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## Adsorption of NO in clinoptilolite-rich zeolitic mineral by concentration pulse chromatography method



Güler Narin\*, Semra Ülkü

Department of Chemical Engineering, Izmir Institute of Technology, Urla, 35430, Izmir, Turkey

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### ABSTRACT

The equilibrium and kinetic parameters for NO adsorption in a clinoptilolite-rich natural zeolitic material from Turkey were determined using the concentration pulse chromatography method. Under the experimental conditions (carrier gas velocities and adsorption temperatures) the micropore diffusion resistance was found to be the mass transfer controlling step. Matching the first moment of the response peaks to the mathematical model the Henry's Law constants and heat of adsorption at zero loading were determined. The axial dispersion, external film, macropore and micropore diffusion coefficients, and activation energy for diffusion of NO in the micropores were calculated from the analysis of the second moments of the response peaks. For successive NO pulses without regeneration between the pulses, the retention times of the response peaks decreased and peak areas increased with the injection number indicating irreversible adsorption. The reversibly adsorbed NO could be desorbed by purging with an inert gas at the adsorption pressure and temperature. Temperature programmed desorption profile obtained by heating the NO saturated adsorbent to 400 °C under inert flow revealed presence of multiple irreversibly adsorbed species in NZ with different thermal stabilities. Desorption of these species was not achieved during the heating up to 400 °C which makes the natural zeolitic material suitable for NO storage rather than for cyclic adsorptive separation processes.

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### 1. Introduction

Nitric oxide (NO) is an important gas from environmental and biological points of view. From the environmental perspective, nitrogen oxides (NO<sub>x</sub>) (NO and NO<sub>2</sub>) are formed by combustion of fossil fuels and of concern because of their adverse effects on public health and the environment. NO typically constitutes 95% of the total NO<sub>x</sub> in the combustion products [1]. On the other hand, it is an extremely important molecule in biology as it plays role in regulation of diverse biological processes including vascular tone, neurotransmission, inflammatory cell responsiveness, defense against invading pathogens and wound healing. NO-storing solids have potential applications as antithrombotic materials [2].

Currently, three-way catalyst is employed for removal of NO<sub>x</sub> in emissions from mobile sources and selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> is applied for stationary sources. The most

significant technical problems in SCR are poisoning of the catalyst and design of the ammonia injection system. Also, the use of ammonia generates problems due to leak and to the difficulties of transport and storage [3]. A variety of ion exchanged zeolites has been tested as catalyst for SCR in which ammonia or hydrocarbons are used as the reducing agent [4–18]. Several other methods have been investigated for elimination of NO<sub>x</sub> including catalytic decomposition [19–22], selective non-catalytic reduction (SNCR) [23] and NO<sub>x</sub> storage-reduction (NSR) [24,25].

Adsorption is a simpler method for the elimination of NO<sub>x</sub>. It allows NO<sub>x</sub> to be adsorbed and subsequently desorbed for the later treatment or direct application. Furthermore adsorption processes does not require additional reagents (e.g., NH<sub>3</sub>) and operate at lower temperatures (<100 °C) [26]. The crucial point in performance of NO<sub>x</sub> adsorption processes is the efficiency of the adsorbent. The adsorbent should have a high adsorption capacity and high selectivity for NO<sub>x</sub>, and low desorption temperature for the ease of regeneration.

Adsorption is the primary step in catalytic reactions. NO adsorption in metal-free zeolites (ZSM-5, 13X, SAPO, Y, β, NaY, NaX, CaA, NaA, ferrierite, mordenite, USY, ZSM-22, MCM-22) [26,27–30],

\* Corresponding author. Present address: Department of Chemical Engineering, Usak University, 64200, Usak, Turkey. Tel.: +90 276 2212121.

E-mail addresses: [guler.narin@usak.edu.tr](mailto:guler.narin@usak.edu.tr) (G. Narin), [semraulku@iyte.edu.tr](mailto:semraulku@iyte.edu.tr) (S. Ülkü).

metal oxide-impregnated or metal (e.g. Cu, Co, Fe, H, Au, V) exchanged zeolites (e.g. Y, beta, ZSM-5, A type, MFI, MOR) have been examined for this purpose [31–47]. Zeolite-based catalysts including transition metal cations exhibited high efficiency in the removal of NO<sub>x</sub>. Recently commercial zeolites (NaX, NaY) and their copper-modified analogues have been evaluated for NO<sub>2</sub> and NO adsorption in the presence of moisture [48]. Chang et al. tested NO<sub>x</sub> adsorption capacity of unsupported CaO and beta zeolite modified with CaO, K<sub>2</sub>O, MgO, BaO, ZnO, MnO, CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> in the presence of O<sub>2</sub> in the feed [49].

After the adsorbent is saturated with NO<sub>x</sub>, the adsorbed NO<sub>x</sub> must be desorbed for the adsorbent to be used again. The application of pressure swing adsorption (PSA) to regenerate the remove NO<sub>x</sub>-saturated adsorbent has been tested using several zeolites (MFI, mordenite, ferrierite, ZSM-5, offretite/erionite, Y, L, and X) exchanged with various metals (Na, Ca, Sr, Ba, Mg, Cu, Ag, Mn, Ni, Zn, Fe, Cr, Ce, La, Co and H) as the adsorbent [26,36–39]. The results of these studies revealed that the total, reversibly and irreversibly adsorbed NO amounts changed with the type and amount of the metal exchanged as well as the zeolite type [26].

