Supporting Information: Why Co-Catalyst-Loaded Rutile Facilitates Photocatalytic Hydrogen Evolution

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1. Catalyst Preparation

A rutile TiO₂(110) single crystal (Surface-net GmbH) was cleaned by several cycles of sputtering (Ar, 1.0 keV, 7×10^{-6} mbar) and annealing at 850 K in vacuum, which results in an atomically flat surface, while the crystal shows a light blue color indicating a slightly reduced surface [r-TiO₂(110)]. Over the course of the experiments, the crystal was sputtered (same conditions), annealed in oxygen atmosphere (1×10⁻⁶ mbar, 820 K) for 20 min and vacuum annealed at 820 K for 10 min. This recipe is known to result in a clean surface with a constant bridge-bonding oxygen (BBO) vacancy concentration.¹

The Pt (99.95% purity, ESG Edelmetalle, Germany) clusters are generated by a laser vaporization source coupled with a quadrupole mass spectrometer (Extrel, USA). In this work, the quadrupole mass spectrometer was operated with the AC-potential only, acting as an ion guide. The resulting size-distribution is then determined by the pressure and voltage settings and kept constant over the course of the experiments.² The Pt clusters are deposited on the r-TiO₂(110) surface under soft-landing conditions (< 1eV/atom in kinetic energy). The resulting catalyst is therefore named Pt_x/TiO₂(110) in the following. Between the experiments, a few cycles in sputtering, lasting in total more than 1h, were employed to facilitate a clean surface. The surface purity is verified by D₂-TPD, since also the smallest contamination of Pt clusters on the surface leads to a desorption feature in a TPD between 200 K and 300 K.

The platinum cluster coverages investigated in this work are displayed in Table 1. The coverages are given in %ML respective to the 1.5×10^{15} surface atoms of the TiO₂(110) surface.³ They are determined by the neutralization current of soft-landed cationic Pt clusters measured by a picoammeter (Keithley 6587).

%ML [cm ²]	Number of clusters [e/nm ²]	Number of clusters [e/cm ²]
0.02	0.003	3×10^{11}
0.1	0.015	1.5×10^{12}
0.12	0.018	1.8 × 10 ¹²
0.5	0.075	$7.5 imes 10^{12}$
1.0	0.15	1.5×10^{13}

Table 1: Cluster coverages used in this work on the $TiO_2(110)$ surface.

Methanol (Chromasolv, \geq 99.9% purity) and Methanol-d₃ (Sigma Aldrich, 99.8 atom % D) are cleaned via several pump-freeze cycles and either introduced by dosing or in a constant background.

2. Catalyst Characterization

The absence of contaminants from the r-TiO₂(110) surface is deduced from Auger Electron Spectroscopy (AES) as shown in Figure S1. Further, the surface of a light blue crystal shows a certain BBO vacancy concentration. The vacancies can be observed either by STM⁴ or by titration experiments.^{3, 5, 6} In this study, the BBO-vacancy density was about $6\pm1\%$ of the Ti-lattice sites as determined by temperature programmed desorption (TPD) of H₂O (Fig. S2).

The cluster size distribution is checked before every experiment and determined by a mass scan over all sizes. The resulting mass spectrum is displayed in Figure S3. The clusters are deposited randomly on the surface and show no preferential adsorption as evidenced by Kelvin Probe Force Microscopy and STM.⁷⁻⁹



Fig. S1: Auger Electron Spectrum of the r-TiO₂(110) surface (a) and Pt_x/r -TiO₂(110) (b). Titanium and oxygen are observed for the rutile TiO₂(110) surface, while a small feature of Pt NOO Peak is observed at 64 eV. The coverage is 1% Pt_x/ML.



Fig. S2: TPD spectra of H₂O on the r-TiO₂(110) surface. In S2a, the TPD of 1.89 ML of H₂O dosed on the surface is shown and is in excellent agreement with literature.⁵, ^{10, 11} The first layer peak is assigned to water desorbing from Ti-lattice sites, while the feature at around 170 K is attributed to water on BBO-sites and multilayer adsorption. Figure S2b shows a smaller coverage, where the hydroxyl recombination peak is clearly observed around 460 K. The grey area indicate the integrated area, that is compared to the integral of the first layer peak in S2a, to obtain a BBO-vacancy concentration of $6 \pm 1\%$ of Ti-lattice sites.



