EUROPEAN SYNCHROTRON RADIATION FACILITY

	Experiment title: In situ XRD study of structural modifications and desorption kinetics of zeolites used for removal of non polar organic compounds from contaminated water	**Experiment number**: CH 3510
Beamline:	**Date of experiment**: from: 08 FEBRUARY 2013 to:11 FEBRUARY 2013	**Date of report**:
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Report:

The aim of this project was to investigate, for the first time by *in situ* time-resolved X-ray powder diffraction, the structural modifications and the desorption kinetics during the thermal regeneration of ZSM-5 zeolites used for removal of non-polar organic compounds from contaminated waters. In particular, we were studied the structural and kinetic response to heating of zeolite ZSM-5 after adsorption of 1,2-dichloroethane (DCE), methyl tert-butyl-ether (MTBE), toluene (TOL) and of a mixtures of these contaminants from aqueous dilute solutions. An hydrophobic zeolite ZSM-5 (Zeolyst International, code CBV28014; SiO2/Al2O3=280) in its as-synthesised for was used as adsorbent. Kinetics and adsorption isotherm batch data were obtained via Headspace Solid Phase Microextraction -Gas Chromatography. Time-resolved diffraction data (temperature range 25°-600°C) were collected at the ID31 beamline at ESRF (Grenoble), using a fixed wavelength of 0.40003(1) Å. Powder diffraction data have been collected as a function of time, both in temperature ramp and isotherm modes in order to obtain information on: i) evolution of the zeolite crystal structure (relocation of extra-framework species and symmetry modifications); ii) site selective kinetic parameters of desorption process. Both kind of information have been crucial to design and optimize the regeneration treatment of zeolites with a very high potential for application in water remediation technologies. The adsorption/desorption behaviour of ZSM-5 loaded with the selected organics was studied using the data cololectd at the ID31 beamline in the temperature range 25-600°C. In all samples, the gradual overlapping of groups of peaks (Figure 1) reveals a monoclinic $P2_1/n$ to orthorhombic *Pnma* phase transition, occuring with a T_c close to 50-70 ± 5°C. This result confirms the well-known crucial influence of the Si/Al

ratio [1-4] as well of the adsorbed extra-framework molecules [5-8] on the monoclinic-orthorhombic phase transition undergone by this zeolite. Up to 70 ± 5°C, the slight increase of unit cell volume can be reasonably related to the relaxation of the interactions between the organics–water molecule complexes and framework O atoms which exert a kind of negative pressure (attractive force) on the surrounding framework (Figure 1). Upon heating the relaxation of the host molecules determines a deformation of both the sinusoidal and straight channels thus causing a unit-cell variations in all temperature range investigated (Figure 2).

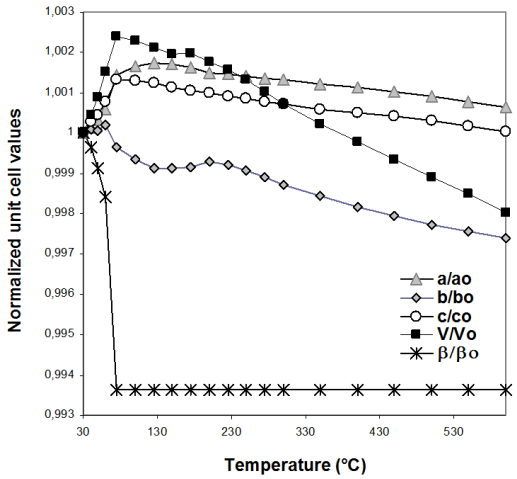

Figure 1. Temperature evolution of the unit cell parameters of ZSM-5-DCE during the *in situ* thermal burning of the organic.

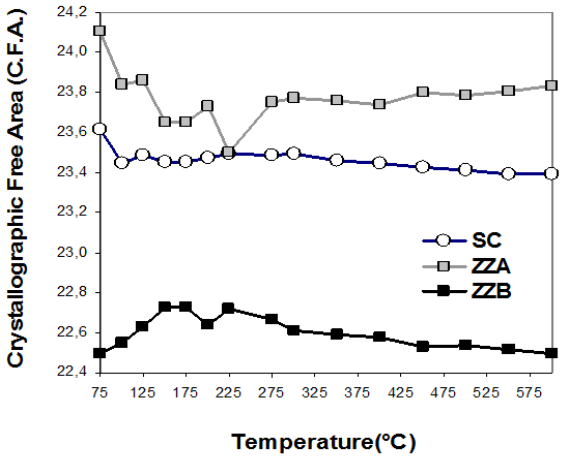

Figure 2. Evolution of Crystallographic Free Area for the 10MR channels as a function of temperature (SC= straight channel, ZZ= sinusoidal channel).

The refined occupancies obtained by the Rietveld method indicates that both organics location and content remained substantially unchanged thus confirming that, after regeneration, Rietveld analysis demonstrated that the adsorption/desorption processes occurred without any significant zeolite crystallinity loss, but with slight deformations in the channel apertures.

These results clearly demonstrated that regeneration of ZSM-5 is effective when thermally treating this environmentally friendly and highly efficient adsorbent at about 350°C thus minimising the cost of the regeneration step of the adsorption process. In conclusion, the use of this adsorbent with unchanged adsorption performances after thermal regeneration under mild conditions appears very promising also over several cycles of the adsorption/desorption process. Once regenerated and reloaded the ZSM-5 zeolite does not show any significant difference in the saturation capacity. Moreover, regenerated zeolite does not exhibit crystallinity loss or deformations in the channel apertures, as well as perfectly regain the unit-cell parameters of fresh material.

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