SUPPLEMENTARY MATERIAL

The influence of catalyst amount and Pd loading on the H$_2$O$_2$ synthesis from hydrogen and oxygen

Nicola Gemo[a,b], Stefano Sterchele[b,c], Pierdomenico Biasi[b,d],*, Paolo Centomo[c], Paolo Canu[a], Marco Zecca[c], Andrey Shchukarev[d], Krisztián Kordás[e], Tapio O. Salmi[b], Jyri-Pekka Mikkola[b,d]

[a]   Dr. N. Gemo, Prof. P. Canu, Dipartimento di Ingegneria Industriale
        University of Padova, via Marzolo 9, 35131, PADOVA, Italy

[b]   Dr. N. Gemo, Dr. P. Biasi, Prof. T. Salmi, Prof. J.-P. Mikkola, Department
        of Chemical Engineering, Åbo Akademi University, Biskopsgatan 8, ÅBO-
        TURKU, 20500, Finland
        E-mail: bpierdom@abo.fi

[c]   Dr. S. Sterchele, Dr. P. Centomo, Prof. M. Zecca, Dipartimento di Scienze
        Chimiche, University of Padova, via Marzolo 8, 35131, PADOVA, Italy

[d]   Dr. P. Biasi, Dr. A. Shchukarev, Prof. J.-P. Mikkola, Department of
        Chemistry, Umeå University, SE-90187 UMEÅ, Sweden

[e]   Dr. K. Kordás, Microelectronics and Materials Physics Laboratories
        University of Oulu, FI-90014 OULU, Finland

        Supporting information for this article is given via a link at the end of the
        document.

Section 1, Catalyst dispersion

The method for the estimation of metal dispersion from TEM data is described in the following. The calculation was based on the average nanoparticle size obtained from the analysis of the size distribution, as assessed from TEM microphotographs. The following hypotheses were assumed:

1) the Pd nanoparticles are spheres, and in each sample they have the same diameter (d_{NP}), equal to the average nanoparticle size;
2) the atomic radius of Pd, r_{Pd}, is 137 pm;
3) the metal in the nanoparticles has the fcc structure;
4) the surface atom are contained in a monoatomic spherical crown and their number is calculated as the difference between the total number of the atoms in a nanoparticle (N_{NP}) and the number of the atoms contained in the spherical "core" (N_C) just beneath the monoatomic spherical crown;
5) the diameter of the spherical "core" (d_C) was calculated as (d_{NP} - $r_{Pd} \cdot \sqrt{3}$); the factor $\sqrt{3}$ was used instead of 2 to allow for the fact that in the compact structures the atoms of a layer sit on holes of the layer immediately underneath;
6) N_{NP} was calculated as the ratio between the volume of the spherical nanoparticle and of the atomic volume;
7) N_C was calculated as the ratio between the volume of the spherical "core" and of the atomic volume
8) per cent dispersion was eventually calculated as $100 \cdot (1-N_C/N_{NP})$

The overall equation for the dispersion is thus the following:

$$D_{Pd} = 100 \left[1 - \left(1 - \frac{r_{Pd}\sqrt{3}}{d_{NP}} \right) \right] \qquad 1$$

Section 2, H₂ conversion analysis

The analysis of H₂ consumption helps to clarify the role of each reaction during the experiments. Moreover, it helps to spot the occurrence of mass transfer limitations. According to the stoichiometry of the reactions involved, the moles of H₂ consumed, $n_{H_2}^R(t)$, correspond to the sum of the moles of H₂O₂ and H₂O produced. Therefore, the actual H₂ consumption at time t, i.e. $X_{H_2}(t)$ was calculated according as:

$$X_{H_2}(t) = \frac{n_{H_2}^R(t)}{n_{H_2}^0} = \frac{([H_2O_2]_t [H_2O]_t +)}{n_{H_2}^0} \qquad 2$$

