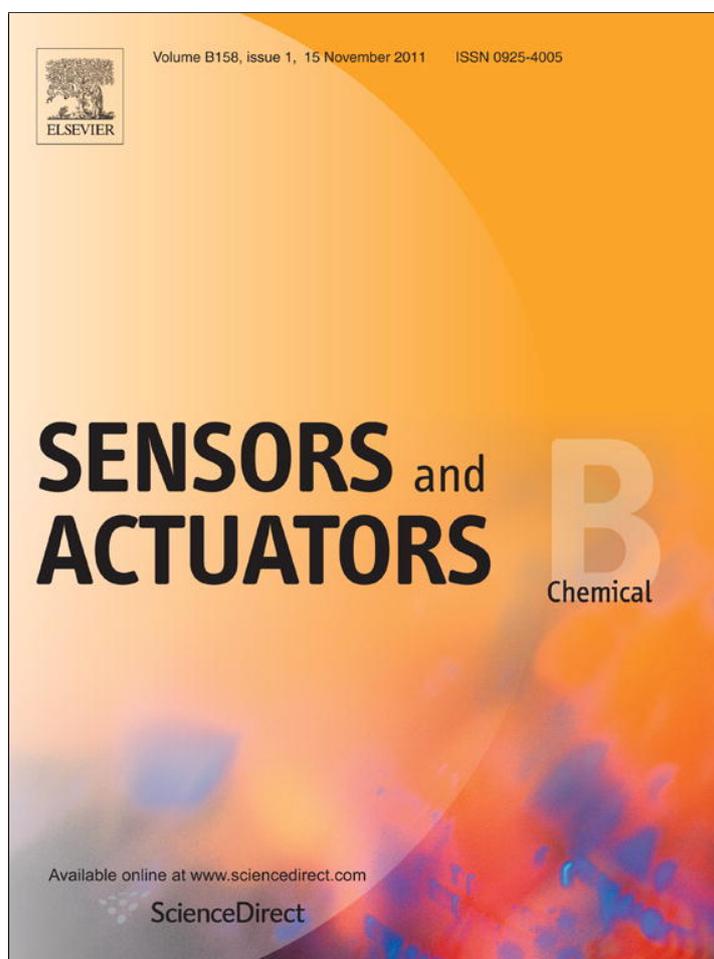


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Ammonia traces detection based on photoacoustic spectroscopy for evaluating ammonia volatilization from natural zeolites at typical crop field temperature

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ABSTRACT

A Brazilian sedimentary zeolite-containing microporous material was characterized by determining its physical and chemical properties (surface area, pore volume, dinitrogen and ammonia desorption rates, oxide composition, and acid site characterization), and compared with two commercial natural zeolites. The characterization of these materials was performed using N₂ adsorption, X-ray fluorescence spectroscopy and temperature programmed desorption (TPD) techniques. Using photoacoustic spectroscopy, the performance of these microporous materials in the adsorption and delayed desorption of nitrogen-containing fertilizers was studied by monitoring the ammonia emission rate after their treatment with ammonium sulfate. Ammonia desorption curves were recorded under 30 °C and 60 °C, aiming to reproduce typical Brazilian cropfield temperature conditions.

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1. Introduction

It is no longer questioned that present-day agricultural practices play a significant role in the unbalancing of the nitrogen cycle, especially the widespread application of fertilizers, which results in plenty of nitrous oxide (N₂O) and ammonia (NH₃) outputs [1–3]. The great amount of greenhouse gases such as N₂O and methane (CH₄) produced by agricultural activities have emerged again the discussion on how to reduce gas emissions from agricultural practices. Other environmental damages that are also related to the use of fertilizers are the pollution of freshwater reservoirs and the degradation of the air quality, which entail eutrophication and acid rain, respectively. Furthermore, although the demand for food has been increasing rapidly, the production of fertilizers does not follow with the same rate [4,5]. Consequently, the improvement of an efficient use of fertilizers is a relevant contribution from the economical and environmental point of view to a sustainable large-scale agriculture [6,7].

