metals

Supporting information

Chemical synthesis and characterization of Pd/SiO2: the effect of chemical reagent

Aram L. Bugaev [1,*], Vladimir A. Polyakov [1], Andrei A. Tereshchenko [1], Ashura N. Isaeva [1], Alina A. Skorynina [1], Elizaveta G. Kamyshova [1], Andriy P. Budnyk [1], Tatiana A. Lastovina [1,*], Alexander V. Soldatov [1]

[1] The Smart Materials Research Center, Southern Federal University, 178/24 Sladkova, 344090, Rostov-on-Don, Russia

* Correspondence: abugaev@sfedu.ru or lastovina.t@yandex.ru; Tel.: +7-863-305-1996

S1. The effect of the initial palladium precursor on the particle size distribution

As reported in Table 1 of the main text, the average nanoparticle size is much bigger in the sample treated by ammonia hydroxide prior to the reduction in comparison with the sample treated in ethanol. Ethanol in known not to react with palladium precursor, and the palladium-containing compound remains $[PdCl_4]^{2-}$. In the case of ammonia hydroxide this compound is modified to $[Pd(NH_3)_4]^{2+}$. According to the literature data [1], the standard redox potential of Pd^{2+}/Pd^0 or $[PdCl_4]^{2-}/Pd^0$ is significantly higher than that of $[Pd(NH_3)_4]^{2+}/Pd^0$. This means that small nuclei of palladium formed in Pd-NPs$_{ammonia,hydrazine}$ are able to move over the surface of silica support and combine with other nuclei forming bigger particles.

Glycols are widely used for the preparation of metal NPs. The reduction reaction is usually activated at temperatures around the boiling point of glycol [2], for PEG, boiling point is about 250 °C. The use of a high-pressure reactor helps to decrease the activation temperature. During the redox reaction PEG can be converted into the butanedione derivative by analogy with ethylene glycol [2]:

$$\mathrm{HOCH_2CH_2OH \rightarrow CH_3CHO + H_2O} \quad (2)$$

$$2/n\mathrm{M}^{n+} + \mathrm{2CH_3CHO \rightarrow CH_3COCOCH_3} + 2/n\mathrm{M} + \mathrm{2H^+} \quad (3)$$

S2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) showed the mass loss with increasing temperature (Figure S1), which correlates with the literature data. For the Pd-NPs$_{PEG}$ sample, there are three mass loss regions in TG curves. The first mass loss in the region from room temperature to 120 °C corresponds to water evaporation. The second weight decrement, from 120 °C to 180 °C, is associated with the decomposition of Si-OR bonds. The huge mass loss between 200 °C and 500 °C is attributed to the decomposition of $Si\text{-}CH_3$ groups connected with PEG and PEG residual on the surface of Pd/SiO_2. For other samples, we can distinguish two main regions: 1) water evaporation from room temperature to ~120 °C and 2) Si-OR bonds decomposition from 120 °C to 200 °C.

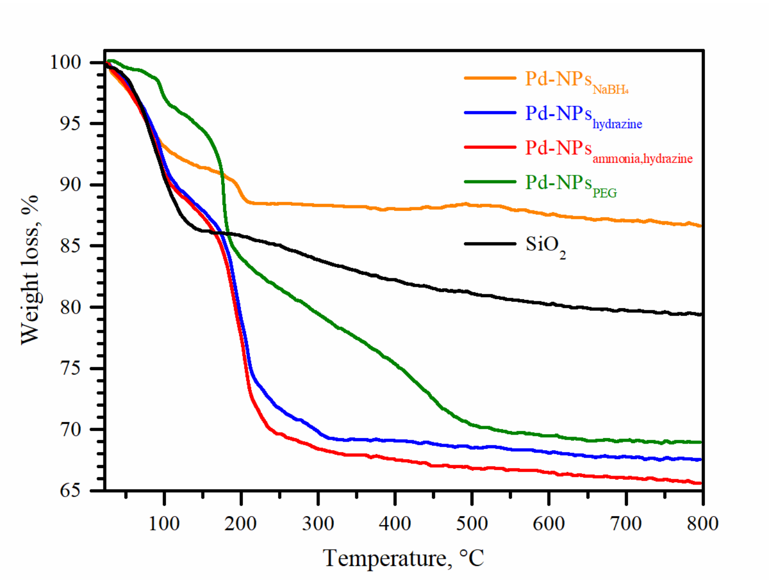

Figure S1. TGA curves for Pd/SiO_2 samples reduced in $NaBH_4$ (orange), in hydrazine: Pd-$NPs_{hydrazine}$ (blue) and Pd-$NPs_{ammonia,hydrazine}$ (red), in PEG (green), and SiO_2 support (black).

References

1. Pomogailo, A. D.; Dzhardimalieva, G. I., Reduction of Metal Ions in Polymer Matrices as a Condensation Method of Nanocomposite Synthesis. **2014**, 13-89. dx.doi.org/10.1007/978-90-481-2567-8_2
2. Yue, H.; Zhao, Y.; Ma, X.; Gong, J., Ethylene glycol: properties, synthesis, and applications. *Chem. Soc. Rev.* **2012,** *41* (11), 4218-44. dx.doi.org/10.1039/c2cs15359a