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

Supplementary Information

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

Eva Morsbach[1], Eike Brauns[2], Thomas Kowalik[3], Walter Lang[2], Sebastian Kunz[1], Marcus Bäumer[1]*

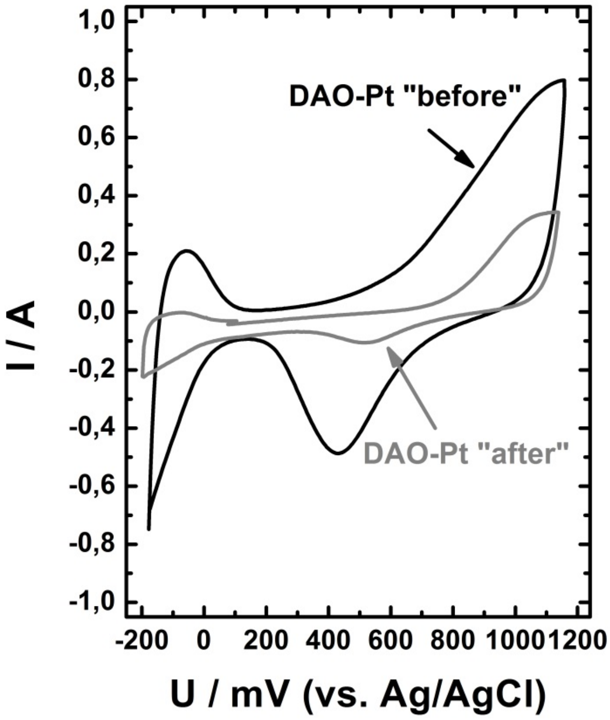

Figure S1: Cyclic voltammogram of DAO-Pt before (black) and after (gray) H_2 oxidation. The Pt reduction peak between 700 – 200 mV (negative sweep) is proportional to the amount of free Pt surface atoms. The shift to higher potentials is due to bigger crystallites (= sintering of NPs).

Figure S1 shows the cyclic voltammogram of DAO-Pt before and after H_2 oxidation. The peak areas of a cyclic voltammogram are proportional to the surface area of the sample. The decreased peak areas after H_2 oxidation confirm a loss of the catalyst's surface area after H_2 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.[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

	"pure" Pt NPs	HDA-Pt	aniline-Pt	DAO-Pt	PDA-Pt	BiPy-Pt
Ligand coverage	0	1	0.92	0.39	0.47	0.34

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.[9]

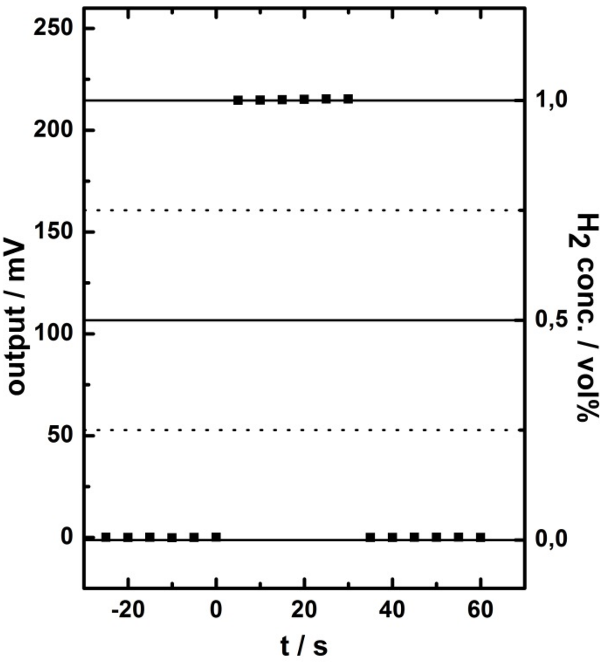

Figure S2: Response of an activated sensor that is kept at operating temperature without the presence of H_2 (t < 0s) towards a hydrogen pulse.

Figure S2 shows the immediate response of an activated sensor that is kept under operating conditions but without the presence of H_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.[6]

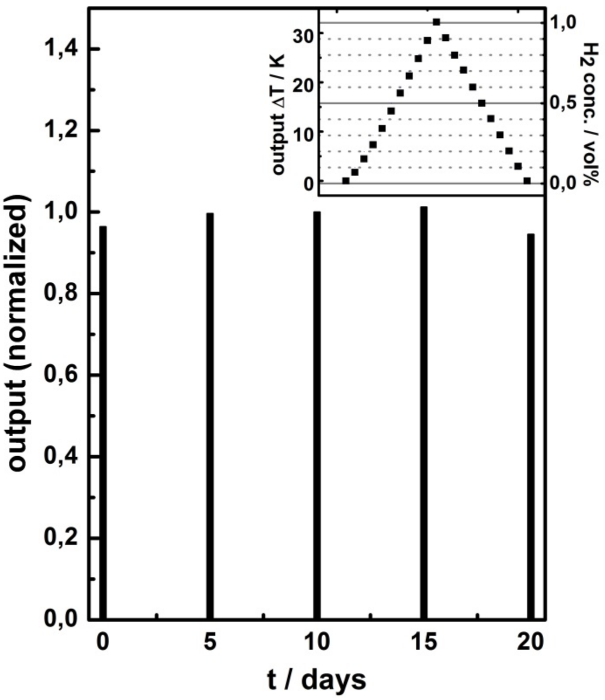

Figure S3: Pulsed long-term measurement of PDA-Pt sensor. The sensor has been kept in an atmosphere without H_2 (0 vol%) and has been exposed to H_2 every fifth day to investigate its performance for repeated measurements over a prolonged period of time. For every measurements the hydrogen concentration has been changed stepwise between 0 vol% and 1 vol% with step sizes of 0.1 vol%, shown as inset. No significant changes of the response times were obtained.

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 1vol% 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.

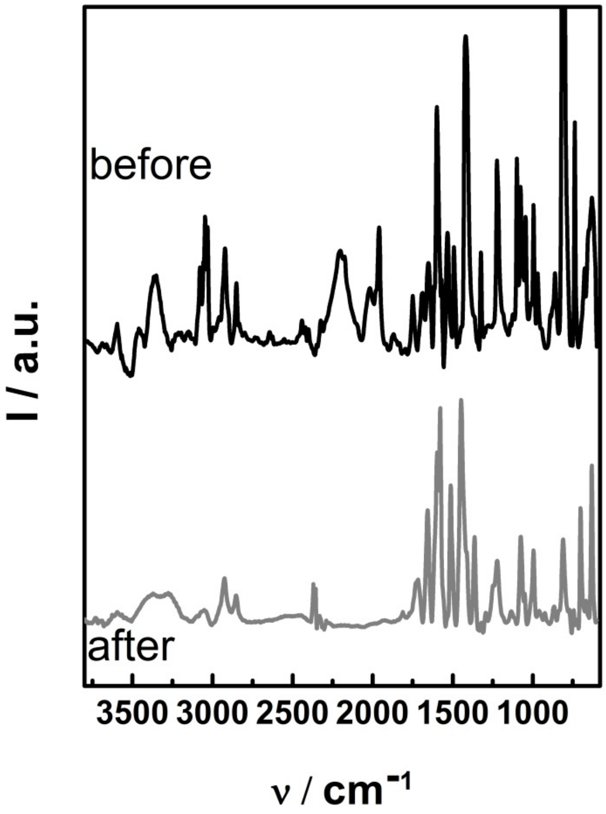

Figure S4: Reflection-IR spectrum of BiPy-Pt before and after H_2 oxidation.