

Supporting information

Study of monometallic Pd/TiO₂ catalysts for the hydrogenation of succinic acid in aqueous-phase

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Catalysts characterization

Experimental

The actual Pd and Cl contents in the prepared catalysts were determined by ICP-OES (inductively coupled plasma optical emission spectrometer, Perkin) with an accuracy of ± 0.1 wt.%.

N₂-physisorption isotherms were collected at -196 °C using a TriStar 3000 apparatus from Micromeritics. Before analysis, samples were previously degassed overnight at 250 °C. The specific surface area, S_{BET}, was determined from the linear part of the BET plot.

The metallic accessibility was determined by H₂ chemisorption using a pulsed technique. To avoid formation of β -Pd hydride phase, H₂ chemisorption was performed at 70 °C. The catalysts were reduced in H₂ flow (1.8 L h⁻¹) at 300 °C for 1 h, then flushed by Ar flow (1.8 L h⁻¹) at the same temperature for 2 h, and finally cooled to 70 °C before H₂ pulses. The value of metallic accessibility or dispersion (D%) was estimated from the ratio of irreversibly adsorbed hydrogen on the Pd total number, considering that one hydrogen chemisorbs on one accessible Pd atom. The average particle size (d) was determined from the metal accessibility value according to Hugues *et al.* [1], who assimilated particles to cubes with one face in contact with the support. The equation is the following:

$$d = 5 \cdot 10^6 M / (D \cdot S \cdot \rho) \quad (1)$$

with M the atomic weight (g mol⁻¹), S the surface by mol of Pd metal (m² mol⁻¹) and ρ the metal volumic weight (g cm⁻³).

Catalysts morphology was studied by transmission electron microscopy (TEM) to estimate the average metallic particle size. The observation was completed with energy dispersive X-ray spectroscopy (EDXS) to ensure accurate localization of metallic particles. Micrographs were collected on a JEOL 2100 instrument (operated at 200 kV with a LaB₆ source and equipped with a Gatan Ultra scan camera). EDX spectroscopy was carried out with

a Hypernine (Premium) detector using the software SM-JED 2300T for data acquisition and treatment.

Powder X-ray diffraction (XRD) patterns of the catalysts were measured for 2 θ comprised between 10 ° to 80 ° (step of 0.03 °, step time of 2 s) using a Bruker AXS D5005 X-ray diffractometer and a CuK α radiation (λ = 1.54184 Å) as X-ray source. Phase identification was made by comparison with JCPDS database.

Temperature programmed reduction (TPR) was performed on Pd catalysts pretreated *in situ* under pure O₂ for 1 h at 300 °C, and cooled down to room temperature before the reduction under a 1.0 vol.% H₂/Ar gas mixture. The temperature range was 25-700 °C with a ramp of 5 °C min⁻¹. The measurements of the H₂ consumption were made in an AutoChem II/Micromeritics apparatus, using a thermal conductivity detector.

X-ray photoelectron spectroscopy (XPS) measurements were collected using a hemispherical analyzer on a Kratos Axis Ultra DLD XPS with a monochromated Al K α X-ray source. Catalysts can be pretreated *in situ* in O₂ or H₂ atmosphere under temperature in a pretreatment cell directly connected to the XPS chamber. After pretreatment, the samples were then cooled to room temperature and moved without exposure to air into the ultra-high-vacuum chamber (10⁻⁹ mbar). Peak fitting was achieved using CASAXPS software. Elemental surface stoichiometries were obtained from peak area ratios corrected by appropriate sensitivity.

The metallic function of the Pd catalysts was characterized by the reaction of cyclohexane dehydrogenation, generally considered as a structure insensitive reaction [2-4]. The reaction was carried out under atmospheric pressure in a continuous flow reactor at 270 °C. Injection of cyclohexane was made using a calibrated motor-driven syringe. The partial pressures were 97 and 3 kPa for H₂ and cyclohexane, respectively. All measurements were performed with a total flow rate of 100 mL min⁻¹ with 20 mg of catalyst, ensuring a conversion lower than 13%. Analysis of the reaction products was performed by gas

chromatography with a flame ionization detector (Varian 3400X) on a HP-PLOT Al₂O₃ “KCl” column. The only detected product was benzene.

