

Supplementary Information

Photocatalyst preparation.

Monometallic. Monometallic Pd and Pt catalysts were prepared by chemical deposition. A required amount of $(\text{NH}_4)_2\text{PdCl}_6$ or H_2PtCl_6 metallic salt was dissolved in 250 mL distilled water and TiO_2 P25 powder (Evonik) was then added. After a 1h stirring to ensure a good salt- TiO_2 contact, chemical reduction of the salt occurred *via* an excess of NaBH_4 as reducing agent, under stirring.¹³ The solution was filtered and washed several time with water, before being dried overnight at 373 K. It is important to note that no thermal treatment was further applied.

Details regarding the action of the NaBH_4 reducing agent can be found in Porta et al. [1].

Au/TiO_2 photocatalysts have been similarly prepared using the HAuCl_4 metallic salt, dissolved in 250 mL distilled water and TiO_2 P25 powder (Evonik) was then added. After a 1h stirring to ensure a good salt- TiO_2 contact, chemical reduction of the salt occurred *via* an excess of NaBH_4 as reducing agent, under stirring. The solution was filtered and washed several time with water, before being dried overnight at 373 K. Again, it is important to note that no thermal treatment was further applied.

Bimetallic. A similar procedure was applied for preparing the $\text{Pd}_x\text{Pt}_{1-x}/\text{TiO}_2$ materials. Required amounts of $(\text{NH}_4)_2\text{PdCl}_6$ and H_2PtCl_6 metallic salt were dissolved in 250 mL distilled water and TiO_2 P25 powder (Evonik) was then added. After a 1h stirring to ensure a good salt- TiO_2 contact, chemical co-reduction of both salts occurred *via* an excess of NaBH_4 as reducing agent, under stirring.¹³ The solution was filtered and washed several time with water, before being dried overnight at 373 K. Again, it is important to note that no thermal treatment was further applied.

In terms of M/TiO_2 compositions, it should be point out that the metal content corresponds to a weight content, whereas the $\text{Pd}_x\text{Pt}_{1-x}/\text{TiO}_2$ P25 corresponds to atomic or molar ratios. $\text{Pd}_x\text{Pt}_{1-x}/\text{TiO}_2$ P25 photocatalysts have been prepared with metal contents ranging from 0.3 to 6 wt.%, and with $\text{Pd}_x\text{Pt}_{1-x}$ bimetallic compositions ranging from $\text{Pt}_{90}\text{Pd}_{10}$ to $\text{Pt}_{10}\text{Pd}_{90}$.

Photocatalytic reactor and Test conditions.

The photocatalytic reaction was carried out in a 260 mm length single pass annular Pyrex reactor made of two coaxial tubes 3 mm apart, between which the reactant mixture was passing through. Extensive details concerning both photocatalytic reactor and device can be found elsewhere [2]. UV-A Illumination was provided by a commercially available 8W black light tube (Philips, TL8W/08 BLB F8T5, $3.8 \text{ mW}\cdot\text{cm}^{-2}$ of irradiance) with a spectral peak centered on 365 nm, located inside the inner tube of the reactor. The photocatalytic performances were obtained by *on-line* analyzing and quantifying both inlet and outlet flows with a microgas chromatography (Quad400P, MTI/SRA-Instruments) through MS5A, PPQ, Stabilwas and OV1 columns coupled to micro thermal conductivity detectors.

