Selective staining of zeolite acidity: Recent progress and future perspectives on fluorescence microscopy

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ABSTRACT

This perspective article highlights recent methodical approaches for probing acid sites in zeolites using selective chemical staining methods. Research and method development on model systems (large zeolite crystals) is presented in close relation to the investigation of industrially relevant catalyst particles for Fluid Catalytic Cracking (FCC) and zeolite-based extrudates. The article begins with an (1) introduction on characteristics of zeolites and industrial catalyst particles, followed by a methodical overview on (2) probing acidity in zeolites, including temperature programmed desorption (TPD), solid state nuclear magnetic resonance (NMR) spectroscopy, and infrared (IR) spectroscopy. Instrumental details on (3) fluorescence microscopy are provided to prepare for the focus on (4) selective staining by probe molecules and oligomerisation reactions to highlight or distinguish materials (i.e. zeolite vs. binder or matrix components) and visualise acid sites within zeolites. Confocal fluorescence yields, in contrast to the other discussed techniques, a high spatiotemporal resolution giving way to exciting prospects such as probing single (fluorescent) reaction products. (5) Concluding remarks and future perspectives envision how Brønsted and Lewis acid sites can be investigated selectively.

Sections: (1) Introduction (2) Probing acidity – methodical overview (3) Confocal fluorescence microscopy – instrumentation (4) Selective staining (5) Concluding Remarks and Future Perspectives.

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1. Introduction

Zeolites are microporous crystalline aluminosilicates used for heterogeneous catalysis in a wide variety of major industrial applications, such as the synthesis of many bulk chemicals as well as the Fluid Catalytic Cracking (FCC) of crude oil into gasoline. Conventional zeolites consist of SiO_4 and AlO_4 tetrahedra, sharing oxygen atoms, forming a negatively charged tetrahedral network. The number of linkages of each tetrahedra give rise to varying channel and cage dimensions, attributing to zeolites valuable shape selective pores in catalysis. Two different types of acid sites are present within zeolite crystals, these are Brønsted and Lewis acid sites [1]. Brønsted acid sites are proton donors, while Lewis acid sites are electron pair acceptors. Brønsted acid sites (acidic OH groups) are commonly generated by ion exchange with NH_4^+, followed by thermal decomposition of the ammonium ions, forming protons which counter balance the negative charge of the framework. The chemical nature of Lewis sites is less distinct, owing to extra-framework Al species and Al atoms positioned in the framework [2]. Acid sites within or on the surface of zeolites promote acid-catalysed transformations, such as Methanol-to-Hydrocarbons (MTH) and

the cracking of long-chain hydrocarbons, an example being n-hexane [3,4]. Since the presence of two types of acidity significantly affects catalytic activity (the other main contributor being accessibility), the acidic properties of zeolitic structures (materials), including MFI (ZSM-5) [5], FAU (Y) [6], BEA (β) [7] and MOR (mordenite) [8], have been the focus of academic and industrial research for decades. Using both standard and advanced characterisation techniques, it is possible to probe both sites in varying levels of detail. Of particular interest are the acid strength, type of acid site (i.e. Brønsted and Lewis sites), as well as their location, amount and density. Zeolites as catalysts are available in a variety of compositions as well as shapes and sizes to tailor to the need. For example, ZSM-5 crystals typically have a size of 0.5–2 μm, although larger crystals (e.g., 20 × 20 × 100 μm) are available as well, while FCC catalysts are characteristically 50–100 μm and zeolite-containing catalyst extrudates have a size up to a few millimetres (Fig. 1). Such catalyst bodies/extrudates, are commonly used on the industrial scale and differ from pure zeolite powder, due to the dispersion of this active phase in a binder and/or matrix. The incorporation of either binder or matrix components to the active phase is reported to improve mechanical and attrition resistance, but they also significantly impact catalytic behaviour. A recent survey by Hargreaves and Munnoch discusses the main benefits and deleterious effects of catalyst-binder composites in comparison to the individual active phase [9].
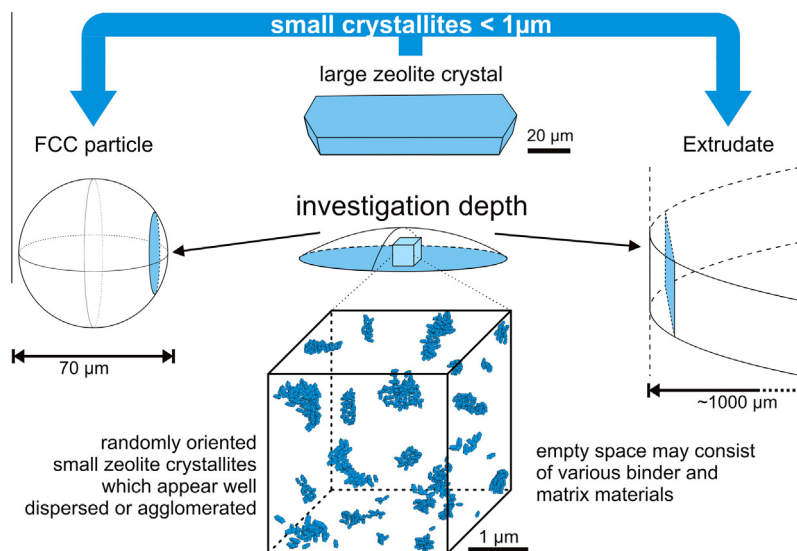

