

Ammonia Loading Detection of Zeolite SCR Catalysts using a Radio Frequency based Method

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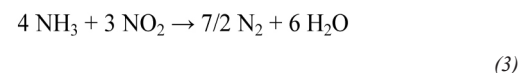
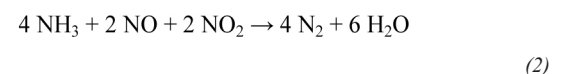
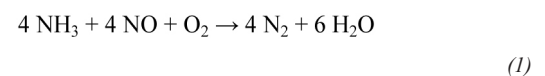
ABSTRACT

Ammonia adsorption on the catalyst surface is a crucial step in the selective catalytic reduction of nitrogen oxides over zeolites with NH_3 as the reducing agent. In this study, two small pore zeolites with chabazite frameworks, H-SSZ-13 and Cu exchanged SSZ-13, are examined. Adsorption of NH_3 on the zeolite causes changing electrical properties of the material. They can be detected by a radio frequency based technique. We have found that with this method it is possible to determine the amount of adsorbed NH_3 on these catalysts, examining both the influences of temperature and NH_3/NO feed gas ratio. At constant temperature, a fairly linear correlation between the resonance frequency and the amount of adsorbed ammonia was observed. Furthermore, this method also allows differentiation between some of the NH_3 adsorption sites.

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INTRODUCTION

In order to meet mandated regulatory standards for Tail Pipe (TP) emissions of Nitrogen Oxides (NO_x) from diesel engines, the Selective Catalytic Reduction (SCR) of NO_x with ammonia (NH_3) as reducing agent has become an industry norm worldwide. This is especially true for heavy duty vehicles. Depending on the NO_x ($= \text{NO} + \text{NO}_2$) composition in the engine out or Feed Gas (FG) exhaust, different chemical reactions with distinct reaction rates proceed to convert NO_x into nitrogen and water [1,2,3,4]. If only NO is present, the "standard" SCR reaction (Eq. 1) occurs. The oxygen for this reaction is readily available from the lean diesel exhaust that typically has O_2 concentration of about 10 % (molar). For an equimolar amount of NO and NO_2 , the so called "fast" SCR reaction (Eq. 2) proceeds, which, as the name suggests, is much faster than the "standard" reaction [1]. Typical diesel FG exhaust contains about 90 % NO and 10 % NO_2 , hence in order to achieve an equimolar NO: NO_2 composition, a Diesel Oxidation Catalyst (DOC) is often used upstream of the SCR. It converts unburned hydrocarbons as well. The reaction with only NO_2 (Eq. 3) is slower than the "standard" and "fast" SCR reactions [2]. The reducing agent NH_3 is derived from an eutectic (32.5 %wt) aqueous urea solution. This urea solution is often referred to as Diesel Exhaust Fluid (DEF) or by its commercial name AdBlue™. The urea solution is injected into the hot exhaust, where it decomposes to ammonia and carbon dioxide through hydrolysis and thermolysis [5].



As catalyst materials, Vanadia-based formulations are also used, but their low hydrothermal stability can be a serious concern, especially when the catalyst is located downstream of a Diesel Particulate Filter (DPF). During regeneration of the DPF, high peak temperatures in the range of 650-700 °C are typical. This high temperature operation may cause a loss of surface area of the Titania support due to the phase transformation of Anatase to Rutile form [3,6,7]. Furthermore, there are also concerns about the Vanadia-based catalysts due to their toxicity [7,8,9]. Metal exchanged zeolites are therefore promising catalysts, not only due to fewer toxic concerns but also because they are lower cost [8]. Additionally, metal exchanged zeolites have been found to show higher SCR activity and selectivity towards N_2 over a wider temperature window than do the Vanadia-based catalysts [6,7,8,9,10,11]. Zeolites with mordenite framework inverted (MFI) structure, especially ZSM-5, and Chabazite (CHA) framework structure, primarily SSZ-13, have been extensively studied for