where $[H_2O_2]_t$ and $[H_2O]_t$ represent the concentrations of H₂O₂ and H₂O at time t, respectively, V^L is the volume of the liquid phase and $n_{H_2}^0$ are the moles of H₂ introduced in the reactor and $n_{H_2}^R$ those that already converted, equal to the moles of water and peroxide produced. Since the value of $n_{H_2}^R$ was independently measured by pressure difference[1] , after its addition to the autoclave, equation (2) also verifies the H₂ mass balance, being X_{H2} from H₂O and H₂O₂ measurements equal to 1 when H₂ disappears. The estimated error was within 5%, confirming the consistency of the experimental procedures and analysis.
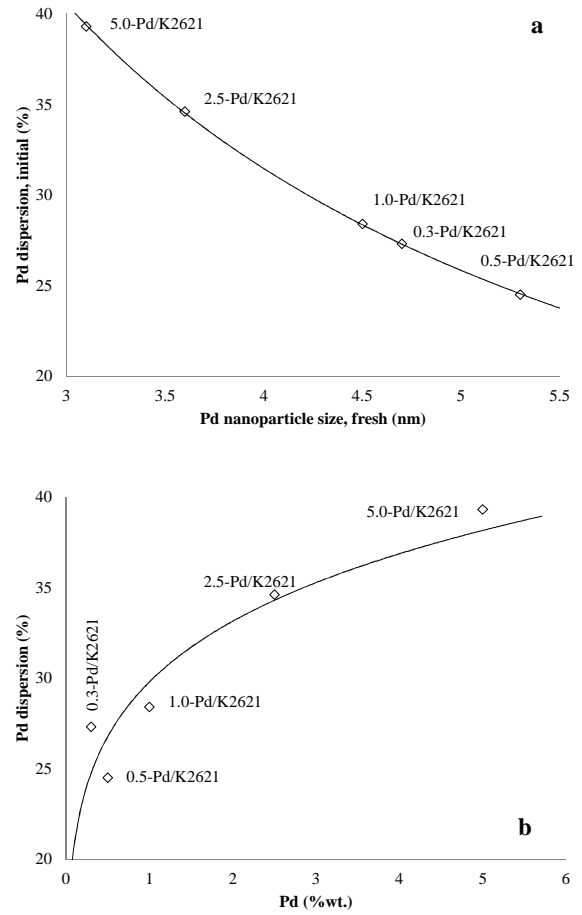
Supplementary Figure 1. Relationship between the nanoparticle size (a) and the Pd load (b) and the metal dispersion in the fresh catalysts X-Pd/K2621. Lines are theoretical predictions based on eq. (1)

The time profiles of H₂ consumption calculated according to Equation (2) are reported in Supplementary Figure 2. A comparison of H₂O₂ and H₂O concentration profiles (Figure 5 and Figure 6 in the manuscript) with the H₂ consumption (Supplementary Figure 2) is extremely interesting. Two stages are clearly identified in each experiment, remarked by the time of complete H₂ consumption ($X_{H2} = 1$). In the first stage, i.e. for $X_{H2} < 1$, all the reactions of Scheme 1 in the manuscript occur, with the synthesis reactions prevailing over hydrogenation and disproportionation; both the peroxide and the water concentrations rapidly increased, though with different rates. H₂O₂ concentration reached a maximum at full H₂ conversion. In the second stage, after H₂ complete conversion, only the disproportionation reaction may occur, lacking H₂. If that is the case, a slow decrease of the H₂O₂ concentration (and a slow increase of the H₂O concentration) is observed. Disproportionation appears very slow compared to all the other reactions (Figure 5 and Figure 6 in the manuscript) and its disproportionation constant can be estimated.
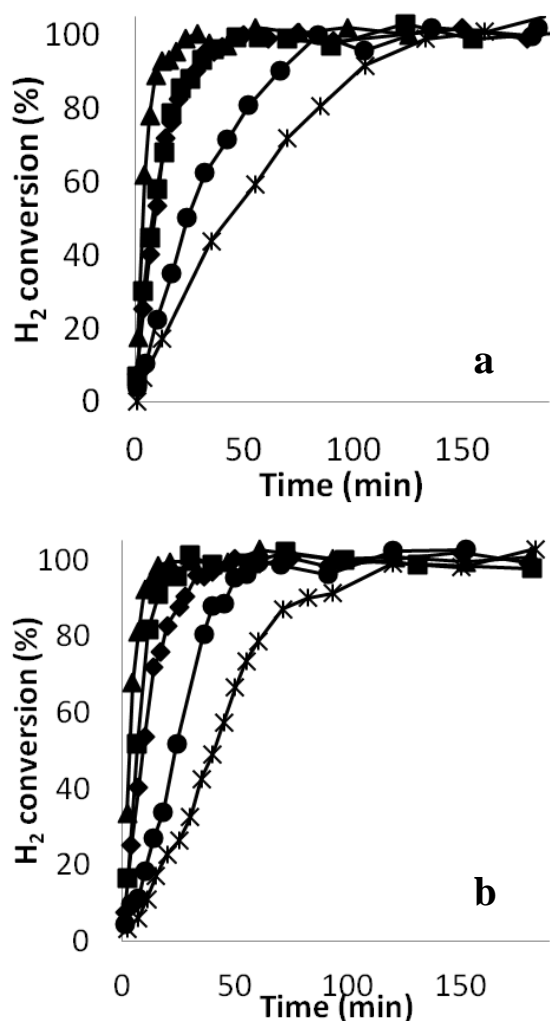
Supplementary Figure 2. H_2 conversion as a function of time with different amounts of 1.0-Pd/K2621 (a; * 0.075 g; ● 0.110 g; ♦ 0.150 g; ■ 0.300 g; ▲ 0.500 g) and the same amount (0.150 g) of different catalysts (b; * 0.3-Pd/K2621; ● 0.5-Pd/K2621; ♦ 1.0-Pd/K2621; ■ 2.5-Pd/K2621; ▲ 5.0-Pd/K2621).

