

Experiment Report Form

	Experiment title: Real-Time Evolution of SAPO Catalysts' Local Coordination during Hydrothermal Treatment	Experiment number: CH-4990
Beamline:	Date of experiment: from: 10.05.2017 to: 15.05.2017	Date of report: 15.06.2017
Shifts:	Local contact(s): Stefano Checchia	<i>Received at ESRF:</i>
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Report:

Motivation

Zeolites are used in catalytic, ion exchange and separation processes in several industries due to their acidic and shape-selective properties [1,2] Silicoaluminophosphates (SAPOs) are a special class of zeolites where a framework of tetrahedrally oxygen-coordinated Al and P has been partially substituted by Si creating a Brønsted acidic site [3]. SAPO-34 is probably the best known SAPO catalyst and is a key material in the industrial conversion of methanol-to-olefins [4]. SAPO-37 can be used in processes such as isomerization of n-decane [5] or isobutene/2-butene alkylation [6]. A critical parameter that promotes structural changes in SAPOs during real-life applications is the presence of humidity. Template-free SAPO-37 is known to have poor structural stability in contact with humidity below 345 K [7]. Although the poor low-temperature stability of SAPO-37 has been known since the early 1990s [8], the mechanism governing the loss of long-range order still remains to be experimentally revealed.

Background

This beam-time is part of long-term, interdisciplinary research activities between the University of Oslo, SINTEF Materials and Chemistry and Inovyn A.S. to provide a conclusive answer on how water attacks and destabilizes the framework SAPO microporous catalysts. The funding project, CATLIFE (P#233848, Research Council of Norway), aims to reveal the mechanism and elucidate the reasons behind the structural deterioration that hydration induces on these SAPO catalyst materials. During a previous beam-time at SNBL/ESRF (**01-02-1111**, September 2016) we revealed the sub-unit cell structural transformations that occur around the points of templates removal of SAPO-37 [9]. Following this, we exposed the template-free SAPO-37 to a variety of hydration loadings in isothermal (313 K) and variable temperature conditions (313 – 473 K). Using high-time resolution SR-XRD we were able to observe, for the first time, the structural changes that water induces in each of the the SAPO-37 cages as it accumulates in its framework [10]. Prolonged exposure of template-free SAPO-37 to hydration below the critical temperature of 345 K leads to amorphization, therefore we needed to employ high-time resolution PDF analysis to study Si-O, Al-O and Si-Al interactions (which should vary significantly with hydration) and pin point changes in the Si local environment.

As far as SAPO-34 is concerned, early NMR studies carried out within the CATLIFE framework have shown changes in the Si local environment during exposure to hydrothermal conditions at 100, 200 and 300 °C. At the same time, very few experimental studies exist in the literature on the hydrothermal stability of the material at the industry-relevant temperatures of 400, 600 and 700 °C with the results at the moment being inconclusive.

Measurement Summary - Results

SAPO-37

Prior to each experiment the as-synthesized SAPO-37 underwent *in situ* calcination and consecutive cooling, while recording a total scattering pattern every 5 s (2 s exposure time).

A) Study of the hydration effect, above and below the critical temperature of 345 K:

- Hydration at 353 K (80 °C)
- Annealing at 423 K (150 °C)
- Hydration at 323 K (50 °C)
- Final annealing at 473 K (200 °C).

Isothermal stay for 2 h at each temperature. The experiment took place in two different hydration atmospheres: He bubbled through water and synthetic air bubbled through water.

Water adsorption on template-free SAPO-37 has shown an order of magnitude stronger uptake of water by the structure at 323, compared to 353 K. DRIFTS showed that annealing the material at 423 K, between the two hydrations, completely removes the water molecules from the material surface. *In situ* SR-XRD showed that water is mostly accumulated in the sodalite (**SOD**) cages, resulting in stretching of the T-O-T bonds of the double 6-rings (*d6R*). The local swelling of the **SOD** cages shrinks the faujasite (**FAU**) cage resulting in volume loss of the unit cell. Excessive hydration results in rupture of the T-O-T bonds in the *d6R*s. The acquired PDF data are expected to provide an answer on whether the **SOD** cages retain their structure after the collapse of the **FAU** cage or if they eventually collapse as well.

B) Study of the hydration effect, in the temperature range 253 – 383 K. Isothermal stay for 10 mins in presence of synthetic air bubbled through water.

Earlier *in-situ* experiments at the RECX lab (University of Oslo), showed that hydration in the temperature range 253 – 293 K has minor effect on the material structure. On the other hand, the effect on the material structure above 293 and below 345 K is quite substantial; The crystallinity loss occurs within

minutes and the unit cell volume decreases despite the water adsorption mechanism that takes place in the same time.