The extent of arable land is insufficient for the infinite expansion of food production, but it is likely that South America can fulfil the promise of supplying the world's increasing requirement for food. Brazil, for instance, has an enormous potential for food production and a large part of its economy is based on agricultural practices, such as the large-scale production of soy bean, fruits and green automobile fuel crops. Nevertheless, due to the heavy rain regimen and high daytime-temperatures, Brazilian soils are typically acidic and poor in nitrogen compounds. The uncontrolled use of large amounts of nitrogen fertilizers is wasteful due to the high levels of ammonia volatilization in tropical soils and thus it is inefficient to remedy the acidity and lack of nitrogen in the typical Brazilian soil. Feasible alternatives for improving fertilizer lifetimes on the soil must be found in order to render agriculture more economically sound and environmentally friendly.

The speedy release process of fertilizers right after they are spreaded over the soil is one of the main causes of waste, which can happen by volatilization or by leaching. Therefore, the detailed knowledge of the kinetics of the volatilization of nitrogen-containing compounds is fundamental for promoting an appropriate usage of fertilizers as a source of nutrient for plants while avoiding excessive environmental damage. It has been shown that minerals like clays and zeolites can be used to control the

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release of fertilizer onto soils, notably at low cost [8]. Furthermore, natural zeolites can readily exchange ions like ammonium (NH_4^+), which is very important for plant feeding [9].

To evaluate and compare the ability of different zeolites to hold ammonium, it is necessary to study the physical and chemical properties of such materials. Studies must focus on factors which are essential in controlling the ion exchange capacity with various nitrogen sources, such as ammonium sulfate and urea, in real time, and under conditions that reproduce closely those that will be found in the crop fields.

Usually, studies on the kinetics of ion exchange with zeolites are performed entirely in the liquid phase. Using photoacoustic spectroscopy (PAS), it is possible to monitor the phase transition from sorbed molecules within the zeolite to the gas phase, *i.e.* their release to the atmosphere, which is the actual process occurring when fertilizers are used in the fields.

PAS is a useful trace gas analysing technique based on infrared spectroscopy with a simple experimental mounting. Its advantages are to be compact, straightforward operation, low cost and high selectivity, and it is highly sensitive. Photoacoustic spectroscopy in the mid-infrared range has found, nowadays, important applications in the detection of trace amounts of environmental and biological important gases such as methane, ammonia, nitrous oxide, ethylene, ozone, and nitric oxide [10–15].

Beginning in the 1970s, gas lasers (such as CO_2) have been increasingly used in photoacoustic spectroscopy as radiation source because of their high power and broad discrete emission range. However, this kind of radiation source demands extensive lab space and its operation can be cumbersome. Over the last few years, numerous applications in PAS have been presented using new solid-state lasers, such as diode lasers (distributed feedback-DFB), quantum cascade lasers and optical parametric oscillators. These sources of radiation operate typically with less power than gas lasers, but their reduced size, ease of operation, narrow and specific emission lines promise good results. As a consequence, many recent articles have shown impressive detection limits, as low as parts per billion (ppb) [10,11]. Nowadays, PAS is largely used for trace gas detection in many applications such as the monitoring of industrial and agricultural emissions [10].

In this work, a study of the chemical and physical properties of zeolite materials is reported together with an analysis of the ammonia–zeolite interaction investigated using PAS. Ammonium sulfate was used as nitrogen source and three different zeolites were assayed.

2. Materials and methods

Three microporous materials were used as ammonia holders: two natural zeolites from Cuba and Chile (furnished by Celta Brasil, Cotia, SP, Brazil) and a Brazilian sedimentary zeolite, produced from a naturally occurring mixture of clays, zeolite and quartz extracted from central-northern Brazil, provided by CETEM and CPRM (Rio de Janeiro, Brazil) [16]. The samples were analysed for physico-chemical properties such as specific surface area, chemical composition, and the strength of their surface acid sites. Photoacoustic spectroscopy was applied to monitor ammonia trace emission at room and near room temperatures (30°C and 60°C) from the materials after saturation treatment with an ammonium sulfate.