ammonia SCR in literature [9,12,13,14,15,16,17]. On H-form zeolites, it was shown that a small Si/Al ratio (module of the zeolite) is favored for high SCR performance due to the higher concentration of acid sites [9,10,17,18]. On the other hand, a high Si/Al ratio improves the hydrothermal stability of the zeolite during operation [7]. Moreover, it is reported in literature that the pore size of the zeolite structure influences the SCR activity. A small pore size prevents deactivation due to dealumination [19,20] or due to adsorption of a large amount of hydrocarbons, particularly during cold start [1,20]. Therefore, chabazites are favored over MFI structures due to their small pores [7,9,10,21,22]. Various exchange metals have been investigated comprehensively in literature as well. It is reported that a higher amount of exchanged metals results in a higher activity but on the other hand reduces hydrothermal stability and leads to higher NH_3 oxidation [10,23,24]. Fe and Cu increase the SCR activity the most compared to the other tested metals. Fe is reported to increase the high temperature activity, whereas Cu shows an excellent low temperature activity [22,25,26,27]. A good low temperature activity is of special importance with regard to the growing number of stop-start operations and hybridization in the mobile sector in the future. On the other hand, a high temperature stability and high temperature SCR activity can be preferred when the SCR system is located downstream of the diesel particulate filter. Based on all these findings, Fe-ZSM-5 and Cu-SSZ-13 are probably the most investigated zeolites for ammonia SCR. Comparing these two materials, both of which are in serial use, Cu-SSZ-13 exhibits a higher standard SCR activity as well as a higher NH_3 storage capacity [22]. For NH_3 -SCR over metal exchanged zeolites, a number of reaction mechanisms are presented in literature. For almost all of these, the initial step involves adsorbed NH_3 on the catalyst surface in form of NH_4^+ ions on Brønsted acid sites [6,9,11,14,18,28,29]. At low temperatures and high NH_3 loadings, ammonia can adsorb weakly on top of each other on these sites via hydrogen bonds as $\text{NH}_4^+ \cdot n\text{NH}_3$ associations [30,31,32]. Furthermore, NH_3 can weakly adsorb on copper exchanged zeolites on alumina or metal related Lewis sites [14,15,16,22,33,34]. While the adsorbed NH_3 is important for the reduction reactions, the stored NH_3 is critical in maintaining NO_x reduction performance during transient operation with its fluctuating exhaust mass flow and feed gas NO_x concentration.

To obtain maximum NO_x conversion and minimum NH_3 slip over the SCR catalyst, it is essential to have knowledge about the current adsorbed amount of NH_3 on the catalyst. Storage based control of urea injection has been proposed by several researchers. Unfortunately, due to a lack of a direct measurement of the storage state, any control algorithm must rely on information from gas sensors located before and after the catalyst [35,36,37,38,39].

The radio frequency based method presented in this work allows for detecting the ammonia loading directly, contactless and *in operando*. In this study, a Chabazite SSZ-13 with and without copper exchange was investigated. Due to NH_3 adsorption, the proton conductivity of the zeolite increases distinctly [30,31]. By monitoring these changes in the material properties of the catalyst material, the NH_3 loading can be determined directly without the need for gas sensors, storage models or map-based approaches. For this purpose, a contactless radio frequency based method is adapted. The applicability of this method has been shown earlier for Fe and Cu exchanged zeolites

[40,41] and recently for Vanadia-based catalyst [42]. Moreover, this technique can be applied to other exhaust gas aftertreatment devices such as to establish the oxidation state of a three-way catalyst [43,44,45,46] or the NO_x loading of a lean NO_x trap [47,48] or soot loading of a diesel particulate filter [49,50].

METHODS

In this work, a radio frequency technique, based on the so called cavity perturbation method, was applied to measure the increase of the proton conductivity of the zeolite due to adsorption of ammonia. For this technique, the metallic catalyst housing serves as a partially filled cavity resonator. Electromagnetic waves are excited by simple coaxial probe feeds (electrically insulated stainless steel stubs). The typical setup of the capacitive probe feeds is shown in [51]. One probe feed is located upstream and the other downstream of the catalyst, thus, electrically, a 2-port network is formed. Metallic wire screens are installed at each end of the housing to define its electrical lengths. Figure 1 shows a schematic description of the test setup.

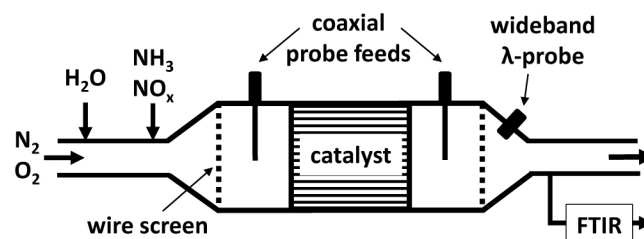


Figure 1. Schematic description of the test setup. The wire screens are used to define the cavity geometry more precisely. They are not mandatory for the principle.

