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Quantifying fluxional behavior in catalytic CeO_2 nanoparticles: toward thermodynamic insight into the stability of surface atomic structures

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Many chemical reactions in heterogeneous catalysis are governed by the influence of small nanoparticles or clusters. Much of current research aims to understand the role of specific atomic structures thought to regulate catalytic activity and selectivity. Recent theoretical insight has pointed to the previously unrecognized importance of dynamic structural rearrangements or so-called fluxional behavior that may arise under working temperatures or reaction conditions [1,2]. These reconfigurations taking place at the surface atoms may modify the energy of the nanoparticle and therefore its thermodynamics, which may give rise to different reaction pathways. In the present work, instead of analyzing these potential reconfigurations occurring on a CeO_2 nanoparticle during conventional reduction process under a H_2 flow and severe temperature conditions, a high electron beam dose has been applied to break the Ce-O bonds and drive this phenomenon. Besides the oxygen release, a high current beam provides a good signal-to-noise ratio which enables the investigation of fast dynamics through direct transmission electron microcopy (TEM) observations.

The time-resolved TEM image series analyzed for the characterization of dynamical effects on a CeO_2 nanoparticle consists of approximately 9,000 single frames acquired at 400 frames per second (21.5 seconds in total) in a Cs-Corrected FEI Titan. The Titan was operated at 300 kV and equipped with a Gatan K2 IS direct electron detector running in integration mode. A high dose of 120,000 $e^-/A^2/s$ was used to drive structural reconfigurations on the nanoparticle [3].

A series of 10-frame, 25 ms time-averaged images of the TEM movie illustrating the CeO_2 nanoparticle acquired at different time points are presented in **Figure 1a-c**. As seen in the figure, the CeO_2 atomic surface structure exhibits surface re-arrangement throughout the observation period. The most dynamics sites are those present on the top surface, where the yellow arrows indicate the appearance/disappearance of atomic-level fluxional behavior induced by the electron beam. In addition to the 3 structures exemplified by the images in the figure, another 8 unique configurations have been identified, including variations mostly occurring at the (111) top surface and at the corners between (111) and (100) facets. The presence of each configuration in every frame of the time-series has been measured and analyzed. **Figure 2a** displays the evolution of two of these configurations after 10-frame averaging, where their presence is indicated with value 1 and their absence with value 0 (1 and 0 mean that the state is present and absent, respectively, for 10 consecutive frames). The quantity can therefore be thought of as a metric to describe the stability of the structure throughout the period of observation. In this case, the stability of structure 1 (black curve) appears higher since it shows a roughly a constant recurrence and mean value of ~0.4, while structure 6 (red curve) appears less stable, being observe briefly during the period marked by the red arrow. Determining the structural configuration present in every frame of the time-series allows on to quantify the transition probability between successive structures. As shown in **Figure 2b**, we have determined that the probability of structure 1 transitioning to structure 5 is about 12 times higher than the structure 1 transitioning to the structure 10 (atomic models given in the figure inset). The transition probability between all the states could be used to derive activation energies through an

Arrhenius analysis, which could yield significant insights into kinetic processes controlling structural transformations in the CeO_2 nanoparticle [4, 5].

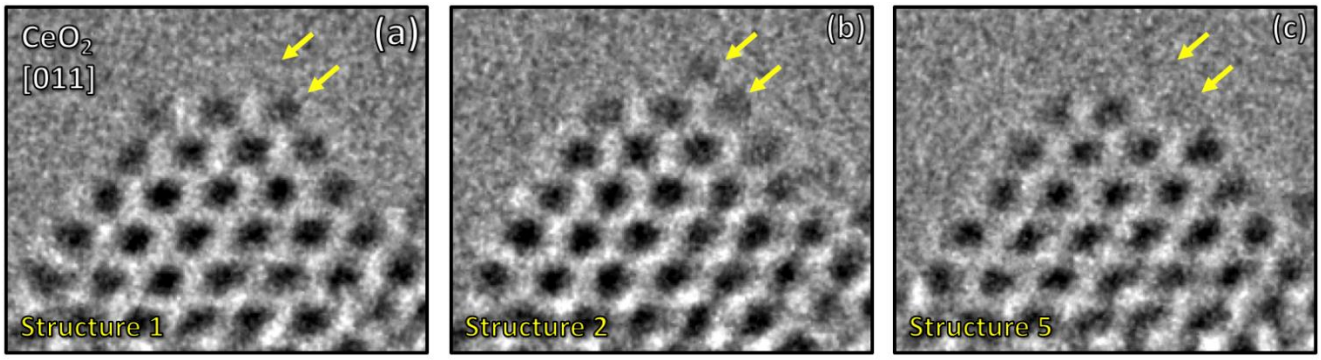

Figure 1. (a), (b) and (c) Structural reconfigurations of a CeO2 nanoparticle undergoing fluxional behavior at the top surface atoms as a result of the high-dose electron beam.

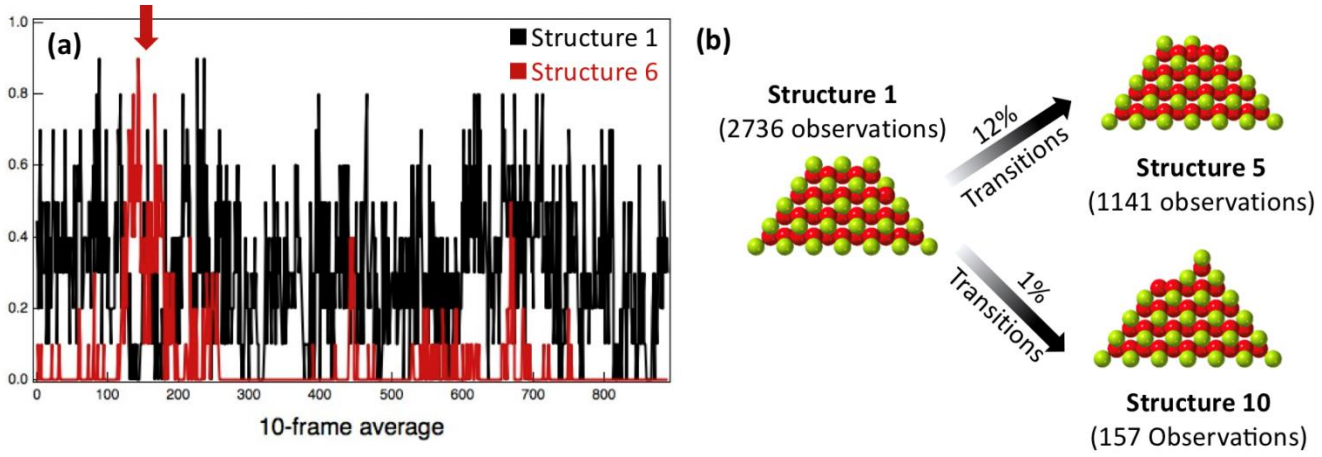

Figure 2. (a) Frequency for structures 1 (black) and 6 (red) along the whole time series averaging every 10 frames. (b) Sketch illustrating three different configurations (1, 5 and 10) with their number of observations. The probability of going from one state to another could be high, like in structure 1 to 5 (common event), or low, like in structure 1 to 10 (rare event).

References

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