Supporting Information

Methanol oxidation on Au(332): Methyl formate selectivity and surface deactivation under isothermal conditions

Christoph D. Feldt[a], Thorren Kirschbaum[a,b], Jian Liang Low[a], Wiebke Riedel*[,a], Thomas Risse[a]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Arnimallee 22, 14195 Berlin*

[b] *Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany*

* Email: wiebke.riedel@fu-berlin.de

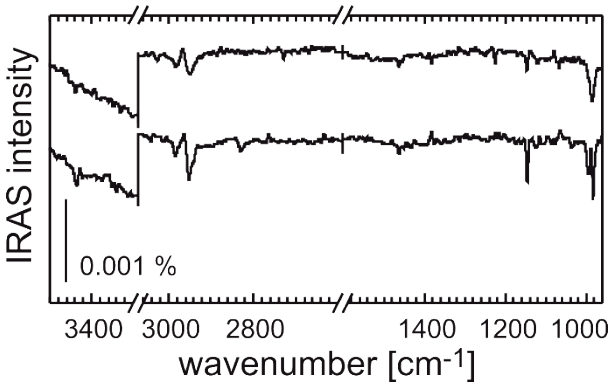

Figure S1 IRAS measurements of 0.1 L (top) and 0.3 L (bottom) ^{13}C-methanol (99 atom % ^{13}C, Sigma Aldrich) adsorbed on clean Au(332) at 120 K.

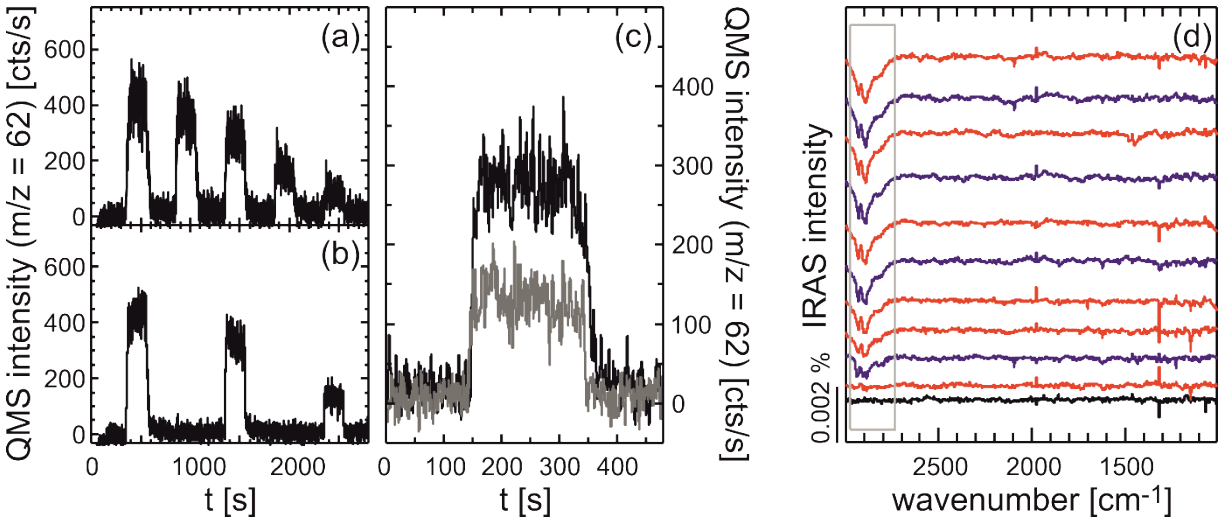

Figure S2 Pulsed isothermal MB experiments of methanol oxidation on Au(332) at 230 K to methyl formate using a different batch of methanol (^{13}C-methanol, 99 atom % ^{13}C, Sigma Aldrich) applying a methanol flux of 52×10^{13} $s^{-1}cm^{-2}$ (p(MeOH) =19.6×10^{-7} mbar) and an atomic oxygen flux of $1.25\cdot10^{-3}$ ML/s ≈ $1.9\cdot10^{12}$ $s^{-1}cm^{-2}$ employing a delay time of (a) 300 s and (b) 800 s between oxygen pulses (methyl formate molecular peak: m/z = 62). In (c) a direct comparison of the third pulses of the measurements with 300 s (black) and 800 s (grey) delay time displayed in (a) and (b) is shown. (d) In situ IRAS measurements conducted for the MB experiment shown in (a) during (blue) and in between (red) the oxygen pulses of the sequence (from bottom to top). The grey box highlights the signals in the CH stretching region attributed to C-H bond containing species accumulation on the surface.

