Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

The effect of Cu and Fe cations on NH_3-supported proton transport in $DeNO_x$-SCR zeolite catalysts

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Theory for impedance spectroscopy (IS)

The complex impedance $Z(\omega)$ is defined as the ratio between the applied complex voltage U and the resulting current I, that is,

$$Z(\omega) = U / I \tag{S1}$$

$Z(\omega)$ can be described by a real part Z' and an imaginary part Z''. Both depend on the angular frequency ω.

$$Z(\omega) = Z'(\omega) + jZ''(\omega) \tag{S2}$$

In the traditional Argand representation (also known as Nyquist plot) of impedance data, the real part Z' is plotted against the imaginary part Z'' of $Z(\omega)$. While the low-frequency phenomena such as the sample/electrode interface polarization can be easily identified by the dominating low-frequency tail, the high-frequency processes are less visible. Modulus plot, which shows the imaginary part of the modulus against the frequency, was thus developed to illustrate the high-frequency processes (see the M'' plots in Fig. S2).[1, 2] The modulus $M''(\omega)$ is defined as

$$M''(\omega) = \omega C_0 Z'(\omega) \tag{S3}$$

wherein C_0 is the capacity of the empty capacitor, i.e. the geometric capacitance.

The modulus plot shows a maximum at the resonance frequency ν_{res} of the system, which is the reciprocal of the relaxation time τ, i.e. the time a perturbed system needs to reach thermodynamic equilibrium

$$\nu_{\mathrm{res}} = 1/\tau \tag{S4}$$

From the thermal shift of ν_{res}, the activation energy E_A of the conductivity process can be derived according to the Arrhenius equation

$$\ln[Y' T] \sim \ln[\sigma(T)] = A + E_A / (k_B T) \quad (S5)$$

where Y' is the real part of the admittance Y ($Y=1/Z$) at the temperature-dependent resonance frequency ν_{res}, σ is the specific conductivity of the zeolite, and k_B is the Boltzmann constant.

Experimental section

Catalyst preparation

Proton-form ZSM-5 zeolite (H-ZSM-5) with a SiO_2/Al_2O_3 ratio of 27 was supplied by the company Clariant and used without any further treatment. Aqueous-phase exchange of copper ion into the zeolite was performed using a 0.0075 mol L^{-1} $Cu(NO_3)_2$ solution at pH 5.5. In a single batch, four grams of H-ZSM-5 zeolite and 600 mL of solution were applied. After ion exchange for 24 h at room temperature, the zeolite materials were filtered, thoroughly washed with distilled water (three times, 1 L water in total), and dried overnight at 100 °C. The obtained powders were calcined in laboratory air at 500 °C for 2 h resulting in the catalyst denoted as Cu-ZSM-5. Iron ion exchange was performed at an elevated temperature of 80 °C for 24 h using a 0.0075 mol L^{-1} $FeSO_4$ solution at pH 5.5. After ion exchange, the zeolite/solution mixture was cooled down to room temperature. Flowing N_2 was supplied in the whole process to protect Fe^{2+} cations in the solution against oxidation upon contact with air. Afterwards, the zeolite materials were filtered, thoroughly washed with distilled water (three times, 1 L water in total), and dried under vacuum for 2 h. The obtained powders were further dried in flowing Ar at 100 °C for 1 h before calcination at 500 °C for 2 h. The synthesized catalyst was denoted as Fe-ZSM-5. For comparison, the H-ZSM-5 zeolite was also calcined at 500 °C in air for 2 h prior to any further use.

