



# Oxidative regeneration of toluene-saturated natural zeolite by gaseous ozone: The influence of zeolite chemical surface characteristics



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## HIGHLIGHTS

- Surface acidity of modified natural zeolite is related to its chemical reactivity.
- Brønsted acid sites are associated to toluene adsorption.
- Lewis acid sites could decompose ozone generating surface active oxygen species.
- Infrared spectra evidence active atomic oxygen and oxidation by-product formation.
- 2NH4Z1 sample shows the highest reactivity toward adsorbed toluene.

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## ABSTRACT

In this study, the effect of zeolite chemical surface characteristics on the oxidative regeneration of toluene saturated-zeolite samples is investigated. A Chilean natural zeolite (53% clinoptilolite, 40% mordenite and 7% quartz) was chemically modified by acid treatment with hydrochloric acid and by ion-exchange with ammonium sulphate. Thermal pre-treatments at 623 and 823 K were applied and six zeolite samples with different chemical surface characteristics were generated. Chemical modification of natural zeolite followed by thermal out-gassing allows distinguishing the role of acidic surface sites on the regeneration of exhausted zeolites. An increase in Brønsted acid sites on zeolite surface is observed as a result of ammonium-exchange treatment followed by thermal treatment at 623 K, thus increasing the adsorption capacity toward toluene. High ozone consumption could be associated to a high content of Lewis acid sites, since these could decompose ozone into atomic active oxygen species. Then, surface oxidation reactions could take part among adsorbed toluene at Brønsted acid sites and surface atomic oxygen species, reducing the amount of adsorbed toluene after the regenerative oxidation with ozone. Experimental results show that the presence of adsorbed oxidation by-products has a negative impact on the recovery of zeolite adsorption capacity.

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## 1. Introduction

Hazardous air pollutants such as volatile organic compounds (VOCs) are typically generated in chemical industries, posing a high risk to human health [1]. Industrial atmospheric emissions have been traditionally controlled using adsorption processes [2,3]. Once

adsorbents are exhausted they need to be disposed or regenerated. Regeneration techniques such as chemical or thermal desorption are normally used by the industry, allowing valuable adsorbate recovery [4]. However, when recovery is not possible, further treatments are needed in order to eliminate adsorbed contaminants [5].

Recently, advanced oxidation processes, such as gas phase catalytic ozonation, have been proposed as an effective alternative to regenerate spent adsorbents [6,7]. Adsorption of toluene on synthetic zeolites (FauY, SilZ and ZSM-5) followed by ozonation, has

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been proposed as a reliable process to oxidise adsorbed toluene on zeolite surface, resulting in a high degree of recovery on adsorption capacity [8–10]. However, there is a lack of information related to the effect of chemical surface characteristics of zeolites in these coupled processes. Separated processes for VOCs and gaseous ozone removal from industrial waste gas streams using synthetic and natural zeolites have been applied [11–16].

On one hand, Brønsted and Lewis acid sites have been claimed as responsible of VOCs removal by adsorption onto natural zeolites [11,12]. It has been indicated that weak base aromatic VOC molecules such as benzene, toluene and *p*-xylene could be adsorbed by a surface mechanism that includes interaction with Brønsted acid sites in the form of proton-donating hydroxyl groups of natural mordenite surface, forming hydrogen bonds; and with Lewis acid sites, generating a Lewis acid–base adduct [12]. On the other hand, weak and strong Lewis acid sites of natural and synthetic zeolites have been identified as the main active sites responsible of gaseous ozone removal [13–16]. Molecular ozone could be adsorbed *via* coordinative bonding at weak Lewis acid sites. Moreover, ozone could transform immediately after adsorption on strong Lewis acid sites and decomposes into O<sub>2</sub> and an active atom of oxygen that could participate in catalytic removal of ozone [15,16].

Unfortunately, the influence of chemical surface properties of natural and synthetic zeolites on VOC removal, using a sequential adsorption-ozonation treatment, at room temperature has not been fully studied yet. In this work, a Chilean natural zeolite is used as starting material; and it is chemically and thermally modified in order to generate a zeolite surface rich in a high content of Brønsted acid sites (using ammonium ion-exchange followed by thermal treatment at 623 K) or Lewis acid sites (using ammonium ion-exchange followed by thermal treatment at 823 K). The nature and strength of acidic surface sites resulting from the applied modification treatments are characterised by Fourier transform infrared (FTIR) spectroscopy using pyridine as a probe molecule. Toluene is chosen here as a target VOCs, since it represents a serious threat to human health [17]. Additionally, FTIR spectroscopy is employed to clarify the surface reaction mechanism that takes place between toluene and ozone on zeolite samples. Finally, zeolite surface active centres are identified and the natures of their interaction toward toluene and ozone are characterised at a molecular level.