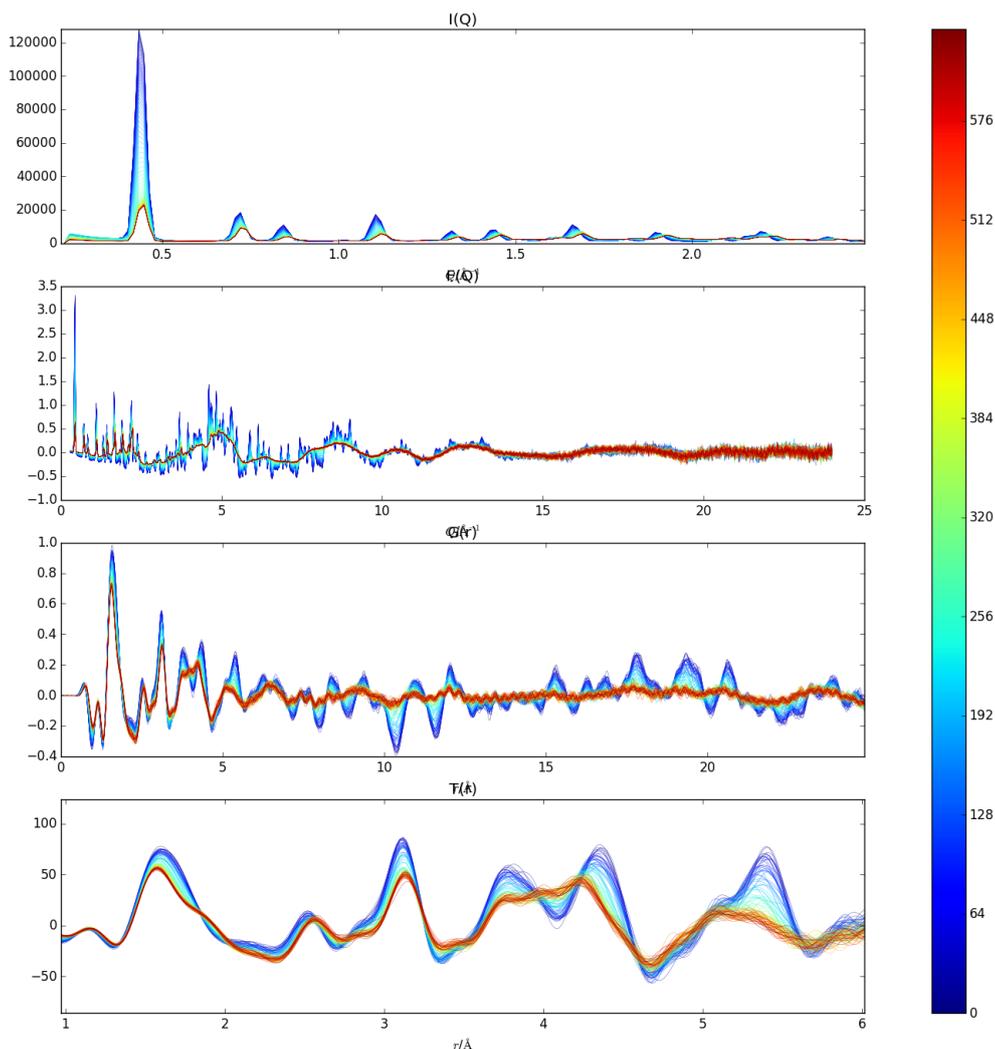


Figure 1: PDFs of template-free SAPO-37 after hydration at 263 K.

Figure 1 shows the local structural changes occurring in the material at 263 K. Hydration results to substantial loss of long-range order, especially above 5 Å, as *in situ* SR-XRD has shown already [10]. Prolonged hydration results in loss of intensity of the sub-5 Å peaks without however losing much of their general features. Preliminary work suggests that the sub-5 Å peaks are most likely related to the **SOD** cages which seem to remain largely intact after the rupture of the **FAU** cage.

A model, to describe the interatomic distances and derived by the acquired PDFs, will be created for the template-free SAPO-37 in a similar way as Readman *et al.* did for the zeolite Na-A [11].

SAPO-34

In a similar way, the as-synthesized double-enriched SAPO-34 sample went through *in situ* calcination and consecutive cooling to 373 K (100 °C), while recording a total scattering pattern every 5 s (2 s exposure time). The template-free material was exposed to hydrothermal conditions at 373, 473, 573, 673, 873 and 973 K for 2 h at each temperature.

The acquired data will be analysed and model describing the local rearrangement of Si-O, Al-O and Si-Al distances will be proposed.

References

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