Physicochemical characterization

The H-form and ion-exchanged zeolites were characterized by X-ray diffraction (XRD), Scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), diffuse reflection ultraviolet-visible spectroscopy (DR UV-Vis) and X-ray photoelectron spectroscopy (XPS). The crystal structures of the zeolites were analyzed by XRD using Cu Kα irradiation. The sample morphologies were studied using a Zeiss DSM 982 Gemini scanning electron microscope, while the sample compositions were analyzed by EDX (Oxford Instruments). DR UV-Vis spectra were recorded in a Perkin-Elmer Lambda 650 UV–vis spectrometer equipped with a praying mantis mirror construction. The samples were diluted by $BaSO_4$ with a zeolite/$BaSO_4$ weight ratio of 10. XPS was performed in a UHV setup equipped with a Gammadata-Scienta SES 2002 analyzer. The base pressure in the measurement chamber was kept at ca. 5×10^{-10} mbar. Monochromatic Al Kα (1486.6 eV, 14 kV, 30 mA) was used as incident radiation, and a pass energy of 200 eV was chosen resulting in an effective instrument resolution better than 0.6 eV. Charging effects were compensated using a flood gun, and binding energies were calibrated by positioning the main C 1s peak at 285 eV, which originates from carbon contaminations. Measured data were fitted using Shirley-type backgrounds and a combination of Gaussian–Lorentzian functions with the CasaXPS software. The surface compositions were obtained by determining the integral area of the Gaussian–Lorentzian functions and correcting the values by the specific atomic sensitivity factors.

The surface acidity of the zeolites was characterized by temperature-programmed desorption using NH_3 as a probe molecule (NH_3-TPD). In each measurement, 50 mg of zeolite samples was loaded into a quartz U-tube reactor. The powders were first dried at 200 °C in flowing helium (50 ml min^{-1}) for 60 min and then cooled to 50 °C. The adsorption of NH_3 was carried out at 50 °C in flowing NH_3 atmosphere (4000 ppm in helium, 50 ml min^{-1}) for 120 min. Subsequently, the reactor was flushed with pure helium (50 ml min^{-1}) for 120 min to remove physically adsorbed NH_3. The desorption of NH_3 was performed in the temperature range from 50 °C to 650 °C with a ramp of 2 °C min^{-1}. The concentration of NH_3 leaving the reactor was recorded by a non-dispersive infrared detector (Emerson Process Management, Rosemount NGA 2000 MLT 4). The detector was calibrated with 4000 ppm NH_3 in helium before each single measurement.

In situ IS measurement

Electrical properties of the zeolites were analyzed by *in situ* IS under dynamic gas conditions, following established protocols reported in our previous work.[1, 3] For a better electrical contact, the zeolite materials were deposited as a thick film on screen-printed inter-digital electrodes (IDEs) being comprising an alumina substrate with gold electrodes on the front side and integrated heater on the back side. For IS measurement, the IDE chip was placed in a stainless steel measuring chamber (with a total volume of 30 cm^3) equipped with a ZnSe-window for contactless temperature monitoring by a spectral pyrometer (KT 19.82, Heitronics), and a digital multimeter (Keithley 2400) for the power supply of the integrated heater. The gas flow through the chamber was regulated by mass flow controllers (MKS 1179A, MKS 1259C MKS-647C, all MKS-Instruments). Impedance response was measured with an impedance analyzer combined with a dielectric interface (SI 1260 and SI 1296, both Solartron). Prior to any IS measurement, the temperature regulation of the IDE chip was calibrated under flowing N_2 conditions. A constant gas flow of 100 sccm was applied in all measurements.

The *in situ* IS studies were carried out in two different modes, i.e. multi-frequency mode (0.1 Hz to 1 MHz) and single-frequency mode (10 KHz), in order to determine the resonance frequency (ν_{res}) of the zeolite catalysts and to improve the time-resolution of the measurements, respectively.

The analysis of multi-frequency IS results are described in the aforementioned theory part. For the single-frequency measurements shown in Figs. 3b, S7 and S9, the IS signals were normalized by setting the smallest value to 0 and the highest value to 1. For the single-frequency measurements shown in Fig. 4c, the IS signals recorded in N_2 and NH_3 were normalized by setting the smallest value to 0 and the highest value to 1, while the IS signals for the subsequent exposure in different atmospheres were normalized by dividing the recorded IS signals with the IS for NH_3-saturated zeolites. Thereby, the different changes in the IS signals for Fe-ZSM-5 and Cu-ZSM-5 by exposure in NO-containing atmosphere can be more clearly visualized.

