Experimental report

18/04/2022

Proposal:	**DIR-170**	**Council:**	4/2019
Title:	Unraveling the structure of Brønsted/Lewis acid sites using probe molecules and smart control of HZSM-5 zeolite (extra)framework composition		
Research area:	Materials		

This proposal is a new proposal

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Samples:
HZSM-5 Zeolite with SiO2/Al2O3 Ratio of 30
HZSM-5 Zeolites with SiO2/Al2O3 Ratios of 23, 30, 50 and 80
Trimethyl phosphine oxide (TMPO)
pyridine anhydrous

Instrument	Requested days	Allocated days	From	To
IN1	6	6	11/10/2021	13/10/2021

Abstract:

Zeolites found a wide range of applications as catalysts in several industrial processes, the properties of these materials can be easily tuned to offer distinct structural and chemical features, allowing for example acid-base and shape/size selective reactions. These solid acid catalysts appeared as a safer alternative to the harmful and corrosive liquid catalysts used in several
industrial processes. Since the overall catalytic properties are extensively dependent on the properties such as the acid site nature (Brønsted or Lewis), location, amount and strength, understanding these properties is mandatory to develop increasingly active and selective acid catalysts. In this proposal, we intend to use INS to gain additional structural insight about the acidic properties of the HZSM-5 zeolite and to assess the location extraframework aluminium (EFAL) species.

Unraveling the structure of Brønsted/Lewis acid sites using probe molecules and smart control of HZSM-5 zeolite (extra)framework composition

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The project underlying this mission at ILL aims at understanding the nature of extraframework aluminium (EFAL) species formed in HZSM-5 zeolite, and their proximity with the framework species. The spatial proximity of EFAL species to the framework species is proposed to play a crucial role in enhancing the catalytic activity of HZSM-5, when the material has a small amount of EFAL species.

For this goal, we prepared samples with distinct framework / extraframework Al ratios by steaming at high temperature (up to 700 ºC). The steaming procedure – which gives rise to increasing EFAL contents – has been optimized by us, and samples were prepared in advance in our laboratory.

During the mission, it was possible to collect the INS spectra for 5 zeolite samples, in the low and medium energy regions:

HZ15 Hydrated

HTZ15 hydrated, steamed at 450 ºC

HTZ15 hydrated, steamed at 600 ºC

HZ15 dry, vacuum 4h, 90 ºC

HTZ15 dry, steamed at 600 ºC, vacuum 4h, 90 ºC

The important sample "HTZ15 dry, steamed at 450 ºC, vacuum 4h, 90 ºC" was intended, but was not possible due to time limitations.

The number of samples recorded was restricted by a 12h period of evaluation of safety conditions, after sample container blow-up incident (to the best of our knowledge, the incident aroused from a tap leak in a sample cell subjected to high vacuum prior to being placed in the cryostat).

The Inelastic Neutron Scattering (INS) spectra were measured at 5 K in the range of energy transfers up to *ca*. 200 meV, with an energy resolution of $\Delta E/E \approx 2\%$. In the present experiment the energy transfer was calculated by subtracting 4.5 meV, the energy of the PG crystals in the ellipsoid, from the energy of the incoming neutrons selected with a focusing Cu(220) single crystal and bent Si(111) and Si(311) reflections.

Figure 1shows INS spectra of HTZ15 sample steamed at 600 ºC, prior and after dehydration with high vacuum (at 90 ºC, during 4 hours). In both cases the sample is "EFAL rich", but in the case of the hydrated sample, the INS profile of water clusters dominates the spectrum.

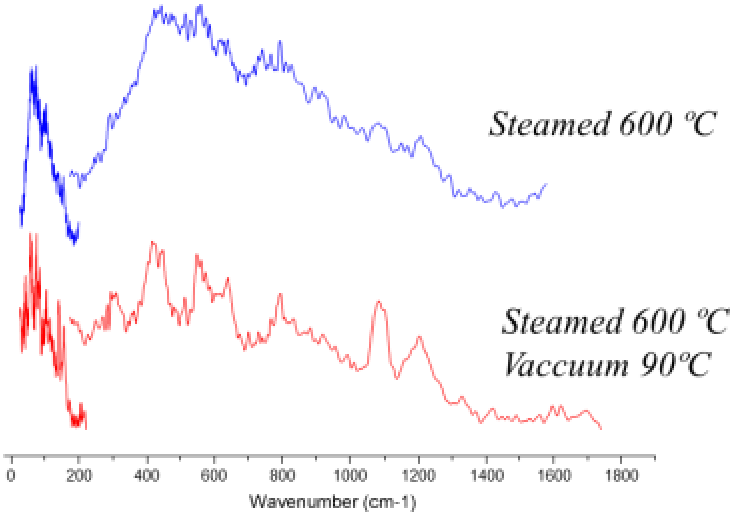

Fig. 1 – INS spectra of zeolite sample "EFAL rich" (steamend at 600 ºC) before and after dehydration (top, bottom, respectively).

