Supporting Information for

Nickel Clusters on TiO_2(110): Thermal Chemistry and Photocatalytic Hydrogen Evolution of Methanol

Moritz Eder[‡,a], Carla Courtois[‡,a], Tim Kratky[b], Sebastian Günther[b], Martin Tschurl[a], and Ueli Heiz[a,]

[a] Chair of Physical Chemistry & Catalysis Research Center, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany

[b] Department of Chemistry & Catalysis Research Center, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany

‡ The authors contributed equally.
*Corresponding Author: ulrich.heiz@mytum.de

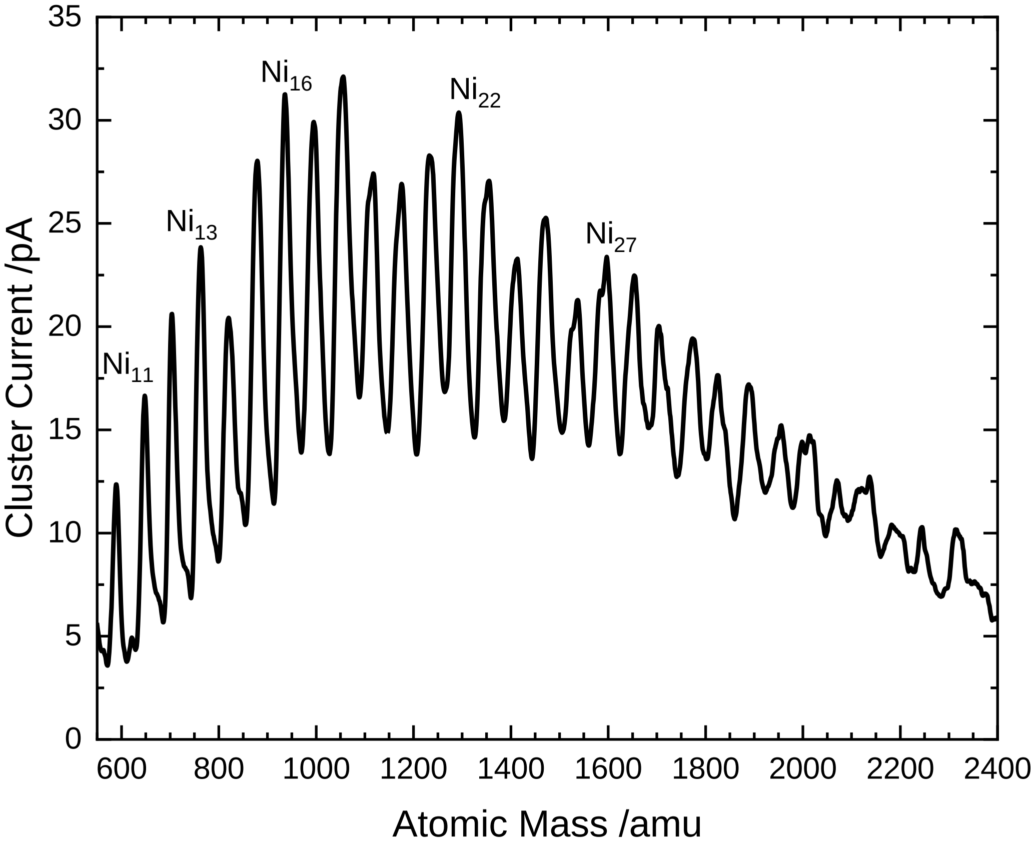

Figure S1. Mass spectrum of the cluster size distribution of Ni clusters from the laser vaporization source. The spectrum is taken after the quadrupole mass filter and shows a size-distribution of Ni_{10} up to Ni_{30}. When depositing in the ion guide mode, all masses lower than Ni_8 are discarded.