2.1. Photoacoustic spectroscopy

2.1.1. Fundamentals

Photoacoustic spectroscopy is a technique based on the infrared (IR) region (near and mid-infrared, 1–11 μm) widely used to

detect the emission of gases in trace levels. The absorption of infrared radiation by a molecule results in the activation of higher-energy rotational–vibrational modes which have specific absorption–energy values. Thus, a group of transitions gives a typical absorption pattern for each molecule, also called molecule fingerprint. The IR radiation is modulated at the resonance frequency of the photoacoustic (PA) cell in order to amplify the PA signal. During the relaxation, heat is transferred in the gas phase and the ensuing adiabatic expansion generates pressure waves, which are detected by microphones set inside the PA cell [18]. The main advantages of PAS are the real time monitoring (continuous flow), low cost, high selectivity, good sensitivity (on the ppb level), ease of operation, and the reduced size of the experimental apparatus.

2.1.2. Experimental setup

The excitation source used was a quantum cascade laser (QCL) [19], with emission wavenumber between 1045 and 1052 cm^{-1} tuned by temperature setting. No significant water absorption is observed in this spectral range, but problems related to ammonia desorption from the PA cell walls induced by water adsorption required the use of a cold trap to remove residual water from the gas samples [20]. In this particular experiment, such procedure has no effective influence on the sensitivity and selectivity of the sensor for detecting ammonia, since the cold trap was also used during the calibration of the PA cell.

For the spectral experiment, the QCL was excited with 20 ns of pulses at 400 kHz of repetition rate (duty cycle 0.8%), while for the concentration measurement experiments the duration of the pulse was altered to 50 ns (duty cycle 2%). A lock-in amplifier (Stanford Research Systems, model SR850) was used to modulate the laser driver at the PA cell frequency resonance (3765 Hz) and to collect the signal from the microphones. A glass flask was used to hold the samples and a homemade heating system based on a peltier element (heating controller Novus 2000) was assembled at the bottom of the sample holder. A zero gas, pure nitrogen (Praxair Inc., 99.95% purity), controlled by an electronic mass-flow controller (Brooks S5650) was used as carrier gas and a flow of 5 L h^{-1} was applied. The lower detection limit of this setup was reported as 66 ppbv (parts per billion by volume) for a signal-to-noise ratio of 3 [11]. Experiments at room and near room temperature (30°C and 60°C) to monitor the ammonia desorption were carried out setting the laser wavenumber at 1046.4 cm^{-1} , which corresponds to the strongest absorption line for ammonia [11] in the spectral range used. At the end of each assay, the laser temperature was raised linearly from -20 to 35°C , resulting in a wavelength scan from 1049 to 1046 cm^{-1} . This procedure was carried out in order to ensure that the signal at 1046.4 cm^{-1} was due solely to ammonia molecules. In order to calibrate the detection system, a certified gas (reference gas) mixture of 5 ppmv (parts per million by volume) NH_3 diluted in nitrogen provided by Praxair Inc. was used. A schematic diagram of the experimental setup is shown in Fig. 1.

2.2. Preparation of the samples

Samples (1250 mg) of each material were mixed in an ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) aqueous solution (7.2 g L^{-1}) and stirred over a magnetic stirring plate for 3 h. Subsequently the materials were filtered using filter paper and 950 mg of each sample was added to the glass sample holder and their ammonia emission rates were monitored by PAS. Ammonia desorption was followed at two different temperatures, namely, 30°C and 60°C , using nitrogen to push the volatilized sample into the photoacoustic cell at constant flow of 5 L h^{-1} .

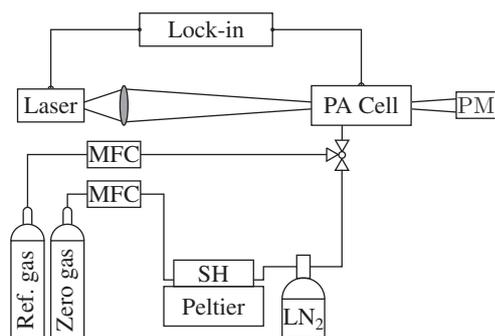


Fig. 1. Schematic diagram of the experimental setup in the PAS. LN₂, liquid nitrogen vessel; MFC, mass-flow controller; PA cell, photoacoustic cell; PM, power meter; SH, sample holder.