Natural zeolites were proposed for gas purification applications rather than bulk separation due to their small pores and small pore volumes [50]. Clinoptilolite [51,52] and NH<sub>4</sub>-clinoptilolite [53] were applied in the removal of NO<sub>x</sub> from stack gases from fuel gas combustion processes. N<sub>2</sub>O and NO adsorption capacities of natural zeolites (erionite, mordenite, and clinoptilolite) from deposits in Mexico were measured in both static and dynamic regimes. The mordenite was found to be the most promising adsorbent for separating N<sub>2</sub>O/NO mixtures [54]. The same research group calculated the isosteric heats of NO adsorption from the adsorption isotherms obtained at 0 °C and 20 °C as 15–46 kJ/mol for mordenite, 15–32 kJ/mol for erionite, and 16–37 kJ/mol for clinoptilolite in the NO loading range of 0–0.7 mmol NO/g [55].

Natural zeolites were also investigated as catalyst in SCR of NO<sub>x</sub>. Cu(II)-exchanged mordenite and clinoptilolite were found to be very active catalysts using NH<sub>3</sub> in excess oxygen and showed high water tolerance [56]. Fe<sup>3+</sup>-clinoptilolite was found to be more active than the commercial vanadia catalyst in SCR of NO with ammonia [57].

Design and optimization of adsorptive separation processes require the adsorption equilibrium and kinetic parameters. Gas chromatography offers an alternative to conventional gravimetric and volumetric methods for experimental adsorption equilibrium and kinetic studies due to its advantage [58]. The adsorption equilibrium and kinetic parameters can be derived by matching the experimental chromatograms to the mathematical model. Chromatography has been applied to determine NO adsorption kinetic and equilibrium parameters for various adsorbents in the literature. Clinoptilolite from Bigadiç region (Turkey) was found to be the most promising adsorbent for the separation of NO from N<sub>2</sub> (air) among the molecular sieves tested, namely synthetic H-mordenite, 4A, 5A, and activated carbon [59]. In another study, higher Henry's law constants and heat of adsorption for NO on the clinoptilolite than on 4A, 5A and H-mordenite were reported. Clinoptilolite gave the highest separation NO/N<sub>2</sub> factors at low concentrations [60]. Galán studied the adsorption of NO on 13X and 5A, alumina (boehmite) and nickel-kieselguhr and copper zinc oxide catalysts by using a chromatographic technique. The low NO adsorption capacity of 13X was explained by absence of interaction between NO molecules and 13X due to the low molecular size of NO in comparison with the effective pore diameter of 13X [61]. In another study, the diffusional resistances for NO were reported to decrease in the following order: natural mordenite > Na-mordenite > H-mordenite > (13X, 5A) indicating the increased ease of flow in the 3-dimensional network. Isosteric heats of adsorption (range from

12.6 kJ/mol to 50.2 kJ/mol) and activation energies (range from 12.6 kJ/mol to 79.6 kJ/mol) decreased in the same order. The differences of these parameters were discussed in terms of the interaction between the adsorbent surface and NO molecules as well as the pore size of the adsorbent relative to the size of the diffusing NO molecules [62].

Recently, synthetic zeolites (LTA and FAU zeolites) exchanged with different transition metal cations (Na<sup>+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, and Mn<sup>2+</sup>) were applied for NO delivery purposes and NO-loaded zeolites exhibited biological activity. The mechanism of the biological effect was release of the loaded NO upon exposure of the NO-loaded zeolite to a moist atmosphere. NO-loaded zeolites were proposed as a cheap and simple alternative to other NO-releasing materials for use in medical applications [63–65].

The present study aims at determining NO adsorption equilibrium and kinetic parameters for a clinoptilolite-rich natural zeolitic material (NZ) from Gördes region (Turkey) using the concentration pulse chromatography method. The NO storage and release properties of this material have been previously examined by our group. In that study total, reversible and irreversible NO adsorption capacities of the material have been determined and it was shown that NZ can store and release NO thereby exhibits antibacterial/bactericidal activity [66].

## 2. Materials and methods

### 2.1. Material

The natural zeolitic material from Gördes region (Turkey) was used as adsorbent in the present study. Preparation and characterization of the zeolitic material (NZ) have been reported in our previous study [66]. Briefly, NZ contains predominantly clinoptilolite (67 wt %) as well as quartz, feldspars and biotite as mineral impurities. NZ is rich in potassium and has SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 5.90.

### 2.2. Concentration pulse chromatography (CPC)

Nitric oxide adsorption equilibrium and kinetic parameters for NZ were determined by the concentration pulse chromatography (CPC) method. This method is a dynamic method of conducting adsorption measurements, which measures the response of a chromatographic column to a pulse in adsorbate concentration.

CPC experiments were performed using the experimental set-up shown in Fig. 1. The column was made from type 316 stainless steel tubing of ¼ inches in outer diameter. Commercially available

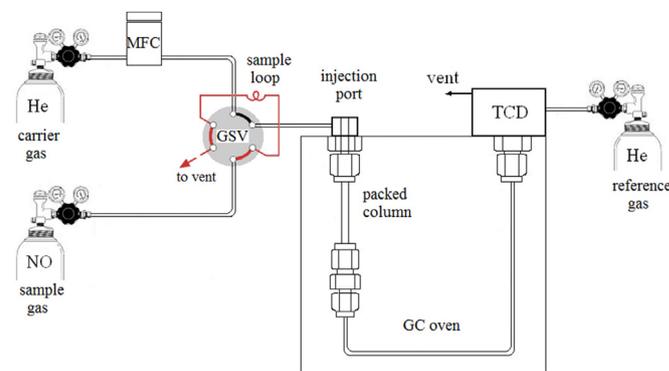


Fig. 1. Experimental set-up used in the concentration pulse chromatography experiments (MFC: mass flow controller, GSV: 6-port gas sampling valve, TCD: thermal conductivity detector).

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