# Electron Transfer in $TiO_2$ and mixed Oxide-Oxide Model Catalysis:
# Impact of $Ti^{3+}$ on the (Photo-)Chemistry of Methanol at Rutile $TiO_2$ (110) Surfaces

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Due to its outstanding properties, titanium dioxide is a promising material for heterogenous (photo-) catalysis. Moreover, $TiO_2$ can be partially reduced under the formation of point defects such as oxygen vacancies and $Ti^{3+}$ interstitials.[1] Both are carriers of electronic charge, leading to a well controllable self-n-doping. This provokes a drastically increased reactivity in thermal and photochemical reactivity. We aim to obtain a systematic understanding for the role of such defects from temperature-programmed reaction (TPRS) studies on Rutile $TiO_2$ (110) single crystals under well-defined UHV experiments.

In detail, we present the defect dependent population of different reaction pathways in the conversion of methanol. Particularly the deoxygenation reaction forming methane as well as the partial oxidation under production of formaldehyde turned out to be highly sensitive towards the presence of $Ti^{3+}$ and different species of oxygen.[2,3] In addition, thermal and photostimulated C-C coupling reactions also appear as $Ti^{3+}$ mediated processes.[4,5]

By deposition of tungsten oxide clusters, we further mimic a model oxide-oxide cocatalytic system. By this, the electron transfer in such materials was investigated in an x-ray photoelectron spectroscopy (XPS) based study. In brief, the deposition of $(WO_3)_n$ clusters enables the accumulation and pinning of $Ti^{3+}$ near the surface for highly reduced $TiO_2$ and additionally allows an increase of the surface Lewis acidity. We suggest the formation of partially anionic $[(WO_3)_n]^{z-}$ clusters by electron transfer from $Ti^{3+}$ towards the clusters.[6] Finally, this material was tested in the thermal and photochemical conversion of methanol. It turned out, that the thermal reactivity is increased under the population of an additional condensation reaction, while the clusters appeared as an inhibitor for methanol photooxidation. [5]

## References

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