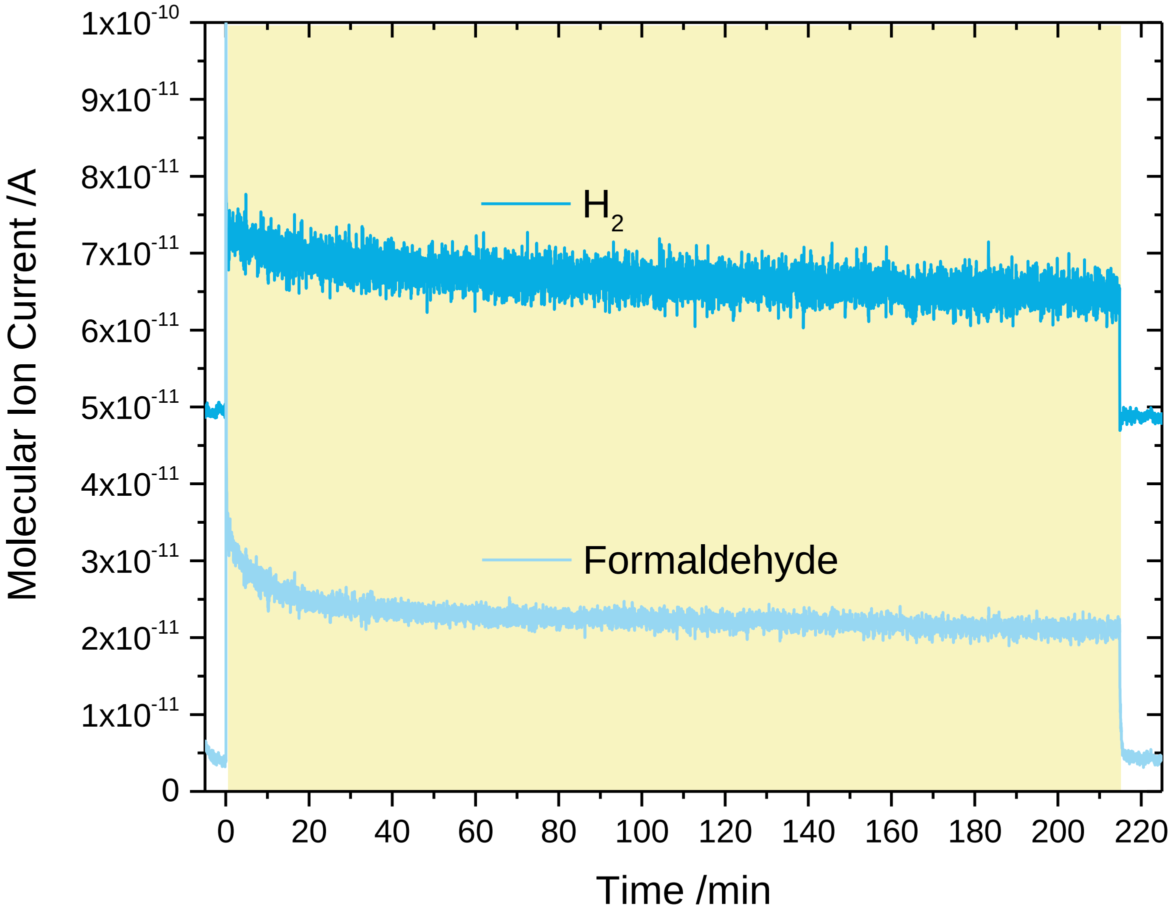

Figure S2. Products of methanol photoreforming on Pt_x/r-TiO_2(110) at 7x10^{-8} mbar alcohol background pressure at 267 K, corrected traces for hydrogen (*m/z 2*), and formaldehyde (*m/z 30)* shown. The colored background highlights the illumination period, where the initial bursts stem from an enhanced methanol concentration on the surface due to its accumulation in the dark. Note that the traces are offset for clarity. With increasing duration of the experiment, no deactivation of the catalyst is evident.

