84	7.59
RF-90-B-EPM	38.0	12.4	147.8	3.84	7.94
RF-95-B-ED	25.7	8.3	---	4.24	7.34
RF-95-B-EPM	37.6	11.3	234.3	4.24	7.95

Apparently, the results obtained do not follow the trend found for other adsorbents where the amount of ammonia adsorbed was found to increase linearly with the amount of water retained in the pores [1]. This is owing to an increase in ammonia adsorption owing to its dissolution in the film of water adsorbed in the pore system. It makes some adsorbents useable only at very high humidity levels. It should also be noted that in all cases the

marked increase in the surface pH was found after ammonia adsorption (neutralization), and all initial samples have a similar surface pH values (acidic).

To understand this behavior the detailed surface characterization of the initial RF resins and their mixtures with bentonite was carried out. This was done to link the behavior to a possible synergistic effect of the binder addition. Since surface chemistry is considered as important for ammonia adsorption, the stress of our analyses is placed on these properties. The FTIR results are collected in Figure 2 where the typical spectrum for bentonite binder is also included.

Here the bands at 792 cm^{-1} , 985 cm^{-1} , 1400 cm^{-1} , 1630 cm^{-1} and 3610 cm^{-1} represent the vibrations of Al-O, Si-O, CO_3^{2-} species, OH of the water molecules and structural OH groups, respectively. The spectra for all three RF resins are very similar with sharp bands at 1085 cm^{-1} , 1210 cm^{-1} , 1470 cm^{-1} and 1600 cm^{-1} representing C-O vibrations from methylene oxide groups, C-OH groups, C-H bending modes in methylene ether bridges, and C=C stretching from the aromatic ring mode conjugated carbonyl and carboxylate groups, respectively [25]. The peaks below 950 cm^{-1} might be due to aromatic C-H bending vibrations.

A broad band between 3220 and 3600 cm^{-1} is linked to OH vibrations, either in water or from surface groups. After the addition of bentonite the bands characteristic for both materials can be clearly distinguished. The sharp band of bentonite at 3610 cm^{-1} representing the structural OH groups is hardly seen with the minimal intensity. These results suggest the physical mixture between the binder and RF resins.

Figure 2. FTIR spectra for the initial samples and those after NH_3 adsorption.

The interpretation of the spectra for the samples exposed to ammonia is rather difficult owing to the fact that the N-H stretching vibration of ammonia should be between 3200-

3500 cm^{-1} [26] and it is also the region where water and OH groups are expected to vibrate. Indeed, after the experiments run in the presence of water, a significant increase in the intensity of the broad band between 3200 and 3600 cm^{-1} is noticed. Interestingly, a sharp band at about 3600 cm^{-1} related to OH also is more intense than that for the initial RF resins-bentonite hybrids. NH_4^+ bending vibrations are expected at 1430 cm^{-1} , which is close to the vibrations of methylene ether bridges present in the materials. Nevertheless, the spectra for the exhausted samples clearly show the broadening of the bands in this region for all samples supporting the existence of ammonium ions in the exhausted samples in both dry and wet conditions, suggesting reactive adsorption.

Following the FTIR findings, potentiometric titration experiments were performed. The proton binding curves and the pK_a distributions for the species present on the surfaces are presented in Figure 3 and Table 2, respectively. Interestingly here, the proton binding curves show the changes in the chemistry of RF-85 and RF-90 upon addition of bentonite. It is especially visible in an increase in the number of groups dissociating over pH 8. The extent of these changes is reverse to the differences found between the amount of ammonia adsorbed in moist and dry conditions. After ammonia adsorption the surface is much more basic and once again a peculiar trend is noticed in the relative position of the proton binding curves (for RF-85-B the amount of groups accepting proton is larger in dry (RF-85-B-ED) conditions than that measured in moist (RF-85-B-EPM) ones. This difference diminishes for RF-90-B-ED and RF-90-B-EPM, and is reverse for RF-95-B-ED and RF-95-B-EPM).

Figure 3. Proton binding curves for the initial and exhausted samples.