In situ IS-DRIFTS measurement

Details of the instrumental design for the simultaneous *in situ* IS-DRIFTS (diffuse reflection IR Fourier transform spectroscopy) measurements were already described in our previous work.[3] The measurement configuration and setup are shown in Fig. S1. The DRIFTS measurements were performed by a VERTEX 70 spectrometer (Bruker) in combination with a Praying MantisTM (Harrick Scientific Products) mirror system for diffuse reflection spectroscopy. The spectra were recorded in the range from 4000 to 650 cm^{-1} with a resolution of 2 cm^{-1} and each consists of 128 single scans. The reflectance is given in Kubelka-Munk (KM) units, which ensures the linearity between the band intensity and the concentration of the adsorbed species. All presented spectra are difference spectra, i.e., a spectrum of the pure sample at the desired temperature was collected in flowing N_2 as background and was subtracted from all further measurements of the series in differently applied gas conditions. From this, only the vibration modes of the adsorbed species and no lattice vibrations are visible in the spectra. The electrical impedance was measured with an Impedance Analyzer combined with a Dielectric Interface (SI 1260 and SI 1296, both from Solartron) enabling measurements in the impedance range up to 10^{14} Ω (±1 %). Before measurements, all samples were held at 400 °C in 10% O_2 flow for at least 1 h to avoid effects of solvent molecules.

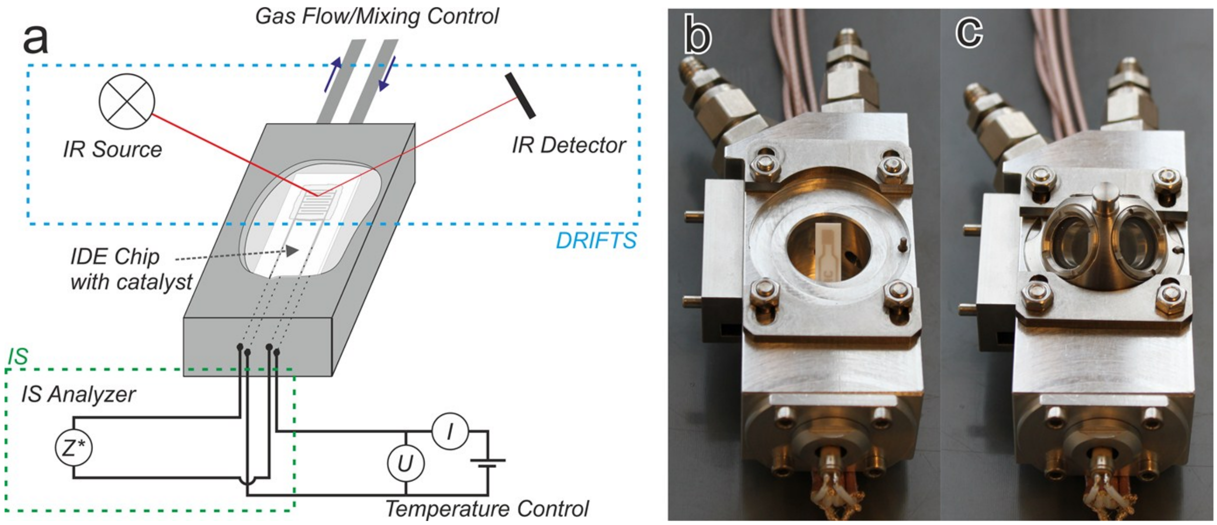

Fig. S1 Simultaneous *in situ* IS-DRIFTS measurements on the same catalyst film. (a) Scheme of the chamber and measurement configuration; (b) Photograph of open chamber; (c) Photograph of chamber with dome. Adapted from Ref 3.

NH_3-SCR tests

The NH_3-SCR tests were carried out in a fixed-bed reactor as described elsewhere.[4] In each test, 0.5 g of catalyst powders was applied, and were pre-treated in 10% O_2 at 375 °C for 3 h prior to the SCR test. After the pretreatment, a gas mixture of 500 ppm NH3, 500 ppm NO, 10% O_2 and 2% H_2O was fed to the reactor to start the SCR reaction. The reaction temperature was decreased stepwise (25 °C per step) from 375 °C to 150 °C. At each temperature, the reaction was maintained for 30 min to achieve steady state. The NO conversion after 30 min was recorded for activity comparison.

Results

Table S1 Chemical compositions of zeolite catalysts

	Si/Al [a]	**Fe/Al or Cu/Al** [a]	**Metal loading wt%** [c]
H-ZSM-5	13.5	0	0
Fe-ZSM-5	14.2	0.18	0.69
Cu-ZSM-5	13.9	0.20	0.99

[a] atomic ratio determined by EDX.