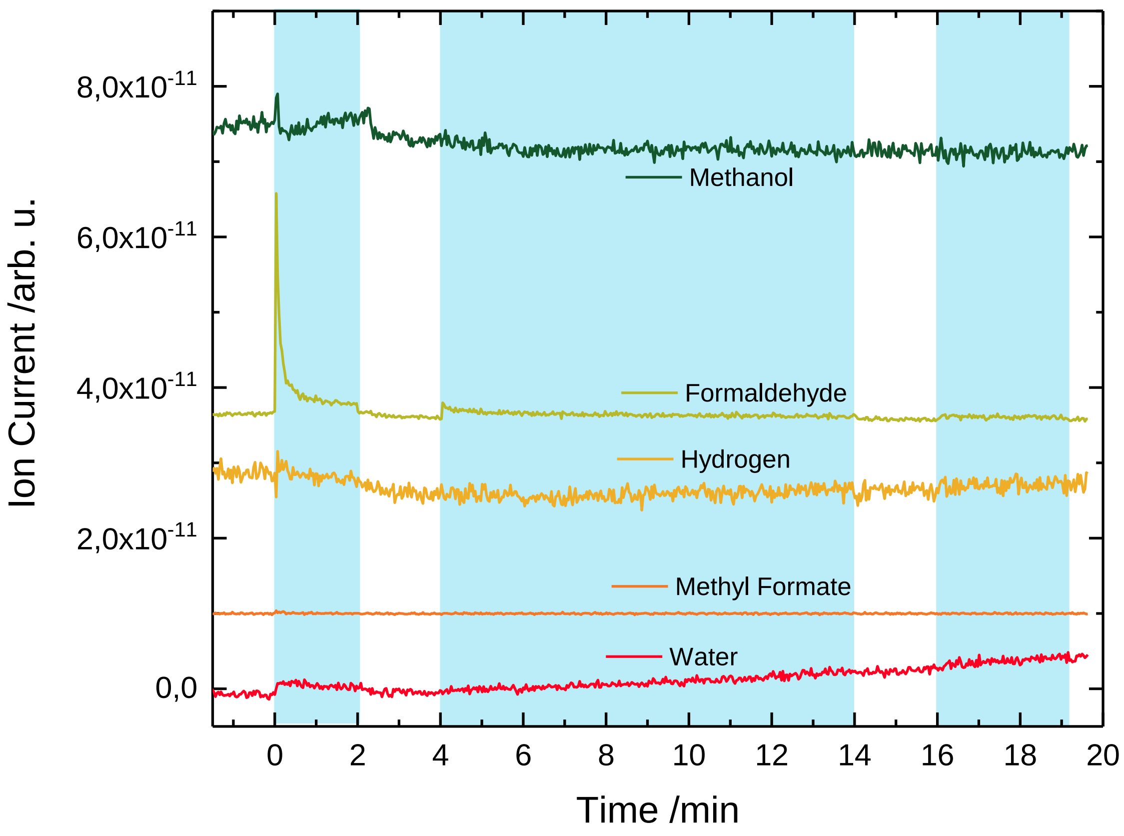

Figure S3. Products of methanol photoreforming on r-TiO_2(110) at $5x10^{-7}$ mbar alcohol background pressure at room temperature (RT), raw traces for hydrogen (*m/z 2*), water (*m/z* 18) formaldehyde (*m/z 30*), methanol (*m/z* 31), and methyl formate *(m/z* 60) shown. The blue background highlights the illumination periods, where the initial bursts stem from an enhanced methanol concentration on the surface due to its accumulation in the dark. Note that the traces are offset for clarity. With increasing duration of the experiment, deactivation of the catalyst is evident as formaldehyde formation under illumination declines.

