

Electronic Supporting Information

Effect of Al content on the strength of terminal silanol species in ZSM-5 zeolite catalysts: A quantitative DRIFTS study without the use of molar extinction coefficients

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S.1 Quantitative analysis of DRIFTS spectra

The purpose of this section is to determine what conversion function for DRIFTS spectra, absorbance or Kubelka-Munk¹ (KM) function, respectively, gives a linear correlation between DRIFTS signal and the concentration of the surface hydroxyl groups such as Brønsted or terminal silanol acid sites.

Diffuse-reflectance IR spectroscopy has several advantages over the very commonly used transmission IR spectroscopy such as simple sample preparation and better applicability for *in-situ* characterisation at high temperatures and pressures. The biggest disadvantage of diffuse-reflectance IR spectroscopy is that experiments are frequently limited to semi-quantitative analyses. However, quantitative IR data analysis is required when the surface concentration and its trend are to be probed. In the best-case scenario, the IR intensity of DRIFTS data is proportional to the concentration of the adsorbed probe molecule. To obtain IR band intensities that are linear to the surface concentration of adsorbed species the KM function is frequently applied to the diffuse-reflectance IR data yielding a linear² calibration curve:

$$KM = f(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k}{s} \quad (\text{S1})$$

The absolute reflectance (R_{∞}) of the scattered radiation is related to the sample absorption coefficient (k) and the scattering coefficient (s) by the KM function. R_{∞} is defined by the scattered intensity divided by the incident radiation and is a function of the wavenumber. The incident radiation is normally not known. Thus, a typical DRIFTS experiment consists of first probing the reflectance $I_{\infty}(\text{reference})$ over highly scattering and poorly absorbing particles as a reference (e.g., KBr powder). After, the reflectance of the sample of interest itself $I_{\infty}(\text{sample})$ is determined. The following ratio is then taken as an estimate for the absolute reflectance (R_{∞}):

$$R_{\infty} \approx \frac{I_{\infty}(\text{sample})}{I_{\infty}(\text{reference})} \quad (\text{S2})$$

However, transforming the acquired DRIFTS data using the KM function curved³⁻⁵ or broken-line shape⁶ calibration curves have been reported as well. For strongly absorbing materials it has been suggested⁴ that the best approximation for the calibration curve can be obtained by calculating the absorbance defined as

$$\text{Absorbance} = \log\left(\frac{1}{R_\infty}\right) \quad (\text{S3})$$

in which R_∞ is the absolute reflectance as defined earlier used in the KM function in (S1). This approach is in analogy to the absorbance measured in transmission mode given by $\log(1/T)$, where T stands for transmission. Both functions, absorbance and KM, are frequently used to linearise the diffuse-reflectance IR intensities. The reasoning for selecting either one is normally not discussed. This is often the case as it is difficult to measure the amount of probe molecule uptake and the diffuse-reflectance IR intensities simultaneously.

To confirm that the DRIFTS setup gives a linear correlation between IR intensities and the concentration of surface hydroxyls, the absorbance, equation (S3), and KM function, equation (S1), were used to transform the acquired raw diffuse-reflectance IR data to absorbance and KM spectra, respectively. The Brønsted peak in the O-H stretching region was then integrated for both conversion functions and all five SARs of H-ZSM-5, respectively. All Brønsted peak areas were normalised by the peak areas of the framework vibrations between 1750 and 2100 cm^{-1} . The concentration of Brønsted Al atoms was independently determined by elemental analysis of the H-form and Na-form of the same ZSM-5 zeolites. To test the linear correlation between DRIFTS signal and surface hydroxyl concentration the integrated and normalised Brønsted absorbance and KM areas were then plotted over the Brønsted Al concentration obtained by elemental analysis, depicted in Figure S1.

The absorbance function illustrated in Figure S1 (left) shows a good agreement between the integrated Brønsted peak area and the Brønsted Al concentration determined by elemental analysis characterisation. Within the experimental error the integrated Brønsted peak area increases linearly with the Brønsted Al concentration. This suggests that the absorbance function is suitable to quantitatively probe the number Brønsted hydroxyl groups in the O-H stretching region and thus likely also the number of terminal silanol sites. However, an independent measurement of the latter was not available. The fitting gives a molar extinction coefficient (ϵ) of $(2.12 \pm 0.10) \times 10^{-4} \text{ cm } \mu\text{mol}^{-1}$, which can be used to calculate the Brønsted Al concentration and its change as a first approximation.

The results for the integrated Brønsted peak area using the KM function plotted over the Brønsted Al concentration determined from elemental analysis is depicted in Figure S1 (right). The correlation is significantly worse and particularly the data point for H-ZSM-5 (23) is too high compared to the other four data points. Hence, the KM function does not seem to be a good choice to quantitatively probe the number of Brønsted hydroxyl groups. In

conclusion, the results obtained for the absorbance and KM calibration curves suggest that absorbance function is the better choice to interpret the diffuse-reflectance IR data quantitatively.

