New insights into the deactivation of fluid catalytic cracking catalysts

Krumeich, F.[1], Ihli, J.[2], Cheng, W.[3], Shu, Y.[3] and van Bokhoven, J.[1,2]

[1] ETH Zurich, Switzerland, [2] Paul Scherrer Institute, Switzerland, [3] W. R. Grace Refining Technologies, United States

Fluid catalytic cracking (FCC) is an important industrial process that converts the heavy fractions of crude oil into gasoline and light olefins. The catalysts in this process are porous composite particles containing zeolites, clays and some minor additives. The catalytic activity of these composites decreases significantly during long-term operation so that their continuous fractional replacement is necessary. As several tons of fresh FCC catalysts are required by major refineries on a daily basis, the extension of the catalyst's lifetime would have an enormous impact. To unravel the structural changes that occur at the nanometer to the micrometer scale and that are behind the observed catalyst deactivation, individual catalyst particles and their pore architecture were studied by different X-ray 3D and electron microscopy imaging techniques and changes of structure and composition were characterized on the micrometer scale (>300 nm) [1-3]. Here, electron microscopy results obtained at the nanometer scale from both pristine and industrially deactivated FCC catalysts are presented and discussed. They reveal unprecedented detail about the structural changes that relate to catalyst deactivation.

Cross-sections of the spherical FCC catalysts with diameters in the range 50 - 100 micrometers were prepared to investigate their internal structure. The SEM image of the cross-section of a deactivated catalyst show a porous and partly fibrous interior structure (Fig. 1). Furthermore, the whole particle is wrapped in a dense envelope which is Si-rich $(Al,Si)O_x$ and contains Fe and Ca according to EDX spectroscopy (Fig. 1). TiO_2 nanoparticles are present as well. HAADF-STEM images (Fig. 2a) recorded at the edge of such a particle show that this envelope is not homogeneous but contains nanoparticles with diameters up to 50 nm. EDXS mappings (Fig. 2b,c) and HRTEM (Fig. 2d) reveal that these particles are Fe_3O_4 (magnetite). Other regions of the envelope contain layer-like calcium enrichments (Fig. 2b,c). The investigation of catalyst particles at different stages of deactivation show a decrease of the porosity of this envelope whereas a thickness plateau is reached at about two micrometers. This envelope does not only block the access to the catalytically active site within the particle but apparently acts also as protective membrane that absorbs poisonous components of the feedstock.

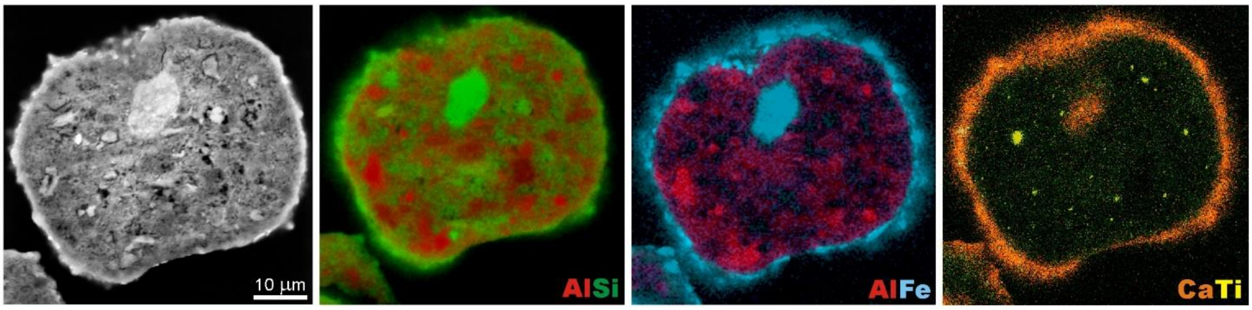

Figure 1: SEM image of the cross-section of a deactivated FCC catalyst particle recorded with back-scattered electrons and with elemental distributions obtained by EDXS mapping.