Fig. S3: Mass spectrum of the cluster size distribution of Pt clusters from the laser vaporization source. The spectrum is taken after the quadrupole mass filter and shows a size-distribution of Pt₇ up to Pt₃₂. When depositing in the ion guide mode, all masses lower than Pt₈ are discarded. The clusters show a log-normal distribution and have a size of about 1 nm in diameter.²

3. Thermal Reaction Products

To understand photocatalytic mechanism on an atomic scale, first the methanol chemistry on r-TiO₂(110) is explored (see Fig. S4) which is found to be in very good agreement with literature.¹²⁻¹⁴ In comparison with Fig. S4, a TPD of 1 L of methanold₃ on Pt_x/r-TiO₂(110) (1% cluster coverage) (Fig. S5) shows significant thermal hydrogen desorption between 250 K and 350 K, accompanied by significant CO desorption between 350 K and 500 K from the Pt clusters.



Fig. S4: TPD of 1 L of methanol on r-TiO₂(110). Molecular methanol mainly desorbs at 270 K from Ti-lattice sites. The high temperature feature at 480 K is associated with recombinative desorption of dissociated methanol and trace amounts of formaldehyde are obtained around 600 K. No molecular hydrogen formation is observed from methanol. The excess hydrogen from formaldehyde formation typically forms water on oxides, as observed from the water desorption at 470 K. The small CO signal at 125 K is attributed to background adsorption. The traces are offset for clarity.



Fig. S5: TPD of 1 L of methanol-d₃ on Pt_x/r -TiO₂(110). In this experiment, isotopically labeled methanol CD₃OH is used to explore the thermal reactions on Pt-loaded TiO₂(110). While the methanol signal is less intense, both molecular and dissociative adsorption are observed on the TiO₂ surface. No intact desorption of methanol or formaldehyde from Pt is observed. Instead, the dehydrogenation products hydrogen and CO ultimately desorb at higher temperature. Methanol-d₃ on Pt is completely decomposed and hydrogen desorbs between 250 K and 350 K. Additionally, CO is observed between 350 and 500 K, as is expected for a CO TPD from Pt nanoparticles on TiO₂(110).¹⁵ Additionally, some water is observed at 240 K. The traces are grouped and offset for clarity.

4. Photocatalytic Activity-Measurements

For the photocatalytic measurements, the catalyst is prepared and moved to the QMS. The pulse energy of the laser is monitored and the reactant is dosed at cryogenic conditions, unless stated otherwise. The crystal is heated to the reaction temperature and then the UV-illumination is started.

To determine turnover-frequencies (TOFs), the catalyst is exposed to a continuous background of a certain methanol pressure and the UV illumination is facilitated and blocked. Areas of constant photoconversion of methanol to H₂ (m/z=2) and formaldehyde (m/z=30) are chosen and both signals are integrated over time. For both species, transmission of the calibrated QMS, ionization cross sections and cracking pattern contributions are taken into account. The following integral area is normalized by the integral of a methanol TPD peak of the Ti-lattice sites (1 ML = 5.2×10^{14}).¹⁰ To calculate the TOF or site time yield (STY), this integral is divided by the time and by the number of active sites for formaldehyde production (0.06 ML, in this case for the BBO-vacancies¹⁴ [see Fig. S2]) to yield a number of molecules per active site per second. Stoichiometry was checked for every catalytic experiment (see Fig. S8). This TOF is possibly still limited by mass transport, but pressures higher than 4×10^{-7} mbar were not investigated to ensure the proper detection by QMS.

The apparent quantum yield (AQY) can be calculated by relating the number of evolved molecules per second to the photon flux:^{16, 17}

$$AQY(\%) = \frac{Product \ molecules \ (s^{-1})}{Photons \ (s^{-1})} \times \ 100 \ (1)$$

In this work, the amount of product molecules (either formaldehyde or hydrogen) is divided by the number of incident photons from the laser.

In the classical picture, two charges are needed to oxidize methanol to formaldehyde as well as reduce protons to H_2 .¹⁷⁻¹⁹ For the lowest photon fluxes (compare to Fig. 3b), a quantum yield of 3.2% is obtained, while in the saturation regime (see Fig. 3b), the quantum yield is about 0.11%.

5. Methanol Photocatalysis on Pt_x/TiO₂(110)

Photocatalytic measurements were performed on the $r-TiO_2(110)$ surface with different loadings of Pt clusters on the surface. Then a background pressure of methanol is applied and the reaction temperature is chosen. The photocatalytic reaction is then started by the UV illumination.

Figure S7 shows, that upon the first illumination a conditioning of the catalyst is observed, that is then constant with every additional illumination. The obtained reaction products are stoichiometric. A one-photon dependence for the H_2 evolution is found for the lowest light intensities, while for the higher ones a saturation regime is observed (Fig. S6).

