Towards a framework for effective experimentation and modelling to characterise solid acids by ammonia temperature programmed desorption

S.K Wilkinson[1,*], J. West[2,*], C. Gücüyener[1], R. Lloyd[1], E.H. Stitt[1], J.L. Casci[1]

1. Johnson Matthey Technology Centre, Belasis Avenue, Billingham, UK, TS23 1LH
2. Johnson Matthey Process Technologies, Belasis Avenue, Billingham, UK, TS23 1LH
* Corresponding author contacts: sam.wilkinson@matthey.com; john.west@matthey.com

Abstract

The characterisation of solid acid catalysts, typically to understand the type, strength and population of surface acid sites is an important step in the development of catalyst performance descriptors for a given process. The temperature programmed desorption of ammonia (NH_3-TPD) is a method commonly used in industry and academia to meet this aim, however there are a number of challenges in interpreting results. These include discretisation of distinct desorption peaks, types of 'site' and decoupling the influence of desorption kinetics from diffusion limitations. Additionally, a number of competing modelling approaches exist in the literature to extract information from the NH_3-TPD.

In this study, we assess a model H-ZSM-5 zeolite by manipulating a wide range of the experimental variables to build a framework of how to maximise understanding from a NH_3-TPD. This includes variation of NH_3 adsorption temperature (to control the extent of adsorption on different sites and/or in different conformations), mass of catalyst (to probe re-adsorption effects along the bed) and the ramp rate during the TPD (to assess impact of transport or kinetic control). Existing models from the literature will be critically analysed against these findings for consistency across the experimental matrix. This will develop an objective-driven roadmap for a TPD user to utilise when testing solid acid materials.

Keywords: zeolite, ammonia, temperature programmed desorption, acidity, model discrimination

Introduction

The characterisation of acidity in solid acid catalysts, such as zeolites, is an important step in developing an understanding of activity and selectivity in a variety of catalytic reactions. There are a variety of descriptors which can be identified from characterisation of solid acids, including the quantity of acid sites, strength and nature (i.e. Brønsted or Lewis acidic). If determined accurately, these chemical descriptors can be correlated with observed performance of catalysts and/or the process of how the solid acid is manufactured. A key aim for solid-acid characterisation methods is to act as an effective fingerprinting tool in understanding catalyst performance.

The temperature programmed desorption of ammonia (NH_3-TPD) is an example of an extensively used technique in both industry and academia. A typical NH_3-TPD experiment will involve a thermal pre-treatment step; adsorption of NH_3 flowing in a carrier gas at a nominal temperature (typically He); outgassing of the sample in the carrier gas to remove 'weakly' adsorbed species; and finally a programmed temperature ramp during which the NH_3 is desorbed from the sample.

The interpretation of results from these experiments can be complex, even for the most well-defined of materials. The challenges in interpreting the NH_3-TPD are well summarised in Gorte (1995) and can include factors such as selection of appropriate temperature ramp rate, NH_3 adsorption/outgassing temperature and mass of catalyst. Such factors influence desorption and re-

adsorption rates during the TPD and can also impact whether kinetic or diffusional effects are rate controlling.

A plethora of modelling approaches has been used to explain and quantify the results from NH_3-TPD. Sharma *et al.*, (1993) used a carefully chosen range of conditions to characterise MFI-type zeolites. Under these conditions, they found desorption and re-adsorption steps to be in equilibrium and were able to calculate consistent heats of adsorption using different carrier gas flow rates.

Later work by Katada *et al.*, (1997) expanded on this approach and developed a model to describe the TPD using the equilibrium assumption, using examples with 1D H-MOR and 3D H-MFI type zeolites. The author's introduced the use of entropy corrections and enthalpy distributions, the latter to account for site heterogeneity. The method has performed well when benchmarked other techniques such as calorimetry, however an extensive criticism of the model inputs over a wider spectrum of TPD conditions has not been performed. Recently, work was published for a variety of solid acid materials using a normal Gaussian distribution fitting approach to describe different acid 'sites' (Arena *et al*., 2015). This led to some materials containing up to four 'sites' and assumed all observations described a kinetically limited desorption process.

Aims

A clear challenge taken from prior work is that the results obtained and the models applied to these results are strongly driven by choice of testing conditions of NH_3-

TPD. Furthermore, the choice of solid acid (total acidity, types of acid site, site strength) will also play a role in shifting where the limiting transport and kinetic regimes will manifest during the TPD. From this, the following aims are targeted in this study:

- Build a framework approach, using a large scope of testing conditions (temp. ramp, catalyst mass, NH_3 adsorption temperature) to challenge the extent of validity of literature models.
- Understand how valid the fitting of (as)symmetric Gaussian profiles to multi-peak NH_3-TPD profiles is in discretising different types of acid site and/or adsorption conformations.
- Challenge the validity of entropy and enthalpy corrections on TPD models across the scope.
- Gain better fundamental understanding of the low temperature acidity peaks in NH_3-TPDs.

