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Atmospheric Gas and Heating Transmission Electron Microscopy with Water Vapor Control

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Water's effects on metal corrosion [1] and catalyst deactivation [2] are well-known and have been under study for decades. On the positive side, water can act as a reactant in hydrogen production reactions, like the water-gas shift (WGS) reaction [3]. With the introduction of aberration correctors, in situ and operando gas and heating transmission electron microscopy (TEM) can reveal structure and composition down to atomic resolution in their working status. However, the investigations of water's influence on gas-solid reactions at an atmospheric environment inside a TEM are limited. This is due to the restricted control over the water vapor flow and the fear of potential leaks that can contaminate the TEM columns. In this work, we will present three application examples of our recently developed Vaporizer for MEMS-based gas and heating TEM: 1) the reversible growth and dispersion of the Au nanoparticles on support materials, 2) the corrosion of FeCrAl alloy and 3) the oscillatory reduction and oxidation of NiAu nanoparticles.

Au dispersed on reducible support materials has important applications in low-temperature water-gas shift reactions. Research on deactivation mechanism of such material under realistic gas environment can help to find more resistant ones. In the first application example, we visualized the agglomeration of Au nanoparticles from CeZrO₄ support under wet gas environment, followed by redispersion under dry oxygen environment, as shown in Fig. 1. The results show complex dynamics and possible regeneration of Au nanoparticles under proper conditions and thus gives practical applications better scopes.

Interrupted cooling water cycle could cause nuclear cladding material Zr to react much faster under water vapor conditions than in vacuum or in dry oxygen. This can cause Zr to break and release a lot of explosive hydrogen gas. As an alternative material to current protective structure material, the FeCrAl alloy's performance under water vapor and heating were investigated in this work.

For NiAu nanoparticles, we firstly investigated three extreme situations: 1) reduction condition without vapor (H₂ & He), 2) reduction condition with highest humidity vapor (H₂, H₂O & He) and 3) only vapor at the highest humidity level (H₂O & He). The particle retained in a structure of Ni core and Au shell in H₂ & He. Loose NiO structure formed outside the particle upon introduction of high humidity vapor (H₂, H₂O & He), and then condensed upon disappearance of H₂ in the inlet gas (H₂O & He). Upon varying the humidity level from 0 to ~50% with H₂ and without H₂, we found an interesting oscillating transition between loose and condensed NiO layer formation, whose periodicity is influenced by the humidity level. Through these application examples, it is evident that the development and application of vaporizers, like the DENSsolutions Climate Vaporizer, can help design more sustainable metal materials and catalysts from fundamental mechanism studies.

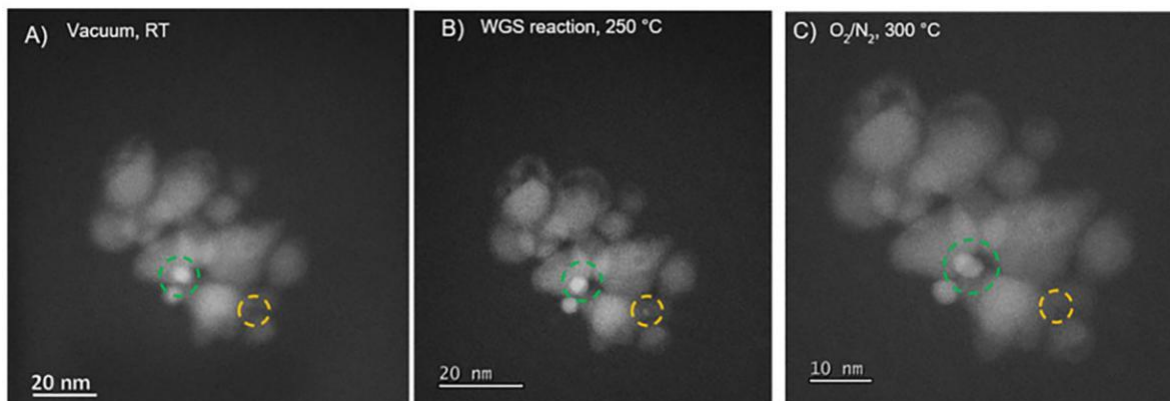
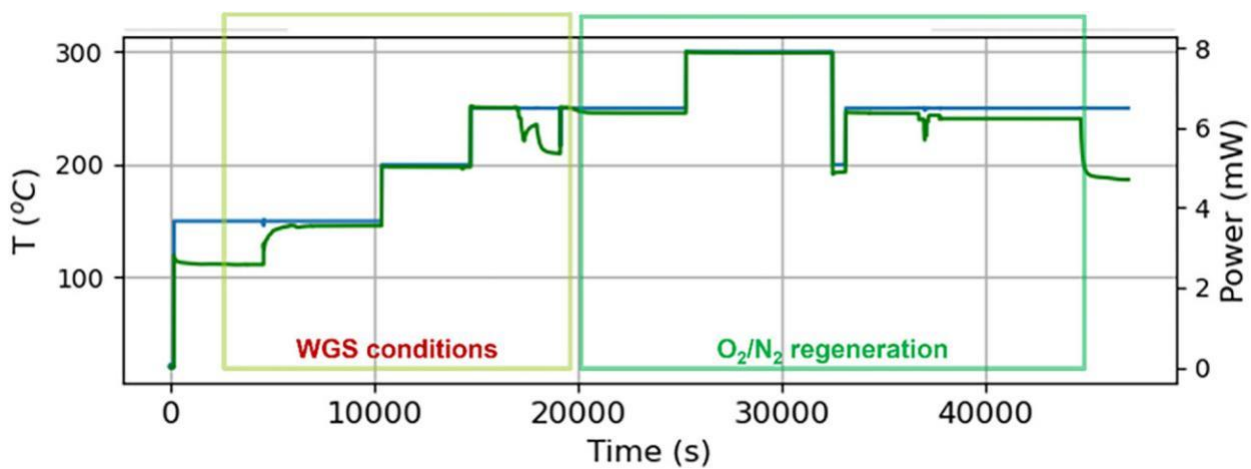


Fig. 1. In situ TEM conditions over time and HAADF-STEM images showing Au segregation and re-dispersion in the 2.5wt% Au/CeZrO₄ catalyst. The light orange circle shows a particle that was not present in the fresh sample, formed during the early stages of the WGS reaction. The green circle shows a particle that was stable under WGS conditions but then grew in size under the oxidative treatment. WGS gas conditions: 2.5 vol% H₂O, 2.7 vol% H₂, 0.67 vol% CO, 0.67 vol % CO₂ + N₂ to balance, 800 mbar.

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