Experimental report

15/12/2015

Proposal:	**7-04-129**	**Council:**	4/2014
Title:	INS study entrapped organic cations within the zeolite cages		
Research area:	Materials		

This proposal is a new proposal

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Samples:
SAS-SiO2(PC13H30)0.2
ITE-SiO2(PC13H30)0.2
PC10H24+ I-
PC13H30+ I-
RTH-SiO2(PC10H24)0.2
RTH-SiO2(PC12H29)0.2

Instrument	Requested days	Allocated days	From	To
IN1 LAG	4	4	03/10/2014	07/10/2014

Abstract:

The aim of this proposal is to study by INS the influence of the size and shape of zeolitic cavities on the rotational/vibrational levels of encapsulated organic cations. The INS data will be analyzed in combination with theoretical calculations using atomistic and quantum techniques.

It is expected that these results could shed light on the zeolite framework stabilization as consequence of the entrapment of organic cations within the zeolite voids.

A set of two different organic cations (structure directing agents, SDA) has been selected that, under certain synthesis conditions, give the same zeolite, RUT-13 (RTH). Being organophosphorous compounds, these structure directing agents are characterised by a strong concentration of positive charge on the phosphorous atom. In fluoride synthesis media, a strong $P^+ \ldots F^-$ electrostatic contribution competes with the van der Waals short range SDA…zeo interaction in order to drive the zeolite formed. The rotation of the methyl groups present in the SDA will be free if van der Waals interactions dominate, but they will be hindered if the Coulombic $P^+ \ldots F^-$ term becomes more important. SDAs can be designed a priori to tune which interactions dominate. The rotational mobility of the SDAs, as well as certain related bendings, has been well tracked (tackled) by Inelastic Neutron Scattering (INS) in order to test this hypothesis. The results yield a valuable knowledge to design specific SDAs for the synthesis of zeolites.

In the final as-synthesised material, it is usual that the intermolecular van der Waals SDA…zeo interactions contain always a small repulsive part which leads to some constraints on specific degrees of freedom of the occluded organic. Hindered rotations or bendings will therefore be expected such as, among other, $-CH_3$ rotations as well as CCH and HCH bendings. These low energy modes, containing hydrogen atoms, are good candidates to be tracked by inelastic neutron spectroscopy (INS), and this is the subjet of the present study.