Since the amount of bentonite added was the same for each sample, these differences are expected to be linked to the differences in the chemistry of xerogels. Even though the differences in the initial pH are not very visible (3.91, 3.84 and 3.85 for RF-85, RF-90 and RF-95, respectively), the numbers of acidic groups detected on the surface differ markedly and it increases in the following order: RF-85 < RF-90 < RF-95 (Table 2). The latter has 35% more acidic groups than has RF-85. The groups detected on the surface must include the carbonyl, phenolic/hydroxyl groups from the RF resins and acidic groups related to aluminosilicate layers from bentonite [27]. The latter should be in minority since the potentiometric titration of bentonite reported elsewhere revealed only 0.210 mmol/g of surface acidic groups with the surface pH in the basic range (pH is 8.78 [24]). Apparently, the addition of bentonite had the more pronounced effects on the average chemistry of the less acidic RF resins and its addition increased the number of acidic groups on the surface of the hybrids based on RF-85, RF-90 and the RF-95 by 69 %, 20 % and 11 %, respectively. That increase for RF-85-B is especially visible in the range of weak acidic groups. The only plausible explanation at this stage of our study is that the interlayer acidic groups of bentonite became somehow available for the release of proton. This might be caused by partial exfoliation of bentonite layers. This process likely happens on the interface between the binder and resins. The oxygen-containing groups of the latter are able to enter and expand the interlayer space of the former. Nevertheless, the adsorption of ammonia on our materials seem to be very complex since there is not linear relationship between the amount adsorbed in each category of experimental set up, and the number of acidic groups on the surface. Taking into account the basicity of ammonia, these groups are expected to be the main NH_3 anchoring centers.

259 **Table 2.** Peak position and numbers of groups (in parentheses; [mmol/g]).

260

Sample	pH	pK _a 4-5	pK _a 5-6	pK _a 6-7	pK _a 7-8	pK _a 8-9	pK _a 9-10	pK _a 10-11	All
RF-85	3.91	4.17 (0.127)	5.29 (0.072)	6.51 (0.199)	7.96 (0.196)	8.87 (0.188)	10.00 (0.489)	11.14 (0.892)	2.163
RF-85-B	4.22	4.22 (0.125)	5.22 (0.136)	6.39 (0.171)	7.77 (0.320)		9.31 (0.528)	11.14 (2.378)	3.658
RF-85-B-ED	7.54	4.11 (0.165)	5.10 (0.173)	6.17 (0.167) 6.98 (0.202)		8.03 (0.303)	9.30 (1.467)	11.09 (2.617)	5.094
RF-85-B-EPM	7.75	4.34 (0.176)	5.42 (0.145)	6.93 (0.244)		8.11 (0.240)	9.22 (1.322)	10.62 (1.286)	3.413
RF-90	3.84	4.25 (0.154)	5.81 (0.138)	6.59 (0.115)	7.76 (0.175)	8.45 (0.209)	9.79 (0.502)	11.15 (1.296)	2.589
RF-90-B	4.15	4.44 (0.092)	5.01 (0.098)	6.24 (0.202)	7.61 (0.282)	8.47 (0.209)	9.66 (0.575)	11.15 (1.628)	3.086
RF-90-B-ED	7.59	4.27 (0.186)	5.16 (0.147)	6.31 (0.159)	7.15 (0.201)	8.24 (0.335)	9.37 (1.506)	11.12 (2.560)	5.094
RF-90-B-EPM	7.94	4.52 (0.199)	5.24 (0.071)	6.34 (0.177)	7.38 (0.238)	8.55 (0.369)	9.38 (1.322)	11.10 (1.713)	4.089
RF-95	3.85	4.36 (0.152)	5.77 (0.125)	6.60 (0.203)	7.92 (0.307)		9.10 (0.295) 9.96 (0.495)	11.10 (1.349)	2.926
RF-95-B	4.24	4.33 (0.095)	5.17 (0.130)	6.50 (0.236)	7.72 (0.247)	8.59 (0.241)	9.62 (0.605)	11.08 (1.717)	3.271
RF-95-B-ED	7.34	4.50 (0.224)	5.82 (0.213)	6.65 (0.113)	7.40 (0.236)	8.63 (0.516)	9.53 (1.125)	11.10 (1.890)	4.317
RF-95-B-EPM	7.95	4.53 (0.207)	5.90 (0.207)	6.75 (0.093)	7.36 (0.201)	8.51 (0.343)	9.40 (1.242)	11.09 (1.601)	3.894

The pK_a distributions (Table 2) for the samples exposed to ammonia clearly show an increase in the number of groups having pK_a between 9 and 10. We link them to the appearance of ammonium ions (pK_a value of ammonium hydroxide is 9.25) [28] indicating acid-base reactions as the main reactive adsorption mechanism. In Table 3 we list the amounts of these new surface species in mmol per gram of an adsorbent and we compared them to the amount of NH_3 adsorbed based on the breakthrough tests. For this comparison one has to remember that the titration experiments are carried out after desorption of weakly adsorbed ammonia, which was generally more pronounced in the experiments run in moist conditions. For RF-85-B, regardless the conditions, about 75 % of adsorbed ammonia is in NH_4^+ . For the other two samples a significantly higher reactivity is found in dry conditions than those in moist ones, suggesting that adsorbed water in this case blocks some reactive sites for ammonia and thus limits the available surface where reactions can take place.

