



Natural zeolite reactivity towards ozone: The role of compensating cations

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HIGHLIGHTS

- ▶ Chemical and thermal treatment enhances catalytic activity of natural zeolite.
- ▶ Modified natural zeolite exhibits high stability after thermal treatment.
- ▶ Reducing the compensating cation content leads to an increase on ozone abatement.
- ▶ Surface active atomic oxygen was detected using the DRIFT technique.
- ▶ The highest reactivity toward ozone was performed by NH4Z3 zeolite sample.

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ABSTRACT

Among indoor pollutants, ozone is recognised to pose a threat to human health. Recently, low cost natural zeolites have been applied as alternative materials for ozone abatement. In this work, the effect of compensating cation content of natural zeolite on ozone removal is studied. A Chilean natural zeolite is used here as starting material. The amount of compensating cations in the zeolite framework was modified by ion exchange using an ammonium sulphate solution (0.1 mol L⁻¹). Characterisation of natural and modified zeolites were performed by X-ray powder diffraction (XRD), nitrogen adsorption at 77 K, elemental analysis, X-ray fluorescence (XRF), thermogravimetric analysis coupled with mass spectroscopy (TGA-MS), and temperature-programmed desorption of ammonia (NH₃-TPD). Ozone adsorption and/or decomposition on natural and modified zeolites were studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Results show that the zeolite compensating cation content affects ozone interaction with zeolite active sites. Ammonium ion-exchange treatments followed by thermal out-gassing at 823 K, reduces ozone diffusion resistance inside the zeolite framework, increasing ozone abatement on zeolite surface active sites. Weak and strong Lewis acid sites of zeolite surface are identified here as the main active sites responsible of ozone removal.

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1. Introduction

Environmental indoor contamination has been added to the list of problems that our modern society has to deal with. Among indoor pollutants, ozone is recognised to pose a threat to human health [1]. Ozone is normally generated in working environments due to the use of photocopiers, laser printers, fax machines and sterilisation apparatus [2]. In airplane cabins, ozone must be purged from air before it can be circulated [3]. Ozone can reduce lung functions, height lung sensitivity to allergens and irritants, and cause chronic damages to lung structure [4]. Microporous materials such as activated carbons have been used during the last decades for ozone

indoor elimination. Recently, low cost natural zeolites have been studied as alternative materials for this purpose.

Zeolites and related microporous materials act as efficient heterogeneous catalysts, as adsorbents, and as molecular sieves in gas separation processes [5]. Zeolites may be used in catalysis or gas adsorption after chemical composition modification, mainly by ion exchange. Ion exchange is an intrinsic property of zeolites; and it is associated with the presence of cations that compensate the negative zeolite structure charge [6]. Various zeolite applications are based directly or indirectly on this property [6].

The influence of surface characteristics of Chilean natural zeolites in gaseous ozone abatement was reported in previous works [7,8]. Lewis acid surface sites were claimed as the main responsible for ozone gaseous elimination, using outgassed natural zeolite at 823 K. However, there are still some doubts related to the effect of zeolite compensating cation content on gaseous ozone removal. Unfortunately, such fundamental aspect has not been studied in detail, being addressed in this article.

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2. Experimental methods

2.1. Materials

Chilean natural zeolite (53% clinoptilolite, 40% mordenite and 7% quartz) was provided by Minera FormasTM. Zeolite sample was sieved to 0.3–0.425 mm, washed with ultra pure water, oven-dried at 398 K for 24 h, and finally stored in a desiccator until further use. Ozone was produced from instrumental dry air supplied by AGA, using an AZCOZON A-4 ozone generator (Vancouver, BC, Canada) rate at 4 g O₃ h⁻¹. Ultra-pure water was obtained from an EASY pure[®] RF II system.

2.2. Modification of compensating cation content in natural zeolite

Four de-cationised zeolite samples were obtained from natural zeolite (NZ) by applying ion-exchange treatments using an ammonium sulphate solution (0.1 mol L⁻¹). Chemical modifications were carried out under shaking for 2 h at 363 K, using solution/solid ratios of 10:1, 20:1 and 30:1. These ammonium-exchanged zeolite samples were denominated NH4Z1, NH4Z2 and NH4Z3, respectively. After the ion-exchange step, samples were rinsed with ultra-pure water at 363 K for 4 h. Ultra-pure water was renovated after washing at 2 h and 3 h. Additionally, a second ion-exchange step was conducted to the NH4Z1 sample using a solution/solid ratio of 10:1. This sample was named 2NH4Z1. All samples were oven-dried at 398 K for 24 h and stored in a desiccator until further use.

Natural and modified zeolite samples were thermally outgassed at 823 K, in a vertical tubular furnace. Zeolite samples (0.15 g) were placed in a quartz fixed-bed flow reactor, and heated at 10 K min⁻¹, under vacuum. When samples reached maximum temperature, isothermal conditions were kept for 2 h, before quenching to room temperature. Thus, zeolite samples were ready to ozone contact.