[b] determined by ICP-OES.

Table S2 Assignments of the characteristic IR bands[3]

Position	**Vibration**	**Assignment**
3400-3100 cm^{-1}	ν (NH_3)	NH_3 bound in 3H-structure
2700-2300 cm^{-1} (max.: 2530 cm^{-1})	ν (NH_3)	Weakly bound NH_3
1616 cm^{-1}	ν (NH_3)	NH_3 bound to Lewis site
1457 cm^{-1}	δ (NH_3)	NH_3 strongly bound to Brønsted site
1267 cm^{-1}	ν (NH_3)	NH_3 bound to Lewis site

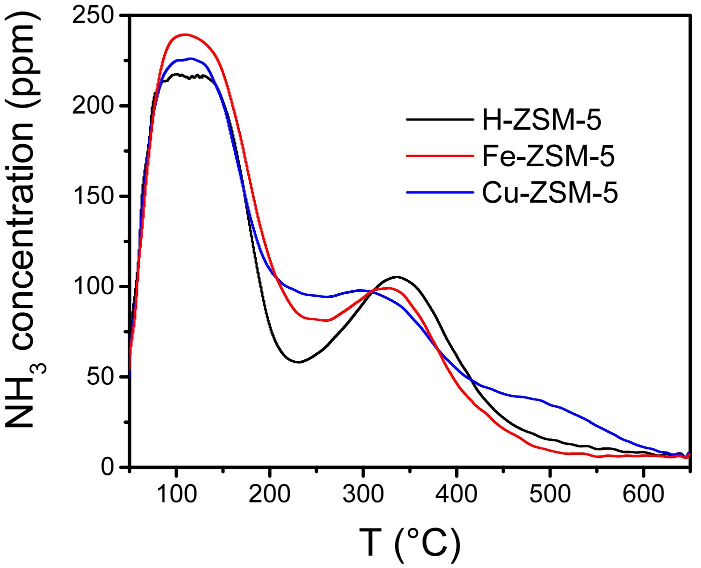

Fig. S2 NH_3 desorption profiles of the zeolite catalysts in NH_3-TPD at a heating ramp of 2 °C min^{-1}.

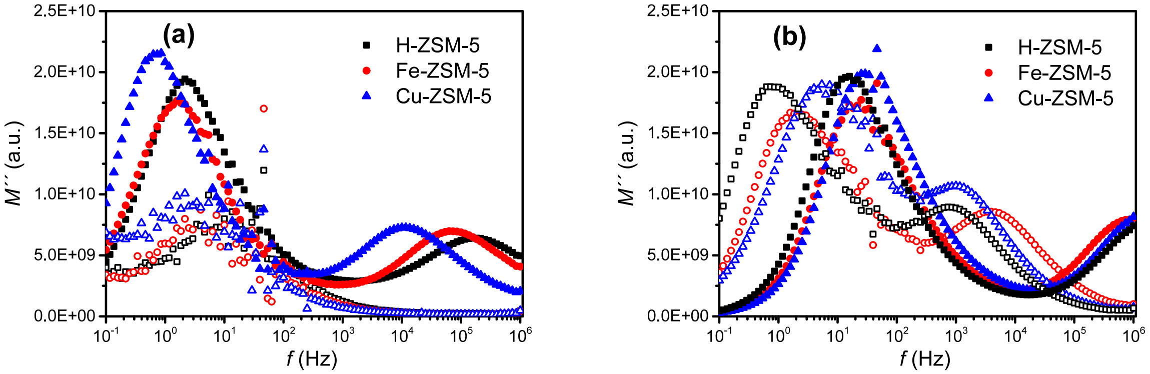

Fig. S3 Modulus plots of the *in situ* IS results in pure N_2 (empty symbols) and 100 ppm NH_3 in N_2 (solid symbols) at 100 °C (a) and 250 °C (b). H-ZSM-5: black squares; Fe-ZSM-5: red circles; Cu-ZSM-5: blue triangles.