Table 3. Comparison of the amount of ammonia adsorbed to the amount of ammonia reacted with the surface groups.

Sample	NH_3 adsorbed (mmol/g)	NH_4^+ (mmol/g)	$pK_a < 7$ (mmol/g)	$pK_a > 7$ (mmol/g)	Total acidic groups (mmol/g)	NH_4^+/NH_3
RF-85			0.398	1.765	2.163	
RF-85-B			0.432	3.226	3.658	
RF-85-B-ED	1.953	1.467	0.707	4.387	5.094	0.75
RF-85-B-EPM	1.824	1.322	0.565	2.848	3.413	0.73
RF-90			0.407	2.182	2.589	
RF-90-B			0.392	2.694	3.086	
RF-90-B-ED	1.794	1.506	0.492	4.602	5.094	0.84

RF-90-B-EPM	2.235	1.322	0.447	3.642	4.089	0.59
RF-95			0.480	2.446	2.926	
RF-95-B			0.461	2.810	3.271	
RF-95-B-ED	1.512	1.125	0.550	3.767	4.317	0.74
RF-95-B-EPM	2.212	1.242	0.507	3.387	3.894	0.56

277

278 The question arises why ammonia adsorption on RF-85-B is insensitive in the presence of
279 water in the system, even though this sample has the highest number of acidic groups,
280 which are expected to be hydrophilic. Interestingly the chemical analysis showed that this
281 RF resin has the lowest content of oxygen (Table 4), although no marked differences in
282 the content of oxygen are found. The similarities in the total oxygen content for all resins
283 and the differences in the number of acidic groups, which in fact are expected to be
284 oxygen based, for hybrid materials suggest that RF-90-B and RF-95-B have a significant
285 number of polar groups not acidic/basic in their nature. Based on the chemical
286 composition of RF resins their surface groups are expected to be both phenolic and ether
287 oxygen groups [19, 20]. From those only the former one should have a weakly acidic
288 character. The latter groups, on the other hand, attract water without providing protons
289 needed for formation of ammonium ions. Bentonite, on the other hand, can provide some
290 oxygen groups originating from its aluminosilicate layers. As the studied resins were
291 prepared using the same formulation (in terms of R/F, R/C and R/W molar ratio), the
292 differences in the surface chemistry must be related to the temperature during the
293 gelation/aging step. As mentioned above, the sol–gel mechanism is initiated by the
294 addition reaction of the RF precursors and cluster growth. While the addition reaction is
295 controlled by the molar ratios used in the precursor's mixture, the rate of the clusters

growth and cross-linking depends on the temperature of the gelation/aging [20]. The increase in the temperature would favor the formation of branched clusters with higher amounts of ether-bridges connecting the aromatic units. However above 85 °C, the fast evaporation rate of the aqueous medium and the changes in the dissociation constants of water and resorcinol (hence modifying the pH) may provoke a phase de-mixing that would affect the development of porosity and the cross-linking arrangement of the monomers. This would explain the fact that RF-85 is the richest in the number of OH groups, despite its lowest oxygen content (Table 4).

Table 4. Elemental analysis for the materials studied (in wt. %).

Sample	C	O	H
RF-85	65.53	29.98	4.47
RF-90	64.10	31.56	4.31
RF-95	62.58	33.09	4.31

Even though a water film can be formed on ether groups in the pore system, ammonia can be only dissolved in it, resulting in an increase in the weak adsorption. The acidic groups, on the contrary, even though they are also polar and thus attract water, dissociate leading to acid-base reactions. The same reaction, however direct, happens in the dry conditions and this is a hypothesized scenario on the RF-85-B hybrid material.

