Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Very small „window of opportunity“ for generating CO oxidation active Au_n on TiO_2

X. Tang, J. Schneider, A. Dollinger, Y. Luo, A. S. Wörz, K. Judai, S. Abbet, Y. D. Kim, G. F. Ganteför, D. H. Fairbrother, U. Heiz, K. H. Bowen, S. Proch

1. Preliminary experiments for TiO_2 cluster studies

Both titanium dioxide clusters and gold clusters were produced via magnetron sputtering. Briefly, gold clusters were generated by sputtering gold targets in Ar/He mixtures, while titanium dioxide clusters were synthesized from titanium targets in Ar/He/O_2 mixtures. The resulting cluster beam was then accelerated and mass selected by passing a magnetic sector field. The mass selected $(TiO_2)_{93}^-$ and Au_n^- cluster beams were further guided by a series of ion optics until they were soft-landed onto the HOPG surface, where TPD was applied to characterize the catalytic activities of size-selected catalysts. The TPD set-up is based on a Hiden HAL/3F PIC quadrupole mass spectrometer. The relative sensitivity factors for CO and CO_2 have been calibrated against purified CO and CO_2 dosing and determined to be 1.125 : 1. The UHV setup which was used for the present work does not allow XPS investigation of the as-deposited clusters without breaking the vacuum which in turn necessitates D_2O-TPD to investigate the surface of TiO_2 materials[1] in order to validate the applied procedures. A virgin $TiO_2(110)$ single crystal has been (***i***) heated at 800 K for 1 h, (***ii***) sputtered with 1 kV Ar^+ ($5 \times 10^{-6}\,torr$) for 20 min (6000 L), and (***iii***) annealed at 800 K for 20 min (*TiO_2[110] procedure*). This crystal was subject to D_2O adsorption at 120 K (100 L) subsequently TPD was measured (see Figure S 1) and compared to literature data. It is known that annealing of $TiO_2(110)$ at 850 K in UHV for ten minutes produces 5 – 10 % oxygen vacancies and the D_2O-TPD of such a surface exhibits two features. One of them is assigned to the desorption of molecularly bound D_2O at Ti^{4+} sites at 270 K and the other one to the recombination of hydroxyl groups that form from the dissociation of water at oxygen vacancy sites at 500 K.[1] The curve obtained by the described procedure only shows the low-temperature feature due to desorption of molecularly bound D_2O while the high temperature feature is completely absent (Figure S 1). This clearly indicates no oxygen vacancies, i.e., oxidized TiO_2. This is also suggested by the appearance of the crystal, while being reduced $TiO_2(110)$ single crystals turn blue due to Ti^{3+} centers, but the applied procedure yields an almost transparent crystal with an off-white color.[2,3,4,5,6]

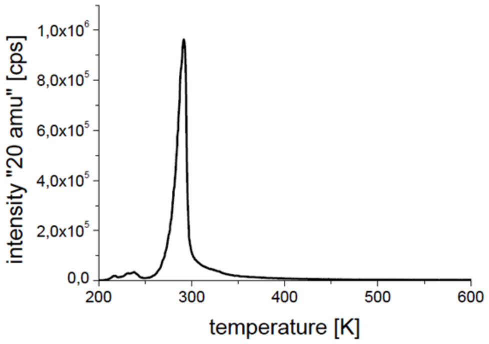

Figure S 1. D_2O-TPD of $TiO_2(110)$ single crystal treated via the *$TiO_2(110)$ procedure* (see text). The TPD ramp has been driven from 200 K to 600 K at a heating rate of 2 K/s.

As second step $^{13}C^{16}O$ desorption from $TiO_2(110)$ single crystal after treatment with above procedure has been monitored and compared to the closest literature results ($^{13}C^{16}O$ adsorption [5 L] at 180 K).[7] In the literature desorption is found at 150 K[8] while for the procedure described above the feature is found at 200 K (see Figure S 2). This comparatively high desorption temperature for CO indicates adsorption on defect sites other than oxygen vacancies. It is, however, consistent with the findings on TiO_2 thin films that at room temperature all CO on the surface is gone (see above). The comparison of the 5 L and 50 L dose shows no shift in the respective peak position and clearly presents first order desorption kinetics (Figure S 2).