In Figure S8, it is shown that the photocatalytic reaction is independent on the used wavelength, when the energy of the photon is higher than the semiconductor's band gap and furthermore independent on pulsed or continuous illumination, at least to a ns-Laser with 20 Hz. In Fig. S10 the thermal H₂ peak from dissociatively adsorbed methanol is shown prior to a photocatalytic experiment with Pt loaded TiO₂(110). The

comparison of O₂ photon-stimulated desorption (PSD) on a bare surface and after the used photocatalyst gives evidence that it is possible to empty all active sites for the oxidation reaction.¹⁴



Fig. S6: The TOF of formaldehyde as a function of the illumination intensity is shown. While for low illumination intensities a linear behavior is found, the signal saturates at higher values. This observation is not in line with a two-photon process, for which a quadratic dependence with light power would arise. The dotted red lines indicate the transition from the regime of first order behavior into the one of saturation. The error bars in energy are determined by the standard deviation of the laser power, while the TOF errors bars are of 10%, except for the one at 5 mW, which represents the standard deviation of four measurements.



Fig. S7: Consecutive photocatalytic experiments with methanol on Pt_x/r -TiO₂(110). The Pt coverage is 0.75% cluster per surface atom and the reaction is carried out at 260 K after adsorption of 1L methanol-d₃. In contrast to Fig. 1(a), no catalyst poisoning is observed after an initial conditioning of the catalyst. Formaldehyde is measured with mass 30, while all hydrogen species are measured on the masses 2, 3 and 4. Between the cycles, the surface is recovered with 1 L of methanol-d₃. In the first experiments, more H₂ is observed, which is attributed to dissociative methanol adsorption and an unknown degree of pre-hydroxylation of the semiconductor. In all runs, the formaldehyde intensity and kinetic decay stays the same and after the conditioning in the first shot, the same holds true for all hydrogen traces.



Fig. S8: Photocatalytic experiments depending on wavelength and illumination conditions with $Pt_x/TiO_2(110)$ and a cluster coverage of 1% in a background of 1×10^{-7} mbar methanol are shown. In a), the sample is illuminated with 250 µJ pulse energy (this corresponds to 5 mW) at 241.8 nm, and with illumination the reaction starts immediately. The reaction stops immediately, when the light is switched off and also runs constant. In panel b), the pulse energy is also hold constant at 250 µJ, but the wavelength is changed to 355 nm. The same amounts of hydrogen and formaldehyde are obtained, also in the second illumination over a time of 45 min. In c), the light source is exchanged from the ns-Laser with 20 Hz to a continuous light source. In this case, this light source is a UV-LED that emits light around 367 nm (see Fig. S9 for details), well above the band gap value for rutile TiO₂ of 3.0 eV. The photocatalytic reaction of methanol shows the same behavior as in a) and b). In panel d), a direct comparison of the LED to laser excitation is shown, while the pulse energy of the laser is only 38 µJ at 241.8 nm and the characteristics show no appreciable difference.



Fig. S9: Light emission characteristics of the UV-LED. The emission is centered around 369 nm with a full-width half maximum of 11.5 nm.



Fig. S10: TPD in a background of 1×10^{-7} mbar methanol on 1‰ Pt_x/TiO₂(110) from 100 K to the reaction temperature at 260 K. After oversaturation of the surface at cryogenic temperatures, some methanol desorption occurs around 250 K as it is expected from Fig. S4. In agreement with Fig. S5, hydrogen desorption from the Pt clusters is observed, too. As methanol adsorbs dissociatively on the TiO₂(110), which is known from STM studies²⁰, the abstracted hydrogen atoms thermally recombine at the Pt clusters and desorb.



Fig. S11: O₂-Photon Stimulated Desorption at 100 K of the r-TiO₂(110)-surface and the Pt_x/TiO₂(110) catalyst after 2 h of photocatalysis. The green trace represents a O₂ PSD from bare surface, that is in excellent agreement with literature. After the catalytic 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. After illumination is turned off, the sample was cooled down to 100 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 by a higher uncertainty due to the additional uncertainty in the starting time of the illumination.)



Figure S12: TOFs at 260 K for a background of $1 \cdot 10^{-7}$ mbar methanol on 1‰ Pt_x/TiO2(110) for a reduced and pre-hydroxylated TiO₂(110). The h-TiO₂(110) was prepared in the same way as in a previous study by Kim *et al.*.²¹

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