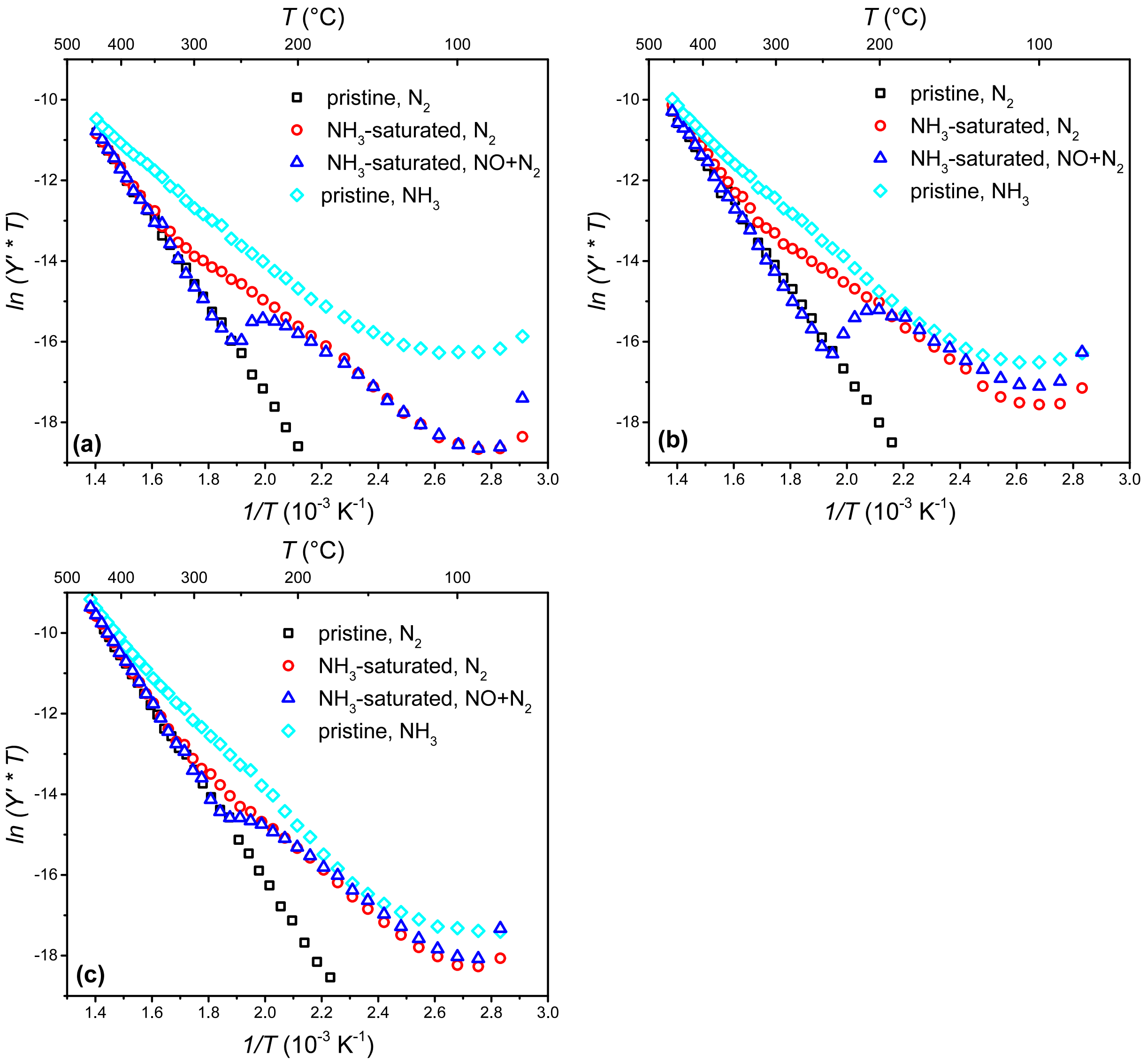

Fig. S4 Arrhenius-like plots of the *in situ* IS results for (a) H-ZSM-5, (b) Fe-ZSM-5 and (c) Cu-ZSM-5 zeolites under different conditions. The *Y′* values were determined according to the impedance data at the low-frequency maxima in the Modulus spectra, and were used for the evaluation of the conductivity under given conditions. Black squares: measurement in N_2 over pristine zeolite; red circles: measurement in N_2 over zeolite saturated by NH_3 at room temperature; blue triangles: measurement in $NO/O_2/N_2$ mixture over zeolite saturated by NH_3 at room temperature; cyan diamonds: measurement in 100 ppm NH_3 in N_2 over pristine zeolite. A pretreatment at 400 °C in 10% O_2 for 1 h was conducted prior to each measurement.