Influence of the activation treatment

Various treatments of thermal activation were tested for the catalyst prepared from the Pd(NH₃)₄Cl₂ precursor salt by IMP method (at pH = 11) on the TiO₂ (P25) support, i.e. a direct reduction at 300 °C or a calcination (at 300 or 400 °C) followed by a reduction (at 300 or 400 °C). The four as-obtained catalysts correspond to the **entries 1 to 4** in Table 2.

On the one hand, dispersion values (D%) determined by H₂ chemisorption show that the Pd accessibility depends on the thermal activation treatments. A dispersion of 13% is obtained for the catalyst activated by direct reduction at 300 °C (Table 2, **entry 1**), compared with 25% when reducing treatment is preceded by a calcination step at 300 °C (Table 2, **entry 2**). These results are in agreement with those obtained by Zou and Gonzales [5] which showed that a direct reduction leads to a low dispersion of palladium on SiO₂ using the same type of Pd(NH₃)₄²⁺ palladium precursor. A calcination before the reduction was observed to improve the dispersion [5,6]. Barbier *et al.* [7] already showed the importance of drying and calcination steps, which, on the one hand, enable the decomposition of the precursor salt complex into a more easily reducible compound and, on the other hand, remove moisture traces that promote the sintering of the metal precursor. The increase in the calcination or reduction temperature (from 300 to 400 °C) induces a very slight decrease in Pd accessibility, taking into account the experimental errors (Table 2, entries 3 and 4 compared with entry 2)

Influence of the nature of the precursor salt

On the TiO₂ (P25) support, five different palladium precursor salts were used to prepare 2 wt.% Pd monometallic catalysts by the IMP method (with or without pH adjustment). After impregnation, the five obtained systems were activated by the same

C300R300 protocol, i.e. calcination followed by a reduction at 300°C (Table 2, **entries 2 and 5 to 8**). The metallic precursors differ by the nature of the chemical species associated with the palladium, mineral or organic, containing chlorinated species or not...

The results reveal that the dispersion of the catalysts is different according to the precursor salt nature. The highest Pd accessibility (33%) is obtained for the catalyst prepared from PdCl₂ salt (entry 6), the K₂PdCl₄ precursor leading to a very badly dispersed metal (2%, entry 8). The classification of the different palladium precursors as a function of the decreasing dispersion of the Pd/TiO₂ (P25) catalysts is the following: PdCl₂ (33%) > Pd_(acac)₂ (28%) > Pd(NH₃)₄Cl₂ (25%) > Pd(NH₃)₄(NO₃)₂ (11%) > K₂PdCl₄ (2%). The lowest dispersion obtained with the Pd(NH₃)₄Cl₂ precursor compared to PdCl₂ was already justified in the literature by several hypotheses, notably on MgO and Al₂O₃ supports [8]. The presence of NH₃ ligands, known as a reducing agent, contributes to the self-reduction of the Pd(NH₃)₄²⁺ complexes in Pd⁰ during the drying and/or calcination, then leading to an agglomeration of the metal particles [9]. Moreover, the formation of N₂ and H₂O can occur during partial decomposition of Pd(NH₃)₄²⁺ into Pd(NH₃)_x²⁺ [10,11], the latter agglomerating more easily in the presence of water. A greater mobility of the precursor salt can also result in a lower metal accessibility.