Methodologies

A model, commercially available, H-ZSM-5 zeolite (Si/Al ratio: 59) was chosen for this case study. NH_3 TPD experiments were carried out using an Altamira Instruments rig connected to a mass spectrometer (Ametek Process Instruments). In a typical experiment, 0.1 g of catalyst was loaded into a 4 mm inner diameter reactor tube. The zeolite was conditioned at 650°C in N_2. NH_3 adsorption then took place using 0.5% NH_3 / He at 40 ml /min (STP). The samples were outgassed in He for up to 10 h. Finally, the TPD ramp was always initiated at 30°C. The key variables explored in this study are catalyst mass (0.05 – 0.2 g), ramp rate (2 – 10 K / min) and adsorption temperature (40 – 180°C).

Results

Figure 1 provides a comparison of the NH_3-TPD results seen based on the NH_3 adsorption temperature.
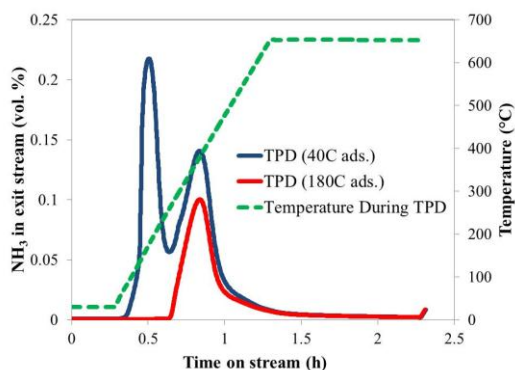

Figure 1: Profile for NH_3-TPD for 0.1 g H-ZSM-5 zeolite, 10 K / min ramp rate, 40 ml / min flow as a function of initial NH_3 adsorption temperature.

A low temperature peak is present in the 40°C test which is not seen in the 180°C test. In both cases, the amount of NH_3 desorbing during outgassing was similar and minimal. The low temperature acidity profile shows a regular, Gaussian-like appearance. The high temperature

peak for both experiments is irregular and features a slow trail of NH_3 release at the end of the ramp. Under these conditions this could point to a diffusion limitation, or a distinctly different (strongly NH_3 bound) surface site.

Taking the 180°C adsorption result as an example, the equilibrium adsorption models of Katada *et al.,* (1997) were applied to the data, using non-linear least squares estimation.
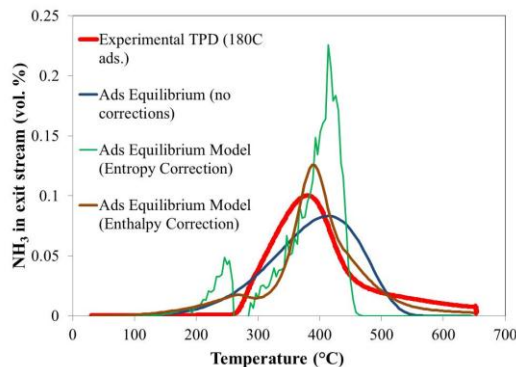

Figure 2: Predictions of different models describing NH_3-TPD for 0.1 g H-ZSM-5 zeolite, 10 K / min, 40 ml / min flow. Total calculated acidity under the experimental peak is 0.199 mol / $kg_{zeolite}$

As the results in Figure 2 show, all of these approaches fail to capture the trends observed. ΔH_{ads} values of 99±4, 156±11 and 164±9 kJ mol^{-1} was estimated for the zero, entropy and enthalpy corrected approaches respectively. Entropy change of adsorption (ΔS_{ads}) meanwhile was -150±1, -406±11 and -154±1 J mol^{-1} K^{-1} respectively, the middle of these values being thermodynamically invalid. The values of the enthalpy corrected approach are closest to previous literature however the predictions are far from satisfactory

Conclusion

Initial results for a model H-ZSM-5 show a complex NH_3-TPD profile which, based on single datasets, is challenging to adequately describe using literature models; predictions and parameter estimates are very sensitive. The presentation will look in depth at the impact of NH_3 adsorption temperature (i.e. controlling and discretising low and high temperature peak region), catalyst mass (i.e. entropy change along the catalyst bed) and ramp rate (i.e. controlling transport/kinetic phenomena) to build an experimental design framework to model these systems. Support will be provided from calorimetry, infra-red methods as well as first principles modelling.

References

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