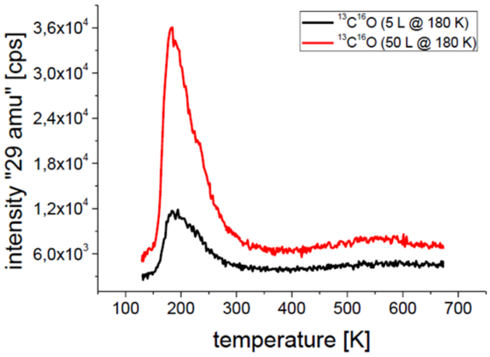

Figure S 2. $^{13}C^{16}O$ desorption from $TiO_2(110)$ after treatment according to the *$TiO_2(110)$ procedure* and adsorption of 5 L (50 L) $^{13}C^{16}O$ at 180 K. The TPD ramp has been recorded with a heating rate of 3 K/s.

2. Blank tests for TiO_2 cluster studies

As first blank test CO oxidation on $TiO_2(110)$ has been carried out and compared to results described in the literature.[8] The crystal has been treated as discussed above and the reaction protocol includes $^{18}O_2$ adsorption at 400 K (10 L) followed by $^{13}C^{16}O$ adsorption at 180 K (5 L) and subsequent TPD from 130 K at a rate of 3 K/s. This procedure results in modest $^{13}C^{16}O^{18}O$ production in the present work (see Figure S 3) and is consistent with data found in the literature. CO is reacted with a probability of approximately 4% as determined via peak integration of CO (200 K, 450 K) and CO_2 desorption (225 K), for sensitivity factors see above. TPD shows again the low temperature desorption feature (200 K) as in case without $^{18}O_2$ dosing and in addition a second broad high-temperature desorption feature at 450 K which is clearly related to the onset of $^{18}O_2$ desorption from the sample (Figure S 3).

The underlying mechanism for the development of this second feature after oxygen dosing is so far unclear but is also found for deposited TiO_2 clusters on HOPG (see below).

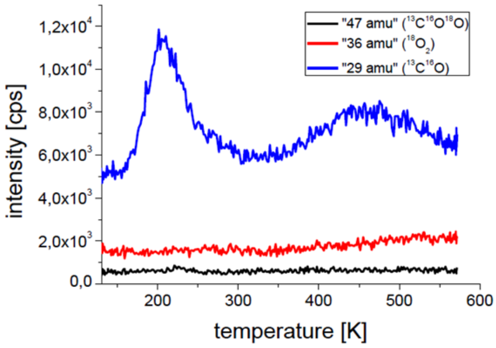

Figure S 3. $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from $TiO_2(110)$ after treatment according to the *TiO₂(110) procedure*, adsorption of 10 L $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K. The TPD ramp has been recorded with a heating rate of 3 K/s.

As next step CO desorption and CO oxidation activity of HOPG were investigated. HOPG annealing requires heating to more than 800 K (the upper limit of the current manipulator), however, without annealing sputtering might create reactive defects at the surface which led to the decision that HOPG is only heated and not sputtered. Literature results from Oh *et al.* suggest that no CO adsorption on HOPG takes place above 200 K.[9] Cleaning of a pristine HOPG sample via the Scotch-tape method, subsequent heating to 473 K for 20 min (*HOPG procedure*) and dosing of 5 L (50 L) of $^{13}C^{16}O$ at 180 K shows a small desorption feature at 180 K (see Figure S 4 left). It remains at this temperature with the sample out of position during the TPD heating curve (Figure S 4 middle) so it must be concluded that no adsorption of CO takes place at HOPG. In case $^{18}O_2$ is dosed to the surface (10 L at 400 K) minute amounts of $^{13}C^{16}O^{18}O$ are desorbed from the surface at 180 K (Figure S 4 right) which is probably also related to desorption from parts of the sample holder.