Some monometallic catalysts were studied by transmission electron microscopy (TEM) in order to verify the palladium dispersion state and to estimate the average particle size. The results suggest that the impregnation of PdCl₂ precursor salt by the ionic exchange method leads to a more homogeneous distribution of Pd particles on the TiO₂ (P25) support than the Pd(NH₃)₄Cl₂ salt (Fig. S1a compared to Fig. S1b). In the case of the 2 wt.% Pd_{Cl(pH=1)}C300R300/TiO₂ (P25) catalyst, the histogram of Fig. S1a confirms the homogeneous palladium distribution with particle sizes mainly comprised between 1 and 2 nm in diameter. On the other hand, the average size of Pd particles estimated from the histogram (1.8 nm) is slightly less than the one deducted from H₂ chemisorption (2.8 nm), (**entry 6**). In the case of

the 2 wt.% Pd_{N-Cl(pH=11)}C300R300/TiO₂ (P25) catalyst (**entry 2**), TEM images (Fig. S1b) show an heterogeneous distribution of the Pd particles. The size of the particles is centered on 2.5 nm. Larger particles as well as Pd particles with sizes inferior to the nanometer were also observed.

XRD analysis was also performed on these catalysts. The Pd_{N-Cl(pH=11)}C300R300/TiO₂ (P25) catalyst (Fig. S2a) shows diffraction peaks characteristic of metal palladium, notably near $2\theta = 40^\circ$, corresponding to a crystallite size of about 20 nm. The diffractograms of the Pd_{Cl(pH=1)}C300R300/TiO₂ (P25) and Pd_{ac}C300R300/TiO₂ (P25) catalysts (not shown) are similar to that of the TiO₂ (P25) support, confirming the good dispersion of their metallic phase as previously highlighted by TEM and H₂ chemisorption. The diffraction patterns of the Pd_{K-Cl(pH=1)}C300R300/TiO₂ (P25) (Fig. S2b) and Pd_{K-Cl(pH=1)}C300R300/TiO₂ (DT51) (Fig. S2c) catalysts show the presence of the characteristic lines of K₂PdCl₄ precursor salt used to prepare these samples. This observation demonstrated that the calcination at 300 °C followed by reduction to 300 °C is not sufficient to decompose this K₂PdCl₄ precursor salt.

Influence of the surface area of the support

The sol-gel synthesized support (TiO₂ (Synth)) was used for the preparation of a Pd catalyst from the PdCl₂ precursor salt *via* the IMP method and activation by C300R300 procedure (Table 2, **entry 12**). Despite of the more important specific surface developed by this support compared to the others (Table 1), the as prepared catalyst presents a metal dispersion value similar to that obtained previously with the Pd_{Cl(pH=1)}C300R300/TiO₂ (P25) sample (Table 2, **entry 6**) prepared in the same conditions but on the TiO₂ (P25) support. Similarly, the specific activities and the TOF values determined for the cyclohexane dehydrogenation are comparable. Palladium surface atoms appear to work in a similar way, even though the chlorine content is more important on the synthesized support. This higher chlorine content can be attributed to its greater specific surface. As a result, chlorine species

would be well distributed on the surface of the synthesized support and the environment of palladium particles would be similar regardless of support, which would explain the similar catalytic performances. Then, the TOF value does not depend on the chlorine content of the catalyst.