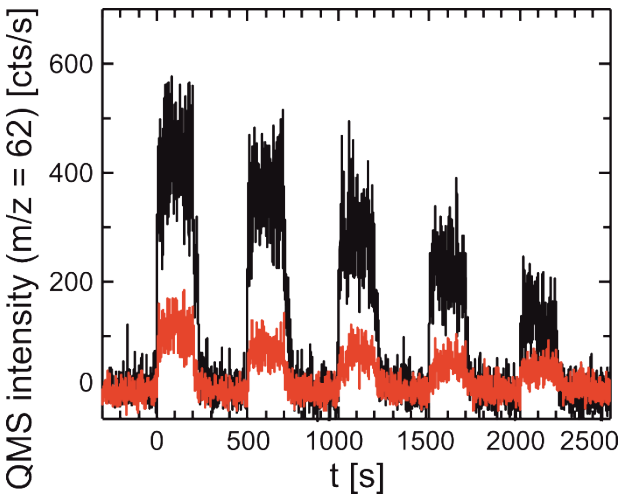

Figure S3 Pulsed isothermal MB experiment on the methanol oxidation to methyl formate on Au(332) at 230 K using a different batch of methanol (^{13}C-methanol, 99 atom % ^{13}C, Sigma Aldrich) applying a methanol flux of 52×10^{13} $s^{-1}cm^{-2}$ (p(MeOH) =19.6×10^{-7} mbar) and an atomic oxygen flux of $1.25\cdot10^{-3}$ ML/s ≈ $1.9\cdot10^{12}$ $s^{-1}cm^{-2}$ for 300 s (black) and 3000 s (red) methanol exposure before the first oxygen pulse. The initial methyl formate formation rate is clearly reduced for the prolonged methanol exposure, even below the rate observed at the end of the experiment with a shorter pre-exposure attesting to the surface deactivation due to methanol or some impurity in methanol.

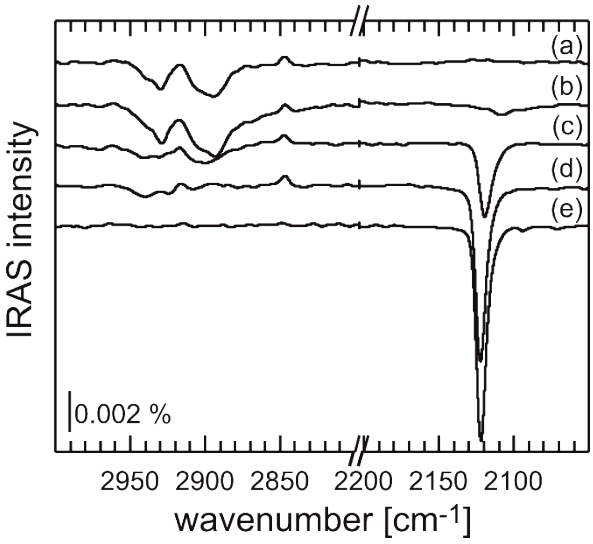

Figure S4 IRAS measurements (a) after a pulsed isothermal MB experiment on the partial oxidation of methanol (different batch: ^{13}C-methanol, 99 atom % ^{13}C, Sigma Aldrich) on Au(332) at 230 K (methanol flux of 52×10^{13} $s^{-1}cm^{-2}$ (p(MeOH) =19.6×10^{-7} mbar), flux of atomic oxygen $0.46\cdot10^{-3}$ ML/s), (b) during subsequent CO exposure (p(CO) = $8.2\cdot10^{-6}$ mbar) at 190 K, and after heating the sample shown in (b) i. vac. to (c) 310 K and (d) 450 K during CO exposure (p(CO) = $8.2\cdot10^{-6}$ mbar) at 190 K, (e) during CO exposure (p(CO) = $8.2\cdot10^{-6}$ mbar) at 190 K for a clean Au(332) surface.