When the NH_3-saturated zeolite catalysts, were exposed to different atmospheres, the different processes (i.e. thermal desorption in N_2 or SCR conversion in NO/O_2) changed differently the temperature-dependent proton conductivity,[1, 3] leading to a distinct ‘SCR window’ in the Arrhenius-like representations (see the difference between the red circles and blue triangles). As compared to H-ZSM-5 (Fig. S4a), the ‘SCR window’ is more clearly visible in case of Fe-ZSM-5 (Fig. S4b), because of the presence of Fe cations serving as active sites for the NH_3-SCR reaction and consequently facilitating the catalytic conversion of surface NH_3 species.[1, 3] Surprisingly, Cu-ZSM-5 displayed a significantly less pronounced ‘SCR window’ (Fig. S4c) than H-ZSM-5 and Fe-ZSM-5, which is unexpected because Cu-ZSM-5 is more SCR-active than Fe-ZSM-5 at low temperatures (Fig. S8).[3] Single-frequency IS studies revealed that proton conducting intermediates formed on Cu-ZSM-5 upon exposure to NO/O2, leading to enhanced proton conductivity against the decaying due to the loss of NH_3 (Fig. 4).

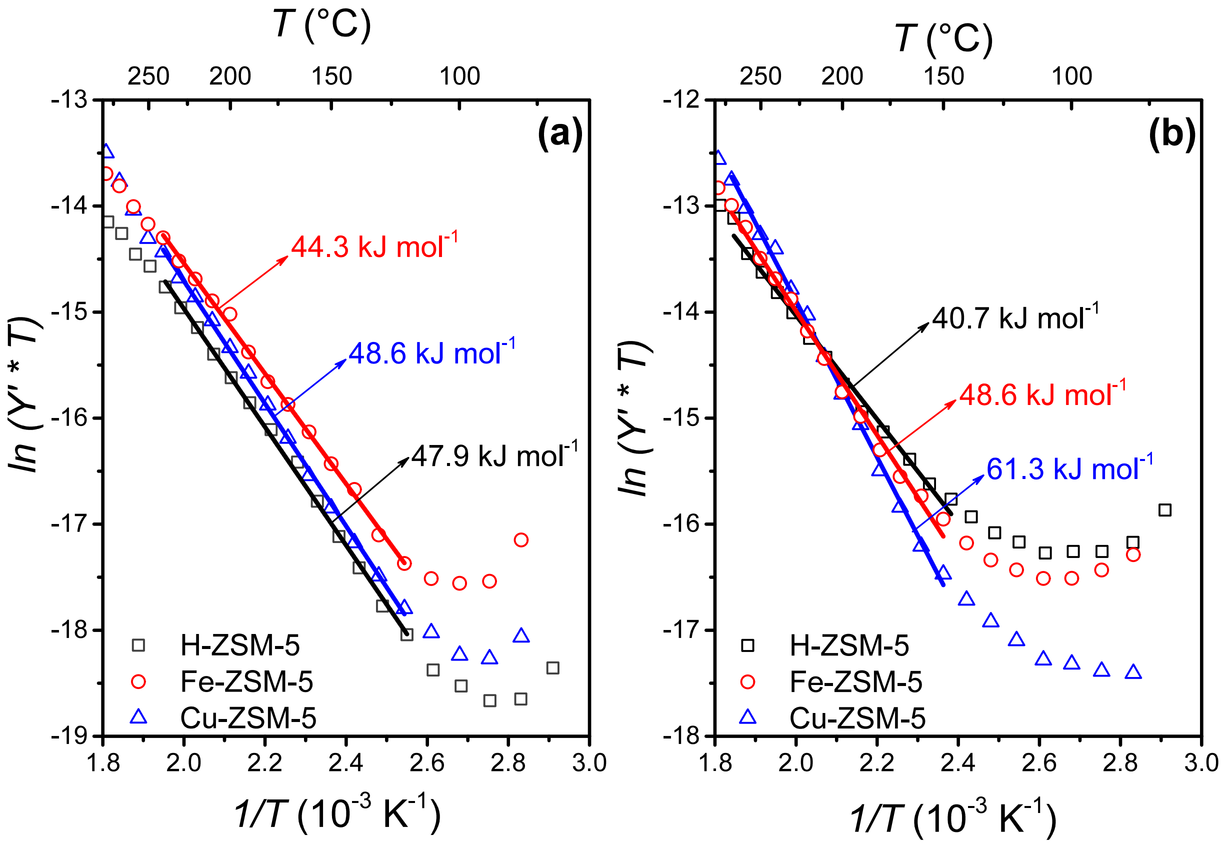

