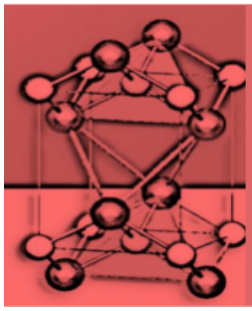

X Workshop on Novel Methods for Electronic Structure Calculations

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Unraveling Reaction Mechanisms in Heterogeneous Catalysis by Oxides: The Dynamic Duo of Infrared Spectroscopy and Density Functional Theory

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A comprehensive understanding of reaction mechanisms is essential for the rational design of catalysts to enhance their catalytic performance. To achieve this goal, the use of in situ and operando infrared (IR) measurements combined with density functional theory (DFT) calculations is crucial. In the context of real industrial processes, various key intermediate species have been postulated following this approach:

- Formate species are proposed as primary intermediates in the synthesis of methanol from CO_2 hydrogenation on palladium-gallium catalysts and in the water gas shift reaction on ceria-based catalysts,
- doping ceria with gallia facilitates hydride formation, significantly impacting the activity for selective hydrogenation of acetylene,
- ethoxy configurations and their transformation on CeO_2 nanocubes and nanooctahedra have a profound effect on selectivity during ethanol steam reforming (similar effects are observed in ceria-gallia and Co-based catalysts), and
- geminal dicarbonyl species on $Cu^{\delta+}$, with $0 < \delta < 1$, appear to be responsible for the heightened activity of reduced $CuGaO_2$ delafossite compared to the oxidized catalyst, specifically under CO oxidation conditions.

These examples underscore the power of the combined IR+DFT perspective in elucidating rational reaction mechanisms.