Fig. 1. Model and industrially shaped zeolite-based catalyst materials: (Top centre) Large zeolite crystals are suitable model systems for microscopy due to their size. The investigated characteristics can be transferred to industrially relevant catalysts, which incorporate small zeolite crystallites well dispersed or agglomerated. (Middle left) Fluid Catalytic Cracking (FCC) particles are spherical with a diameter of about 50–100 μm and extrudates (middle right) are often in a cylindrical shape, with a diameter of about 0.5–2 mm. (Bottom centre) Zeolite crystallites are mixed with various binder and matrix components, required for the overall performance of the industrial catalyst particle.

The basis of this concept article will focus on the state-of-the-art and recent developments, aimed at studying acidity of zeolite materials of varying degrees of morphological complexity, making use of various recent micro-spectroscopic characterisation techniques.

2. Probing acidity – methodical overview

This section provides an overview of a selection of methods, which allow to probing zeolite acidity. The illustrations in Fig. 2 are meant as a guideline.

Temperature programmed desorption (TPD), illustrated in the upper left panel of Fig. 2, is a method based on the interaction strength of a probe molecule with a specific site, i.e. the adsorption enthalpy. Thus, during a (linear) temperature increase, probe molecules will desorb at specific temperatures, depending on their adsorption enthalpy at the desorption site. Obviously, stronger interactions would be recorded at higher desorption temperatures compared to weaker bound probe molecules. Typically, TPD experiments are combined with other methods, such as infrared spectroscopy (IR) [10–12], thermogravimetry (TGA) [12] and calorimetry [13], to crosslink and validate the peaks in the thermograms to a specific site. Furthermore, selective probe molecules and suitable reference materials increase the accuracy to interpret TPD results. Common probes are Ar [14], N$_2$ [15], CO [10,16,17], NH$_3$ [10], pyridines [11] and amines [12,18] (also alcohols, nitriles, thiols, ketones and diethylether [19]), which do all have certain advantages and disadvantages. Selected examples will be discussed below and the interested reader is advised to consult the cited literature and related references therein for further details then described here.

The interaction of a probe molecule with an acid site requires free electrons/electron density. Most of the molecules mentioned above do have a free electron pair, which can overlap with an empty orbital (Lewis site) and provide electron density to a proton of a Brønsted site. The inert gas Ar is a probe molecule due to the polarisability of its electron shell. The polarisation of the Ar molecule increases with the strength of the acid site and, therefore, the

interaction between the two. Experiments are carried out between 100 and 250 K to accurately determine heats of adsorption [14].

Nitrogen-containing molecules, i.e. NH$_3$, amines and pyridines, are widely applied for TPD measurements [10–12,18]. In addition to adsorption of probe molecules, they may undergo reactions. Strong Brønsted acid sites (OH stretching vibration at 3540 cm^{-1} [12]) deaminate primary, secondary and tertiary amines, thus, at higher temperatures a desorption peak containing NH$_3$ and the respective alkene of the alkyl chain is observed [18]. This is illustrated in the top left of Fig. 2. Weakly bound (physisorbed), chemisorbed and strong acid sites are distinguished in combination with IR spectroscopy [12,18].

The IR vibration frequencies of OH groups and probe molecules are characteristically altered upon interaction of their empty and filled molecular orbitals, respectively. Hydroxyl groups typically appear between 3800 and 3200 cm^{-1} in the IR spectrum, depending on their location inside/outside the zeolite crystal. Their IR frequency shifts bathochromically when interacting with a base (free electron pair). CO, NH$_3$ and N$_2$ can enter small zeolite pores, whereas larger molecules like pyridine, ketones and ethers are prevented from entering. This size exclusion effect is depicted in the centre panel of Fig. 2. Spectral evidence is provided by the pyridine adsorption spectra on zeolite HY in the bottom left: external surface OH-groups and those in large cages are reached by the pyridine molecule, their OH-frequency correspondingly shifted. IR bands which correspond to Brønsted sites located in the small cages however, remain unaffected. Furthermore, additional features appear in the fingerprint-region of the pyridine spectrum upon adsorption. Brønsted and Lewis acid sites are distinguished by bands at 1540 cm^{-1} and 1455 cm^{-1}, respectively [2].

Carbon monoxide, as a smaller probe molecule, reaches pores/cages, which pyridine could not enter. The IR spectra on the bottom of Fig. 2 show that all OH-bands are shifted from their original position after CO adsorption, in contrast to pyridine adsorption, as discussed above. CO is a versatile molecule to examine electron donating effects. When interacting with metal ions, the CO stretching frequency shifts to higher and lower wavenumbers with respect to the free CO molecule (v_{CO} = 2143 cm^{-1}) depending on electron donation and back-bonding, respectively, observed in me-