The identification of the bands ascribed to the EFAL forms is more evident in Fig. 2, by comparing a dehydrated steamed sample (EFAL rich) with a dehydrated bare sample (no EFAL forms expected). The INS bands centred at *ca*. 790 cm^{-1}, 1090 cm^{-1} and 1200 cm^{-1}, deserve particular attention as possible "EFAL modes".

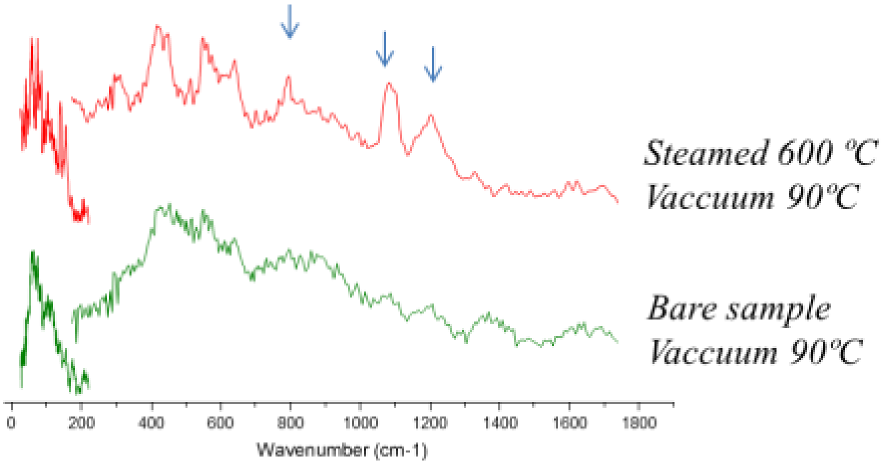

Fig. 2 – INS spectra of zeolite sample "EFAL rich" (steamend at 600 ºC) before and after dehydration (top, bottom, respectively).

DFT methods offer extreme and valuable assistance in the analysis and interpretation of INS spectra by predicting vibrational normal mode eigenvectors. The combination of INS with DFT methods yields a very accurate yet convenient systematic approach to test molecular models and interpret experimental spectra. To assist the assignment of the possible EFAL modes observed, calculations for several EFAL structures proposed in the literature [1] were performed (geometry optimization and frequency calculations with *Gaussian 09*, simulated spectra with *Mantid*'s *AbINS*).

Figure 3 shows some preliminary results, by comparing the experimental INS spectrum with the simulated spectrum for two EFAL models, labelled 1 and 3. The calculated INS spectrum for most of the EFAL models is similar to the EFAl-1 shown. Only the model EFAL-3 is able to produce INS bands in the region highlighted.

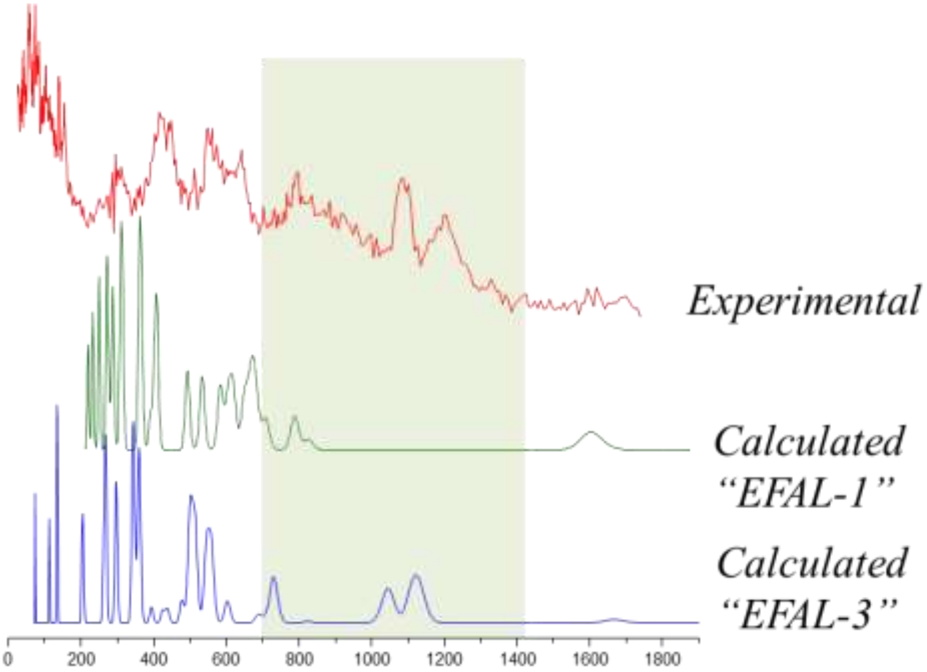

Fig. 3 – Comparison of experimental INS spectrum of zeolite sample "EFAL rich" (top line) with the simulated spectra obtained for two EFAL models (EFAL-1 and EFAL-3).

Reference:

[1] *Towards a better understanding of Lewis acidic aluminium in zeolites*. M. Ravi, V. L. Sushkevichand J. A. van Bokhoven, Nat. Mat. **19** (2020) 1047-1056.
DOI: 10.1038/s41563-020-0751-3