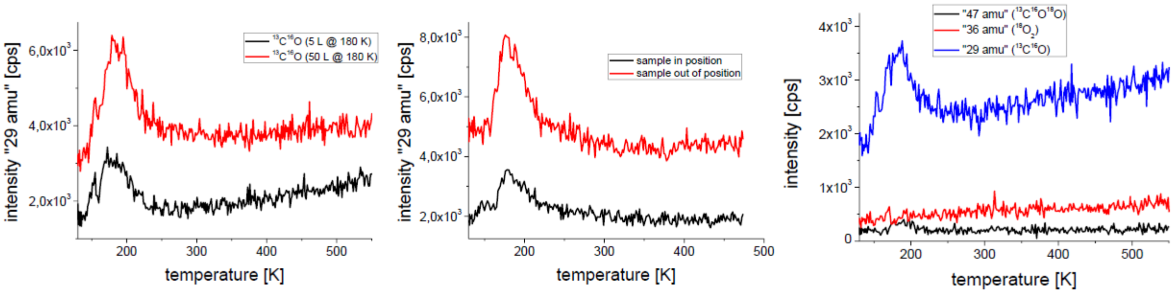

Figure S 4. Left. $^{13}C^{16}O$ desorption from HOPG after treatment according to the *HOPG procedure* and adsorption of 5 L (50 L) of $^{13}C^{16}O$ at 180 K. Middle. $^{13}C^{16}O$ desorption with sample in and out of position after adsorption of 5 L of $^{13}C^{16}O$ at 180 K. Right. $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from HOPG after treatment according to the *HOPG procedure*, adsorption of 10 L $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K. The TPD ramp has been recorded with a heating rate of 3 K/s in all cases.

The final experiment in this subsection is the deposition of $(TiO_2)_{93}^-$ onto HOPG. $(TiO_2)_{93}$ clusters were chosen because previous work has shown that large titanium dioxide clusters tend to form fractal structures on HOPG with high surface areas.[10] The full monolayer of $TiO_2(110)$ contains 5×10^{14} atoms/cm² and it was chosen to deposit approximately 0.3 monolayer equivalents, i.e., 2×10^{12} clusters within the 5 mm × 5 mm deposition spot (ca. 80 pA for an hour). An AFM image of the as-deposited cluster spot shows good coverage of the

HOPG surface and an average cluster height of approximately 1.2 nm (Figure S 5). According to simple calculations, assuming clusters exhibit bulk density (4.23 g/cm^3) and spherical structures the diameter of $(TiO_2)_{93}$ should be around 1.8 nm which is significantly larger than the average height of the clusters on the HOPG surface (Figure S 5). A deformation of the cluster on HOPG could account for the height difference.

An AFM tip usually has a tip-dilation effect which limits the resolution in the lateral direction. As a result of this, AFM will not be an ideal technique to measure the size (diameter) of the gold clusters. In addition, due to the weak interaction between the titania clusters and the HOPG surface the tip tends to pick up clusters from the support which oftentimes results in measurement artifacts. However, we think we will be able to disclose structures of the gold clusters on titania particles by future ISS measurements in similar fashion like in experiments carried out by Lee et al.[11] On the other hand does the very sharp size-dependent behavior in TPD experiments already point to intact clusters landed on the previously deposited titania particles.

A very systematic STM study on Au_n (n = 1 - 8) deposited onto TiO_2(110) has been conducted which illustrates the basic behavior of this type of clusters.[12] Here, it is already described that starting from Au_2 stable clusters are observed on the single crystalline surface and that 2d-3d transition takes place at Au_5. Moreover, Au_8 is found to be dissociating to a percentage of < 5% into two Au_4 clusters which do not show significant activity towards CO oxidation either.[11,13]

This sample was also dosed with $^{13}C^{18}O$ (5 L and 50 L) at 180 K and subject to the CO oxidation procedure (see Figure S 6). The CO desorption behavior can now be compared to single crystal TiO_2(110) [Figure S 2] and pristine HOPG (Figure S 4 left, middle). In all cases peak positions for the 5 L and 50 L dose do not shift and nondissociative interaction between CO and the surface can be assumed. Compared to TiO_2(110) the main desorption feature is shifted to higher temperatures, 240 K for $(TiO_2)_{93}$/HOPG as compared to 200 K for the single crystal surface. This suggests stronger binding of the CO molecules to the cluster surface probably due to more defect sites at the clusters compared to a single crystalline surface. In comparison, the $^{13}C^{16}O$ desorption feature is roughly one order of magnitude smaller for the composite material which is accounted for by the coverages, 30% ML vs. 100% ML, if one takes into account that these 30% ML form larger clusters covering less than 30% of the surface. If compared to HOPG (or CO desorbing from the heating wires, sample holder, etc.) the desorption feature is shifted about 60 K (Figure S 4, left) to higher temperatures and so it is concluded that $(TiO_2)_{93}$ clusters are solely responsible for the adsorption/desorption behavior of the composite material. The CO oxidation experiment on $(TiO_2)_{93}$/HOPG revealed similar CO reaction probabilities (5%) are observed as on the single crystal surface (Figure S 4 right), only shifted to higher temperatures (240 K). Like in the case of TiO_2(110) a second high temperature desorption feature is found for the composite material after $^{18}O_2$ dosing which is also associated with the desorption of $^{18}O_2$ at around 450 K. The intensity of $^{13}C^{16}O$ for the low-temperature desorption feature is much higher for TiO_2(110) than for the high-temperature desorption feature while on the composite material this is reversed.