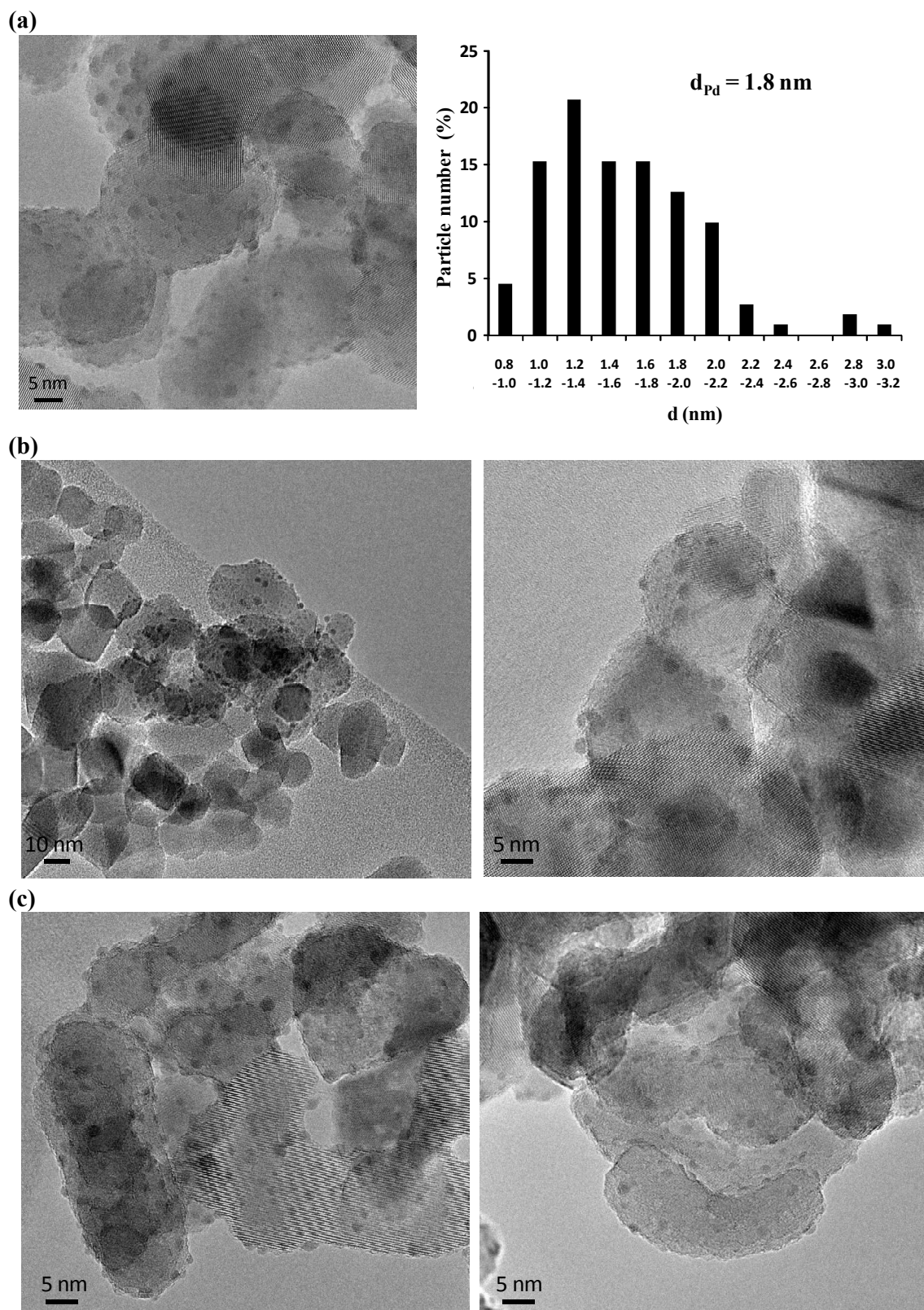


Figure S1. Representative TEM images obtained for:
 (a) 2 wt.% $\text{Pd}_{\text{Cl}(\text{pH}=1)}\text{C300R300}/\text{TiO}_2$ (P25), (b) 2 wt.% $\text{Pd}_{\text{N-Cl}(\text{pH}=11)}\text{C300R300}/\text{TiO}_2$ (P25), and
 (c) 2 wt.% $\text{Pd}_{\text{Cl}(\text{pH}=1)}\text{C300R300}/\text{TiO}_2$ (DT51).

