Supporting Information

Heterogeneity of oxygen reactivity: key for selectivity of partial methanol oxidation on gold surfaces

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Experimental Details

All experiments were conducted in an ultrahigh vacuum apparatus which is described in detail elsewhere.[1] In brief, the apparatus consists of two chambers which can be separated by a mechanical gate valve. One chamber is equipped with a sputter gun (IQE 11/35, SPECS), a MCP LEED system (Omicron), an Auger spectrometer (PHI 11-010, PerkinElmer) and a quadrupole mass spectrometer (Prisma, Pfeiffer) with a self-made Feulner cup,[2] mounted onto the mass spectrometer to increase sensitivity for temperature-programmed reaction (TPR) experiments. The second chamber contains two effusive molecular beams (MB)[3] and a thermal oxygen atom source (Dr. Eberl MBE-Komponenten GmbH) which can be modulated by automated valves and shutters. A stagnation flow monitor, equipped with a high precision ion gauge (360 Stabil-Ion, Granville-Phillips) is mounted for pressure detection at the sample position. A quadrupole mass spectrometer (MAX-500HT, Extrel) is used for time resolved measurements of gas phase species ($H_2{}^{18}O^+$ at 20 a.m.u.) during pulsed, isothermal MB experiments. A movable flag consisting of a stainless-steel lever connected to a non-reactive quartz plate was used to block direct exposure of the sample in reference MB experiments. The round Au(332) single crystal (10 mm diameter, 2 mm thick, MaTecK) is fixed onto a BN heater (HT-01, Momentive) by means of Mo clamps. A 0.2 mm hole in the crystal edge is used to connect a type K thermocouple. The sample temperature is measured and controlled by a commercial PID controller (Eurotherm). The BN heater is attached to a Mo holder connected to a liquid nitrogen cooled copper block, which enables sample cooling to 100 K. The Au(332) single crystal was cleaned by repeated cycles of Ar^+ ion sputtering (1keV, 5 – 6 µA, 15 min) and subsequent annealing to 1000 K for 10 min.[4-6]

For TPR experiments, ^{16}O ($^{16}O_2$, Air Liquide, 99.998 %) atoms were supplied by the thermal atomic oxygen source (T = 1630 °C, 1.35 mbar $^{16}O_2$ backing pressure) with an atom flux of $4.0 \cdot 10^{12}$ s^{-1} cm^{-2}. The oxygen flux was determined by TPD measurements assuming a saturation coverage of $2.9 \cdot 10^{15}$ atoms cm^{-2} (corresponding to 2.1 monolayers (ML) defining 1 ML as one oxygen atom per Au surface atom $1.4 \cdot 10^{15}$ atoms/cm^2). This number was evaluated by referencing the integrated $^{16}O_2$ (m/z = 32) peak intensity of a fully covered Au(332) to the desorption of O_2 from a 2x2 O superstructure on Pt(111), which amounts to 0.25 ML.[7, 8] Oxygen was adsorbed onto the Au(332) surface at 250 K and subsequently, methyl formate (Sigma Aldrich, ≥ 99.8 %), cleaned by repeated freeze-pump-thaw cycles, was dosed onto the ^{16}O pre-covered Au(332) at 110 K using a manual leak valve. The methyl formate exposure was quantified by the pressure difference during exposure as compared to the base pressure, measured by an ion gauge calibrated to N_2 pressure. Deviations in the indicated pressure for methyl formate and N_2 due to differences in ionization probability were accounted for by measurements of methyl formate and argon individually dosed into the chamber by a molecular beam using the same backing pressure. For the difference in indicated pressure and considering the correction factor between argon and N_2 given by the manufacturer's manual, a correction factor for methyl formate was deduced. The TPR experiments were conducted by programmed temperature ramps (110 K – 800 K, 2 K·s^{-1}) and simultaneously monitoring time-resolved m/z = 18 ($H_2{}^{16}O^+$), m/z = 32 ($^{16}O_2{}^+$), m/z = 44 ($C^{16}O_2{}^+$) and m/z = 60 ($HC^{16}O^{16}OCH_3{}^+$) with a quadrupole mass spectrometer (-100 eV, 0.1 s). The analog output signals were converted into a digital signal with a polling rate of 10 ms and matched to the sample temperature by a self-written computer software. Next to the TPR measurement of Au(332) exposed to both activated oxygen and methyl formate, also, for each applied exposure, reference measurements with Au(332) exposed to merely oxygen or methyl formate were conducted to gauge on one hand the amount of reacted methyl formate and to determine on the other hand signals due to desorption from the sample holder as well as due to fragmentation in the mass spectrometer. The integrated intensities of the CO_2 desorption in the TPR experiments as measured on m/z = 44 were determined by different approaches. On one hand, the off-set corrected spectra were directly integrated in the corresponding temperature range and subsequently the integrated intensity of the oxygen or methyl formate reference measurements was subtracted in the corresponding temperature range. While this approach is well-suited for the CO_2 desorption at 320 K, where no strong signals are observed for the reference measurements, the low temperature CO_2 desorption peaks required a different method. Therefore, all CO_2 desorption features were also fitted to reproduce the experimental spectra taking also in this approach the difference between the TPR measurement and the corresponding references. The error bars shown in Fig. 2c were estimated from the difference in area obtained by the different integration approaches. The amount of reacted methyl formate in the TPR experiment was estimated from the integrated intensity on m/z = 60 with respect to the reference measurement with merely methyl formate, i.e. without oxygen. Assuming a sticking coefficient of unity for methyl formate at 110 K, it was found that 24 % of the initially provided 0.11 L methyl formate reacted in the TPR with the Au(332) surface pre-exposed to 0.13 L atomic oxygen. Considering the separately measured fragmentation pattern of methyl formate on m/z = 60 and m/z = 44, the number of desorbing methyl formate molecules and the fragmentation pattern of CO_2 on m/z = 44, the absolute number of CO_2 molecules formed in the TPR measurements on the methyl formate oxidation on Au(332) was estimated from the integrated intensities of the desorption peaks corrected for the reference measurements. For the feature at 185 K, methyl formate desorption coincides with CO_2 formation. Therefore, the integrated intensity measured on m/z = 60 was rescaled according to the measured fragmentation pattern of methyl formate and subtracted from that of the TPR experiment. It should be noted that also other (partial) oxidation products may contribute to the intensity at 185 K on m/z = 44, as other m/z traces show this feature.[9]

