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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_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 *in situ.* We introduce a setup combining impedance spectroscopy (IS) and infrared spectroscopy in diffuse reflection mode (DRIFT) for *in situ* measurements on zeolites under SCR-related conditions. By means of this gas sensing approach, we observed the formation of ammonium ion (NH_4^+) intermediates resulting from the interaction of NO and NH_3 on Fe-ZSM-5 catalysts. The formed NH_4^+ intermediates, indicating the activation of NO in the presence of adsorbed NH_3, were found to correlate to the NH_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_3−SCR reaction over Fe-zeolite catalysts.

Key words: Impedance spectroscopy, DRIFTS, NH_3-SCR mechanism, proton transport, Fe-ZSM-5.

Introduction

One key strategy to reduce nitrogen oxides (NO_x) emissions from lean-burn engines is the selective catalytic reduction using NH_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_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 *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_3-loaded Fe-ZSM-5 shows a higher proton conductivity then the pristine one below 350 °C due to the support of the adsorbed NH_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_2 (SCR-related conditions) decreases much faster than under N_2 (i.e. due to pure NH_3 desorption). These results allow us to identify the interval in which NH_3 is consumed by SCR, and, therefore, in which the main information about SCR can be derived.

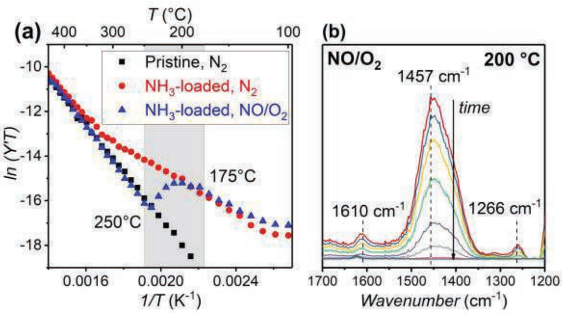

Fig. 1. Arrhenius plots for pristine and NH_3-loaded Fe-ZSM-5 under different gas conditions (a); Time-resolved in situ DRIFT spectra of NH_3-loaded Fe-ZSM-5 in NO/O_2 at 200 °C (b).

Fig. 1b depicts the time-resolved spectra obtained for NH_3-loaded Fe-ZSM-5, during exposure to NO/O_2 atmosphere centered in the "SCR temperature interval" (200 °C). Thereby we observe the progressive consumption of NH_3 following the decrease in intensity of the characteristic bands, associated to NH_3 on Fe sites (1266 cm^{-1}), on Lewis sites (1610 cm^{-1}) and on Brønsted sites (1457 cm^{-1}) [3]. 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 NH_3-loaded Fe-ZSM-5 was exposed to NO/O_2 only after an interval under N_2 or NO (Fig. 2a and 2b, respectively). In both situations, the proton conductivity (I_{IS}) seems to be strongly correlated to the 1457 cm^{-1} DRIFTS signal, attributed to NH_4^+ ions formed on the Brønsted sites. Interestingly, both I_{IS} and DRIFTS intensity, experienced a slight increase in NO/O_2 after exposure to N_2 (Fig. 2a). In contrast, this evolutionary trend is not observed, when the catalyst is exposed first to NO before applying NO/O_2. Furthermore, under NO, the catalyst shows a significantly higher I_{IS} signal compared to the measurement under N_2 (Fig. 2b). These results show that the co-adsorption and interaction of NH_3 and NO on the Fe(III) sites leads to the formation of supplementary NH_4^+ 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 NH_3, leads to the formation of an NH_4^+ intermediate.

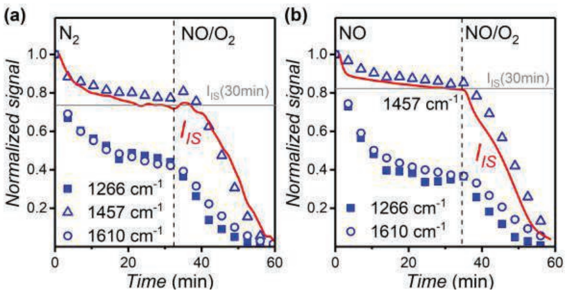

Fig. 2. Normalized ion conductivity signal (I_{IS}, red line) and DRIFTS signal at characteristic wavenumbers (blue symbols) of NH_3-loaded Fe-ZSM-5 exposed to different gas atmospheres at 175 °C. The horizontal black line highlights the I_{IS} values after 30 minutes, used to calculate ΔI_{IS}. (adapted from [6])

IS-DRIFTS and NH_3-SCR activity

The formation of NH_4^+ intermediates reflect the activation of NO in the presence of NH_3. The proton conductivity enhancement (i.e. the difference between I_{IS} after 30 min in NO and I_{IS} after 30 min in N_2, 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 ΔI_{IS}, and therefore a higher presence of highly mobile NH_4^+ 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 NH_4^+ intermediates, but also their favoring effect to the SCR activity of Fe-ZSM-5. The formation of NH_4^+ intermediates may serve as a potential "descriptor" for the design of active Fe-zeolite catalyst for NH_3−SCR.

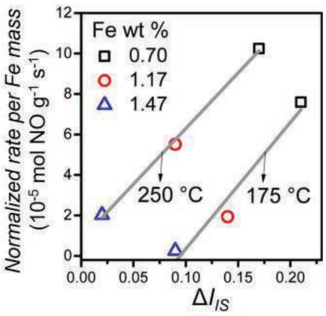

Fig. 3. Correlation between NH_4^+ intermediate formation (associated to ΔI_{IS}) and NO reduction rates for zeolites with varied Fe-loaded ZSM-5 catalysts at different temperatures (reproduced from [6]).

References

[1] R. Zhang, N. Liu, Z. Lei, B. Chen, *Chem. Rev.* 116, 3656-3721 (2016); doi: 10.1021/acs.chemrev5b00474.

[2] M.E. Franke, U. Simon, R. Moos, A. Knezevic, R. Müller, C. Plog, *Phys. Chem. Chem. Phys.* 5, 5195-5198 (2003); doi: 10.1039/b307502h.

[3] K. Góra-Marek, K. Brylewska, K.A. Tarach, M. Rutkowska, M. Jabłońska, M. Choi, L. Chmielarz, *Applied Catalysis B: Environmental* 179, 589-598 (2015); doi:1 0.1016/j.apcatb.2015.05.053.

[4] P. Chen, S. Schönebaum, T. Simons, D. Rauch, M. Dietrich, R. Moos, U.Simon, *Sensors* 15, 28915-28941 (2015); doi: 10.3390/s151128915.

[5] C. Paolucci, A.A. Verma, S.A. Bates, V.F. Kispersky, J.T. Miller, R. Gounder, W.N. Delgass, F.H. Ribeiro, W.F. Schneider, *Angew. Chem., Int. Ed.* 53, 11828-11833 (2014); doi: 10.1002/anie.201407030.

[6] P. Chen, M. Jabłońska, P. Weide, T. Caumanns, T. Weirich, M. Muhler, R. Moos, R. Palkovits, U. Simon, *ACS Catal.* 6, 7696-7700 (2016); doi: 10.1021/acscatal.6b02496.