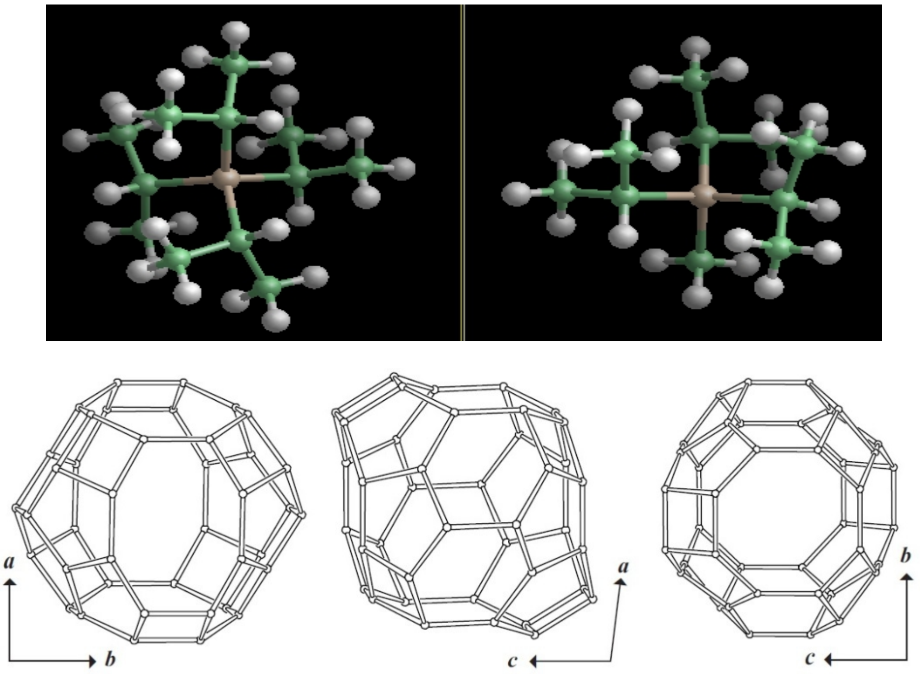

Figure 1. (top) Phosphonium cations, tetrapropylphosphonium, that we call ADE-1 (left) and triisopropylmethyl (right) phosphonium, that we call ADE-2, used as SDAs for the synthesis of pure silica RUB-13 (RTH). (bottom) Three views of the *rth* cavity in RTH zeolite.

INS results in IN1 have shown that there are clear differences between the INS spectra of iodide salts of organic cations (cation 1 and 2) and the same cations occluded in RTH zeolite (Figure 2). Hence, it is obvious that there are differences in the phonon modes of the organic cations as iodide (not entrapped) and as encapsulated in RTH zeolite, particularly at low wavenumbers. Preliminar calculations using an atomistic forcefield approach allowed us to quantify the differences in two specific frequencies associated to rotation and bond bending modes and roughly there is a good agreement between calculated and INS data. The low energy region can not be studied by Raman or IR spectroscopies owing to the presence of very strong overlapping bands corresponding to silica framework. The RTH spectrum does not show any INS peak, confirming that the RTH host (SiO_2) is absolutely free of hydrogen.

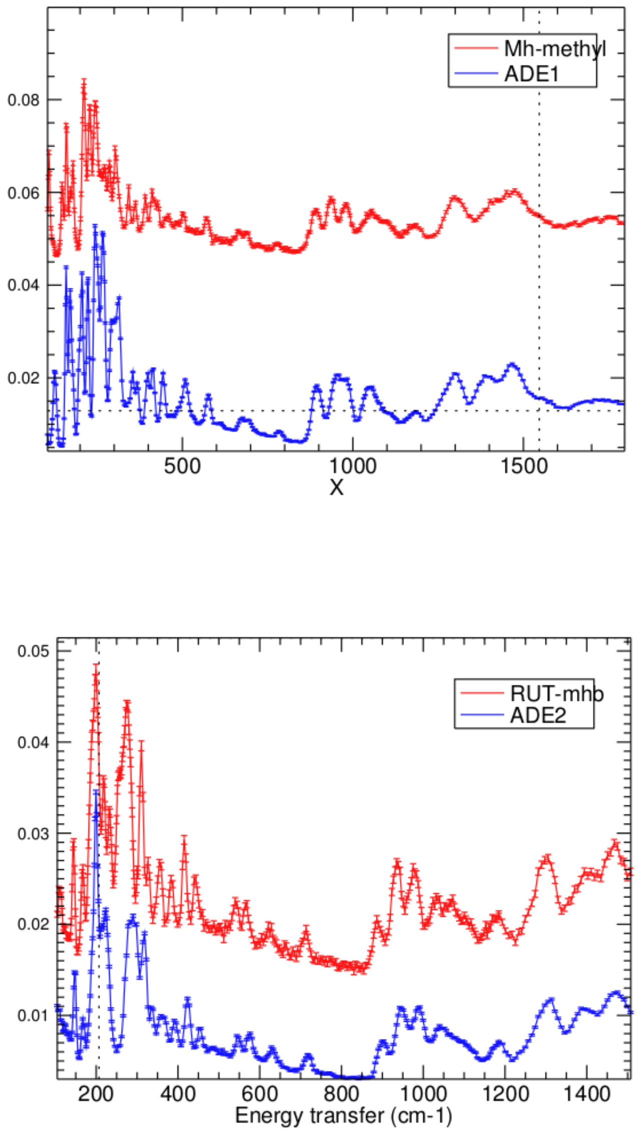

Figure 2. INS spectra of ADE-1 (top) and ADE-2 (bottom) in solid state and occluded in RTH zeolite