A Gas Sensing Approach to Gain Insight into the Mechanism of DeNOx-SCR over Fe-ZSM-5 Catalysts

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Abstract:
In order to meet the legislative emission requirements for NO\textsubscript{x} emission, selective catalytic reduction (DeNOx-SCR) catalysts, in particular zeolites, are used. To improve their catalytic performance, an in-depth understanding of the reaction mechanisms is required based on an analysis of the physicochemical properties, preferably \textit{in situ}. We introduce a setup combining impedance spectroscopy (IS) and infrared spectroscopy in diffuse reflection mode (DRIFT) for \textit{in situ} measurements on zeolites under SCR-related conditions. By means of this gas sensing approach, we observed the formation of ammonium ion (NH\textsubscript{4}+) intermediates resulting from the interaction of NO and NH\textsubscript{3} on Fe-ZSM-5 catalysts. The formed NH\textsubscript{4}+ intermediates, indicating the activation of NO in the presence of adsorbed NH\textsubscript{3}, were found to correlate to the NH\textsubscript{3}-SCR activity of Fe-ZSM-5 catalysts at low temperatures. These findings, which are not easily achievable by conventional methods, provide new and important perspectives to understand mechanistically the NH\textsubscript{3}-SCR reaction over Fe-zeolite catalysts.

Key words: Impedance spectroscopy, DRIFTS, NH\textsubscript{3}-SCR mechanism, proton transport, Fe-ZSM-5.

Introduction
One key strategy to reduce nitrogen oxides (NO\textsubscript{x}) emissions from lean-burn engines is the selective catalytic reduction using NH\textsubscript{3} as reducing agent (DeNOx-SCR). Among the catalysts employed, metal-exchanged zeolites are the most widely used. Particularly, Fe-exchanged ZSM-5 zeolite demonstrated SCR activity in a wide temperature range and thermal durability under operative conditions [1]. At the same time, proton conducting zeolites are well known sensing materials for NH\textsubscript{3} detection [2]. The stringent legislative emissions requirements require further improvement of SCR catalysts driven by an advanced mechanistic understanding of the catalytic cycle. In this context impedance spectroscopy (IS) in combination diffuse-reflection infrared Fourier transform spectroscopy (DRIFTS) applied \textit{in situ} allowed us to gain important and unique information on the catalytic properties of Fe-ZSM-5.

Combining IS and DRIFTS
IS data are represented in an Arrhenius plot (Fig. 1a), that shows the temperature dependent proton conductivity. NH\textsubscript{3}-loaded Fe-ZSM-5 shows a higher proton conductivity than the pristine one below 350 °C due to the support of the adsorbed NH\textsubscript{3} to the proton transport [2]. Performing measurements under different gas conditions, it was possible to individuate a temperature range (175-250 °C) in which the proton conductivity under NO/O\textsubscript{2} (SCR-related conditions) decreases much faster than under N\textsubscript{2} (i.e. due to pure NH\textsubscript{3} desorption). These results allow us to identify the interval in which NH\textsubscript{3} is consumed by SCR, and, therefore, in which the main information about SCR can be derived.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Arrhenius plots for pristine and NH\textsubscript{3}-loaded Fe-ZSM-5 under different gas conditions (a); Time-resolved \textit{in situ} DRIFT spectra of NH\textsubscript{3}-loaded Fe-ZSM-5 in NO/O\textsubscript{2} at 200 °C (b).}
\end{figure}
Fig. 1b depicts the time-resolved spectra obtained for NH₃-loaded Fe-ZSM-5, during exposure to NO/O₂ atmosphere centered in the “SCR temperature interval” (200 °C). Thereby we observe the progressive consumption of NH₃ following the decrease in intensity of the characteristic bands, associated to NH₃ on Fe sites (1266 cm⁻¹), on Lewis sites (1610 cm⁻¹) and on Brønsted sites (1457 cm⁻¹). Thanks to the IS-DRIFTS setup already described elsewhere [4], similar experiments under SCR conditions can be combined with single-frequency IS measurements, obtaining combined plots as shown in Fig. 2a-b. Here NH₃-loaded Fe-ZSM-5 was exposed to NO/O₂ only after an interval under N₂ or NO (Fig. 2a and 2b, respectively). In both situations, the proton conductivity (Iₓₛ) seems to be strongly correlated to the 1457 cm⁻¹ DRIFTS signal, attributed to NH₄⁺ ions formed on the Brønsted sites. Interestingly, both Iₓₛ and DRIFTS intensity, experienced a slight increase in NO/O₂ after exposure to N₂ (Fig. 2a). In contrast, this evolutionary trend is not observed, when the catalyst is exposed first to NO before applying NO/O₂. Furthermore, under NO, the catalyst shows a significantly higher Iₓₛ signal compared to the measurement under N₂ (Fig. 2b). These results show that the co-adsorption and interaction of NH₃ and NO on the Fe(III) sites leads to the formation of supplementary NH₄⁺ ions, suggesting that a mechanism similar to the redox cycle in Cu-exchanged zeolites [5] is followed: during the reduction of Fe(III) to Fe(II), a proton is generated on the adjacent Brønsted site, that, interacting with adsorbed NH₃, leads to the formation of an NH₄⁺ intermediate.

**IS-DRIFTS and NH₃-SCR activity**

The formation of NH₄⁺ intermediates reflect the activation of NO in the presence of NH₃. The proton conductivity enhancement (i.e. the difference between Iₓₛ after 30 min in NO and Iₓₛ after 30 min in N₂, see Fig. 2a-b) has been found to be relatable to the NO reduction rate (Fig. 3). Specifically, in catalysts with low Fe-loading, where isolated or dimeric Fe species are predominant (verified by means of UV/Vis and XRD data), a higher reducibility of Fe(III) coincides with a more pronounced change in ΔIₓₛ, and therefore a higher presence of highly mobile NH₄⁺ ions. These results demonstrate that a typical gas sensing approach, i.e. the combination of IS and DRIFTS applied in situ, allows not only to observe the formation of NH₄⁺ intermediates, but also their favoring effect to the SCR activity of Fe-ZSM-5. The formation of NH₄⁺ intermediates may serve as a potential “descriptor” for the design of active Fe-zeolite catalyst for NH₃-SCR.

![Fig. 2. Normalized ion conductivity signal (Iₓₛ, red line) and DRIFTS signal at characteristic wavenumbers (blue symbols) of NH₃-loaded Fe-ZSM-5 exposed to different gas atmospheres at 175 °C. The horizontal black line highlights the Iₓₛ values after 30 minutes, used to calculate ΔIₓₛ. (adapted from [6])](image)

**Fig. 3.** Correlation between NH₄⁺ intermediate formation (associated to ΔIₓₛ) and NO reduction rates for zeolites with varied Fe-loaded ZSM-5 catalysts at different temperatures (reproduced from [6]).

**References**


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