

Experimental report

28/09/2023

Proposal: DIR-290

Council: 4/2023

Title: Unraveling the structure of Brønsted/Lewis acid sites using smart control of HZSM-5 zeolite EFAL composition
(Continuation)

Research area: Materials

This proposal is a new proposal

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Samples: HZSM-5 Zeolites with SiO₂/Al₂O₃ Ratio 15
HZSM-5 Zeolites with SiO₂/Al₂O₃ Ratio 25

Instrument	Requested days	Allocated days	From	To
IN1	2	2	08/09/2023	10/09/2023

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 smart control of HZSM-5 zeolite EFAL composition (Continuation)

DIR-230 *Experimental Report*

The project underlying this mission is a continuation project and builds upon the successful outcomes of the project entitled "Unraveling the Structure of Brønsted/Lewis Acid Sites Using Probe Molecules and Smart Control of HZSM-5 Zeolite (Extra)Framework Composition" (hereafter referred to as "DIR-170"). For this goal, we prepared samples with increased extraframework/framework Al ratios by steaming at high temperature (ca. 600 °C). The steaming procedure – which gives rise to increasing EFAL contents – has been optimized by us, and samples were prepared in advance in our laboratory. Besides increasing the EFAL contents, the steaming procedure also decreases the number of Brønsted acid sites and increases the number of silanol nests.

During the mission, it was possible to collect the INS spectra for 7 zeolite samples, in the medium energy region and the “empty can” spectrum:

Description

- (1) Z15-450 dry, steamed at 450 °C, vacuum 4h, 90 °C (missing in previous mission)
- (2) Z15-NS dry, non-steamed, vacuum 4h, 90 °C
- (3) Z15-600, steamed at 600 °C, cleaned with HNO₃ 0.1 M
- (4) Z15-600 dry, steamed at 600 °C, cleaned with HNO₃ 0.1 M, vacuum 4h, 90 °C
- (5) Z15-NS, non-steamed, cleaned with HNO₃ 3 M
- (6) Z15-NS dry, non-steamed, cleaned with HNO₃ 3 M, vacuum 4h, 90 °C
- (7) Silicalite, calcinated silicalite (no Al)
- (8) *Empty can.*

Cleaning the steamed samples with HNO₃ diluted removes the “free” EFAL from the zeolite channels. Cleaning the non-steamed samples with HNO₃ concentrated is expected to remove the Aluminium ions from the framework.

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.

Figure 1 compares the INS spectra of steamed zeolite samples at two temperatures, in the hydrated and dehydrated forms. The dehydration process of the zeolite sample steamed at 450 °C (#1) seems to be less complete than the observed for the sample steamed at 600 °C (DIR-170), but the main features are still visible.

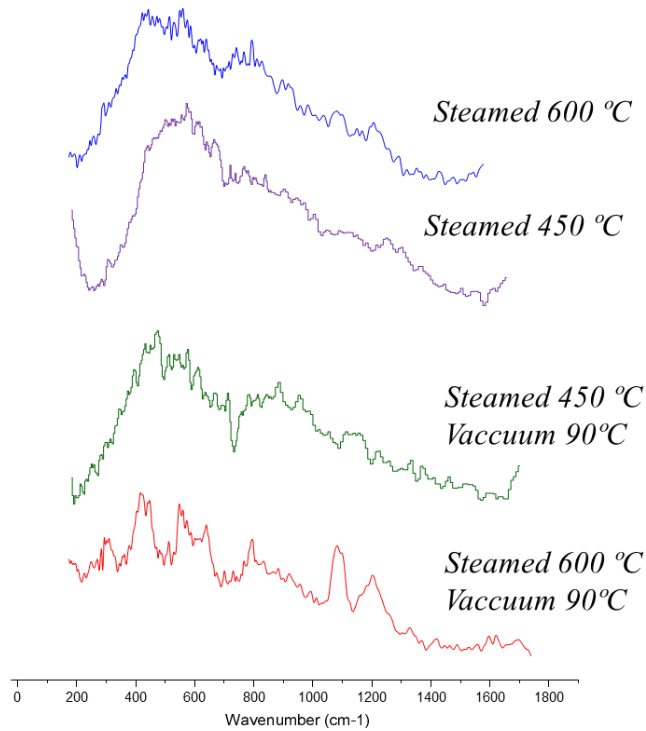


Fig. 1 – INS spectra of zeolite samples “EFAL rich” (steamed at 450 ° and 600 °C) before and after dehydration (vacuum, 90°C).

Figure 2 illustrates the effect of dehydration on the sample cleaned with concentrated HNO₃ (in order to remove the Aluminium ions from the framework). The difference spectrum evidences the presence of amorphous water.