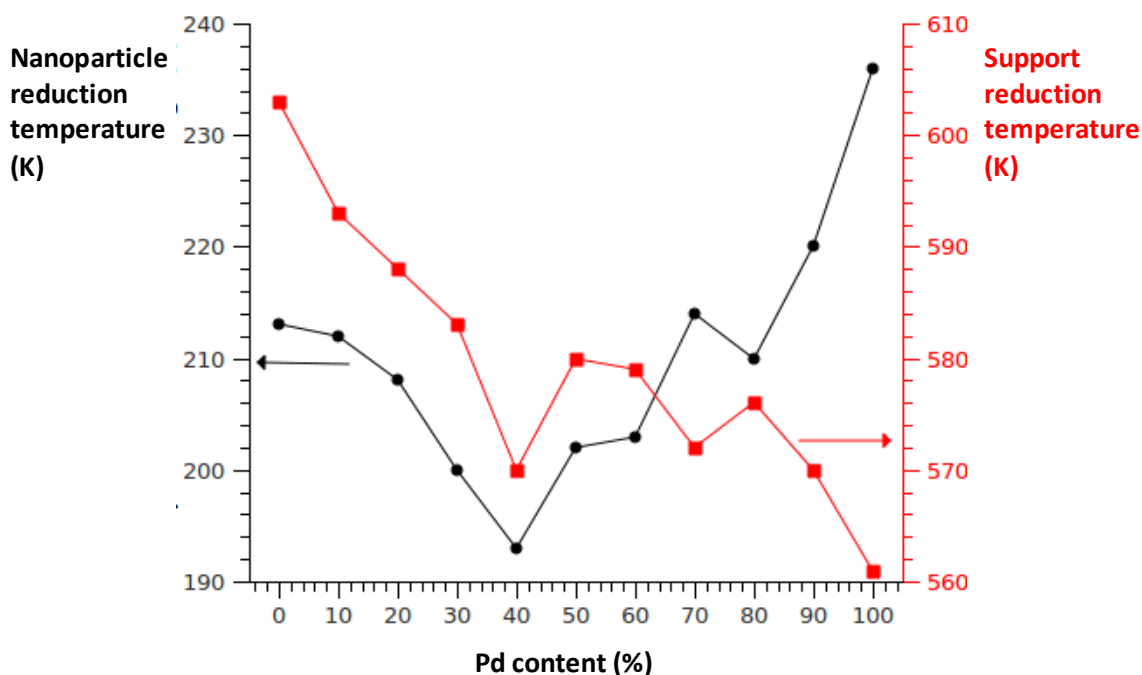
100 mg of photocatalytic material was evenly coated on the internal side of the 28 mm *i.d.* external tube by evaporating a catalyst-containing ethanol slurry to dryness (20 mL of ethanol). The annular reactor was coated with 100 mg of photocatalyst, corresponding to a coverage density of $0.25 \text{ mg}\cdot\text{cm}^{-2}$. The reaction was then performed at a total flow rate of 200 mL/min, with 250 ppmv of inlet CO concentration, a relative humidity ranging from 0% to 60%, 25 vol.% of He and balanced with dried air. A total flow rate of 200 mL/min corresponds to a gas velocity of 1.7 cm/s and a residence time of 13.7 s. In the case of simultaneous CO and acetone elimination, the acetone concentration was set at 1800 ppmv.

Additional characterization and discussion relative to the Pd_xPt_{1-x}/TiO₂ photocatalysts.

We present here additional characterization by CO adsorption-FTIR and H₂-Temperature Programmed Reduction of Pd_xPt_{1-x}/TiO₂ photocatalysts, as a function of the palladium content.

Hydrogen - Temperature Programmed Reduction of Pd_xPt_{1-x}/TiO₂ photocatalysts.

Pd_xPt_{1-x}/TiO₂ photocatalysts have been characterized by Temperature Programmed Reduction, recorded between 193 K and 773 K, with a heating rate of 6 K/min and under a 10% H₂/Ar flow. Bare TiO₂ is reduced under hydrogen flow at 873 K, but the metal catalyses the reaction by hydrogen atom *spill-over*, and thus the reduction temperature of TiO₂ modified by metallic particles is decreased. The Figure below shows both nanoparticle and support reduction temperatures for the different Pd_xPt_{1-x}/TiO₂ materials. Between both single metals, platinum is reduced at the lower temperature. By contrast, nanoparticles up to about 70% of Palladium displayed an even lower reduction temperature, probably as a result from stronger Pt-Pd interactions within the nanoparticles, which lead to more reducible nanoparticles. One can note that the support reduction temperature by *spill-over* quasi-linearly decreased from 603 K to 561 K for platinum and palladium, respectively. Thus the incorporation of palladium into the nanoparticles resulted in the decrease in the support reduction temperature. This can be seen as the evidence of the linear increase with the bulk palladium content, of the palladium content which contributing to the *spill-over* (*i.e.* located at the surface). This is in agreement with the absence of any surface segregation effect.



CO adsorption-FTIR.