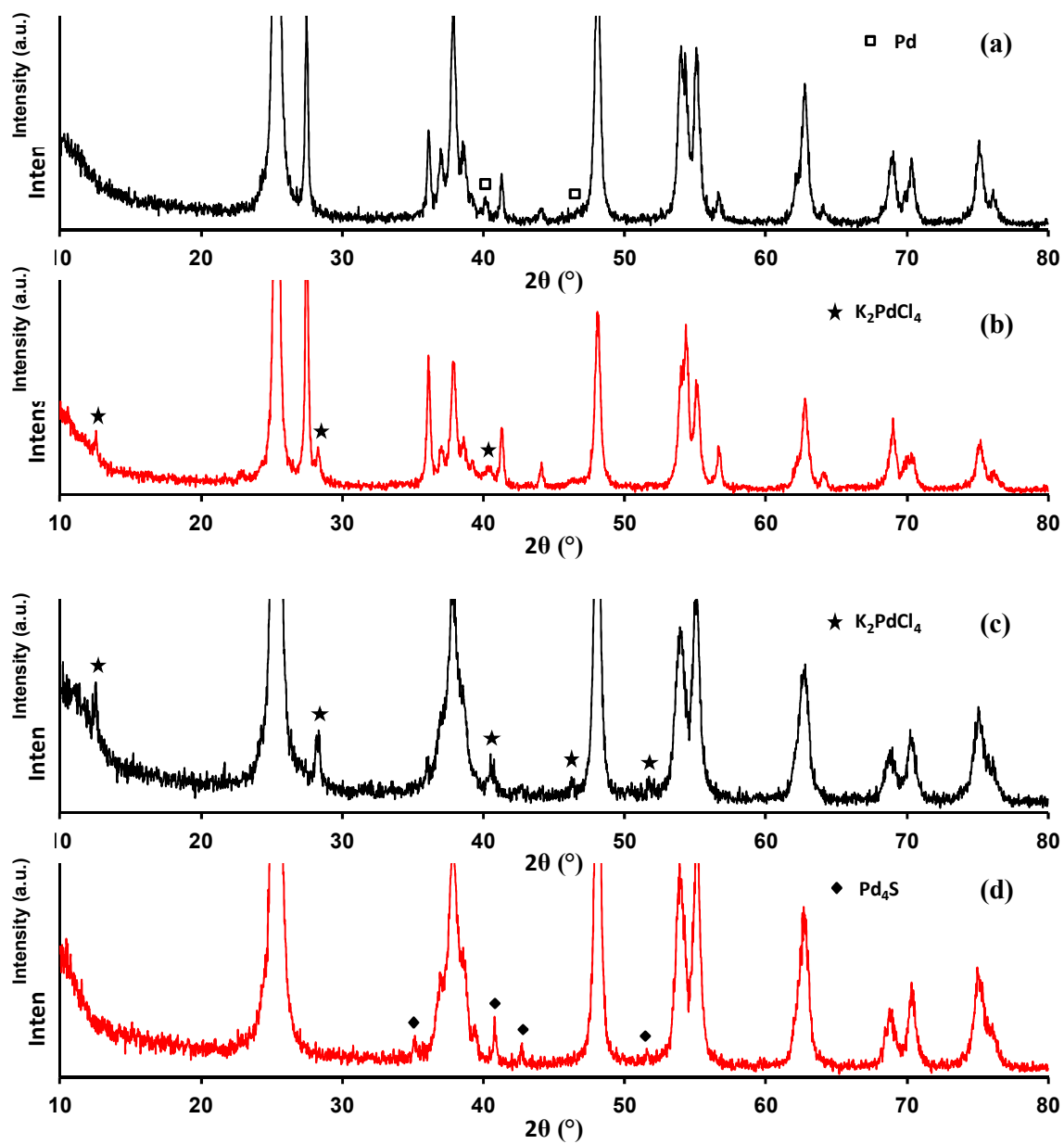


Figure S2. Diffraction patterns of the monometallic catalysts:
 (a) Pd_{N-Cl}(pH=11)C300R300/TiO₂ (P25), (b) Pd_{K-Cl}(pH=1)C300R300/TiO₂ (P25),
 (c) Pd_{K-Cl}(pH=1)C300R300/TiO₂ (DT51), (d) Pd_{N-Cl}(pH=11)C300R300/TiO₂ (DT51).

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