2.3. Physical–chemical characterisation of natural and modified zeolite samples

X-ray powder diffraction (XRD) was applied to natural and modified zeolite samples in order to evaluate mineralogical and structural changes. XRD was performed with a Bruker AXS Model D4 ENDEAVOR diffractometer, equipped with a copper X-ray tube and Ni filter. Powdered samples were mounted on quartz plates and stepped scanned over the angular range 3–70°(2θ), a step size of 0.02 and a time/step of 0.2 s. X-ray generator was fixed at 40 kV and 20 mA.

Surface area of natural and modified zeolite samples were obtained by nitrogen adsorption isotherms, using a Micromeritics Gemini 3175 as described elsewhere [7,8]. Samples were previously degasified at 623 K for 12 h under vacuum. Surface areas (*S*) of natural and modified zeolite samples were calculated from nitrogen adsorption data, applying the Langmuir equation.

Elemental analyses were performed on a LECO CHN 2000 apparatus. Samples of 0.1 g were put inside the oven at 1173 K and burned in the presence of excess oxygen to ensure complete combustion. Gaseous combustion products were evacuated using He (100 cm³ min⁻¹) and the nitrogen content of modified zeolite samples was registered by a thermal conductivity detector, previously calibrated with ethylenediaminetetraacetic acid (EDTA).

X-ray fluorescence (XRF) allowed determination of bulk chemical composition of natural and modified zeolites by using a RIGAKU Model 3072 spectrometer. This is a dispersive wave spectrometer equipped with a Rhodium X-ray generator, four crystal diffractors (LIF200-SC, LIF200-PC, PER, TAP100), and two detectors. 5 g of lithium tetraborate were thoroughly mixed with 0.5 g sample in

an agate mortar. Then, it was placed in a Pt–Ru crucible, together with lithium iodine before spectrometric determination [9].

Thermogravimetric analyses (TGA) were performed on a NET-ZSCH thermobalance ST409PC, coupled with a quadrupole mass spectrometer (MS) detector. Natural and de-cationised zeolite samples (0.025 g), without thermal out-gassing treatment, were heated up to 950 K (heating rate of 10 K min⁻¹) under He flow (100 cm³ min⁻¹) and the change in sample weight in relation to change in temperature was registered (TG curve). A derivative weight loss curve was also obtained as function of temperature (DTG curve). Simultaneously, the temperature difference between Al₂O₃ reference crucible and the sample was recorded and the differential temperature was plotted against temperature. Thus, a differential thermal analysis (DTA) provides data on the transformations that occur in zeolite samples (DTA curve). Moreover, during TGA analysis, evolved gases were monitored with a quadrupole mass spectrometer detector (QMS 403C), recording the change of ammonia and water concentration by following the mass-to-charge ratio (*m/z*) at 16 and 17, respectively.

Acid site density of zeolite samples was determined by applying the ammonia temperature-programmed desorption method (NH₃-TPD) [10]. NH₃-TPD is one of the most conventional methods for global acid site characterisation of zeolites. Natural and modified zeolite samples (0.15 g) were previously outgassed at 823 K (10 K min⁻¹ heating rate) for 2 h under Ar flow (50 cm³ min⁻¹). Then, they were allowed to adsorb the saturated ammonia vapour from the ammonium hydroxide solution until reaching saturation at 373 K (in order to minimise physical adsorption of ammonia). Finally, ammonia saturated zeolites were placed into the TPD equipment coupled with a thermal conductivity detector (TCD). Samples were heated from 293 to 973 K at a rate of 10 K min⁻¹ in Ar flow (100 cm³ min⁻¹). The conductivity changes of the evolved gas were plotted against temperature and the acid site strength and density were estimated. The temperature range in which most ammonia was desorbed; is related to the acid strength distribution. The total amount of chemisorbed ammonia is proportional to the number of acid sites per unit mass of the adsorbents (acid site density) [11].

2.4. Experimental system

Ozone abatement experiments were carried out in a quartz fixed-bed flow reactor (4 mm ID) at 293 K and 101 kPa, loaded with 0.15 g zeolite. Untreated (NZ) and treated (NH4Z1, NH4Z2, NH4Z3, 2NH4Z1) zeolite samples were used. Ozone removal experiments were conducted after the thermal treatment at 823 K was completed and room temperature was quenched. Typically, the reactor was continuously fed with an O₂/O₃ gas mixture at 740 cm³ min⁻¹, and 0.345 μmol O₃ dm⁻³ (C_{O3in}). These operating conditions were selected from preliminary experiments aimed at reducing mass transfer effects. Ozone concentrations in the reactor outlet stream (C_{O3out}) were monitored on-line by continuous absorbance measurement at 255 nm, using an UV spectrophotometer (Bausch & Lomb TU-1810 S). The exhaust gas stream was sent to an ozone trap before discharging to the ambient air. Data were registered as function of time and processed using UV-Win 5.0 software. Once the outlet ozone concentration equalled the inlet level, the O₃/O₂ flow was stopped and argon gas was fed into the reactor system for 10 min, before removing the zeolite.

2.5. DRIFTS study of ozone–zeolite surface interactions

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used in order to confirm ozone molecule adsorption and/or ozone decomposition by-products on natural and modified zeolite samples [12]. DRIFTS measurements were carried out using