Table 1
Chemical composition of the Chilean, Cuban and Brazilian zeolites determined by X-ray fluorescence.

| Composition (%) | Chilean | Cuban | Brazilian |
|--------------------------------|---------|-------|-----------|
| SiO ₂ | 74.5 | 71.1 | 62.5 |
| Al ₂ O ₃ | 15.0 | 14.6 | 16.3 |
| CaO | 5.3 | 7.3 | 9.5 |
| K ₂ O | 1.9 | 2.4 | 2.5 |
| SO ₃ | 1.9 | 1.9 | 2.1 |
| Fe ₂ O ₃ | 1.1 | 2.2 | 6.0 |

2.3. Temperature programmed desorption – NH₃ (TPD – NH₃)

A homemade setup for temperature programmed desorption (TPD) experiment was used to analyse the acidity of the materials. Ammonia adsorption was previously promoted by exposing the samples to pure ammonia (99.9%) over a period of 15 min at 100 °C. A temperature ramp ranging from 100 to 500 °C, with a heat rate of 5 °C min⁻¹, was subsequently applied to induce ammonia desorption. Ammonia was detected with a thermal conductivity sensor. Helium was used to push the desorbed ammonia from the sample holder into the detector at 30 mL min⁻¹. After the end of the temperature ramp, the sample temperature was kept at 500 °C for 1 h.

2.4. Kjeldahl method

The remaining NH₃ was extracted from the zeolites treated with ammonium sulfate by dissolving the samples in 100 mL of an aqueous solution of potassium chloride (KCl) (2 mol L⁻¹). In order to induce ammonia volatilization, the pH of the solution was raised to 7.5, by adding an aqueous solution of sodium hydroxide (40%, w/v). Ammonia was collected from the steam distillation in a Kjeldahl distiller [21] and quantified by titration using an aqueous solution of sulfuric acid (5 mmol L⁻¹) [22].

3. Results and discussion

X-ray fluorescence spectroscopy was used to determine the oxide composition of the three materials (EDX-700, SHIMADZU). The chemical composition of the samples is presented in Table 1. Silicate and aluminate contents in the Chilean and Cuban zeolites are typical of naturally occurring zeolites [23]. On the other hand, the incongruent oxide ratios found for the Brazilian sedimentary sample are related to the fact that this material is a mixture of stilbite, quartz and clays [16]. The later is probably responsible for the higher concentration of Fe₂O₃ therein detected.

The specific surface area and pore volume were determined by dinitrogen adsorption and the Brunauer–Emmet–Teller (BET)

Table 2
Textural analysis of the types of zeolites.

| Sample | Specific area (m ² /g) | Pore volume (× 10 ⁻³ cm ³ /g) | Mean pore diameter (Å) |
|-----------|-----------------------------------|---|------------------------|
| Chilean | 193.7 | 89.4 | 48.2 |
| Cuban | 72.2 | 25.6 | 77.5 |
| Brazilian | 8.8 | 1.0 | 115.1 |

method, using an Autosorb-1C (Quantachrome) equipment [17]. According to the BET surface analysis results shown in Table 2, the Chilean zeolite has a surface area nearly 22 times larger than the Brazilian sample. The number of molecules that undergo adsorption depends on the surface composition and its total area, thus it is expected that a large area will support a larger number of adsorption sites. Similarly, the pore volume of each material followed the same trend, that is, 89.4 × 10⁻³ cm³/g for the Chilean zeolite, 25.6 × 10⁻³ cm³/g for the Cuban material and 1.0 × 10⁻³ cm³/g for the Brazilian material. The small surface area and pore volume found for the Brazilian sample are influenced by its mineral composition, which includes some quartz, a significant amount of clay, as well as stilbite [16].