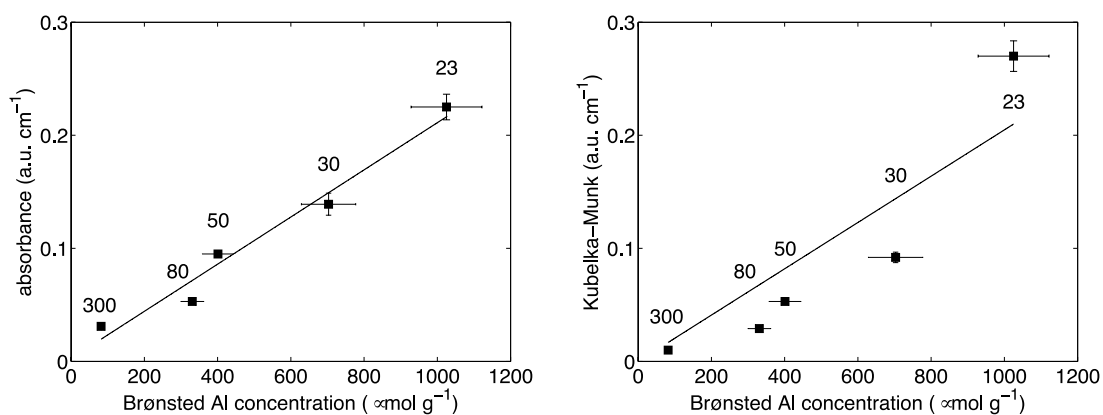


Figure S1. Framework vibration normalised areas of activated Brønsted IR peak ($\sim 3610 \text{ cm}^{-1}$) for **(left)** absorbance function and **(right)** KM function over Brønsted Al concentration obtained by elemental analysis of H-form and Na-form of ZSM-5 with different SAR (300, 80, 50, 30 and 23 from left to right) at 300 K. Straight line represents fit to linear equation.

Some IR studies have reported that diffuse-reflectance experiments are strongly affected by particle size and packing density of the sample bed leading to significant errors due to experimental results not being reproducible.^{2,7} However, the results presented in Figure S1 (left) show that the errors for the Brønsted IR peaks exhibit a maximum value of 5% determined by repeating the experiments three times. Hence, the normalisation by the area of the framework vibrations seems to consider the different sample weights. Furthermore, the particle size of the H-ZSM-5 samples ranges from 1.18 to 4.10 μm suggesting that the particle size does not significantly affect the results.

In summary, it has been shown that the absorbance function performs better in giving a linear DRIFTS signal intensity for the Brønsted hydroxyls in the O-H stretching region.

S.2 XPS characterisation

The XPS experiments were carried out by Johnson Matthey (Johnson Matthey Technology Centre, Sonning Common). The H-ZSM-5 powder samples were dusted onto carbon tape and thereby attached to a sample stub. Care was taken to avoid signals from the tape contributing to the study. The XPS experiments were conducted with a Thermo Escalab 250. The radiation used was monochromatised aluminium K_{α} radiation with a 650 μm spot size. Charge compensation was provided by the in-lens electron flood gun at a 2 eV setting and the "401" unit for "zero energy" argon ions. Sensitivity factors after Scofield⁸ used in quantification were carried out. The energy scales were corrected to the silicon 2p (Si_{2p}) signal maxima, 103.3 eV. In this regard, 2p refers to the primary orbital quantum number (2) and the orbital type (p).

To validate the total Al concentration in H-ZSM-5 zeolites obtained by elemental analysis XPS experiments were conducted to access the Al concentration on the H-ZSM-5 surface. The typical maximum penetration depth of XPS in ZSM-5 is ~ 6 nm,⁹ thus, the characterisation technique is mainly sensitive to the Al species present on the ZSM-5 surface. In contrast, elemental analysis probes the bulk composition. However, knowledge of the surface Al concentration is crucial for adsorption and reaction applications of ZSM-5 zeolites.¹⁰

The comparison of the surface Al concentration obtained by XPS experiments and the total Al concentration determined by elemental analysis characterisation is shown in Figure S2. A good agreement is observed between both experimental characterisation techniques. This suggests that most of the Al present in the five H-ZSM-5 zeolite samples is situated at the surface as has been observed elsewhere.¹¹ However, it must be noted that the surface composition of ZSM-5 can be significantly different to one of the bulk.¹² Nonetheless, the elemental analysis results will be used for any further correlation of IR results with the total Al concentration due to the agreement with the XPS results depicted in Figure S2.

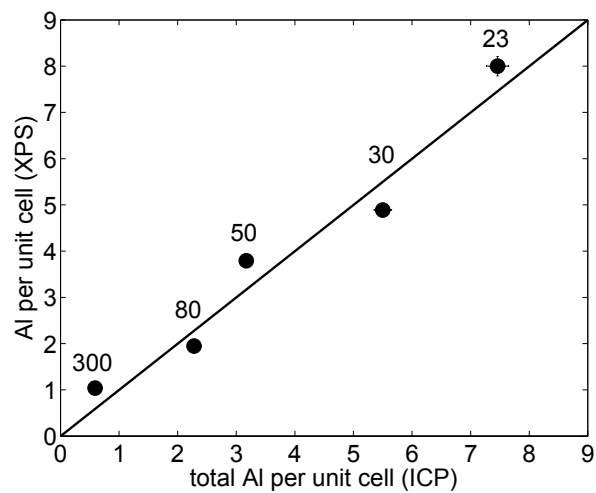


Figure S2. Comparison of Al concentration per unit cell obtained by XPS, on the y-axis, and elemental analysis, on the x-axis, characterisation for H-ZSM-5 with varying SAR (300, 80, 50, 30 and 23 from left to right).

