

Stability and Local Environment of Transition Metal Ions in Vapor Phase Grown MgO Nanocrystals

Matthias Niedermaier^a, Thomas Schwab^a, Paolo Dolcet^b, Gregor Zickler^a, Johannes Bernardi^c, Silvia Gross^b, Annette Trunschke^d and Oliver Diwald^a

^aChemistry and Physics of Materials, University of Salzburg, 5020 Salzburg, Austria

^bChemical Sciences, University of Padova, 35131 Padova, Italy

^cUSTEM, Vienna University of Technology, 1040 Vienna, Austria

^dInorganic Chemistry, Fritz Haber Institute, 14195 Berlin, Germany

Structure and functional properties of mixed metal oxide nanoparticle systems are subject to stability and composition of related surfaces and interfaces. For vapor phase grown non-equilibrium solids, annealing induced ion diffusion provides efficient means to adjust the surface composition and, thus, functional properties of the material.

In the present study we will discuss the transformation behavior of diluted transition metals (e.g. Fe, Co) in MgO nanocrystals, which were prepared by chemical vapor synthesis. Vacuum annealing changes the properties of the resulting non-equilibrium solids toward thermodynamic equilibrium and provides means to control impurity localization and to trigger phase separation. [1]

By combining structural (XRD, TEM) and spectroscopic (XAS, XPS) characterization techniques, we tracked valence state and local chemical environment changes of admixed transition metal ions (TMI). Impurity concentration determines whether TMI are effectively diluted within the particles or additional effects, like enhanced ion diffusion and particle coarsening at elevated temperatures occur. This leads to clustering of Fe³⁺-Mg²⁺ vacancy complexes and, after annealing to T = 1173 K, surface migration as well as the nucleation of a magnesioferrite phase. [2] With regard to catalytic properties associated with TMI in MgO host lattices, the here presented insights underline that reorganization in the course of catalytic reactions on oxide nanoparticle catalysts is an important issue in terms of distribution and location of functional defects.

[1] A. R. Gheisi, Part. Part. Syst. Char. 2017, 34, 1700109.

[2] M. Niedermaier, J. Phys. Chem. C 2017, 121, 24292.