

Binding of NO₂ in BaY Faujasite Catalysts: *In situ* Time-resolved X-ray Diffraction Studies

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Introduction

The reduction of harmful NO_x species emitted by internal combustion engines, factories and power plants has been a daunting task for controlling environmental pollution.[1] Zeolites possess unique features as gas adsorbents, gas separators, and catalysts.[2] BaY faujasite zeolites have been reported to be very promising catalysts for the non-thermal plasma-assisted catalytic reduction of NO_x species.[3-5] In order to understand these processes we have determined the structures of the NO_x species and the Barium cations in the zeolite under a wide range of conditions using *in situ* time-resolved X-ray diffraction.[6]

Materials and Methods

A BaY faujasite zeolite with a Si/Al ratio of ~2.6 was prepared from a NaY zeolite obtained from Zeolyst International (CBV 100) following procedures described elsewhere[3]. Time-resolved X-ray diffraction experiments on the dehydration and NO₂ adsorption/desorption on these samples were carried out at beamline X7B ($\lambda = 0.922 \text{ \AA}$), National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, with a MAR345 image plate detector.

The structures were determined and refined with powder diffraction analysis tools.[7]

Results and Discussion

Figure 1 shows the series of powder diffraction patterns obtained during adsorption and desorption of NO₂. The strongest line (111) provides an indication of the contents of the zeolite supercage (Figure 2). High values are indicative of nearly empty while low values suggest nearly full cages.

Consistent with the reported FT-IR results, three different ionic NO_x species (NO⁺, NO⁺-NO₂, and NO₃⁻) were observed in the NO₂-dosed, dehydrated BaY zeolite. The stabilities of the NO_x species are attributed to the strength of the interactions between the NO_x, the cations, and the framework. Likewise, the population of Ba cations at different locations strongly depends on the amount of NO_x species; and Ba cations migrated between different locations as a consequence of NO₂ adsorption/desorption. Figure 2 shows the local geometry of the NO_x species in the vicinity of the Ba²⁺ ions bound to the six membered rings in the supercage.

Significance

This work provided a direct observation of Ba cation migration to the different locations in the zeolite to accommodate the binding of the NO_x molecules. This unique feature plays a pivotal role in the catalytic performance of the BaY zeolite.

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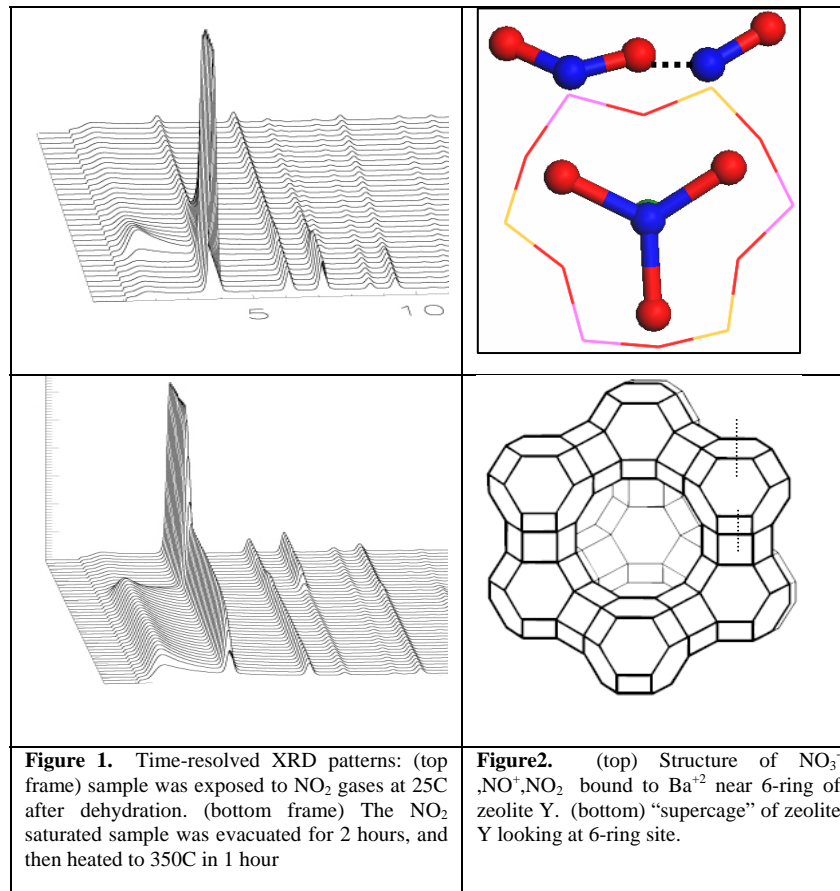


Figure 1. Time-resolved XRD patterns: (top frame) sample was exposed to NO₂ gases at 25C after dehydration. (bottom frame) The NO₂ saturated sample was evacuated for 2 hours, and then heated to 350C in 1 hour

Figure 2. (top) Structure of NO₃⁻, NO⁺, NO₂ bound to Ba²⁺ near 6-ring of zeolite Y. (bottom) "supercage" of zeolite Y looking at 6-ring site.

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