As suggested above, the presence of phenol/hydroxyl groups in the polymeric chains could cause a partial exfoliation of the polymer chains between the clay layers, especially in the case of RF-85-B, for which a significant increase in acidity was found. X-Ray

patterns collected in Figure 4 provide a direct proof for this exfoliation process. For all initial resin/bentonite hybrids, at the diffraction angle when d_{001} of bentonite should be seen (see diamond in Figure 4) only broad peaks are revealed supporting the loss of ordered structure. On the other hand, after adsorption of ammonia at moist conditions the rearrangement of the clay layers is clearly seen by the peak at 7.1° representing $d_{001}=1.23$ nm. This might happen as a result of the reaction of ammonia with phenolic/hydroxyl groups and thus their withdrawal from the clay interlayer space. Interestingly, we do not observe the d_{001} peaks of bentonite after adsorption in dry conditions. This suggests that water in the system promotes the reaction of ammonia with the resin functional groups on the interface between resin and the binder.

Not without importance are the differences in the porosity of the original RF resins. The nitrogen adsorption isotherms collected in Figure 5 show the characteristic shape for micro/mesoporous materials. Based on the complex shapes of the hysteresis loops, the mesopores are structurally very heterogeneous and they are more complex in RF-85 than in RF-95. RF-90 has the porosity in-between the two other samples. From all three samples, RF-85 is the most porous with the highest surface area and the volume of micropores. These factors contribute to the high dispersion of oxygen on the surface. That oxygen is either in groups contributing from phenols or ether. Regarding the polar groups, their high surface dispersion decreases the probability of the pore blocking by water and should allow the migration of ammonia to the surface acidic groups when the adsorption is run in moist conditions.

Figure 4. XRD pattern for the initial RF resins, with bentonite (B) and after ammonia adsorption (diamond: d_{001} peak of bentonite).

The addition of bentonite changes the porosity drastically and once again the biggest change (a decrease) in surface area is found for RF-85-B (47%) followed by RF-90-B (40%) and RF-95-B (37%). This effect is linked to the blocking of small pores in RF resins by attached bentonite layers. Exfoliation of these layers increases the extent of surface area by increasing the contact/interface with the surface of RF resins. After ammonia adsorption further decrease in surface area and porosity is noticed in a whole range of pore sizes (Figure 5 and Table 5) owing to blocking of some pores by the products of surface reactions and by reversal of the exfoliation process. The decrease is more pronounced after ammonia adsorption in moist conditions, which can be linked to the increased amount of NH_3 adsorbed, especially for RF-90-B and RF-95-B. A decrease in the surface area for RF-85-B with similar amounts of NH_3 adsorbed at both conditions might be linked to a change in bentonite/RF interface as a result of interaction with ammonia. That sample was originally most acidic and exposure to ammonia affects its surface chemistry to greatest extent.

353

354 **Figure 5.** N_2 adsorption isotherm at $-196\text{ }^{\circ}\text{C}$ for the materials studied.

Table 5. The parameters of porous structure calculated from nitrogen adsorption measurements.

Sample	S_{BET} (m^2/g)	V_{t} (cm^3/g)	V_{meso} (cm^3/g)	V_{mic} (cm^3/g)
RF-85	526	0.49	0.35	0.14
RF-85-B	277	0.25	0.18	0.07
RF-85-B-ED	246	0.22	0.16	0.06
RF-85-B-EPM	204	0.17	0.12	0.05
RF-90	485	0.45	0.33	0.12
RF-90-B	289	0.26	0.19	0.07
RF-90-B-ED	252	0.24	0.18	0.06
RF-90-B-EPM	186	0.16	0.11	0.05
RF-95	476	0.42	0.30	0.12
RF-95-B	300	0.29	0.22	0.07
RF-95-B-ED	280	0.27	0.21	0.06
RF-95-B-EPM	201	0.18	0.13	0.05

A peculiar trend in ammonia concentration during the desorption process (a spike on the desorption curves on RF-85-B and on RF-90-B) can be explained by the removal of ammonia adsorbed on the centers of various adsorption energies and thus the differences in the kinetic of the desorption process (Figure 1). Apparently, there is a delay in the desorption of ammonia from the surfaces of these two samples and the effect is stronger for the most acidic samples and it decreases with a decrease in surface acidity. This effect can be related to removal of ammonia interacting with the acidic centers of exfoliated clay layers (aluminosilicates). Since these centers can be at the interface between the

resin and clay phases, they can be located in small pores and besides exhibiting strong adsorption energy, their location can also contribute to the observed behavior. This effect is not observed in the moist conditions since here the removal of water with dissolved ammonia governs the desorption process at the beginning.