For the isothermal oxidation of methanol and methyl formate, the atomic oxygen source was modified. An additional quartz tube connected to a differential pumping stage was mounted. The source was operated at 1700 °C at an $^{18}O_2$ (97.39 %, Eurisotop) backing pressure of 3 mbar corresponding to an atom flux of $6.9\cdot10^{11}\,cm^{-2}s^{-1}$. Within one experiment, 31 oxygen pulses with a length of 30 s were dosed onto the Au(332) followed by a delay time of 100 s without oxygen exposure. Methanol-^{13}C (99 atom % ^{13}C, Sigma Aldrich) and methyl formate (≥ 99.8 %, Sigma Aldrich), were cleaned by repeated freeze-pump-thaw cycles and dosed onto the Au(332) surface by means of effusive molecular beams. The molecular fluxes of methyl formate ($1.2\cdot10^{15}\,cm^{-2}\,s^{-1}$) and methanol ($4.2\cdot10^{13}\,cm^{-2}\,s^{-1}$) were calculated according to calibrations with the beam monitor using Ar. Time resolved mass spectra (1 mA, - 70 eV) were recorded simultaneously with a time constant of 2 s using a pulse counting amplifier. Reference measurements placing a non-reactive quartz flag in front of the sample were conducted to account for background reactions in the chamber. TPD spectra after isothermal MB experiments were recorded in a temperature range of 310 to 800 K with a heating rate of 2 $K\cdot s^{-1}$ simultaneously recording m/z = 32 ($^{16}O_2^+$), m/z = 34 ($^{16}O^{18}O^+$), m/z = 36 ($^{18}O_2^+$) and m/z = 46 ($C^{16}O^{18}O^+$). $^{18}O_2$ and methanol-^{13}C were used to discriminate the produced water and CO_2 in the oxidation reaction from naturally abundant $H_2{}^{16}O$.