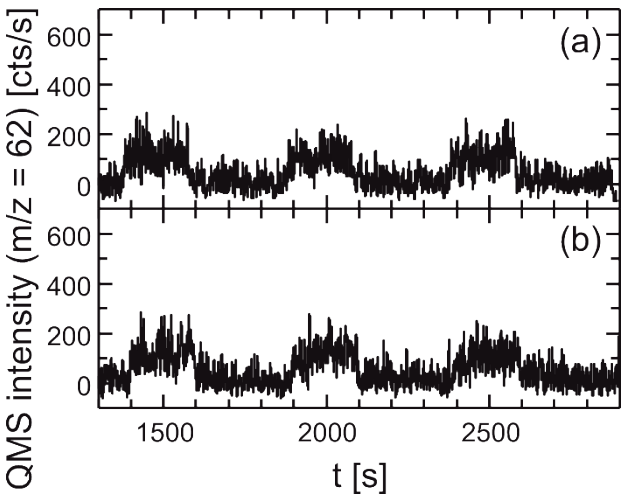

Figure S5 Pulsed isothermal MB experiments of methanol oxidation on Au(332) to methyl formate (molecular peak: m/z = 62) at 230 K using a different batch of methanol (^{13}C-methanol, 99 atom % ^{13}C, Sigma Aldrich) applying a methanol flux of 4×10^{13} $s^{-1}cm^{-2}$ (p(MeOH) = $1.6\cdot10^{-7}$ mbar) and an oxygen flux of $0.46\cdot10^{-3}$ ML/s displaying the last three pulses of the measurement. (a) Experiment conducted on a clean Au(332) surface. (b) The Au(332) surface was initially deactivated for methyl formate formation by a pulsed isothermal MB experiment at 230 K applying a high methanol flux of 52×10^{13} $s^{-1}cm^{-2}$ (CO IRAS after sequence shown in Fig. S3) and subsequently heated i. vac. to 450 K, before conducting the displayed experiment at 230 K applying the same fluxes of methanol and atomic oxygen as in (a). The methyl formate formation rates are comparable demonstrating a lifting of the surface deactivation by the thermal treatment.

Analysis of ^{12}C-methanol

To further investigate the impurities contained in the ^{12}C-methanol (Roth, 99.98 %, Charge 903951) GC-MS and LC-MS were conducted (see experimental details below). In brief, GC-MS did not show any impurities, as compared to UPLC-grade methanol. In LC-MS, several trace impurities were observed including trifluoroacetic acid and a plasticizer used in PE as well as other unidentified components. However, due to a lack of further information, such as characteristic IRAS signals, it is impossible to determine which of the trace impurities causes the surface deactivation under methanol-rich conditions.

The samples were analyzed by UPLC-ESI MS using an Acquity UPLC system connected to a Synapt G2-S HDMS by Waters Co., Milford, MA, USA in both modes, (+)-ESI and (-)-ESI and compared with UPLC grade MeOH (BioSolve BV, Valkenswaard, NE). The principal settings of the mass spectrometer as well the gradient program and other LC parameters are found in the following: [injection volume: 3 µL; sample temperature: 15 °C; flow rate: 0.3 mL/min; solvent: A1: water, 0.1 % FA, B1: acetonitrile, 0.1 % FA; gradient: 0-30 min 20-90 % ACN, 30-31 min 90-100 % ACN, 31-36 min 100 % ACN, 36-37 min 100-20 % ACN, 37-40 min 20 % CAN; chromatogr. separating column: ACQUITY UPLC ® HSS T3 1.8 micrometer, 2.1 mm x 100 mm, column temperature: 40°C, calibration range: 50-600 Da (Natrium Formiate), measurement range: 50-600 Da; source temperature: 90 °C; desolvation temperature: 250 °C; cone gas: 1 L/h; desolvation gas: 600 L/h; nebulizer gas: 6.5 bar; capillary voltage: (+)-ESI: 3.2 kV ; (-)-ESI: 2.7 kV, sample cone: 40 V; source offset 80 V]

For analysis by GC-MS, a 7820A GC coupled to a 5977E MSD, Agilent Technologies Co., Santa Clara, CA, USA, was used (column: HP-5MS Ultra Inert 30m, 0,25mm, 0,25 µm; dead time: ~1,3 min; GC program: 50 °C to 300 °C, rate 20 °C/min; 0.5 µL, split 5:1; MS method: solvent delay 1 minute; m/z 40 to m/z 500).