4. Conclusions

This paper shows that, upon addition of the clay binder, phenolic resins of specific composition/surface chemistry can be used as efficient adsorbents of ammonia. Their original powdered form excludes their application in a pristine form in dynamic conditions. An important finding is that the amount adsorbed is relatively high and it might not be affected by the presence of moisture in air. This scenario happens when a resin with a high number of acidic/phenolic functionalities is used. Its chemical and morphological composition allows the exfoliation of the clay binder resulting in an increase in the number of acidic groups, which are strong adsorption centers for ammonia in dry conditions. Polar oxygen groups also increase the amount of ammonia adsorbed, although the adsorption is weak. Moreover, they attract water in the moist conditions promoting dissolution of ammonia in water film. The majority of ammonia is adsorbed following acids-base reactions with surface functional groups. Even though, taking into account the stability of our hybrid adsorbent (bentonite swelling in water and a low thermal stability of resin) the conventional regeneration (through ion exchange or heat treatment) over consecutive cycles seemed rather not feasible, it is interesting to point out that the spent adsorbents of basic properties have a potential to be used as an acidic gases separation media.

Acknowledgments

This work was partially supported by the Spanish MINECO (CTM2014/56770-R). COA thanks her Salvador de Madariaga Mobility Action (PRX12/00290).

References

- [1] M. Seredych, A. V. Tamashausky, T. J. Bandoz, Graphite oxides obtained from porous graphite: The role of surface chemistry and texture in ammonia retention at ambient conditions, *Adv. Fun. Mater.* 20 (2010) 1670-1679.
- [2] T. J. Bandoz, Towards understanding reactive adsorption of small molecule toxic gases on carbonaceous materials, *Catal. Today* 186 (2012) 20-28.
- [3] M. Goncalves, L. Sanchez-Garcia, E. de Oliveira Jardim, J. Silvestre-Albero, F. Rodriguez-Reinoso, Ammonia removal using activated carbons: Effect of the surface chemistry in dry and moist conditions, *Environ. Sci. Technol.* 45 (2011) 10605-10610.
- [4] T. J. Bandoz, C. Petit, On the reactive adsorption of ammonia on activated carbons modified by impregnation with inorganic compounds, *J. Coll. Interf. Sci.* 338 (2009) 329-345.
- [5] A. M. B. Furtado, Y. Wang, M. D. LeVan, Carbon silica composites for sulfur dioxide and ammonia adsorption, *Micropor. Mesopor. Mater.* 165 (2013) 48-54.
- [6] A. M. B. Furtado, J. Liu, Y. Wang, M. D. LeVan, Mesoporous silica-metal organic composite: synthesis, characterization, and ammonia adsorption, *J. Mater. Chem.* 21 (2011) 6698-6706.

- 410 [7] C. Petit, T. J. Bandoz, Engineering the surface of a new class of adsorbents: Metal-
411 organic framework/graphite oxide composites, *J. Coll. Interf. Sci.* 447 (2015) 139-151.
- 412 [8] H. Jasuja, G. W. Peterson, J. B. Decoste, M. A. Browe, K. S. Walton, Evaluation of
413 MOFs for air purification and air quality control applications: Ammonia removal from air.
414 *Chem. Eng. Sci.* 124 (2015) 118-124.
- 415 [9] J. F. Van Humbeck, T. M. McDonald, X. Jing, B. M. Wiers, G. Zhu, J. R. Long,
416 Ammonia capture in porous organic polymers densely functionalized with Brønsted acid
417 groups, *J. Am. Chem. Soc.* 136 (2014) 2432-2440.
- 418 [10] C. Petit, K. Kante, T. J. Bandoz, The role of sulfur-containing groups in ammonia
419 retention on activated carbons, *Carbon* 48 (2010) 654-667.
- 420 [11] M. Seredych, C. Petit, A. V. Tamashausky, T.J. Bandoz, Role of graphite precursor
421 in the performance of graphite oxides as ammonia adsorbents, *Carbon* 47 (2009) 445-456.
- 422 [12] C. Petit, C. Karwacki, G. Peterson, T. J. Bandoz, Interactions of ammonia with the
423 surface of microporous carbon impregnated with transition metal chlorides, *J. Phys.*
424 *Chem. C* 111 (2007) 12705-12714.
- 425 [13] C. Petit, B. Mendoza, T. J. Bandoz, Reactive adsorption of ammonia on Cu-based
426 MOF/graphene composites, *Langmuir* 26 (2010) 15302-15309.
- 427 [14] C. Petit, T. J. Bandoz, Enhanced adsorption of ammonia on metal-organic
428 framework/graphite oxide composites: Analysis of surface interactions, *Adv. Funct.*
429 *Mater.* 20 (2010) 111-118.
- 430 [15] S.-Y. Wang, J.-Y. Ma, Z.-J. Li, H. Q. Su, N. R. Alkurd, W.-L. Zhou, L. Wang, B.
431 Du, Y.-L. Tang, D.-Y. Ao, S.-C. Zhang, Q. K. Yu, X.-T. Zu, Surface acoustic wave

