In-situ/ Opernado (S)TEM on Mass Selected Pt Clusters Deposited on CeO_2 for CO Oxidation Catalysis

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The study of model catalyst systems with mass selected Pt, Pd and Pt-Pd clusters on nanostructured metal oxide supports like CeO_2, Al_2O_3 in exhaust gas environments can be helpful to understand the fundamental processes in catalytic reactions of exhaust gases, to unravel the complex relationship between the structure and the catalytic properties. *In-situ* TEM can be of aid to track the dynamic transient stages involved such as structural or morphological changes of clusters under catalytic reaction conditions. In this work the behavior of size selected Pt clusters (50-200 atoms) deposited on CeO_2 support are studied using advanced scanning transmission electron microscopy (STEM) techniques, under pure gas environments (H_2, Ar, O_2, CO, CO_2) and during CO oxidation (with CO and O_2).

Size selected Pt clusters are deposited using an ultra high vacuum (UHV) cluster ion beam deposition (CIBD) system[1] on top CeO_2 thin films, which is deposited on *in-situ* TEM nanoreactors. Pt clusters are characterized calculating the pair distribution function from 4D-STEM datasets. The morphology changes in the clusters, cluster-support interaction, cluster-gas interaction etc. are studied realtime in pretreatment and exhaust gas environments using *in-situ* STEM imaging & spectroscopy. The CO_2 generation and the level of conversion at different temperatures can be qualitatively studied using high sensitivity residual gas analyzer (RGA). Figure 1(a) shows the 4D-STEM image of Pt_{55} deposited directly onto Si_3N_4. The integrated PDF of all Pt_{55} clusters is compared to the PDFs simulated for Pt_{55}-FCC and Pt_{55}-icosahedron (Fig. 1(b)).

In-situ (S)TEM on Pt_{200} supported on CeO_2 at pretreatment conditions (oxidation and reduction cycles at 300-500°C) are done and the clusters are found stable at both reducing and oxidative atmospheres. The clusters dynamics under catalytic reaction conditions (in CO & O_2 atmospheres) are tracked *in-situ* at different temperatures from 200-700°C. With continuous imaging, the clusters are found hopping through CeO_2, sintering only at 200-300°C. The movement is not identified at higher temperatures when tracked with the electron beam. Clusters in the areas which are not tracked with e^- beam are found coalesced, moved to other locations at higher temperatures. This shows that the effect of the electron beam on the reaction sites are inevitable and has to be taken into account during acquisition.

To summarize, the study concentrates on the structural characterization of Pt clusters using 4D-STEM PDF. The results show clear differences from bulk FCC-Pt and more resemble towards isomeric shapes. Comparison of PDFs of Pt_{55} icosahedron at various orientations confirms shift of pair distances and intensity variations according to the changes in diffraction intensities with different orientation. Additionally, *in-situ* evaluation of the model catalyst system shows changes in the morphology as well as movement and sintering of the clusters on CeO_2 under catalytic reaction conditions.

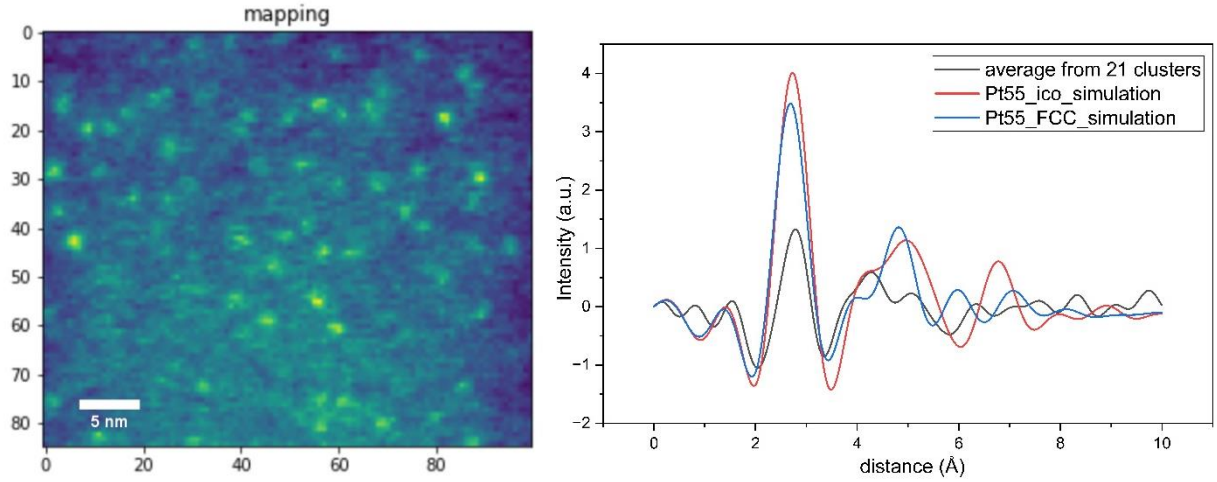

Fig 1: a) 4D-STEM map of Pt_{55} clusters on Si_3N_4, b) Comparison of background subtracted Pt_{55} PDF with Pt_{55}-FCC and Pt_{55}-ico simulated PDFs

Reference:

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