Fig. S5 Arrhenius plots of the *in situ* IS results at temperatures between 80 °C and 280 °C for H-ZSM-5 (black squares), Fe-ZSM-5 (red circles) and Cu-ZSM-5 (blue triangles) under different gas conditions. (a): measurement in pure N_2 over zeolite saturated by NH_3 at room temperature; (b): measurement in 100 ppm NH_3 in N_2 over pristine zeolite. The Y' values were determined according to the impedance data at the low-frequency maxima in the Modulus spectra.

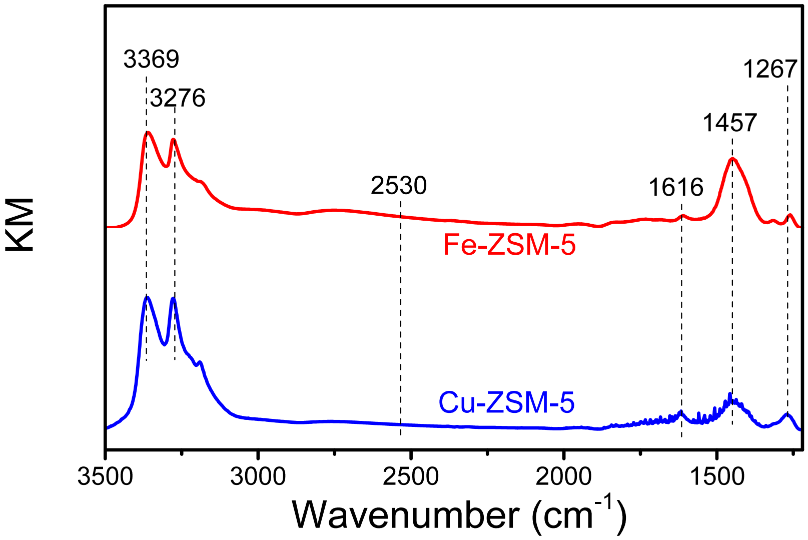

Fig. S6 DRIFT spectra taken over zeolites after NH_3 saturation at 250 °C.

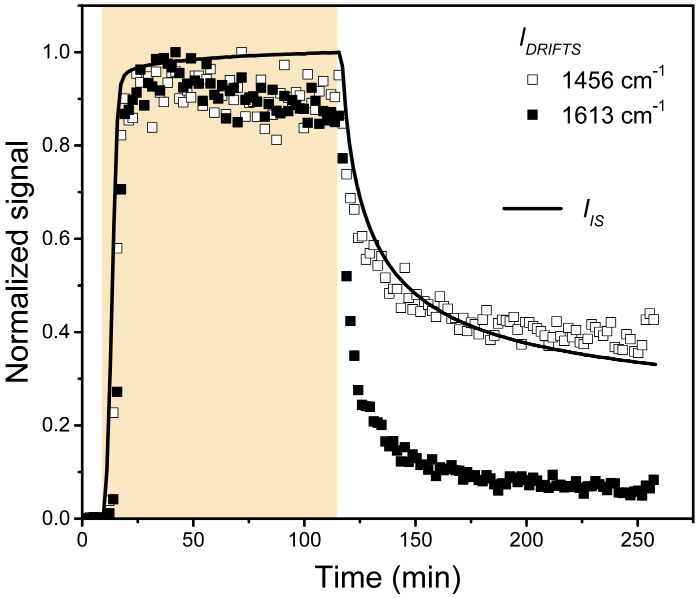

Fig. S7 Simultaneously measured IS signal at 10 kHz (I_{IS}; solid lines) and DRIFTS signals after KM transformation (I_{DRIFTS}; symbols) during the loading and thermal desorption of NH_3 over H-ZSM-5 at 100 °C (b). The colorful background in (b) indicates the period with NH_3 (100 ppm in N_2) supply to the system. I_{DRIFTS} at 1456 cm^{-1} (empty symbols) and 1613 cm^{-1} (filled symbols) are attributed to the bending vibrations of NH_4^+ ions on Brønsted acid sites and bending vibrations of NH_3 species on metal Lewis sites, respectively. The IS and DRIFTS signals were normalized by setting the smallest value to 0 and the highest value to 1.