- 432 ammonia sensor based on ZnO/SiO₂ composite film, J. Hazard. Mater. 285 (2015) 368-
433 374.
- 434 [16] Y. Tang, Z. Li, X. Zu, J. Ma, L. Wang, J. Yang, B. Du, Q. Yu, Room-temperature
435 NH₃ gas sensors based on Ag-doped γ -Fe₂O₃/SiO₂ composite films with sub-ppm
436 detection ability, J. Hazard. Mater. 298 (2015) 154-161.
- 437 [17] Y. Wang, L. Zhang, N. Hu, Y. Wang, Y. Zhang, Z. Zhou, C. Peng, Ammonia gas
438 sensors based on chemically reduced graphene oxide sheets self-assembled on Au
439 electrodes, Nanoscale Res. Lett. 9 (2014) 251.
- 440 [18] N. A. Travlou, M. Seredych, E. Rodríguez-Castellón, T. J. Bandoz, Insight into
441 ammonia sensing on heterogeneous S- and N- co-doped nanoporous carbons, Carbon
442 2015, doi:10.1016/j.carbon.2015.10.049.
- 443 [19] R. W. Pekala, Organic aerogels from the polycondensation of resorcinol with
444 formaldehyde, J. Mater. Sci. 24 (1989) 3221-3227.
- 445 [20] E. Isaacs-Paez, M. Haro, E. J. Juarez-Perez, R. J. Carmona, J. B. Parra, R. Leyva-
446 Ramos, C. O. Ania, Fast synthesis of micro/mesoporous xerogels: textural and energetic
447 assessment, Microp. Mesop. Mater. 209 (2015) 2-9.
- 448 [21] <http://cms.lanl.gov/chem.htm>.
- 449 [22] J. Jagiello, Stable numerical solution of the adsorption integral equation using
450 splines, Langmuir 10 (1994) 2778-2785.
- 451 [23] J. Jagiello, T. J. Bandoz, J. A. Schwarz, Carbon surface characterization in terms of
452 its acidity constant distribution, Carbon 32 (1994) 1026-1028.

- [24] M. Seredych, A. V. Tamashausky, T. J. Bandosz, Surface features of exfoliated graphite/bentonite composites and their importance for ammonia adsorption, *Carbon* 46 (2008) 1241-1252.
- [25] M. C. Gutiérrez, F. Rubio, F. del Monte, Resorcinol-formaldehyde polycondensation in deep eutectic solvents for the preparation of carbons and carbon-carbon nanotube composites, *Chem. Mater.* 22 (2010) 2711-2719.
- [26] J. Zawadzki, M. Wisniewski, In situ characterization of interaction of ammonia with carbon surface in oxygen atmosphere, *Carbon* 41 (2003) 2257-2267.
- [27] G. Kortum, W. Vogel, K. Andrusso, Dissociation constants of organic acids in aqueous solutions, Butterworth, London, 1961.
- [28] M. Seredych, T. J. Bandosz, Removal of ammonia by graphite oxide via its intercalation and reactive adsorption, *Carbon* 45 (2007) 2130-2132.

Captions to the Tables

Table 1. The NH_3 breakthrough capacities, water adsorbed and the pH values for the samples run in dry and moist conditions.

Table 2. Peak position and numbers of groups (in parentheses; [mmol/g]).

Table 3. Comparison of the amount of ammonia adsorbed to the amount of ammonia reacted with the surface groups.

Table 4. Elemental analysis for the materials studied (in wt. %).

Table 5. The parameters of porous structure calculated from nitrogen adsorption measurements.

Captions to the Figures

Figure 1. Ammonia breakthrough curves measured in dry and moist conditions (inset: magnification of desorption branches for RF-85-B and RF-90-B at different scale).

Figure 2. FTIR spectra for the initial samples and those after NH_3 adsorption.

Figure 3. Proton binding curves for the initial and exhausted samples.

Figure 4. XRD pattern for the initial RF resins, with bentonite (B) and after ammonia adsorption (diamond: d_{001} peak of bentonite).

Figure 5. N_2 adsorption isotherm at -196°C for the materials studied.