

Revealing the Working Active Sites of M1 phase for Ethane Oxidation

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At the heart of understanding heterogeneous catalysis lies the identification of the nature and structure of active sites – an ensemble of atoms new pathways for the desired reactions. Active sites facilitate reactant/product molecules absorption/desorption, bond rearrangement and electron exchange, but active sites often undergo themselves geometric and electronic structural changes under working conditions. In the field of oxidative dehydrogenation (ODH) of alkanes, understanding the catalytically relevant sites in the most promising catalyst – a complex MoVNbTe oxide in its crystalline form designated as M1 phase – remains as one of the greatest challenges [1, 2]. Among various structural characterization tools, environmental annular dark-field scanning transmission electron microscopy (ADF-STEM) offers unique directly interpretable incoherent imaging of potential catalytic sites at the atomic level [3, 4]. In this work, we demonstrate systematic ADF-STEM analysis of the atomic configuration of the M1 (001) basal plane, where active sites are proposed to be located, after quenching from the ethane ODH operation temperature of 400 °C in the presence of various gas feeds.

Fig. 1 summarizes the structural evolution of the same M1 (001) at various heating durations under each carefully chosen atmospheric condition including: 1) (S)TEM vacuum ($\sim 10^{-8}$ mbar, an unwanted high-vacuum required by conventional (S)TEM as used in [5]), 2) inert He of 0.9 mbar (to bridge the pressure gap), 3) pure oxidative atmosphere with an oxygen partial pressure of 0.9 mbar and 4) the ethane ODH reaction atmosphere. Here, we employed a dedicated field-emission ETEM (FEI Titan 80-300), equipped with differential pumping system allowing controlled gas pressure around the sample, and a resistant coil double-tilt Gatan heating holder. To alleviate heating-introduced sample drifting and off-zone, we adopted a slow-heating-and-fast-quenching protocol that preserves the development of M1 structure at different reaction stages for atomic STEM observation.

To achieve a sound sampling statistics, we developed an automated line profile analysis capable of robust locating and effectively subtracting intensity and atomic displacement information over 200 studied structure units (marked by diamonds) for each STEM image. This in-depth analysis reveals unexpected structural modifications of atomic sites round the cation site S2 in the M1 (001) plane when exposed to different gas feeds at different heating duration. Combining STEM image quantification and simulation as well as *ab initio* (density functional theory) simulations of the temperature-induced transformations of the atomic structure and associated electronic structure changes, we propose a new model for the M1 active sites under working conditions for ethane oxidation as well as for the evolution of such active sites from the room-temperature stable catalyst precursor.

References:

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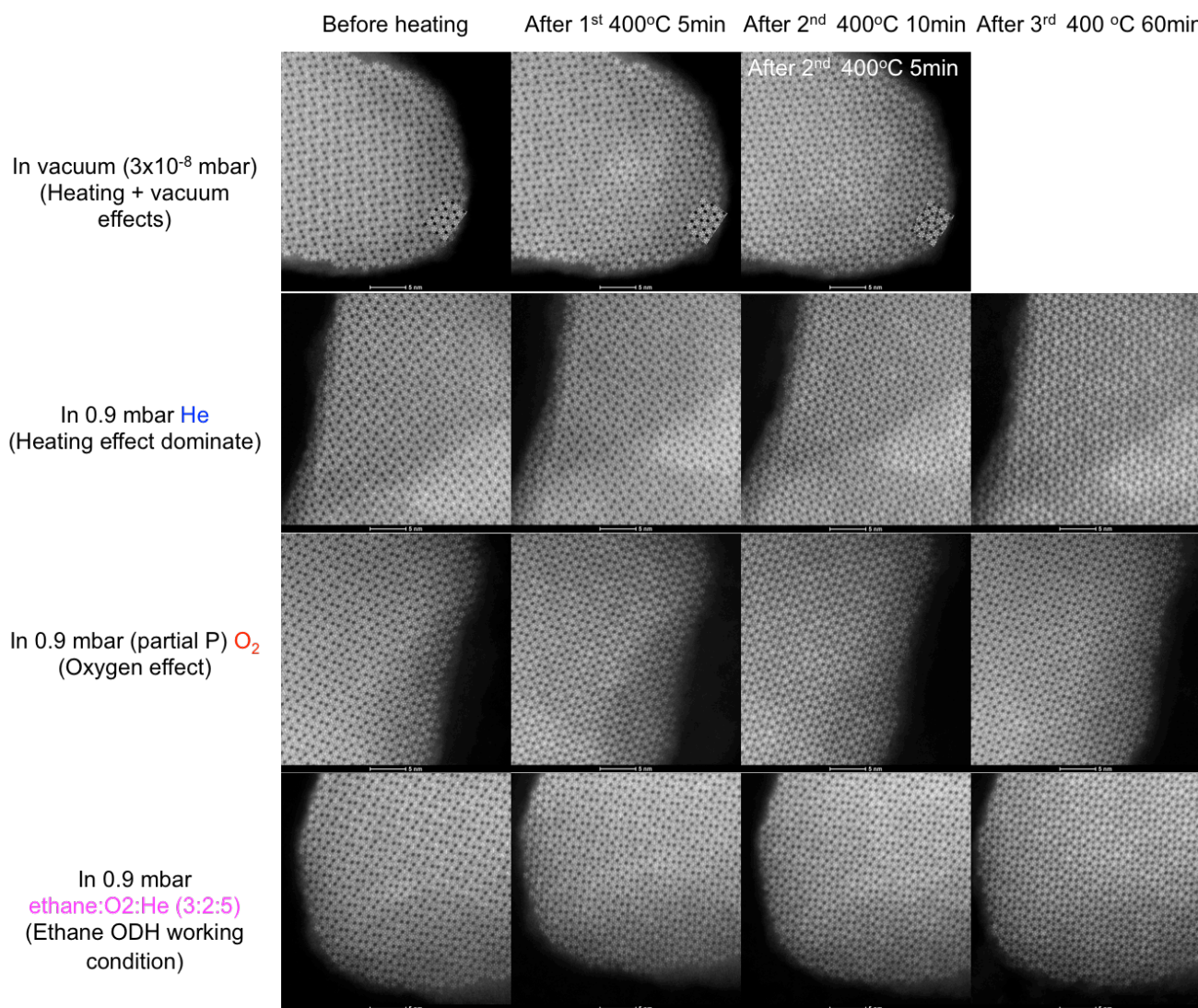


Figure 1. Atomic resolution ADF-STEM snapshots of M1 (001) planes before and after thermally treated for different heating durations in four systematically selected atmospheric conditions. The inserts in the 1st row are simulated STEM images from M1 crystal with modified S12-Te(O) occupancy and atomic displacement.