The mean pore diameter is also listed in Table 2. Although the smallest mean pore diameter of 4.8 nm was obtained for Chilean sample, this will not hinder the access of ammonium ions, which have an ionic radius equal to 0.143 nm [24,25]. Therefore all zeolite materials analysed here have pore radius size large enough to admit the ammonium ions. However, during the rapid ammonia desorption induced by raising the temperature, a small pore diameter could be a limiting factor that contributes to increase the resistance for the release of ammonia.

Figs. 2 and 3 show the rate of ammonia emission per unit of mass from the zeolite samples at 30 °C and 60 °C, respectively, monitored by photoacoustic spectroscopy with the laser tuned to an emission radiation of 1046.4 cm⁻¹. The Cuban zeolite emitted more ammonia than Brazilian and the Chilean zeolite at either temperature. At 30 °C, a mean rate of ammonia emission of 30.1 μL h⁻¹ g⁻¹ (with a 4.9 μL h⁻¹ g⁻¹ of standard deviation, calculated after three replications as shown in Figs. 2 and 3) was found for the Cuban zeolite and mean values, respectively of 8.7 ± 1.8 μL h⁻¹ g⁻¹ and 0.7 ± 1.0 μL h⁻¹ g⁻¹ were obtained for the Brazilian and Chilean samples. The amount of ammonia emitted from the Chilean zeolite at 30 °C is near to the detection limit of the PAS technique (66 ppbv).

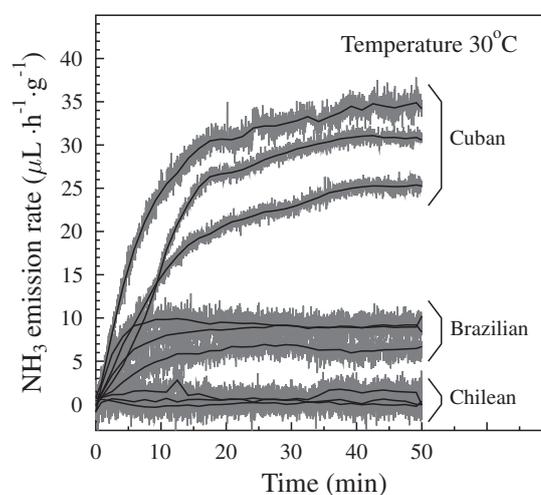


Fig. 2. Time evolution of ammonia emission rate from zeolites treated with ammonium sulfate at 30 °C. The solid lines are an interpolation of the data taking into account the average of y-values in every window of 100 points.

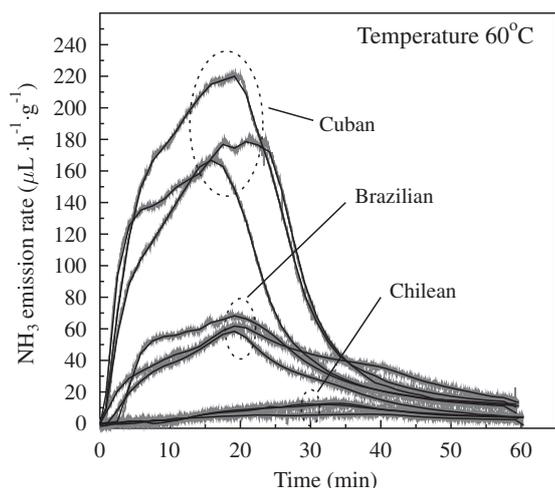


Fig. 3. Time evolution of ammonia emission rate from zeolites treated with ammonium sulfate at 60 °C. The solid lines are an interpolation of the data taking into account the average of y -values in every window of 100 points.

