

Oscillatory redox behavior of nickel catalysts observed by operando SEM

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Background

A catalytic cycle in heterogeneous catalysis involves the adsorption, reaction, and desorption of species on the surface of an active catalyst. This cycle repeats as long as the catalyst remains active and is linked to the concept of turnover frequency - defined by chemists to estimate the number of conversions per active site per unit of time. The cyclic behavior that occurs at the molecular or atomistic level involves catalyst restructuring and cannot be separated from the larger scale processes involving collective phenomena of heat and mass flow. Under reaction conditions, the coupling of processes dominating at different time and length scales can give rise to complex dynamics that are observable at both microscopic and macroscopic levels [1,2].

The aim of this work is to investigate how catalytic function emerges in the interplay between reactive species and catalyst. We employ operando scanning electron microscopy to study the simple model system of hydrogen oxidation. This reaction is known to exhibit oscillatory behavior characterized by periodic variations in the reaction rate [3]. This is primarily due to the dynamic and cyclic interplay between the adsorption of reactants, the formation of water, and the autocatalytic formation and reduction of nickel oxide.

Methods

The experiments were conducted using a FEI Quanta 600F Environmental Scanning Electron Microscope (ESEM) at pressures between 20 to 30 Pa. The instrument is attached to a home-built gas feeding system and equipped with a home-built laser heating stage. For reactivity studies, an electron ionization quadrupole mass spectrometer was used. Images were recorded using the gaseous secondary electron detector.

Results

As hydrogen and oxygen are adsorbed and react to form water, the surface periodically transitions between a highly active metallic state and a less active oxidized state. Changes in the oxidation state of the surface result in a change in the secondary electron yield and are detected as brightness variations. In the case of reactions carried out on polycrystalline nickel foils, a dependence of the reactivity on the grain orientation is observed, as well as spillover coupling at grain boundaries and a complex, spiral-like pattern of propagating reaction fronts on some of the grains. Superimposed on the grain dependent surface dynamics are collective oscillations associated with reaction induced variations in gas phase composition. By varying the oxygen flow or temperature, i.e., one of the key control parameters, we are able to systematically follow the transition of the system from a steady state to oscillatory, and ultimately chaotic behavior. Notably, bifurcations are observed, marking shifts in the system's behavior. Switching from a polycrystalline foil to single crystals removes coupling effects due to grains with different activity and shows the formation of intriguing spiral waves under otherwise steady state conditions. Our results reveal the complexity of simple reactions and provide valuable insights into the most relevant coupling mechanisms. It furthermore demonstrates that catalysis cannot be understood based on ex-situ studies.

Conclusion

On the polycrystalline Ni foil, oscillatory behavior between oxidized and reduced states correlates with significant changes in catalytic activity. The reactivity is influenced by the orientation of the surface grains. In contrast, the single crystal (100) Ni surface exhibits initial oscillations that stabilize into spiral-like reaction fronts. Unlike the transient patterns observed on the polycrystalline foil, these spirals are persistent. The stability is attributed to the absence of neighboring grain interactions which typically introduce complexities and destabilize reaction fronts on polycrystalline surfaces.

Graphic:

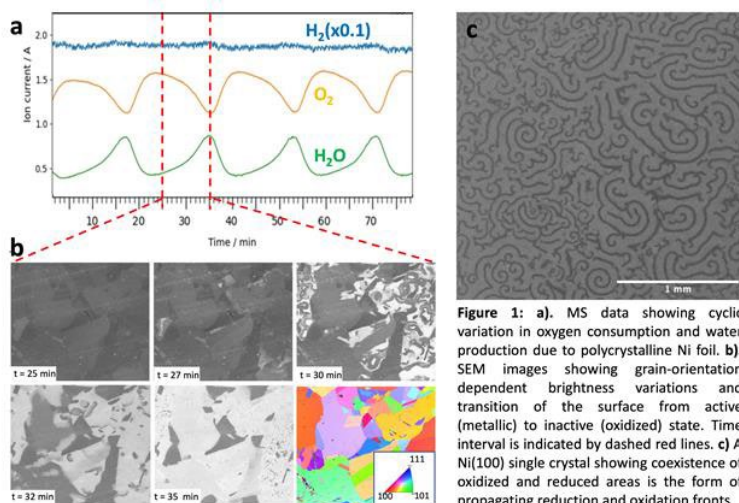


Figure 1: a). MS data showing cyclic variation in oxygen consumption and water production due to polycrystalline Ni foil. b). SEM images showing grain-orientation dependent brightness variations and transition of the surface from active (metallic) to inactive (oxidized) state. Time interval is indicated by dashed red lines. c) A Ni(100) single crystal showing coexistence of oxidized and reduced areas in the form of propagating reduction and oxidation fronts.

Keywords:

Operando SEM, Oscillations, Dynamic Catalyst

Reference:

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