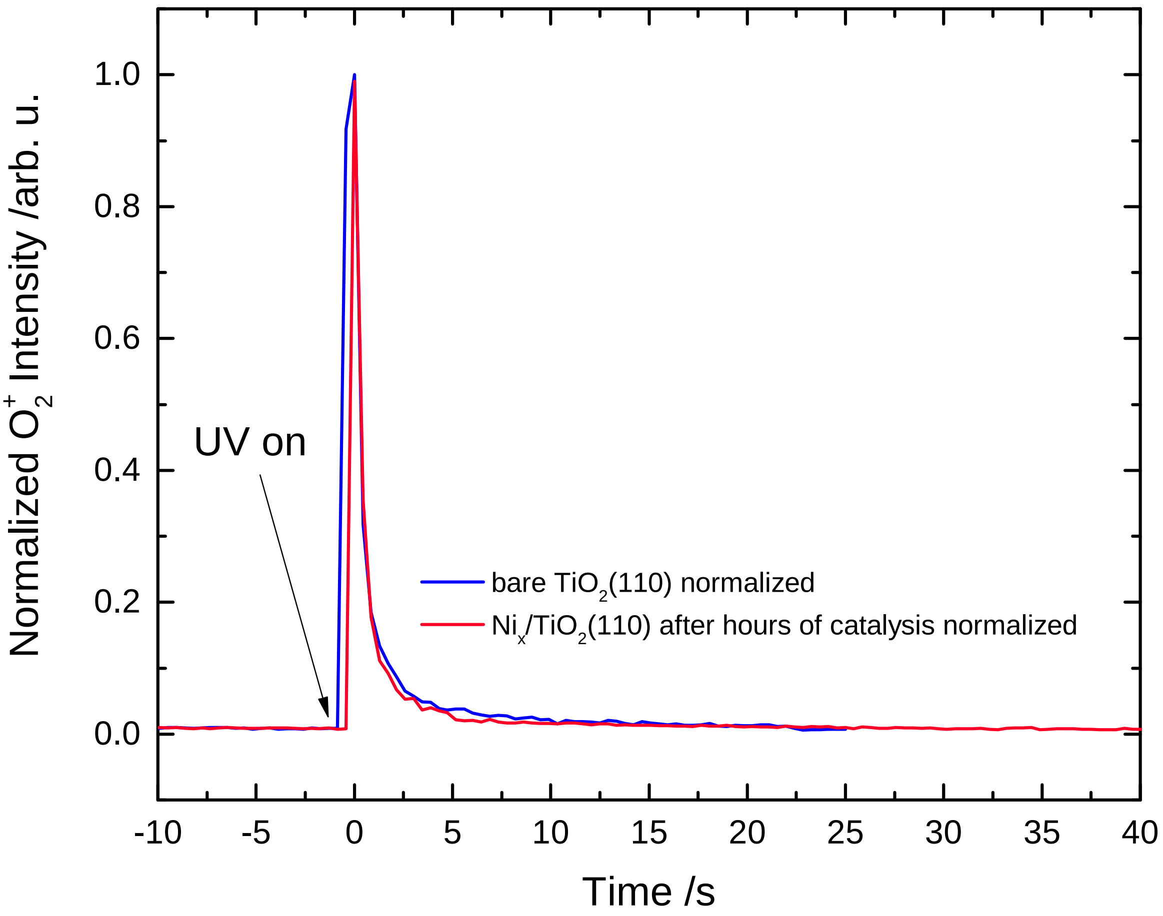

Figure S4. Normalized O_2 photon-stimulated desorption (PSD) spectra on r-$TiO_2(110)$ and $Ni_{16\text{-}45}$/r-$TiO_2(110)$, trace *m/z* 32 shown. For r-$TiO_2(110)$, after dosing 20 L of O2 at cryogenic temperatures, the crystal surface was illuminated at 241.8 nm. For $Ni_{16\text{-}45}$/r-$TiO_2(110)$ after the experiment, the methanol background is turned off and the sample was illuminated for another 15 min to deplete all the methanol from the photo-oxidation sites. The illumination is turned off, the sample cooled down to 130 K and exposed to 20 L of oxygen, to saturate the surface. Upon UV illumination, the same intensity and kinetics for the O2 PSD are observed as for the bare sample, indicating that the number of photoactive sites stays constant and that the methanol at least in the active sties was completely converted. (Note that the signals only slightly deviate in their maximum values from each other. This is caused due to the uncertainty in the starting time of the illumination as well as deviations by the QMS when the recording data points.)

