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Electronic Supplementary Information

Nuclear spin relaxation as a probe of zeolite acidity: a combined NMR and TPD investigation of pyridine in HZSM-5

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Limiting cases for TPD analysis of desorption energetics

Our TPD analysis is performed assuming desorption from a homogeneous surface, where the temperature dependence of the desorption rate constant k_{des} may be described by the Arrhenius equation

$$k_{des} = A\exp\left(\frac{E_{des}}{RT}\right). \qquad \text{(S1)}$$

Here E_{des} is the energy of desorption, T the temperature, R the gas constant and A the pre-exponential factor.

A general expression describing the relationship between TPD desorption peak temperature T_p, heating rates β and desorption energetics may be written[1,2]

$$(2+\alpha)\ln\left(T_p\right) - \ln\left(\beta\right) = \frac{E_{des}}{R}\frac{1}{T_p} + C. \qquad \text{(S2)}$$

Here the formal definitions of α, C and E_{des} depend on the rate-limiting process controlling the observed TPD desorption data. A series of measurements utilising different heating rates therefore facilitates a plot of $(2+\alpha)\ln\left(T_p\right) - \ln\left(\beta\right)$ against $1/T_p$, yielding a gradient equal to E_{des}/R.

Three limiting cases may influence our TPD experiments:[1]

(a) *Desorption kinetics*: This condition is valid if the carrier gas flow rate is high, such that the probability of re-adsorption events is negligible. Here E_{des} is the activation energy for desorption and $\alpha = 0$. The term C is given by

$$C = \ln\left(\frac{E_{des}}{AT_p}\right). \qquad \text{(S3)}$$

(b) *Adsorption equilibrium*: Under this condition re-adsorption events occur as per surface equilibrium conditions, with the rate of such events limited by the availability of unoccupied adsorption sites. Here E_{des} is equal to the heat of desorption ΔH_{des} and $A = 0$. The term C is given by

$$C = \ln\left(\frac{(1-\theta)^2 V \Delta H_{des}}{\exp\left(\Delta S_{des}/R\right) F R}\right). \tag{S4}$$

Here θ is the fractional surface coverage at the maximum desorption rate, V is the volume of the solid within the catalyst bed under investigation, F is the carrier gas flow rate and ΔS_{des} is the entropy change upon desorption.

(c) *Diffusion limitations*: If mass transport throughout the pore network is slow then diffusion limitations will control the rate of observed desorption. Here E_{des} is again equal to the heat of desorption ΔH_{des} and A is a coefficient that describing the type of diffusion within the pore network (e.g. $\alpha =$ 0.5 for Knudsen diffusion). The term C is given by

$$C = \ln\left(\frac{l^2 \Delta H_{des}}{\pi^2 \exp\left(\Delta S_{des}/R\right) R D}\right), \tag{S5}$$

where l is the pore length and D the diffusion coefficient of the adsorbate.

To determine the limiting case for our HZSM-5 zeolites the effect of carrier gas contact time W/F was investigated, where W is the sample mass and F the flow rate. Figure S1 highlights the sensitivity of T_p to this ratio across ~2 orders of magnitude for the HZSM-5 zeolite with SAR = 23, with an increase in contact time resulting in higher T_p values. According to work of Niwa *et al*. this observation is indicative of case (b) described above, wherein re-adsorption events influence the observed desorption rate;[3–5] this limiting condition is assumed relevant across the range of zeolites investigated here and we assign the measured desorption energetics to the heats of desorption ΔH_{des}. The dashed line within Figure S1 indicates the W and F conditions used to compare pyridine desorption energetics across the TPD experiments detailed within the main text, with $W =$ 10 mg of each material exposed to a flow rate of $F =$ 40 ml min^{-1}.

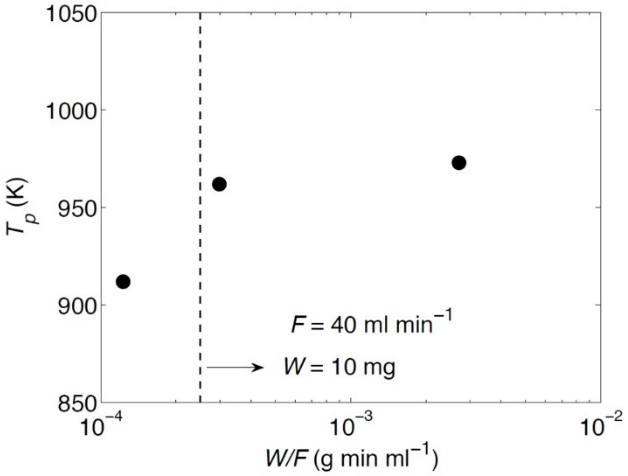

Figure S1. Dependence of the peak temperature at maximum desorption rate T_p for pyridine in HZSM-5 with SAR = 23 as function of carrier gas contact time, expressed as the ratio of sample mass W and flow rate F. TPD measurements were performed at a constant heating rate of 10 K min^{-1}.

References

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