Supplementary Information

Ligand-stabilized Pt nanoparticles (NPs) as novel materials for catalytic gas sensing: Influence of the ligand on important catalytic properties

Eva Morsbach¹, Eike Brauns², Thomas Kowalik³, Walter Lang², Sebastian Kunz¹*, Marcus Bäumer¹

Figure S1: Cyclic voltammogram of DAO-Pt before (black) and after (gray) H₂ oxidation. The Pt reduction peak between 700 – 200 mV (negative sweep) is proportional to the amount of free Pt surface atoms. The shift to higher potentials is due to bigger crystallites (= sintering of NPs).

Figure S1 shows the cyclic voltammogram of DAO-Pt before and after H₂ oxidation. The peak areas of a cyclic voltammogram are proportional to the surface area of the sample. The decreased peak areas after H₂ oxidation confirm a loss of the catalyst’s surface area after H₂ oxidation. Additionally, the Pt reduction peak (negative sweep between 200-700 mV) shifts to higher potentials, which indicates that
bigger Pt crystallites instead of nanoparticles are the catalytically active species.\textsuperscript{13} It can thus be concluded that the deactivation of the sensor can be related to sintering of the catalytically active NPs.

**Table S 1: Ligand coverage of Pt NPs for different ligands**

<table>
<thead>
<tr>
<th>Ligand coverage</th>
<th>“pure” Pt NPs</th>
<th>HDA-Pt</th>
<th>aniline-Pt</th>
<th>DAO-Pt</th>
<th>PDA-Pt</th>
<th>BiPy-Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand coverage</td>
<td>0</td>
<td>1</td>
<td>0.92</td>
<td>0.39</td>
<td>0.47</td>
<td>0.34</td>
</tr>
</tbody>
</table>

The ligand coverages for ligand-linked NPs have been determined via the electrochemical surface area. Determination via elemental ratios by AAS/elemental analysis does not reflect the ligand coverages due to different degrees of cross-linking for the bifunctional ligands.\textsuperscript{9}

---

*Figure S2: Response of an activated sensor that is kept at operating temperature without the presence of H\textsubscript{2} (t < 0s) towards a hydrogen pulse.*

Figure S2 shows the immediate response of an activated sensor that is kept under operating conditions but without the presence of H\textsubscript{2}. No additional activation is required after the pre-treatment and the sensor achieves 90% of its maximum output of 220 mV within <150 ms.\textsuperscript{6}
An essential requirement for hydrogen sensors is a constant response towards H\(_2\) over several runs. Figure S3 shows a long-term run of a PDA-Pt sensor that was kept at operating conditions for several weeks without a constant stream of hydrogen. Every 5th day the sensor was exposed to 1 vol% of H\(_2\) and the output signal was recorded. During these measurements, the hydrogen concentration has been increased and decreased stepwise from 0 vol% to 1 vol% H\(_2\) with stepsizes of 0.1 vol% H\(_2\). The stepwise response of the sensor towards H\(_2\) on day 20 is displayed as an inset in Fig.S3. All obtained changes were within the limit of the experimental accuracy.
Figure S4: Reflection-IR spectrum of BiPy-Pt before and after H₂ oxidation.