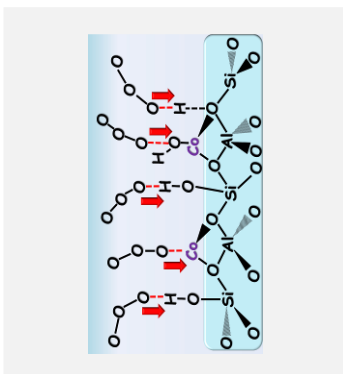


Evidences of the effect of chemical surface sites of natural and cobalt-modified natural zeolite during the abatement of ozone emissions using DRIFTS *operando* studies

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In this study, ozone adsorption and/or catalytic decomposition onto natural and cobalt modified natural zeolite were studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Natural zeolite was chemically and thermally modified by a succession of two ion-exchange with ammonium sulfate, thermal out-gassing at 350°C, and impregnation with cobalt ions (0.07 mol dm⁻³) followed by thermal out-gassing at 350°C. The acidic character of natural and modified zeolite samples were established using temperature-programmed desorption of ammonia (NH₃-TPD). Results evidenced that ozone is adsorbed and decomposed at strong Lewis acidic sites, whereas ozone adsorption products interact with surface OH groups. Additionally, DRIFTS studies indicate that nitrous species are adsorbed at acidic sites, reducing the capacity to decompose ozone when ozone is generated from air.

Introduction

Ozone at tropospheric level poses serious environmental and occupational health hazards. Ozone can increase sensitivity to bronchoconstrictors and allergens, and may facilitate the development of asthma. In working environments ozone is formed due to the use of laser printers, photocopiers, sterilization apparatus and ozone generators for air and water treatment [1]. Cars and power plant emissions are precursors of ozone outdoor formation [2]. Ozone decomposition has been reported over metal oxide catalysts [3-9]. However, the high investment costs, become a major obstacle for full-scale application, and alternative materials should be found. Recently, low cost stable natural zeolites have been used as alternative materials [10-12]. Lewis acid sites were claimed as the main responsible for ozone gaseous elimination, using outgassed natural zeolite at 550°C [10]. Transition metal modified natural zeolites could act as an alternative and low cost catalyst to effectively abate ozone, exhibiting greater activities than the parent natural zeolite. In this work, the influence of the structure, framework composition of natural and cobalt-modified natural zeolites on the catalytic activity in the ozone gaseous abatement are established. Finally, surface reaction mechanisms that represent the catalytic elimination of ozone using natural and cobalt-modified natural zeolite are proposed.

Material and Methods

Natural zeolite (NZ) was provided by the Chilean mining company "Minera Formas". NZ was ground and sieved to 0.300–0.425 mm; then was rinsed with ultra pure water, oven-dried at 125 °C for 24 h, and stored in a desiccator until its further use. This zeolite is composed of clinoptilolite (53%), mordenite (40%), and quartz (7%) and has been previously characterised using standard techniques,

as indicated elsewhere [13]: apparent density, 2.3 g cm⁻³; BET surface area, 281 m² g⁻¹; total pore volume, 0.24 cm³ g⁻¹; with a Si/Al of 5.05; and mainly composed of SiO₂ (72.97%) and Al₂O₃ (14.45%) followed by CaO (5.68%), Fe₂O₃ (2.53%), Na₂O (2.15%), K₂O (0.9%), MgO (0.59%), TiO₂ (0.48%), SO₃ (0.08%), P₂O₅ (0.05%), MnO (0.05%), SrO (0.04%), and ZrO₂ (0.02%).

Ozone was produced from dry synthetic instrumental air using an AZCOZON ozone generator, featuring variable ozone generation rates in the concentration range from 9000 to 22000 ppmv.

Co was used here as active transition metal (Mt) for natural zeolite modification. It was supplied in the form of metal salt by MERCK (Darmstadt, Germany) as cobalt nitrate (Co(NO₃)₂·6H₂O) with purity > 99%. Natural zeolite was chemically and thermally modified by a succession of two ion-exchange with ammonium sulfate, thermal out-gassing at 350°C, and impregnation with cobalt ions (0.07 mol dm⁻³) followed by thermal out-gassing at 350°C, as indicated before [13].