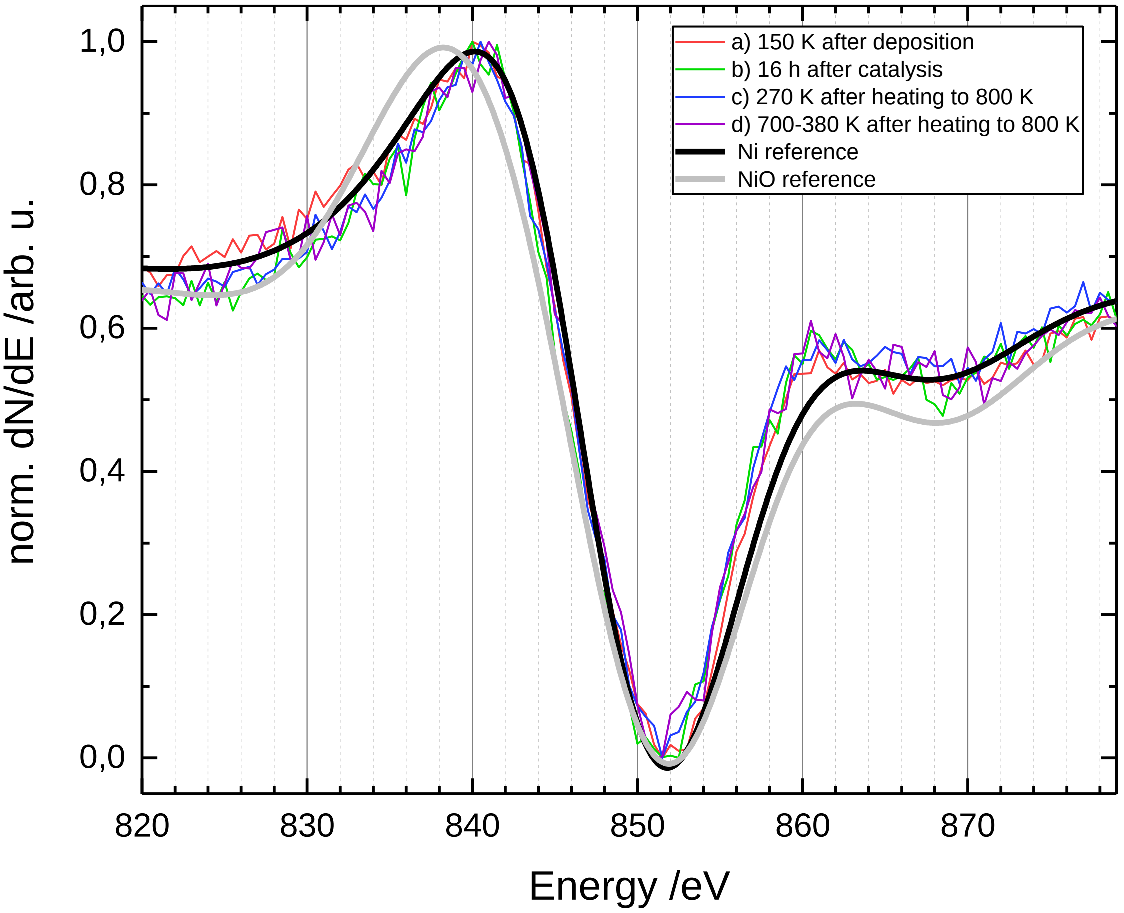

Figure S5. Excerpt of the Auger spectra of the Ni_x/r-TiO_2(110) surface from **Figure 5** in the manuscript, normalized to the maximum peak intensity between 800 eV and 900 eV (Ni). Two reference curves outline the progression of metallic Ni (black) and NiO (grey) references for comparison. The auger spectra were recorded with a primary electron energy of 3 keV.