A vector network analyzer (VNA, Anritsu MS2025) was utilized to measure the scattering parameters (reflection and transmission) in the range from 2 to 6 GHz. These parameters denote the ratios between the complex wave amplitude of the ingoing (a_j) and outgoing waves (b_i) where j denotes the ingoing and i the outgoing port. Consequently, S_{11} is the reflection and S_{21} the transmission parameter. Standing electromagnetic waves form inside the resonator at the resonance frequencies. These frequencies depend on the catalyst material and the overall geometry of the resonator cavity, and are also influenced by temperature due to the decreasing electrical conductivity of the catalyst material and thermal expansion of the resonator. The resonant frequencies can be determined by local extrema in the frequency spectrum of the recorded scattering parameters. Due to an increase of the proton conductivity of the catalyst because of adsorption of NH_3 , the electromagnetic field is perturbed to a larger extent. This causes a shift in the resonance frequencies. In this article, only the frequency of the lowest resonance mode, the TE_{111} mode, is observed. More detailed information of the radio frequency based technique can be found in literature [52,53].

All tests were performed on a laboratory synthetic exhaust gas test bench using a total gas flow of 40 l/min (equivalent to a gas hourly space velocity of 11 000 h^{-1}). All experiments were carried out with N_2 as carrier gas and 5 vol. % H_2O and 7 % NO_x in the background gases. All gas flows were controlled by mass flow controllers (MFCs).

Brooks). The downstream gas concentrations of H_2O , NH_3 , NO , NO_2 , and N_2O were monitored by a Fourier Transformed Infrared Spectroscopy (FTIR) analyzer (Nicolet Antaris IGS) and O_2 by a wideband lambda probe (Bosch, LSU 4.9), as outlined in Fig. 1. The zeolites H-SSZ-13 and a serial production copper exchanged SSZ-13, coated on honeycomb-structure cordierite drill cores with 6.0 cm (2 3/8") in diameter and 7.6 cm (3") in length, were mounted in a stainless steel canning and sealed by glass wool.

The adsorbed amount of NH_3 on the catalyst was calculated by balancing the inlet and outlet gas concentrations according to Eq. 4.

$$m_{\text{NH}_3} = \rho_{\text{NH}_3} \cdot \dot{V} \cdot \int (c_{\text{NH}_3, \text{in}} - c_{\text{NO}_x, \text{in}} - c_{\text{NH}_3, \text{FTIR}} + c_{\text{NO}_x, \text{FTIR}}) dt \quad (4)$$

In Eq. 4, m_{NH_3} is the mass of adsorbed ammonia on the catalyst and $\dot{V}$ is the volumetric gas flow rate and ρ_{NH_3} is the density of ammonia at the corresponding temperature. $c_{\text{NH}_3, \text{in}}$ and $c_{\text{NO}_x, \text{in}}$ are the NO_x and NH_3 feed gas concentrations (MFC output data) respectively, and $c_{\text{NH}_3, \text{FTIR}}$ and $c_{\text{NO}_x, \text{FTIR}}$ are the measured downstream gas concentrations. By matching the shift of the resonance frequency with this balance, the stored amount of NH_3 can be correlated with the radio frequency signal.

The feed ratio, α , is defined by

$$\alpha = \frac{c_{\text{NH}_3, \text{in}}}{c_{\text{NO}_x, \text{in}}} \quad (5)$$

RESULTS AND DISCUSSION

H-Form Chabazite (H-SSZ-13)