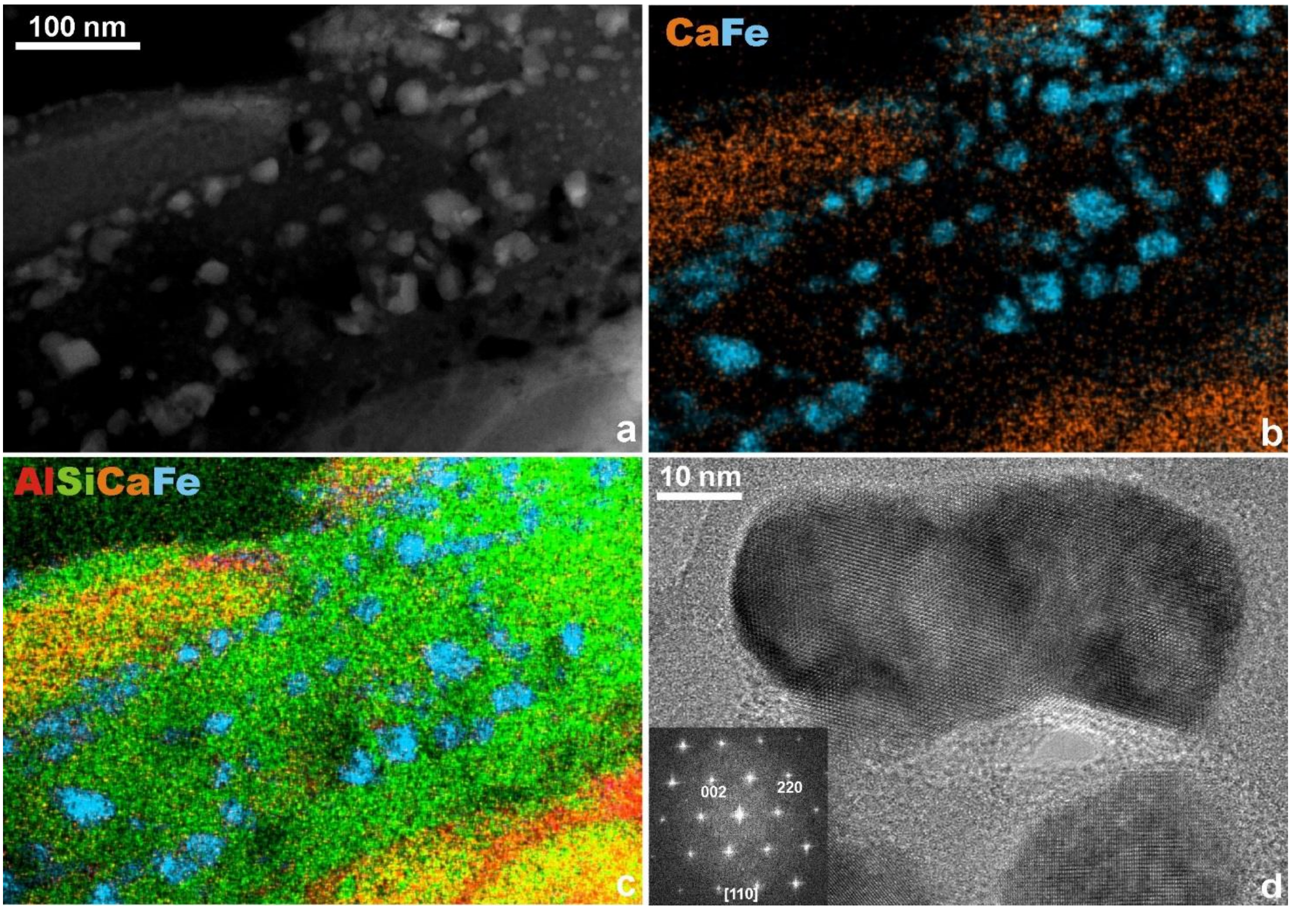

Figure 2: (a) HAADF-STEM image of envelope details and (b) CaFe and (c) AlSiCaFe distribution. (d) HRTEM image of a Fe_3O_4 particle in [110] orientation and its Fourier transform (inset).

[1] da Silva Mader, Holler, Haberthür, Diaz, Guizar-Sicairos, Cheng, Shu, Raabe, Menzel, van Bokhoven *ChemCatChem* **2015**, *7*, 413.

[2] Ihli, Jacob, Holler, Guizar-Sicairos, Diaz, da Silva, Ferreira Sanchez, Krumeich, Grolimund, Taddei, Cheng, Shu, Menzel, van Bokhoven *Nat. Commun.* **2017**, *8*, 809.

[3] Ihli, Sanchez, Jacob, Krumeich, Borca, Huthwelker, Cheng, Shu, Grolimund, Menzel, van Bokhoven *Angew. Chem. Int. Ed.* **2017**, *56*, 14031.

Acknowledgements: Electron microscopy was performed at the Scientific Center for Optical and Electron Microscopy (ScopeM) of ETH Zurich.