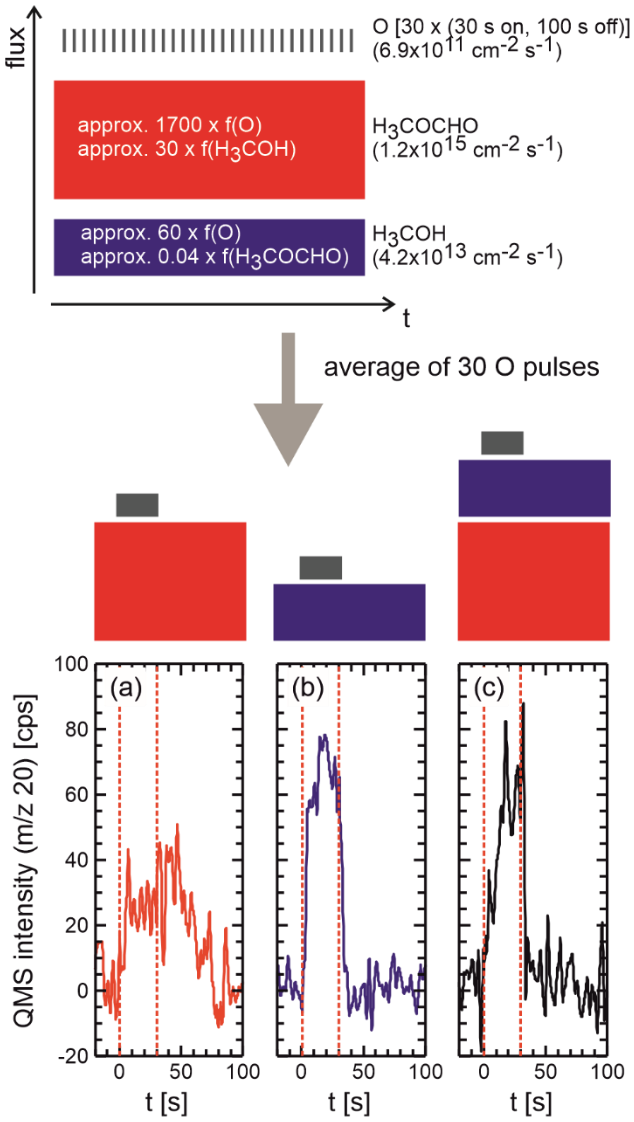

Figure S0 Schematic representation of pulse sequence applied in isothermal molecular beam (MB) experiments on the oxidation of methyl formate and/or methanol on Au(332).

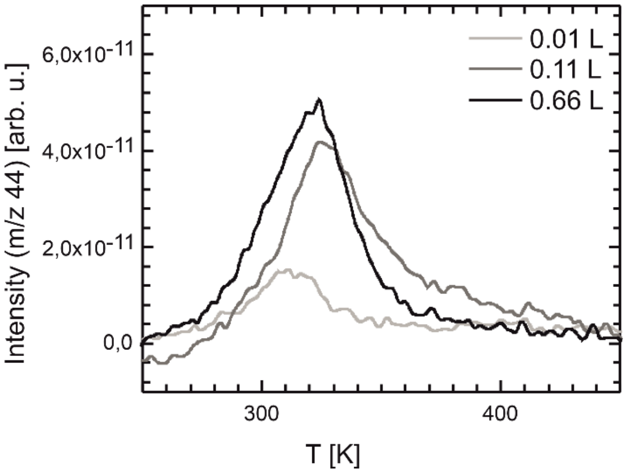

Figure S1 CO_2 desorption at 320 K from Au(332) pre-covered with 0.13 ML activated oxygen and varying exposures of methyl formate. While CO_2 desorption increases for raising the methyl formate exposure from 0.01 L to 0.11 L, it remains nearly constant for a further increase to 0.66 L.

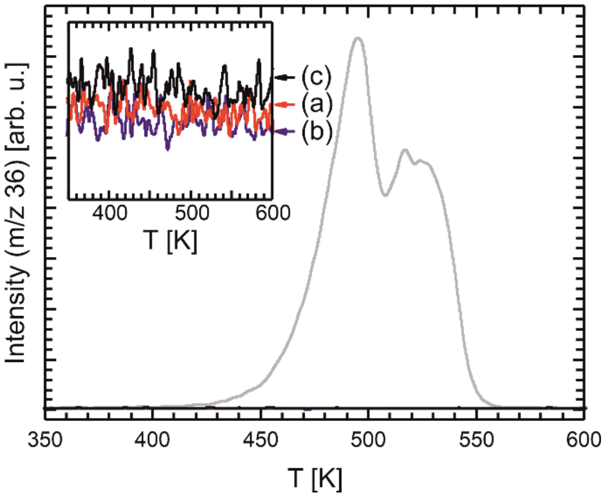

Figure S2 TPD spectra of $^{18}O_2$ (m/z = 36) after the pulsed isothermal molecular beam experiments shown in Fig. 2. The inset shows the $^{18}O_2$ TPD after pulsed MB oxidation experiments of (a) methyl formate (red), (b) methanol (blue) and (c) a co-feed of methanol and methyl formate (black). Next to the oxidation experiments, also a reference (grey) is shown where the experiment was conducted without applying methanol or methyl formate.

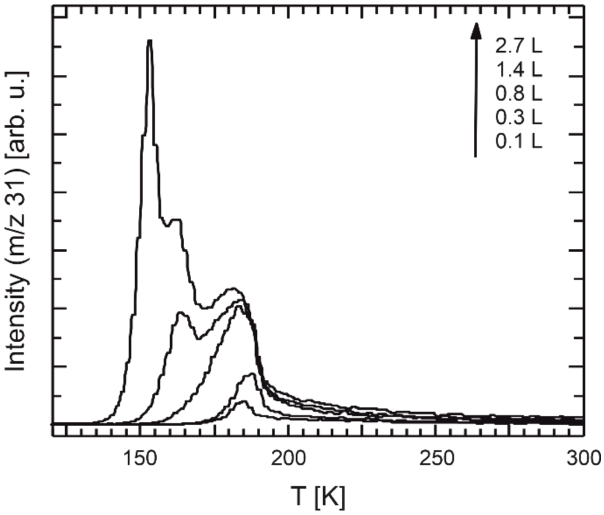

Figure S3 Methanol desorption from Au(332) for varying exposures of methanol.

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