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Microstructural evolution of zeolitic nanocrystals for CO2 capture by Environmental in-situ TEM

Dr. Simona Moldovan[1], Mr Edwin Clathworthy[2], Mrs. Kalthoum Nakouri[3], Mrs. Svetlana Mintova[2]
[1]CNRS, Rouen University, Groupe de Physique des Materiaux, Rouen, France, [2]Normandie University, ENSICAEN, Laboratoire de Catalyse et Spectrochimie, Caen, France, [3]TOTALEnergies, Solaize, France

In the current context of demographic evolution resulting in the considerable increase in greenhouse gas emissions, the academic and industrial community allocates more and more resources to the development of new solutions for capturing, storage and recovery of these undesirable products, the main component of which is carbon dioxide (CO2). Micronsized zeolites such as FAU, LTA or TiSi are currently the most widely used for CO2/CH4 separation, but they have disadvantages such as reduced accessibility of pore volume, slow CO2 kinetics, low regeneration and low cycling, and high costs of organic templates used for their synthesis. In this context, functionalized nanosized zeolites (RHO type) with fully accessible active internal and external surfaces and high crystalline yields were synthesized [1]. Considering the ultimate atomic resolutions (<1 Å) achieved in a TEM, and the in-situ capabilities available nowadays, the in-situ environmental TEM is the only approach able to allow the real-time exploration of the impact of specific parameters such as the gas flow, pressure, temperature on the nanosized crystals evolution upon reactions. It allows the real-time analysis of parameters such as crystal size, the proportion of open/closed pores and/or crystalline facets.

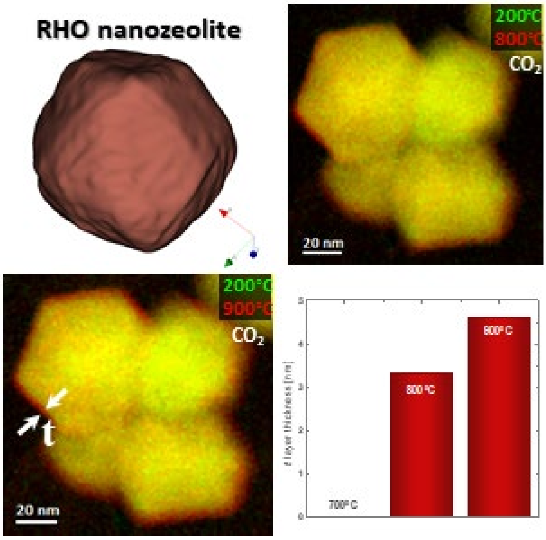
In this study, we focus on and the microstructural changes of nanosized RHO zeolites analyzed by the MET in-situ Environmental under a CO2 flux under high temperatures and pressures.

The STEM-HAADF 2D and 3D observations were carried out on a double corrected Analythical JeolARM 200CF equipped with a Jeol Centurio EDS detector and a Quantum GIF. The in-situ experiments were performed by using an Environmental-Cell from Protochips [2] which has been employed under 1 bar of CO2 flow and for temperature increased from 25 to 900 °C with a heating rate of 10 °C/min. Owing to the high sensitivity of zeolites upon electrons irradiation, the STEM observations were carried out at well-defined temperatures (the beam was turned off during the heating steps).

The RHO nanozeolite was initially heated under Ar at 200 °C, and images under these conditions were taken as references. Maintaining the temperature at 200 °C, CO2 was then contacted with the sample followed by heating and imaging at 700°C, 800 °C and 900 °C. No significant lattice expansion occurs between 200 and 700 °C, when the RHO nanosized zeolite is exposed to CO2. However, the visible expansion of the crystals at 800 °C is consistent with the structural flexibility behavior under air where we observed a substantial increase of the lattice parameter (0.2221 Å) from 700 to 800 °C due to the change in symmetry of the crystalline structure from non-centrosymmetric to centrosymmetric [1]. Superposition of the very same nanozeolite crystals recorded at different temperatures revealed distinct differences in the size of the discrete nanocrystallites. Specifically, the images recorded at 800 °C [3] and 900 °C superimposed with the reference images taken at 200 °C under CO2 show a clear difference in the size of the nanosized crystals, corresponding to an expansion of the particle-matrix by 3 nm and 4.8 nm, or 9% and 15% of the average particle size, respectively. The increase in the volume of RHO crystals was evaluated on the basis of 2D micrographs and corroborated with the exploration of the volume of nanocrystals obtained by electron tomography. The particle expansion between 800°C and 900°C is accompanied by a sharp change of the nanocrystal's microstructure. The crystals morphology remains stable up to 1000°C.

This original study highlights for the first time the flexibility and the microstructural stability of RHO nanosized zeolite at high temperatures under CO2 exposure by in situ HRTEM.

Graphic:



Keywords:

In-situ ETEM-CO2, Flexible RHO zeolites,

Reference:

[1] E. Clathworthy et al., ACS Appl. Energy Mater. (2022), 5, 6032–6042.
[2] https://www.protochips.com/solutions/in-situ-tem-solutions/in-situ-gas-cell/
[3] E. Clathworthy et al., J. Am. Chem. Soc. 2023, 145, 28, 15313–15323.