Experimental report

13/02/2019

Proposal: 7-04-164 **Council:** 4/2018

Title: Investigation of the Brønsted acidsites in H-ZSM-5 model catalysts: How does Si/Al ratio affect acid strength and Al location?

Research area: Chemistry

This proposal is a new proposal

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Samples: |H+n| [AlnSi96-n O192]-MFI , n < 27

Instrument	Requested days	Allocated days	From	To
IN1 LAG	3	3	17/09/2018	20/09/2018
IN5	4	0		

Abstract:

Zeolites are widely used industrial heterogeneous aluminosilicate catalysts. Even though they are well studied, exact locations of active sites as well as acid strengths of individual sites remains elusive. ZSM-5 is one type of zeolites with orthorhombic Pnma unit cell and pore diameters of about 5.5 Å. The challenge in characterizing Al location and acid strength lies in the difficulty to distinguish between the Si and Al atoms in X-ray diffraction experiments. We have synthesized defect-free ZSM-5 samples with varying Al content. In catalysis, the varying Al content has large effects that have often been ascribed to variations in acid strengths or the spatial proximity of acid sites.

In the proposed project we intend to investigate the location and strength of zeolitic acid sites by means of inelastic neutron scattering (INS) in the fundamental state. Furthermore it is planned to measure the samples at catalytically relevant conditions (T > 473 K) in order to characterize the T-dependent acid strengths as well as the proton's mobility. For this purpose quasi-elastic neutron scattering (QENS) is the adequate technique that we plan to use.

Experimental Report for Proposal 7-04-164 at IN1 Lagrange

Investigation of the Brønsted acid sites in H-ZSM-5 model catalysts: How does Si/Al ratio affect acid strength and Al location?

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Zeolites are widely used industrial heterogeneous aluminosilicate catalysts. Even though they are well studied, exact locations of active sites remains elusive. ZSM-5 is one type of zeolites with orthorhombic Pnma unit cell and pore diameters of about 5.5 Å. The challenge in characterizing Al location is the difficulty to distinguish between the Si and Al atoms in X-ray diffraction experiments. We have synthesized defect-free ZSM-5 samples with varying Al content. In catalysis, the varying Al content has large effects that have often been ascribed to variations in acid strengths or the spatial proximity of acid sites. In the present project we intended to investigate the location of zeolitic acid sites by means of inelastic neutron scattering (INS) in the fundamental state at the the ***IN1 LAGRANGE (ILL)***.

We investigated H-ZSM-5 samples with different Al contents. H-ZSM-5 is a widely used acidic catalyst with 48 possible locations for protons (12 T sites each with 4 oxygen atoms). We obtained INS data for H-ZSM-5 samples with Si/Al of 30, 50 and 100. These spectra however looked rather similar (**Figure 1**).

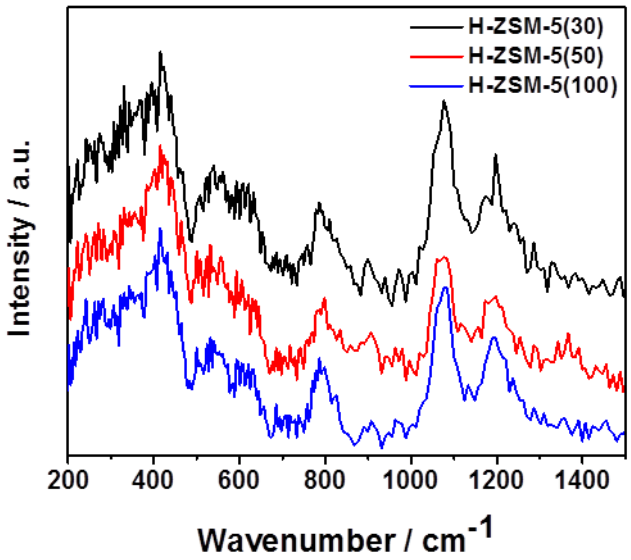

Figure 1. INS spectra for H-ZSM-5 with Si/Al ratios of 30 (black), 50 (red) and 100 (blue) respectively.

During the three days on IN1 Lagrange we had measured amongst others a blank aluminum cell and several different H-ZSM-5 zeolites. The raw data files recorded were from *11911* to *11949* and exported with the available software. Signal smoothing was performed to improve the signal to noise ratio (**Figure 2**).