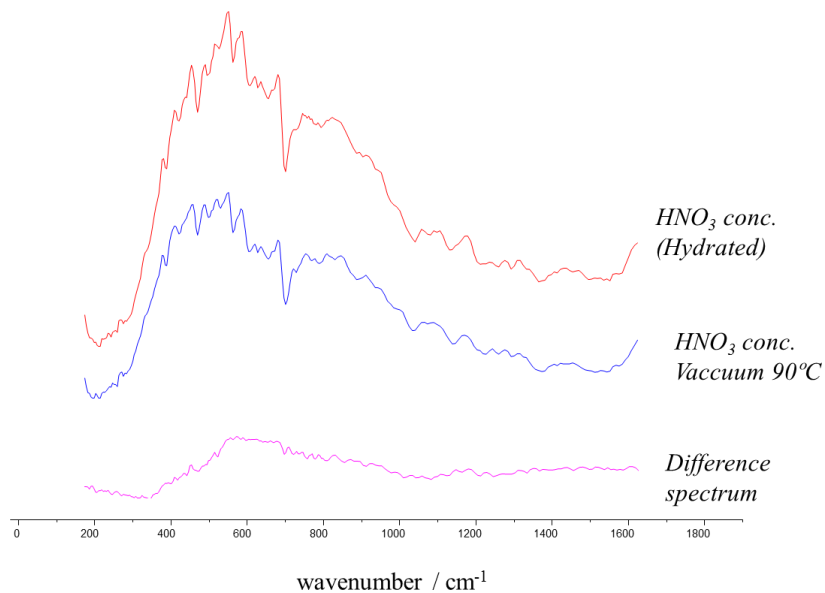


Fig. 2 –INS spectra of non-steamed zeolite sample, cleaned with concentrated HNO₃, before (top) and after (middle) dehydration in vacuum at 90 °C. Line in bottom shows the difference spectrum.

Figure 3 compares three dehydrated samples with different pre-treatments. The non-steamed sample cleaned with concentrated HNO₃ (#6) is labelled “No Aluminium”, as

the treatment is used to remove the aluminium ions in the framework. The sample steamed at 600 °C (DIR-170) is labelled “EFAL rich”. And the steamed sample cleaned with diluted HNO₃ (#4) is labelled “No EFAL”. This comparison is intended to allow the identification of spectroscopic signatures of EFAL species, Bronsted acid sites, and silanol nests.

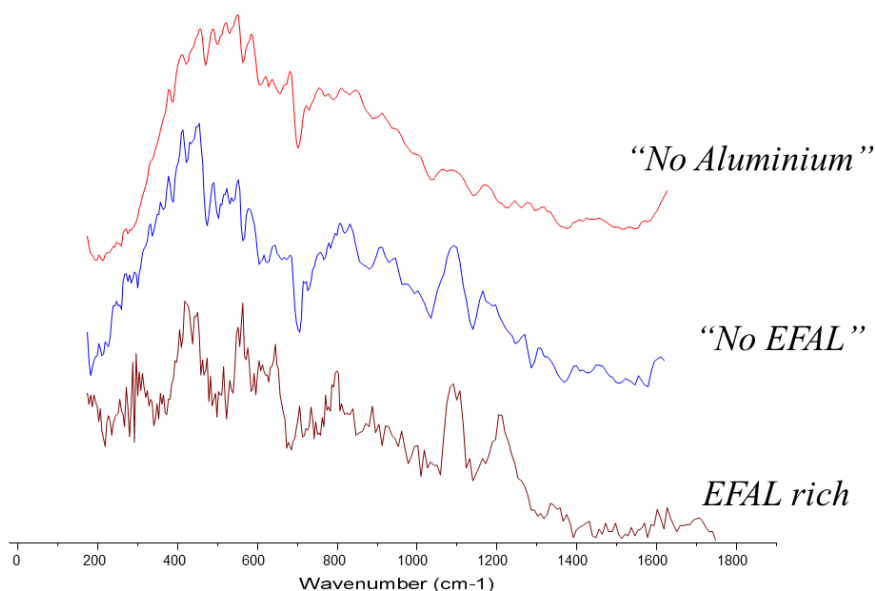


Fig. 3 – Experimental INS spectra dehydrated samples with different pre-treatments. From top to bottom, non-steamed sample, cleaned with concentrated HNO₃; Steamed sample, cleaned with diluted HNO₃; EFAL rich sample (steamed at 600 °C).

This work is currently part of a Master thesis in Chemistry, at the University of Aveiro.