

MS13-O3**Cation migrations and Brønsted sites formation in NH₄-form of zeolite omega: a combined in situ time-resolved Synchrotron and Neutron powder diffraction study**

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Acidic zeolites are usually exploited by petroleum industries as high-performing catalysts. Thus far, they have been successfully employed with different purposes, such as isomerization of xylenes, paraffin hydro- isomerization, catalytic cracking, and heavy oil hydrocracking [1]. Their catalytic properties arises from the presence of protons bonded to framework oxygen atoms, which act as Brønsted acid sites. To predict the zeolite performances as acid catalysts, a detailed structural study is needed in order to determine location, nature, strength and density of acid sites. Based on this, the aim of this work is to give an exhaustive picture of thermal behaviour of zeolite omega (a synthetic counterpart of the natural mazzite zeolite) [2] in its NH₄-form, from RT to 900 °C in order to follow the structural modifications induced by calcinations of ammonium ions. The formation of Brønsted sites was also monitored by neutron diffraction in order to detect their location. A sample of zeolite omega (Na_{6.6}TMA_{1.8}(H₂O)_{22.2}[Al_{18.4}Si_{27.6}O₇₂]-MAZ) was synthesized at the Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, (CNRS, Montpellier, France) and then NH₄-ion exchanged three times at Room Temperature and other three times at 90 °C (Na_{2.4}TMA_{0.9}(H₂O)_{4.2}(NH₄)_{20.0}[Al_{18.4}Si_{27.6}O₇₂]). The “in-situ” time resolved diffraction measurements were performed at ESRF, Grenoble (heating rate was 5°C/min). The loss of extraframework species (residual TMA and NH₄) was accompanied by strong deformation to the zeolite framework (*i.e.*, variation on O-O distances and T-O-T angles for 6MR, 8MR and gmelinite cage) and by Na cations migration towards the 6MR. The decrease in T-O₂-T angle causes a shift of O₂ framework oxygen towards the centre of gmelinite cage, as proved by the decrease of O₁-O₂ distance addressed by the formation of a O₂-H Brønsted acid site, whose location was highlighted by neutron powder data collected at the diffraction beamline D2B (ILL Grenoble). The neutron structure refinement showed that the mean T-O distances are consistent with Si, Al disorder, showing that the small difference (0.015 Å) indicate that more Al is in T₂ (or A) than in T₁ (or B) in agreement with the results obtained from single crystal X-ray refinement of natural mazzite [3]. Above 770 °C, the strongly inhomogeneous lengthening of the T-O₅ distance indicates that a dealumination process occurs. All these informations provide a basis for the interpretation of the omega shape selectivity in reactions of growing importance in the oil and petrochemical industries.

References:

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