## 2. Materials and methods

### 2.1. Materials

Chilean natural zeolite (53% clinoptilolite, 40% mordenite and 7% quartz) was provided by Minera Formas. Zeolite sample was ground and sieved to 0.3–0.425 mm; then was rinsed with ultra pure water, oven-dried at 398 K for 24 h, and stored in a desiccator until further use. Natural zeolite was modified by acid treatment using HCl (2.4 mol dm<sup>-3</sup>), and by ion-exchange using ammonium sulphate (0.1 mol dm<sup>-3</sup>), as reported elsewhere [14]. Acid-treated zeolite and ion exchanged zeolite were named ZH2.4 and NH4Z1, respectively. A second ion-exchange treatment was conducted to the NH4Z1 sample and a new zeolite sample with different chemical surface properties was obtained (2NH4Z1), as described in previous work [14]. Zeolite samples were thermally out-gassed in an oven at 623 K or 823 K (heating rate 10 K min<sup>-1</sup>) during two hours prior to adsorption-ozonation experiments.

Toluene (99.8% purity) was provided by MERCK. Ozone was produced *in situ*, from synthetic dry air, using a Traigalaz 5LO ozone generator. The inlet concentration of ozone was fixed at 24.3 g dm<sup>-3</sup> in all experiments.

### 2.2. Physical–chemical characterisation of zeolite samples

Surface area of zeolite samples were obtained by nitrogen adsorption at 77 K, after zeolite out-gassing overnight at 623 K and 823 K, under vacuum [14]. Bulk chemical composition of natural and modified zeolite samples was obtained by X-ray fluorescence (XRF) using a RIGAKU Model 3072 spectrometer [18]. Density measurements of zeolite samples were carried out in an AccuPyc 1330 pycnometer using helium (99.995% purity) and registering the helium pressure change in a calibrated chamber [19]. Physical and chemical surface characteristics of natural and modified zeolite samples are listed in Table 1. Surface areas (*S*) were calculated by applying the Langmuir adsorption model to nitrogen adsorption data. After acid treatment of natural zeolite, the surface area and the Si/Al ratio increase for ZH2.4, as a consequence of a de-cationisation and de-alumination mechanisms [20]. The high value of ZH2.4 surface area could be related to an enhancement on zeolite microporosity. During the de-alumination process, the exchange of hydrated cations by H<sup>+</sup> could have risen micropore accessibility, eventually blocked before the acid treatment [20]. Pore opening expansion could result also from a de-cationisation process, generating the so-called “open structures” that could lead to a decrease in diffusion resistance inside the zeolite framework [14]. Additionally, surface areas of NZ and ZH2.4 samples decrease after thermal treatment at 823 K. This could be related to the interaction of compensating cations and water in the zeolite framework. During the out-gassing process at 823 K, water molecules leave the zeolite, destabilising the zeolite charge structure. In order to correct this, it has been suggested that compensating cations in the zeolite framework, form bonds with network oxygen atoms, affecting the zeolite structure channels [15]. However, in the ammonium-exchanged zeolites, surface areas are increased after thermal treatment at 823 K. Such increase in the value of surface areas could be related to the elimination of ammonium due to thermal out-gassing at 823 K, thus reducing any blocking effect on microporous structures [15].

Results summarised in Table 1 also show that the content of compensating cations of zeolite samples decreases after the chemical treatments applied here. Although the de-cationisation treatment using ion-exchange with ammonium sulphate effectively reduces the amount of compensating cations (Na, K, Mg, Ca); the Si/Al ratio of the zeolite framework does not show a significant change. A considerable amount of calcium and sodium cations migrates to the solution during chemical modification, while magnesium and potassium cations are exchanged at a lower extent. Magnesium and potassium cations seem to be hard to access due to their large radius (e.g. Mg<sup>2+</sup> has an atomic radius of 0.16 nm; whereas K<sup>+</sup>, Ca<sup>2+</sup> and Na<sup>+</sup> have an atomic radius of 0.133 nm, 0.104 nm and 0.098 nm, respectively). Sodium ions in natural clinoptilolite zeolites have been reported to be weakly bonded to zeolite lattice and are easy to remove [21]. Moreover, helium pycnometry technique reveals the true density of zeolite samples. The value of true density of NZ decreases from 2.30 to 2.26 g cm<sup>-3</sup> after acid treatment. In the case of ammonium-exchanged zeolites, density values fall to 2.10 and 2.11 g cm<sup>-3</sup> for NH4Z1 and 2NH4Z1, respectively.

Acidic properties were determined by Infrared (IR) spectroscopic using pyridine as a probe molecule (99.5% purity supplied by Fluka) in a conventional IR cell of a Nicolet Magna-IR 550 spectrometer, using a pressed disc containing 2 mg of the zeolite sample and 100 mg of KBr, according to experimental procedures reported elsewhere [22]. Samples were previously out-gassed at 623 K or 773 K for 2 h, and then pyridine was introduced into the IR cell at 293 K and maintained for 24 h. After that, non-adsorbed pyridine was removed at 423 K, 523 K, 623 K, 723 K or 773 K (heating temperature) under vacuum. This thermal desorption procedure allows to determine the acidity strength of Lewis and Brønsted

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