In-situ XRD and SEM Study of Ni Colloid Formation from Ni Spinel Oxides

Alec C. Ladonis,[1] Brenden E. Hill[1], Michelene Hall,[1] Robert Koch,[1] and Scott T. Misture[1]
[1]*Inamori School of Engineering, Alfred University, Alfred, NY 14802*

In-situ techniques offer insights into reaction mechanisms that may be missed entirely when studying complex materials systems. Nickel aluminate spinel is an interesting case study, where reducing atmospheres extract reducible cations from the MAl_2O_4 spinel starting phase. Subsequent re-oxidation at low temperature causes resorption of the metal into the oxide, thus enabling regeneration of the metal colloids in applications such as heterogenous catalysis. The spinel materials are highly tailorable with substitution of cations onto the lattice as well as the formation of metastable non-stoichiometric compounds which show promise as catalysts for dry methane reforming with good resistance to sulfur poisoning and high turnover frequencies (TOFs) near 4.

Here we present *in-situ* powder X-ray diffraction and *in-situ* scanning electron microscopy of nickel aluminate spinel systems. The combined techniques together reveal the complex nature of spinels, highlighting the phase and surface reactions under non-ambient conditions, allowing us to track reaction progress, structure, and microstructure evolution during oxidation-reduction reactions. We demonstrate mass surface diffusion and coalescence of Ni particles over the defective spinel support under slightly oxidative conditions via *in-situ* microscopy. We highlight coarsening of Ni colloids and surface migration of the particles despite strong anchoring to the support oxide. While the diffraction studies (both neutron and X-ray) indicate that the reaction progresses (in the limit of full Ni reduction, which is not possible) as: $NiAl_2O_4 \rightarrow \sim Al_2O_3 + Ni$, the microscopy study suggests that the oxide surfaces are in fact massively defective, allowing rapid mass transport and remarkable surface changes that are enhanced by electron beam interactions.

We present this interesting and puzzling result, and tie it back to the functionality in oxidative sulfur removal and high TOFs in the dry methane reforming reaction.