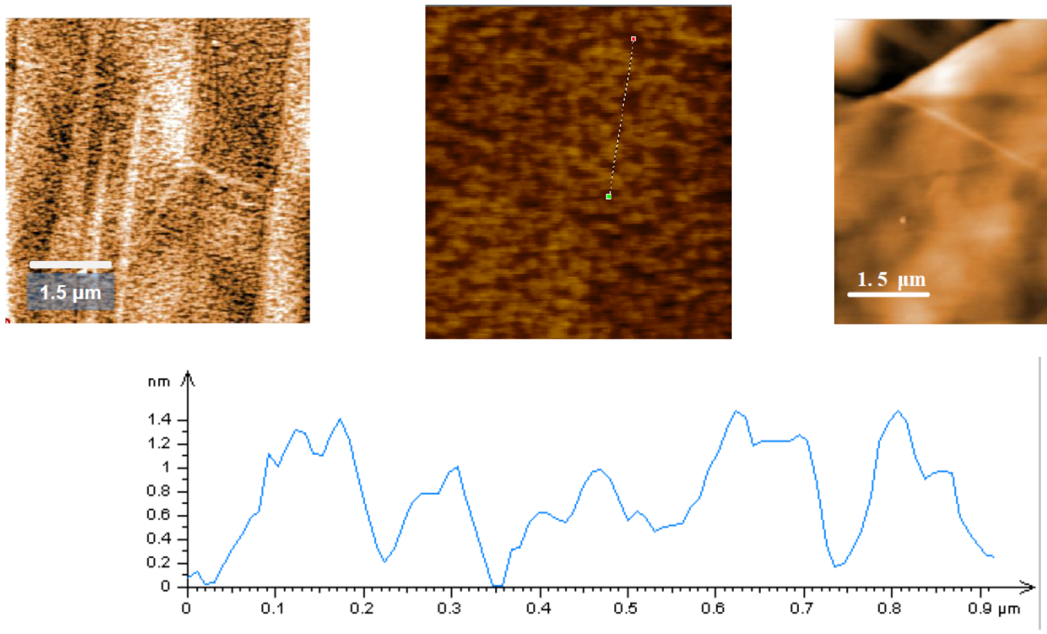

Figure S 5. Left. AFM image of 30% ML $(TiO_2)_{93}$/HOPG. Middle. Average height trace taken along the dashed line. Right. AFM image of HOPG for comparison.

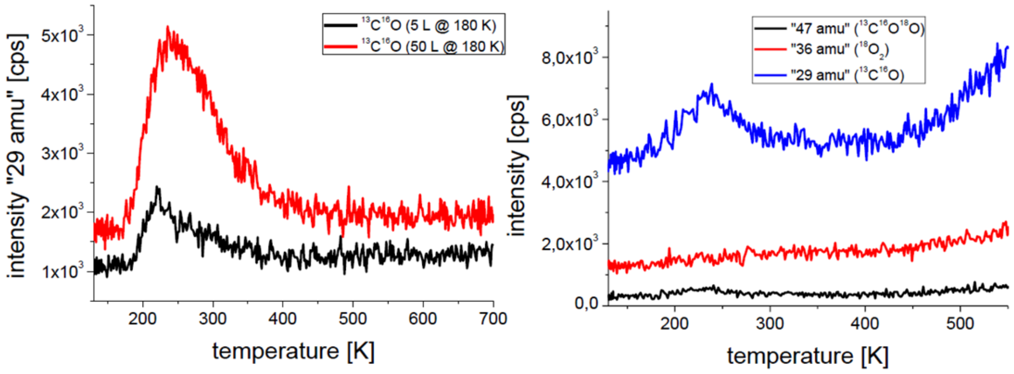

Figure S 6. Left. $^{13}C^{16}O$ desorption from 30% ML $(TiO_2)_{93}$/HOPG after adsorption of 5 L (50 L) of $^{13}C^{16}O$ at 180 K. Right. $^{13}C^{16}O$, $^{18}O_2$, and $^{13}C^{16}O^{18}O$ desorption from 30% ML $(TiO_2)_{93}$/HOPG after adsorption of 10 L $^{18}O_2$ at 400 K and 5 L of $^{13}C^{16}O$ at 180 K. TPD ramps have been recorded with a heating rate of 3 K/s in all cases.

