doi:10.1017/S1431927613004649
Microsc. Microanal. 19 (Suppl 2), 2013

Electron Tomography Studies to Unravel the 3D Nanostructure of Zeolite Catalysts

Krijn P. de Jong

Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands

Nanostructured catalysts play a key role in chemical processes ranging from oil refining to synthesis gas conversion. One important component of many industrially relevant heterogeneous catalysts are zeolites. Zeolites are crystalline microporous alumino silicates that can also be used, for example, as molecular sieves in separation. As catalyst the micropores (< 2 nm) of the zeolite framework provide beneficial activity and shape selectivity for a given chemical reaction, but can also set severe limitations on the diffusion of reactants and products. Hence zeolite based catalysts are structured on the nanoscale to reduce the size of the microporous regions or to introduce additional components such as metal nanoparticles. In this talk we intend to unravel the 3D nanostructure of complex zeolite catalysts using electron tomography [1].

In a first example, mesoporous zeolites used for hydro-isomerisation and cracking of heavy oil fractions to transportation fuels are considered. Introducing mesopores (2 – 50 nm) into zeolite crystallites by acid and base leaching is beneficial for mass transfer to restrict secondary cracking to gases. Electron tomography is used to assess the mesopore network and its consequences for catalysis [2]. Figure 1 shows the mesopore network with unprecedented clarity in a zeolite Y crystal. Here the trimodal porosity, in particular, combining micropores (~1 nm), small mesopores (~3 nm) and large mesopores (20-50 nm) provided unique selectivity in hydrocracking [2]. Moreover, the meso- and micro-porosity of these zeolite Y samples was quantified using advanced image analysis techniques [3].

In the second example the introduction of platinum nanoparticles inside zeolite Y crystals is discussed. These Pt/Y crystals are widely used as bi-functional catalysts. The proximity of the metal function and the acid function is crucial for catalyst performance. Quantitative ET revealed that the majority of the Pt nanoparticle were 1-2 nm in size and they were placed within the microprous regions of the zeolite crystal. Most interestingly, in carefully synthesized Pt/Y samples we found that within one zeolite Y crystal the Pt particles are uniformly dispersed, however, from one crystal to another the total density of Pt particles varied up to a factor of 35 [4,5].

The third example deals with $Pt/Al_2O_3/Y$ structures. In such catalysts the alumina serves as binder and as carrier of the Pt, in some cases. Our results show that the Pt distribution can be rationally linked to catalyst synthesis [6].

In summary, ET combined with image analysis provides quantitative data on the morphology of mesoporous zeolites which cannot be obtained by any other technique. This approach establishes a new basis for the quantitative interpretation of the impact of synthesis conditions on mesoporosity, metal and binder size, amount or distributions thus paving the way for a rational design of catalysts with defined activity, selectivity, and stability.

References:

[1] H. Friedrich *et al*, Chem. Rev. **109** (2009) p. 1613.
[2] K.P. de Jong *et al*, Angew. Chem. Int. Ed. **49** (2010) p. 10074.
[3] J. Zecevic *et al*, Angew. Chem. Int. Ed. **51** (2012) p. 4213.
[4] J. Zecevic *et al*, Micropor. and Mesopor. Mater. **164** (2012) p. 99.
[5] J. Zecevic *et al*, submitted for publication to ACS Nano.
[6] J. Zecevic *et al*, unpublished results.

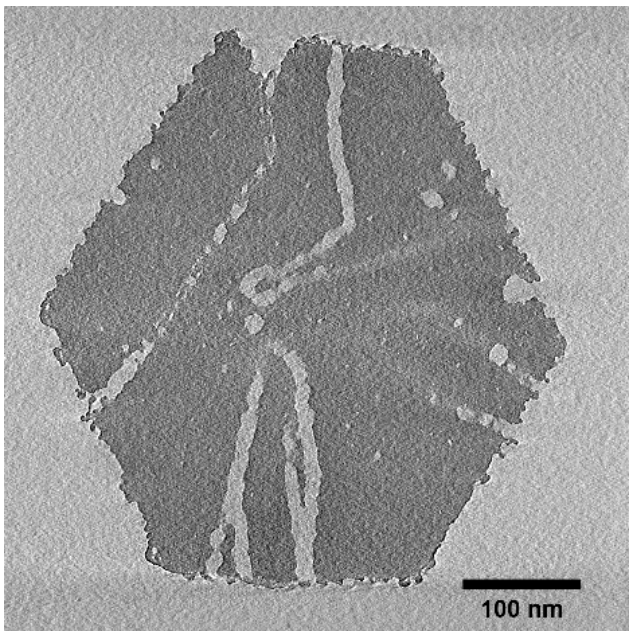

Figure 1. Numerical slice from an electron tomogram of mesoporous zeolite Y. Bright channels are mesopores with a diameter of 20-40 nm; uniform dark grey area is the crystalline zeolite lattice.

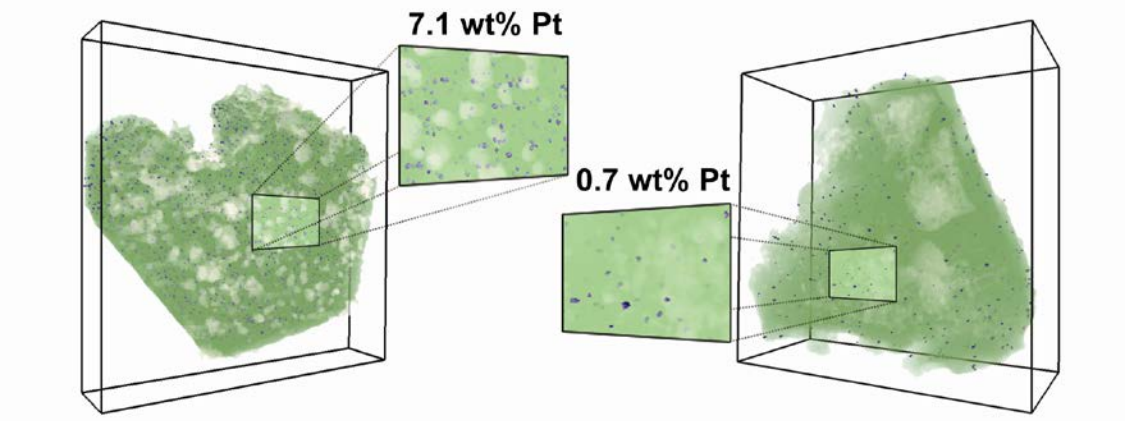

Figure 2. Volume rendering of two Pt/Y zeolite crystals; green = zeolite lattice, white = mesopores; blue = Pt nanoparticles (1-2 nm in size). Both crystals display a uniform distribution of Pt particles, however, at vastly different Pt loading and thereby density of the Pt particles.

https://doi.org/10.1017/S1431927613004649 Published online by Cambridge University Press