S.3 Additional IR spectra

The IR spectra of the H-ZSM-5 zeolites with varying SAR before and after probe molecule adsorption, that is, after pyridine or collidine adsorption at 300 and 423 K, were already shown in the main work but are illustrated again in Figure S3 with a much wider range of wavenumbers (2000 to 4000 cm^{-1}).

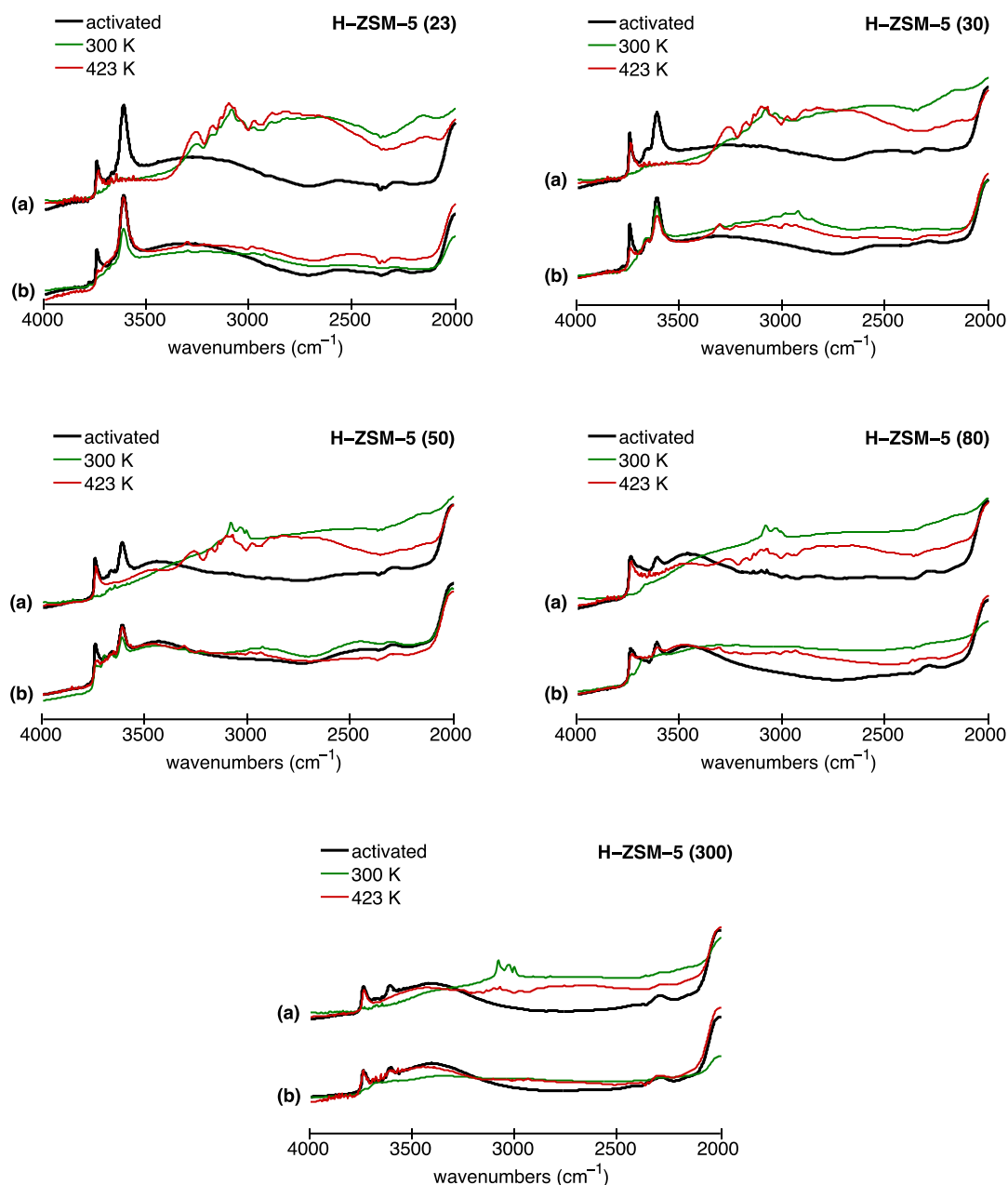


Figure S3. Framework vibration normalised IR spectra of H-ZSM-5 with varying SAR for (a) pyridine and (b) collidine adsorption at 300 and 423 K, respectively, for wavenumbers between 2000 and 4000 cm^{-1} : (black line) activated form, (green line) after adsorption at 300 K, (red line) after adsorption at 423 K. The y-axis (absorbance a.u.) in each plot has the same scale so spectra can directly be compared.

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