Phenomenology of the dealumination in Faujasite Y zeolitic catayst

Dr Valentina Girelli Consolaro[1], Dr Virgile Rouchon[2], Dr Walid Baaziz[1], Dr Sharmin Sharna[3], Dr Stefan Stanescu[3], Mme Anne-Lise Taleb[2], Dr Gerhard Pirngruber[2], Prof Ovidiu Ersen[1]
[1]Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS, Stasbourg, France, [2]IFP Energies Nouvelles (IFPEN), Etablissement de Lyon, Solaize, France, [3]Synchrotron SOLEIL, Gif-sur-Yvette, France

Background incl. aims
The dealumination is one of the most efficient strategies for designing optimized catalysts of zeolite-type [1]. In aluminosilicates such as the zeolite Y, which is a widely employed material in the field of the heterogeneous catalysis, the dealumination involves the removal of Al atoms in the 4-fold coordination (with oxygen) from the crystalline zeolitic framework thus leading to an acquired hydrothermal stability and an interconnected hierarchical porosity [2], which are both beneficial properties in catalytic reactions. Although, the mechanism of structural rearrangement after the extraction of the framework Al atoms (FAL) from their tetrahedral sites turning into extra-framework Al atoms (EFAL), the evolution of the mesopores (pores from 2 to 50 nm of diameter), the elemental distribution of Si and Al as well as the chemical speciation between the FAL and EFAL are still considered as hot topics in the subject [3]. Our study aims indeed to provide an understanding of the phenomenology of the dealumination at the nanometric space resolution by combining different TEM-based approaches.

Methods
For this research work, a series of 4 zeolites Y at subsequent stages of a multi-step dealumination process, mainly obtained by alternating thermal treatments under steam and chemical treatments, was considered. A first hydrothermal treatment (steaming 1, 620°C and 80% humidity) is performed on the commercial CBV300 (Zeolyst) zeolite Y in a reactor and followed by a NH4 ionic bath, a second hydrothermal treatment (steaming 2, 700°C and 80% humidity) and a HNO3 (1M) leaching. These zeolites undergoing such protocol were characterized by Electron Tomography, STEM EDX, STEM EELS together with synchrotron STXM XAS in order to locate the chemical signatures of Si and Al within the grain and correlate with morphological modifications.

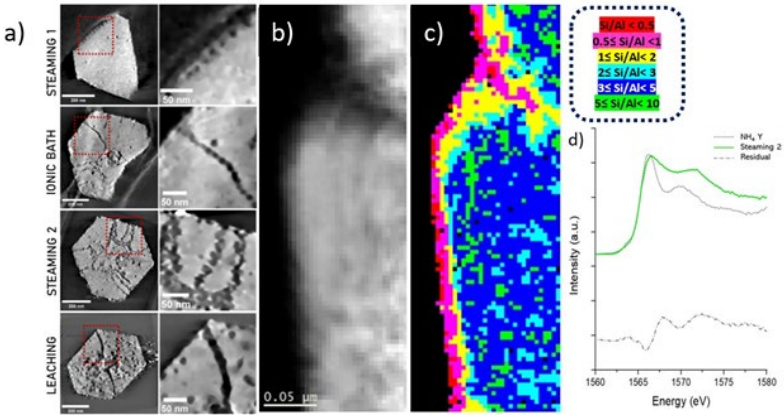
Results
The results of the electron tomography highlight the presence of a well developed system of mesopores that is structured in cavities and channels converging towards the core of the grains of zeolites. The facets of the zeolites Y are mainly belonging to the {111} smmetry and the results show the preferential elongation of the mesopores parallelly to the basal facets. Moreover, most of the channeling mesopores propagate at the intersection between two plans of the {111} simmetry. At more advanced steps of the dealumination, the mesoporous network is observed in conjunction with some extra material on the edges of the zeolite, inside its microporous matrix and into the mesopores. This extra-framework material, that is suspected to be amorphous, is associated to a phase enriched in Al as it is observed with the STEM EDX analysis. The characterization by STEM EELS on the K-edge of Al and Si reveals the gradient of these two elements on the edge of the grain and at the mesopore mouth. The Si/Al ratio is provided for this extra-framework material, that we consider as EFSiAl (Extra-Framework Silica Alumina) and, for the first time, related to morphological aspects at the nanometric scale. Moreover, the analysis by STXM XAS on the Al K-edge shows that the signal arising from such areas is mainly tetrahedral, in contrast with the current idea that the EFAl sites are octahedral α-alumina type. These findings could be interpreted by assuming the flexibility of the the framework and its reversibility to 4-fold Al under experimental vacuum

conditions. Although, small traces of 6-fold Al persist in the XAS spectrum and might provide a proof of the difference in terms of structure and stochiometry of the EFSiAl phase.

Conclusion

This study has evidenced the role of the {111} family of plans as preferential symmetry for the development of the mesoporous network within Faujasite Y zeolites during dealumination treatments. At the single crystal scale, the removal of material inside the grain is coupled in parallel with the presence of areas enriched in Al. This is termed as the EFSiAl phase, and it is considered as a collateral product of the dealumination. The EFSiAl is mainly observed at the edges of the grain and inside the mesopore. Contrarily to the expectations arising from the literature which tend to assign to the Al sites of the extra-framework material the 6-coordination, our results show a principal tetrahedral signal even for the Al on the EFSiAl phase.

Graphic:



Keywords:

Zeolites, Hierarchical porosity, 3D-TEM, Spectro-Microscopy

Reference:

[1] Verboekend, D., Vilé, G., & Pérez-Ramírez, J. (2012). Hierarchical Y and USY zeolites designed by post-synthetic strategies. Advanced functional materials, 22(5), 916-928. https://doi.org/10.1002/adfm.201102411
[2] Scherzer, J. (1984). The Preparation and Characterization of Aluminum-Deficient Zeolites. In T. E. Whyte, R. A. Dalla Betta, E. Derouane, & R. T. Baker (Eds.), Catalytic Materials: Relationship between Structure and Reactivity 248, 157-200. https://doi.org/10.1021/bk-1984-0248.ch010
[3] Van Bokhoven, J. A., Nabi, T., Sambe, H., Ramaker, D. E., & Koningsberger, D. C. (2001). Interpretation of the Al K- and LII/III-edges of aluminium oxides: Differences between tetrahedral and octahedral Al explained by different local symmetries. Journal of Physics Condensed Matter, 13(45), 10247–10260. https://doi.org/10.1088/0953-8984/13/45/311