As expected, the rate of ammonia emission at 60 °C for all zeolites increased, compared to that measured at 30 °C, and a maximum of emission was found. This maximum can be related to the desorption of ammonia (activated by the temperature increase to 60 °C) from a physisorbed state. In this work, the mean value of $187.5 \mu\text{L h}^{-1} \text{g}^{-1}$ (standard deviation = $29.6 \mu\text{L h}^{-1} \text{g}^{-1}$) of the maximum of ammonia desorption was calculated after three replications for the Cuban zeolite. The mean of the maximum of emission rate obtained for the Chilean zeolite was found to be $10.4 \mu\text{L h}^{-1} \text{g}^{-1}$, and for the Brazilian material reached $62.7 \mu\text{L h}^{-1} \text{g}^{-1}$ (with 4.4 and $6.0 \mu\text{L h}^{-1} \text{g}^{-1}$ standard deviations, respectively).

Consequently, in order to identify the most appropriate application of each zeolite as a fertilizer microporous carrier, it is important to take into account the demand for organic nutrient of each plant species. These results point, therefore to the Cuban zeolite as an outstanding material to be used for cultivating crops which demand high amounts of nitrogen owing to its higher ability to hold and release ammonium at typical field temperatures.

Comparing the effect of raising the temperature on the desorption rates, a remarkable enhancement of desorption rate was observed for Chilean zeolite. While the desorption rate for Cuban zeolite and the Brazilian material increased respectively, by factors of 6 and 7 as a result of the temperature change from 30 to 60 °C, the ammonia desorption rate for the Chilean sample increased by a factor of about 15. This indicates that an activation temperature higher than 30 °C is essential to promote desorption in the Chilean zeolite. The fact that the ratio of increase of ammonia emission rate for the Brazilian sample is similar to that recorded for the Cuban zeolite is an indication that both materials probably carry the same type of adsorption sites.

After the desorption measurements at 30 and 60 °C the remaining nitrogen found in the zeolite samples was determined by using the total Kjeldahl nitrogen method, whose results are summarized in Table 3. Taking into account the errors inherent to such a quantification method, it is plausible to point out that the remaining concentration of organic nitrogen in the Brazilian material is no more than half of the concentration found for the Cuban and Chilean zeolites.

A TPD peak for samples treated with NH_3 was obtained at 220 °C for the Cuban and the Brazilian materials, while for the Chilean sample the peak is found at 200 °C [26]. The total area below the TPD curves for the three kind of zeolite is shown in Table 4. The total area normalized by the mass is expressed in arbitrary units (a.u.).

Table 3

Nitrogen content (mg) in the materials determined by the total Kjeldahl nitrogen method. The measurements were made with the same samples treated with ammonium sulfate used in the assay of ammonia desorption at 30 and 60 °C by PAS.

| Sample | N (mg) | |
|-----------|--------|-------|
| | 60 °C | 30 °C |
| Chilean | 10.6 | 10.5 |
| Cuban | 10.0 | 11.1 |
| Brazilian | 4.9 | 4.0 |

Table 4

Temperature programmed NH_3 desorption analyses.

| Material | Saturated with NH_3 |
|-----------|------------------------------|
| Cuban | 7266 a.u. g^{-1} |
| Chilean | 5645 a.u. g^{-1} |
| Brazilian | 4384 a.u. g^{-1} |

A relative comparison of the data from the all materials analysed reveals that the Cuban zeolite presents a higher concentration of acid sites owing to the largest desorption area found for such zeolite when treated with NH_3 . The ratio of 0.6 between the areas obtained for the Brazilian material and the Cuban zeolite is reasonable since a concentration of 66.8% of stilbite was found in the composition of the Brazilian sedimentary material [16].

4. Conclusion

The results presented in this work demonstrate the feasibility of the photoacoustic spectroscopy technique for detecting the release of ammonia from zeolite materials treated with ammonium sulfate. The influence of the temperature on the rate of ammonia desorption was clearly demonstrated when the temperatures of the samples were increased to 60 °C, resulting in a significant increase in the emission rate of ammonia. Temperature programmed desorption and Kjeldahl methods showed that the Brazilian material has the ability to retain half of the quantity of ammonium held by the Cuban zeolite. This study proves that even impure zeolite-containing minerals such as the Brazilian sedimentary material analysed is feasible as a carrier of nitrogen which can be slowly released to the soil in tropical fields conditions, with the added advantage of its very low cost.

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