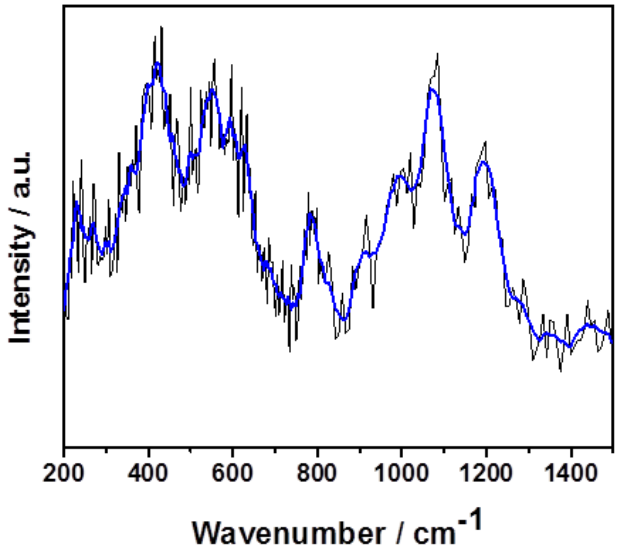

Figure 2. Data smoothing performed on original data improving signal to noise ratio.

In the following months we developed a method to use small clusters for computation of frequencies. For data evaluation, the strategy was to first optimize periodic crystal structures by ab-initio simulations, and then perform frequency computation on small reduced clusters. These clusters are carved out of the periodic structures and serve as a very good estimate of geometry for vibrational analysis (**Figure 3**). Two modes of vibration are distinguished; OH valence stretch (ν_{OH}) exploited in our high temperature IR study, and Si-OH in-plane deformation (δ_{OH}). Besides in-plane bending, out-of-plane deformations (γ_{OH}) can be observed by INS. The latter are however vibrating in a region strongly affected by zeolite framework overtones. In the final data treatment we will focus on in-plane bending vibration bands for fitting with computational data. The latter are currently also not optimal in the 200 – 600 cm^{-1} spectral range since terminal SiH_3 caps strongly affect the signal in this region. The δ_{OH} mode is well coupled with the neighbouring atoms and provides a good fitting region also opposing to the stretching modes.

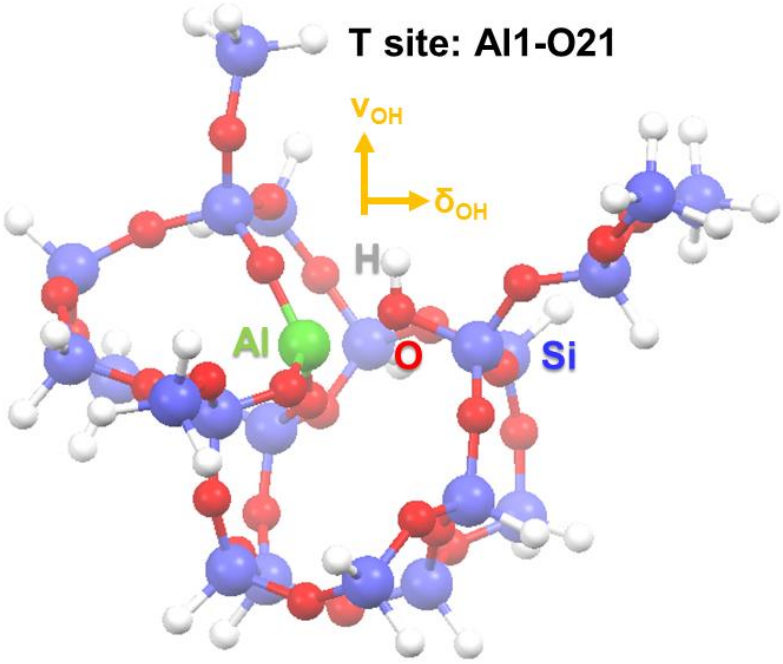

Figure 3. One of 48 possible sites for a proton to be located, namely the Al1-O21 site

Having observed very similar INS spectra for the three investigated samples we now also have to confirm that the collected data are meaningful and would actually differ as a function of H location. Therefore it will be necessary to measure further samples wher the protons will be surrounded by a differing environment, respectively samples completely without protons (all silica sample). The latter test will allow to ensure that the observed signal is actually a result of protons interacting with the zeolite framework.