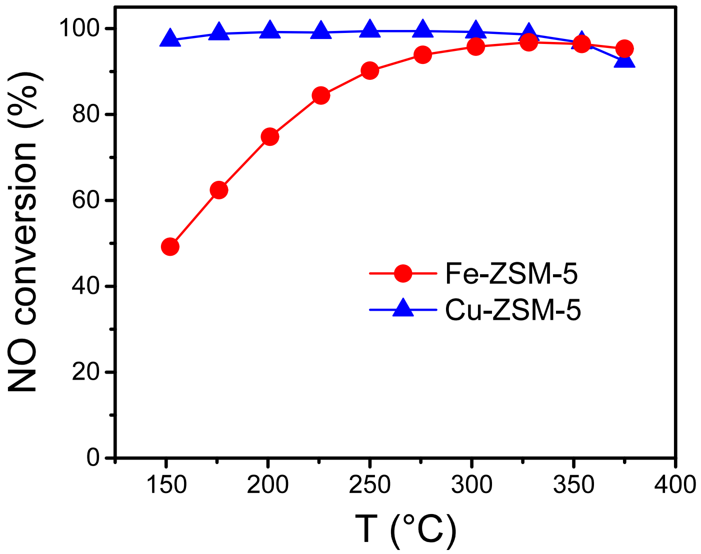

Fig. S8 Measured conversion of NO in the NH_3-SCR tests over Fe-ZSM-5 and Cu-ZSM-5. The Testing conditions: 0.5 g catalyst; a total flow rate of 1 L min^{-1}; 500 ppm NH_3, 500 ppm NO, 10% O_2, 2% H_2O.

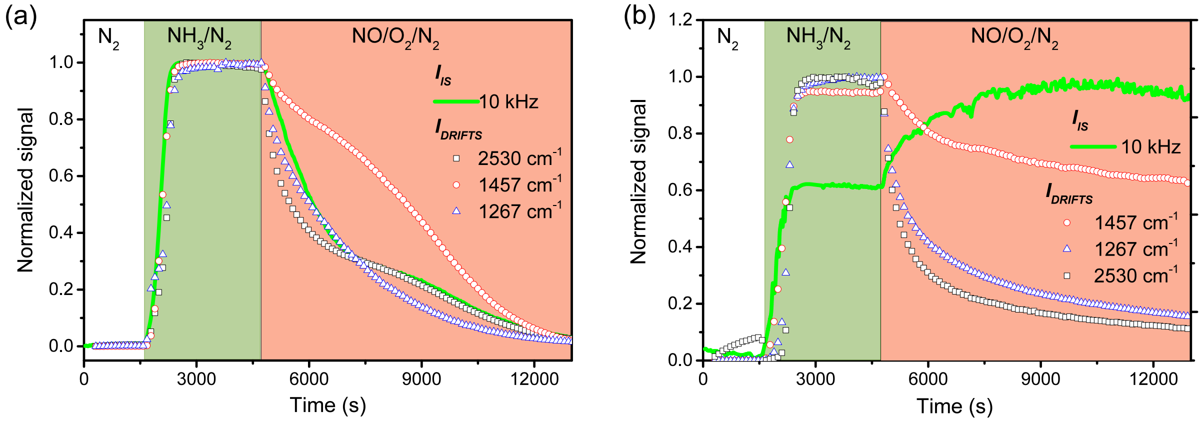

Fig. S9 Time-course of normalized I_{IS} and I_{DRIFTS} signals (normalized by setting the smallest value to 0 and the highest value to 1) for Fe-ZSM-5 (a) and Cu-ZSM-5 (b) during exposure to the indicated atmospheres at 100 °C. Fig. S9b is part of a submitted manuscript.

References

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