Supporting Information

Same Size, Same Support, Same Spectator? Selective Acetylene Hydrogenation on supported Pd Nanoparticles

Given the finite thickness of the a-SiO_2 films on Pt(111) and Mo(211) reported in this work, the main concern/issue might be an active contribution of the underlying metal (Pt(111), Mo(211)) during catalysis by diffusion or incorporation of substrate atoms in the oxide film, as described by Freund[1–3]. To elaborate on thin-film characterization, IRRAS measurements were conducted for both the a-SiO_2/Pt(111) and a-SiO_2/Mo(211), respectively. Figure S1a shows the characteristic vibrational Si-O bands at 1238 and 1252cm^{-1} and a broad shoulder down to 1100 cm^{-1} associated with asymmetric longitudinal phonon vibrations for both support materials. In contrast to the Pt-based system, a chemical bond between oxygen and Mo yielding Mo-O-Si vibrations can be found spectroscopically around 1051 cm^{-1} [4].
Moreover, TPD measurement were performed and Figure S1b depicts deuterium desorption from a-SiO_2/Pt(111) and a-SiO_2/Mo(211). No m/z=4 desorption is detected after dosing 0.4/sA D_2 on a clean a-SiO_2 thin-film without metal loading. Thus, on the one hand, the metal single crystal is fully covered by a-SiO_2, as described previously[5]. On the other hand, no D_2 desorption hints towards no substantial amount of substrate metal atoms incorporated in the thin-film.

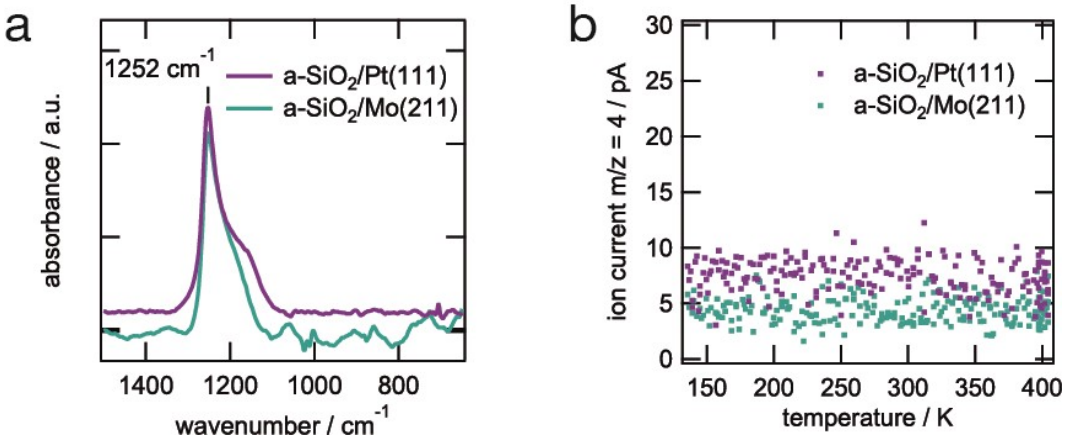

Figure S1: a: IR absorption spectrum of clean a-SiO_2/Pt(111) and a-SiO_2/Mo(211) with characteristic vibrational bands 1238 and 1252 cm^{-1} with a shoulder down to 1100 cm^{-1}. Mo exhibits a Mo-O-Si bond yielding an additional band at 1051 cm^{-1}. b: Desorption spectrum of D_2 (m/z=4) after dosage of 0.4/sA D_2 on clean a-SiO_2/Pt(111) and a-SiO_2/Mo(211).

Furthermore, CO and D_2O TPD experiments were performed to exclude metal substrate atoms present in the a-SiO_2 film, see figure S2. After dosing 0.1/sA (D_2O) and 1/sA (CO) of the respective molecule, no desorption feature for CO (m/z=28) and D_2O (m/z=20), except physisorption below 150 K were found, indicating unperturbed and fully closed films grown on Pt(111) and Mo(211).

