



NO_x adsorption over a wide temperature range on Na-ZSM-5 films

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Abstract

NO_x adsorption over a wide temperature range (30–350 °C) on monolith supported Na-ZSM-5 films were studied with a gas flow reactor. The nature of the adsorbed species was further investigated by in situ infrared spectroscopy. Depending on the adsorption temperature, three different ranges of thermally stable species were observed on Na-ZSM-5 films. In addition to the role of cationic sites and residual hydroxyl groups in zeolite frameworks, it was found that the formation of nitric acid plays an important role in NO₂ adsorption. Nitrate species were formed during adsorption by two mechanisms. The nitrates formed via nitric acid and involving NO formation had lower thermal stability than those formed through an NO₂ disproportionation reaction.

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1. Introduction

Zeolites are alumina silicates with a well-defined crystalline structure with cavities and pores of molecular dimensions. Positively charged cations are often required in the structure to balance the charge. These cations are exchangeable and influence the catalytic and transport properties of the zeolite. These characteristics make zeolites promising materials for catalysis and separation applications. Among the different types of zeolites, the MFI type in particular (i.e., ZSM-5 and silicalite-1) is widely used and studied.

For separation applications, zeolite crystals may be intergrown to form a film on a porous support material, resulting in a zeolite membrane. The selective permeation of a certain component through zeolite membranes strongly depends on both the adsorption properties and mobility of the component in the zeolite. Zeolite powder samples are commonly used to study the adsorption of components on zeolites.

However, a direct adsorption study using a zeolite film with crystal morphology similar to that of the membranes can lead to a better understanding of the adsorption and transport properties for a membrane. Recently, it was possible to coat monolithic and other structured support materials with binder-free zeolite films [1–3], and the films were catalytically active [2,3]. However, it has been found that the presence of defects in thick films could increase the effective diffusivity and eventually reduce catalyst selectivity [4,5].

NO_x adsorption on catalytic materials has been an important research topic for the development of transport and stationary exhaust after treatment systems. Investigations of NO_x adsorption on cation-exchanged zeolites have been reported in a number of publications. It has been found that NO is much more weakly adsorbed than NO₂ on several cation-exchanged zeolites [6,7] and requires a low temperature for storage [8,9]. To obtain storage of NO, oxidation to NO₂ is required [6,10,11]. Depending on the nature of the zeolite, various adsorbed NO_x species may exist. Infrared studies, mostly at near-ambient temperatures, show that in most cation-exchanged zeolites, surface nitrate species are formed after NO_x exposure, and the species are mainly located on the metal sites [7,11–14].

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However, there is no information now available concerning NO_x adsorption on the zeolite in the form of a film. The present work is devoted to a study of the adsorption of NO_x on an oriented Na-ZSM-5 film supported on a cordierite monolith. The presence of adsorbed NO_x species is studied by temperature-programmed desorption (TPD) and in situ DRIFT spectroscopy. In this report an adsorption mechanism is also proposed. The results from this work give valuable insights into NO_x adsorption and transport in Na-ZSM-5 films or membranes.

2. Experimental

2.1. Sample preparation

The Na-ZSM-5 film samples were prepared on cordierite monoliths. The monoliths consist of 188 channels in the cross section with a channel dimension of 1×1 mm. A detailed description of the sample preparation procedure has been reported elsewhere [2]. The monoliths were seeded with 60-nm silicalite-1 seeds [15,16] and hydrothermally treated repeatedly at atmospheric pressure at 75°C for 48 h. The seeded monolith samples used in this work were hydrothermally treated 12 times in a synthesis solution with a molar composition of 3 TPAOH:25 SiO_2 :0.25 Al_2O_3 :1 Na_2O :1600 H_2O :100 EtOH. Between hydrothermal treatments the samples were rinsed with 0.1 M aqueous ammonia solution and treated with ultrasound for 10 min. After the last hydrothermal treatment the samples were rinsed in a 0.1 M aqueous ammonia solution for 4 days and treated with ultrasound for 1 h each day. To remove precipitated zeolite from the ends of the monoliths, the monoliths were polished on each side to a length of 75 mm.

A powder sample for in situ DRIFT spectroscopy measurements was prepared from a synthesis solution with the same composition as that used for film growth. The resulting ZSM-5 crystals were hydrothermally treated for 72 h at 100°C , but without the support and silicalite-1 seeds [2]. To remove the template material, the monolith and powder samples were finally calcined at 550°C for 6 h with a heating and cooling rate of $1.75^\circ\text{C min}^{-1}$.

The samples were characterized by scanning electron microscopy (SEM) (Philips XL 30) and with nitrogen sorption (Micromeritics ASAP 2010). It was found that the surface area of the support is negligible compared with the total surface area of the sample [5]. Therefore, the zeolite loading was determined from gas sorption data (BET), with the surface area of ZSM-5 powder ($415 \text{ m}^2/\text{g}$) as a reference [5,17]. The elemental content of the powder sample was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.2. Adsorption–desorption measurements

NO_2 adsorption measurements were performed in a gas-flow reactor. The reactor consisted of a horizontal quartz tube with a length of 880 mm and a diameter of 22 mm and was equipped with a circular electrical heating element on the outer surface of the tube. To regulate the gas temperature and measure the sample temperature, two thermocouples were placed in the reactor. The monolith sample was sealed in the quartz tube with glass wool to prevent the gas flow from bypassing the channels. The two thermocouples were inserted into channels near the center of the monolith and from the downstream end of the monolith. One thermocouple was inserted about 5 mm into the monolith, whereas the second thermocouple traversed the entire length of the monolith so that it protruded about 10 mm out of the upstream end. We minimized heat loss by enclosing the reactor with glass wool insulation. Before NO_2 adsorption, the sample was pretreated with 8% O_2 in argon at 500°C for 15 min at a total flow rate of 3000 ml/min (STP). After the pretreatment, the sample was cooled to the adsorption temperature and equilibrated in an argon flow. For the adsorption, a gas mixture at a total flow rate of 2600 ml/min (STP) containing 600 ppm NO_2 in argon was prepared in a gas mixer (Environics 2000) consisting of several mass flow controllers. The temperature was regulated with a temperature controller (Eurotherm), with the use of the measurement from the thermocouple positioned 10 mm in front of the sample. After adsorption, the sample was flushed with only argon at the adsorption temperature. Finally, to release all of the adsorbed species, the sample was heated from the adsorption temperature to 550°C with a temperature ramp of $20^\circ\text{C}/\text{min}$ in an argon atmosphere during TPD.

In some experiments, the sample was also exposed to NO in argon. The influence of NO on the adsorbed species was investigated at 350°C . The sample was first equilibrated with 600 ppm NO_2 for 20 min. After establishment of equilibrium, the sample was flushed with argon for 5 min. Subsequently, at the same temperature, 600 ppm NO in argon was introduced at the inlet. In addition, the influence of NO was further studied by NO_2/NO co-adsorption experiments. During adsorption and desorption the outlet gas composition was analyzed online with a chemiluminescence detector (Ecophysics CLD 700 EL ht). The amount of adsorbed/desorbed NO_x was quantified from the area under corresponding concentration curves of adsorption, flushing, and TPD.

2.3. In situ DRIFT spectroscopy measurements

In situ DRIFT spectroscopy measurements were performed with a rapid scan method with a Bio Rad FTS6000 spectrometer. The zeolite powder was placed in a sample holder assembly in a Harrick Praying Mantis DRIFT cell. The gases were supplied by individual mass flow controllers with a total flow rate of 200 ml/min (STP). Before NO_2 ad-

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