Experiments were carried out in an U-type fixed-bed flow reactor at 20°C loaded with 0.3 g zeolite sample. In regular tests, the reactor was continuously fed with 75 cm³ min⁻¹ at STP of an O₂/O₃ gas mixture with a concentration of 9000 ppmv O₃. Ozone concentration in the reactor outlet stream was monitored on-line using an ozone analyser BMT 963 (BMT Messtechnik GmbH, Berlin, Germany), until the effluent concentration of gaseous ozone reached stationary state. Ozone removal efficiency was calculated when the reactor reached the stationary state condition, taking into account the inlet and outlet ozone concentrations.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied to distinguish the chemical interaction features that take place between surface sites of the NZ and of the cobal

modified natural zeolite sample (Z-Co) and O₃ generated from pure oxygen and from dry synthetic air.

DRIFTS *operando* studies were performed using a commercial DRIFTS cell (PIKE DiffuIR™), with a KBr window (32 × 3 mm) and a gas flow system set on a Nicolet™ iS™50 spectrometer (Thermo Fisher Scientific Inc., USA) equipped with a DTGS detector. NZ or Z-Co was loaded into a ceramic cup with a porous base. After that, the loaded cup was placed into the PIKE DiffuIR™ chamber. The signal measured on a mirror was used as reference. Before the measurement, the sample was post-treated inside the chamber following the preparation parameters. Then, the sample was cooled down to 20 °C under vacuum (3 × 10⁻³ hPa) and a spectrum of the sample without ozone was measured. Spectra were collected as an average of 30 scans with a resolution of 1 cm⁻¹ between 4000 and 720 cm⁻¹. In *operando* DRIFTS studies ozone was generated not only from dry synthetic air (21% O₂ purity balanced in nitrogen) but also from pure oxygen (99.5% purity) provided by Air Liquide Chile. In both cases, the inlet concentration of ozone was rated at 22000 ppmv.

An O₂/O₃ gas mixture was passed through the PIKE DiffuIR™ chamber during 60 min and spectra were registered as a function of time. At the same time, the concentration of ozone in the reactor outlet stream was registered on-line using a BMT 963 ozone analyser (BMT Messtechnik GmbH, Berlin, Germany). PIKE TempPro™ software was used for temperature control and data collection. Results were processed with OMNIC 9.0 software.

Results and Discussion

Figure 1 shows the evolution of DRIFTS spectra upon zeolites contact with gaseous ozone (generated from pure oxygen) between 4000 and 3300 cm⁻¹. DRIFTS *operando* study revealed that different mechanism took place for ozone abatement over natural zeolite and cobalt-modified natural zeolite.

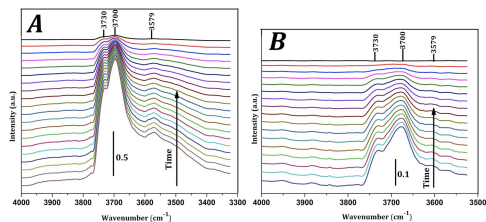


Figure 1. DRIFTS spectra of natural zeolite sample (A), cobalt modified zeolite sample (B) in the range between 4000 and 3300 cm⁻¹. Operating conditions: 30 mg of zeolite sample, 75 cm³ min⁻¹, inlet concentration of ozone 22000 ppmv generated from pure oxygen, at 20 °C.

In both zeolites, ozone basic molecules are adsorbed and decomposed at strong Lewis acidic sites, leading to decomposition by-products that interact with zeolite OH groups forming H-bonding. In cobalt-modified natural zeolite, ozone molecules

interact with cobalt cations (Lewis acid sites). Over strong Lewis acidic sites (Z-Co) ozone is dissociated and adsorbed atomic oxygen and superoxide species are observed at the Z-Co surface. The latter species could contribute to catalytic chain decomposition reactions of ozone. The new Lewis acidic sites generated from cobalt introduction into the zeolite matrix play a very important role in ozone adsorption and abatement.

Conclusions

Cobalt-modified natural zeolite could be effectively used as alternative and low cost catalyst to destroy ozone emissions from working environments after a sequence of chemical and thermal treatments. Cobalt modified natural zeolite enhance ozone removal compare to the parent natural zeolite. DRIFTS analyses evidence the formation of new active sites after Cobalt was exchanged on natural zeolite, leading to an increase on ozone gaseous elimination. Ozone abatement over natural and cobalt modified natural zeolite are due to a combined mechanism that includes ozone adsorption and decomposition at strong Lewis acidic sites. DRIFTS results also show that such acidic sites are poisoned by nitrous adsorbed species when ozone is generated from air, reducing zeolite capacity to decompose ozone. These results suggest that the nature and strength of surface active sites play a fundamental role in the surface reaction mechanism of ozone gaseous removal.

Acknowledgments

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