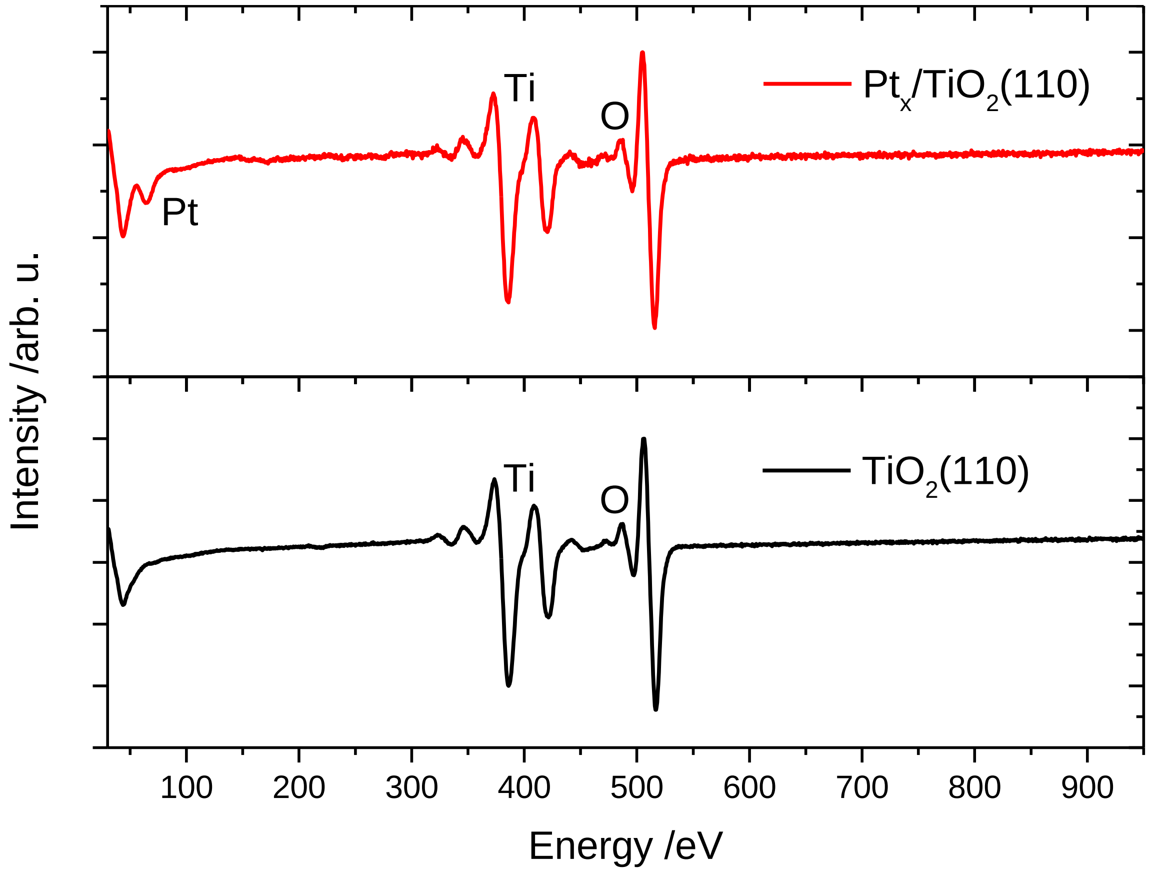

Figure. S6. Auger Electron Spectra of the clean r-TiO$_2$(110) surface (bottom) and Pt$_x$/r-TiO$_2$(110) after methanol photocatalysis and subsequent annealing to 800 K (top). Only titanium and oxygen are observed for the r-TiO$_2$(110) surface, while a small feature of the Pt NOO Peak appears at 64 eV on Pt$_x$/r-TiO$_2$(110). The coverage is 0.3% Pt>47/ML.