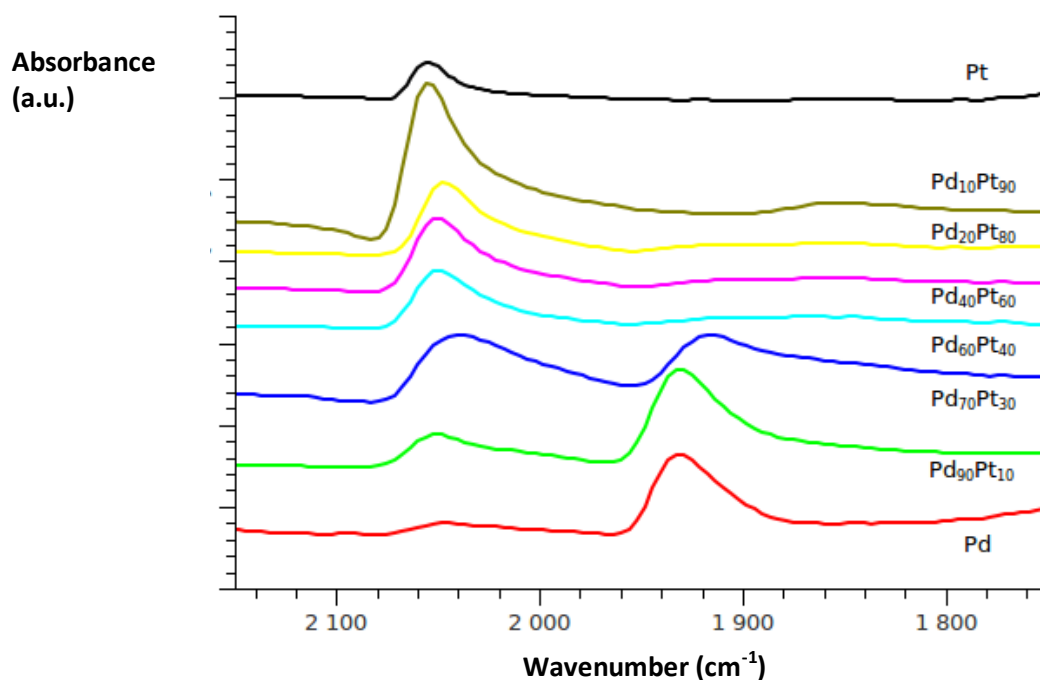
CO adsorption followed by FTIR spectroscopy has been recorded on a Bruker Vertex 80 IR spectrometer equipped with a Global IR source and a liquid Nitrogen MCT 318 detector (peak-to-peak resolution of 8 cm⁻¹). Hydrogen electrode is used as reference electrode, and a platinum wire is used as counter-electrode.

The Figure below shows the CO vibration wavenumber for the different Pd_xPt_{1-x}/TiO₂ materials. The adsorption of CO on Pt nanoparticles is characterized by an adsorption band at 2047 cm⁻¹,

corresponding to the linearly-adsorbed CO on Pt. On pure Pd, two adsorption modes are observed, a bridged one, strongly pronounced, at 1921 cm^{-1} , and a second one, linear and with weak intensity, at 2041 cm^{-1} .

The bridged CO adsorption on Pd needs to adjacent Pd atoms to occur. However, up to 70% of Pd (blue curve), no bridged adsorption is observed. The band located at 2045 cm^{-1} is attributed to both contributions, *i.e.* linearly adsorbed CO on Pt and on Pd atoms, what can explain the band broadening. Further, for richer Pd content, the probability to locate two adjacent Pd atoms for performing a bridged adsorption increases, and we observe the appearance and increase in the peak at 1920 cm^{-1} for $x \geq 70\%$.

Increasing the Pd content, increasing the CO(bridged)-to-CO(linear) ratio. It seems that both metals are located at the nanoparticle surface and that the surface composition linearly changes with the nanoparticle composition. This conclusion is in good agreement with the following observation: closer the nanoparticle composition from $x=0.5$ ($\text{Pd}_{50}\text{Pt}_{50}$), stronger the shift towards lower wavenumbers. Indeed, for mono-metallic particles, for which one adsorption mode is dominant, the dipole-dipole coupling is important and leads to a strong shift towards higher wavenumbers. By contrast, for bimetallic particles, linear and bridged CO adsorption occurs, and also the vibration wavenumber is different on Pt and on Pd. As a result from that, the coupling phenomena is weaker and results in a shift towards lower wavenumbers compared to the case with stronger coupling effect. This effect explains the band shift towards lower wavenumbers observed on bimetallic nanoparticles, and also the fact that this shift is maximal for compositions close to $\text{Pd}_{50}\text{Pt}_{50}$.



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- [1] F. Porta, L. Prati, M. Rossi and G. Scari, *J. Catal.*, 2002, **211**, 464.
- [2] V. Keller, P. Bernhardt, F. Garin, Photocatalytic oxidation of butyl acetate in vapor phase on TiO_2 , Pt/TiO_2 and WO_3/TiO_2 catalysts, *J. Catal.*, 2003, **215**, 129.