Initially, the ammonia storage of the H-form chabazite catalyst was studied to investigate the capability of the radio frequency-based method. The catalyst core was therefore saturated at first with NH_3 to determine the overall storage capacity at the respective temperature. Afterwards, the catalyst was flushed with background gas to allow the weakly bonded ammonia to desorb from the catalyst surface. Eventually, NO_x was admixed to convert the remaining strongly bonded NH_3 on the catalyst according to the SCR reactions (1,2,3). In Fig. 2, an experiment of this kind is shown at 250 °C. In Fig. 2a, the inlet (MFC data, dashed) and outlet (FTIR data, solid) gas concentrations of NH_3 , NO and NO_2 are shown. Figure 2b displays the resonance frequency and Fig. 2c the calculated adsorbed amount of NH_3 in gram per liter catalyst volume according to Eq. 4. At the onset, only 5 % H_2O and 7 % O_2 balanced with N_2 were fed and a stable baseline of the RF signal was obtained. After 10 min (at t_1), 500 ppm NH_3 was admixed. Although NH_3 was not detected downstream of the catalyst by the FTIR analyzer for the next 12 min, the resonance frequency immediately started to decrease as soon as NH_3 was added. The decrease continued linearly in combination with an increase in the calculated amount of NH_3 stored on the catalyst. Only after NH_3 broke through downstream and reached the same 500 ppm concentration as the inlet at t_2 , indicating that the catalyst was saturated with ammonia, did the RF signal remain on a constant level. The calculated adsorbed mass on the catalyst amounted to 0.62 g per

liter catalyst volume at that point. At t_3 , the NH_3 supply was stopped, resulting in a decrease in the downstream concentration of NH_3 . This NH_3 slip during the interval from t_3 to t_4 is attributed to the desorption or release of the weakly bonded NH_3 . Since, according to Fig. 2c, only a small fraction of the ammonia was weakly bonded at 250 °C, the resonance frequency increased only slightly and the stored amount decreased marginally during the desorption period. At t_4 , the NH_3 concentration from this desorption phase reduced to 0 as indicated by the FTIR. The RF signal and the stored amount at this time instance both reached a constant value, indicating that all the weakly bonded NH_3 desorbed. The remaining strongly bonded NH_3 was then converted with 250 ppm NO and 250 ppm NO_2 , which were introduced at t_4 . The conversion proceeded according to the "fast" SCR reaction (Eq. 2). This can be seen by a fast increase of the RF signal seen immediately after t_4 when all the input NO_x was converted, as indicated by zero NO_x detected at the outlet. At t_5 , the resonance frequency returned to its unloaded value and the downstream NO_x concentration matched the inlet values of 250 ppm for each component, indicating both zero NO_x conversion and that the catalyst had achieved a zero NH_3 storage state. This is also mirrored in the calculated amount of stored NH_3 . By comparing the RF signal and the stored amount, one can recognize a clear correlation between the resonance frequency and the NH_3 loading on the catalyst.

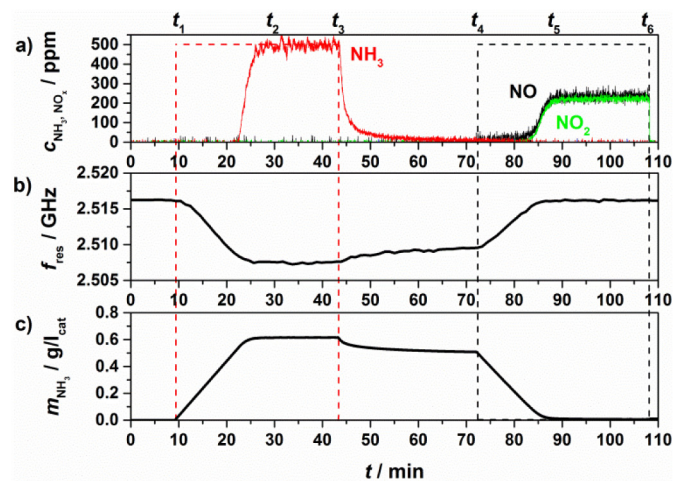


Figure 2. Storage experiment on H-SSZ-13 at 250 °C. a) Inlet (dashed) and outlet (solid) gas concentrations of NH_3 (red), NO (black) and NO_2 (green), b) resonance frequency and c) calculated amount of NH_3 adsorbed on the catalyst.

Similar experiments were performed at 200, 250, 300 and 350 °C with NH_3 feed concentrations of 25, 50, 100, 200, 300, 400 and 500 ppm. In Fig. 3, the adsorbed amount of ammonia on the catalyst at saturation (t_2 in Fig. 2) is shown over the feed concentration for all temperatures. It is obvious from Fig. 3 that the adsorption capacity reduces with temperature. This is in line with expectation. Furthermore, it is also seen that the amount of NH_3 adsorption increases with ammonia concentration in the feed gas, more precisely on the partial pressure of NH_3 . These observations agree well with literature [54]. The increase in storage with c_{NH_3} can be explained by the multiple NH_3 layer hypothesis discussed previously. It is hypothesized that the weak layer bonding can be increased with