As *conclusion from preliminary experiments* and *blank tests* it can be drawn that (***i***) the described treatment of the TiO_2(110) single crystal leads to D_2O-TPD results which are comparable to the literature.[1] (***ii***) It is found that oxygen vacancies are not formed (oxidized materials) and adsorption of CO probably takes place on other defect sites on the crystal. In both cases (TiO_2[110] and $(TiO_2)_{93}$/HOPG) the high temperature desorption feature of D_2O at around 500 K is absent clearly ruling out oxygen vacancies (see Figure S 1 and Figure S 7). (***iii***) HOPG as a substrate does not bind CO as described in current literature.[9] In the composite material $(TiO_2)_{93}$/HOPG CO adsorption behavior is dominated by deposited titania particles. (***iv***) CO oxidation blank tests on the single crystal and the composite material show low CO reaction probabilities of approximately 5%.

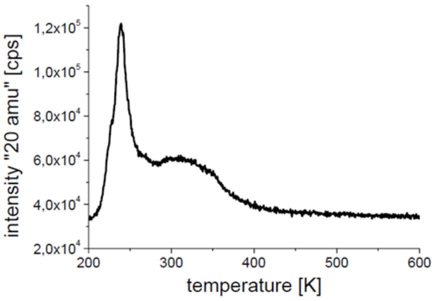

Figure S 7. D_2O-TPD of 30% ML $(TiO_2)_{93}$/HOPG. The TPD ramp has been driven from 200 K to 600 K at a heating rate of 2 K/s.

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[1] W. S. Epling, C. H. F. Peden, M. A. Henderson, U. Diebold, *Surf. Sci*. **1998**, *412/413*, 333-343.

[2] W. Göppel, G. Rocker, R. Feierabend, *Phys. Rev. B* **1983**, *28*, 3427-3438.

[3] J.-M. Pan, B. L. Maschhoff, U. Diebold, T. E. Madey, *Surf. Sci*. **1993**, *291*, 381-394.

[4] G. Lu, A. Linsebigler, J. T. Yates, Jr., *J. Phys. Chem*. **1994**, *98*, 11733-11738.

[5] S. Fischer, A. W. Munz, K.-D. Schierbaum, W. Göpel, *Surf. Sci*. **1995**, *337*, 17-30.

[6] U. Diebold, J. F. Anderson, K.-O. Ng, D. Vanderbilt, *Phys. Rev. Lett*. **1996**, *77*, 1322-1325.

[7] W. E. Kaden, W. A. Kunkel, F. S. Roberts, M. Kane, S. L. Anderson, *J. Chem. Phys*. **2012**, *136*, 204705.

[8] W. E. Kaden, T. Wu, W. A. Kunkel, S. L. Anderson, *Science* **2009**, *326*, 826-829.

[9] J. Oh, T. Kondo, D. Hatake, Y. Iwasahi, Y. Honma, Y. Suda, D. Sekiba, H. Kudo, J. Nakamura, *J. Phys. Chem. Lett*. **2010**, *1*, 463-466.

[10] X. Tang, X. Li, Y. Wang, K. Wepasnick, A. Lim, D. H. Fairbrother, K. H. Bowen, T. Mangler, S. Noessner, C. Wolke, M. Grossmann, A. Koop, G. Gantefoer, B. Kiran, A. K. Kandalam, *J. Phys. Conf. Ser.* **2013***, 438*, 012005.

[11] S. Lee, C. Fan, T. Wu, S. L. Anderson, *J. Chem. Phys.* **2005**, *123*, 124710.

[12] X. Tong, L. Benz, P. Kemper, H. Metiu, M. T. Bowers, S. K. Buratto, *J. Am. Chem. Soc.* **2005**, *127*, 13516-13518.

[13] S. Lee, C. Fan, T. Wu, S. L. Anderson, *J. Chem. Phys.* **2005**, *123*, 124710.