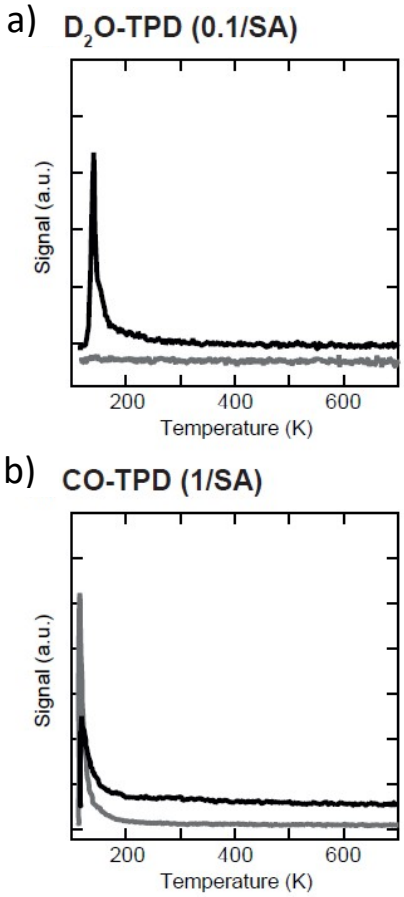

Figure S2: TPD of probe molecules on a-SiO_2 supported on Pt(111) and Mo(211): The amount of dosed molecules are given per surface atom (SA). For D_2O m/z=20 was monitored, and for CO m/z=28.

The possibility of incorporation of support material atoms during ethylene hydrogenation was considered too. The active participation of the support material might lead to the creation of a capture zone by spill-over, which was used to explain CO oxidation of size-selected Pd clusters supported on MgO(100). The direct spill-over would, in this case, lead to ethylene or hydrogen adsorption onto the support and subsequent diffusion to the active metal component, where the reaction takes place. Diffusion of dissociatively adsorbed D_2 on the metal to the support would result in the formation of surface silanol groups, which have not been observed experimentally by IRRAS experiments.
Thus, the surface sensitive characterization of the synthesized thin-films shows no indications for uncovered metal substrate or metal-atom incorporation in the film, altering the surface chemistry of the film or the deposited Pd_n-particles.

Cracking-pattern analysis via MatLab

Below, a Cracking pattern implantation for quantitative data evaluation – Exemplary MatLab source code – can be found, based on the cracking patterns for the investigated m/z ratios found in literature [6,7].

```
clear all;
clc;

A=[ 100 23 157 64;
    0 100 231 220;
    0 0  37 55;
    0 0 100 19]

b=[31.29786959  7.1782     0.369863    0.321661;
16.68243314    5.68726     0.234108    0.294768;
11.31786799    3.75862     0.177465    0.212484;
8.400860468    2.87068     0.174119    0.16173;
6.934829535    2.14974     0.0600183   0.184048;
5.535981604    1.77098     0.0536415   0.187794;
4.674012108    1.51626     0.0744638   0.158978;
4.295078759    1.26553     0.0724996   0.178637;
4.298189701    1.03897     0.066513    0.18815;
3.205695667    0.972467    0.104781    0.195823;
3.628694241    0.863145    0.0471521   0.222695;
3.052017068    0.731704    0.0499693   0.167026;
2.908128732    0.611449    0.0284203   0.127262;
2.336051126    0.621957    0.0681886   0.134296;
2.743460093    0.568178    0.0752409   0.148168;
2.076864893    0.489337    0.0271474   0.145289;
1.607430133    0.433026    0.0601058   0.112568;
1.928591497    0.300708    0.0362324   0.126477;
1.615915683    0.310071    0.0705088   0.148052;
1.907903267    0.446189    0.0280443   0.157499;
0.958511672    0.361403    0.0438559   0.155365;
1.505722882    0.332444    0.0546669   0.168024;
0.945026981    0.21122     0.033272    0.151365;
1.372076904    0.311736    0.0462998   0.182028;
1.630137223    0.174595    0.0889294   0.191375;
1.321586478    0.290529    0.04076     0.190154;
2.86601        0.212976    0.0590531   0.170478;
1.680239233    0.258763    0.0726462   0.111461;
0.588709024    0.228596    0.0426132   0.122099;
1.326398817    0.251319    0.0843497   0.115808
]';

c=[100 100 100 55]';

x=A\b

w=x'*diag(c)

xlswrite('SiO2P111_ethyl.xls',w,'tab5','E5')
```

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