A quantitative comparison of the H_2 consumption rates is interesting: in case of external mass transfer limitation, the H_2 consumption rate should be observed to increase proportionally less and less with increasing amount of the active metal. H_2 consumption rate can be estimated as slope of the H_2 conversion time profiles (Supplementary Figure 2). In a batch reactor, the profiles of H_2 conversion will never be linear in time (unless the reaction rate is independent of reactants concentration, i.e. all partial reaction orders=0), so that a unique definition of the slope is arbitrary. However, Supplementary Figure 2 shows that H_2 consumption was quite linear up to values even higher than 60% (this is likely not true, but still an acceptable approximation, for the two experiments with the 0.075 and 0.110 g of 1.0-Pd/K2621; Supplementary Figure 2a, * and ●). Hence, $X_{H2} = 0.6$ was chosen as the reference value to estimate the H_2 consumption rate Note that this convention is more general than taking the slope at a fixed reaction time, whose value can change dramatically for different conditions (of temperature, catalyst concentration, etc). $X_{H2} = 0.6$ is indeed achieved at very different times. Estimated values are reported in Supplementary Figure 3, as a function of Pd in the liquid phase. A direct correlation with Pd amount is evident, clearly proving that all the experiments were carried out within the kinetic regime.
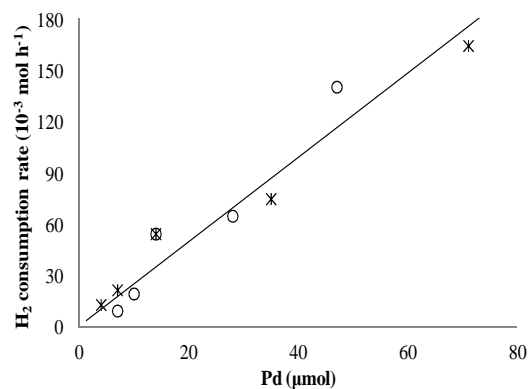

Supplementary Figure 3. H_2 consumption rates at 60% H_2 conversion: ○, alternating catalyst amount (1 wt.% Pd/K2621); *, alternating Pd content (catalyst amount 0.150 g).

For the first set of experiments this profile is expected, since the same catalyst was used. For the second set of experiments, i.e. varying the Pd loading of the catalyst, this is not obvious, because both the metal amount and its dispersion were changed from one experiment to another. However, the total palladium amount was changed from 4 to 71 µmol (almost a 20-fold increase), but the metal dispersion, i.e. the specific active surface area, underwent a less than two-fold change. In fact, the total amount of the surface palladium, i.e. the total active surface area, depends almost exclusively on the Pd load (0.150 g of catalyst were used in this set of experiments). As a consequence, the total Pd amount was directly proportional also to the surface Pd amount employed (Supplementary Figure 4).

Section 3, Disproportionation reaction

After H_2 complete conversion (second stage of the experiments), the disproportionation of H_2O_2 into water and O_2 was the only reaction occurring, if any, and causes the slow decrease of H_2O_2 concentration. Interestingly, it was slower than the reactions taking place in the first stage of the process (Figure 5 and Figure 6 in the manuscript). With the 0.3-Pd/K2621 and 0.5-Pd/K2621 catalysts (Figure 6 in the manuscript) the decrease of the peroxide concentration was negligible. The disproportionation apparent kinetic constant (k'_d) was estimated from the analysis of the experimental data collected after H_2 complete conversion using the integrated form of the first order kinetic law:
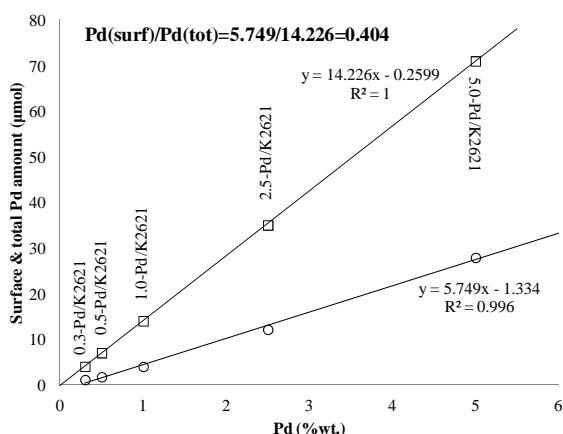
Supplementary Figure 4. Relationship between the Pd load of the catalysts and the surface (○) and total (□) Pd amount.
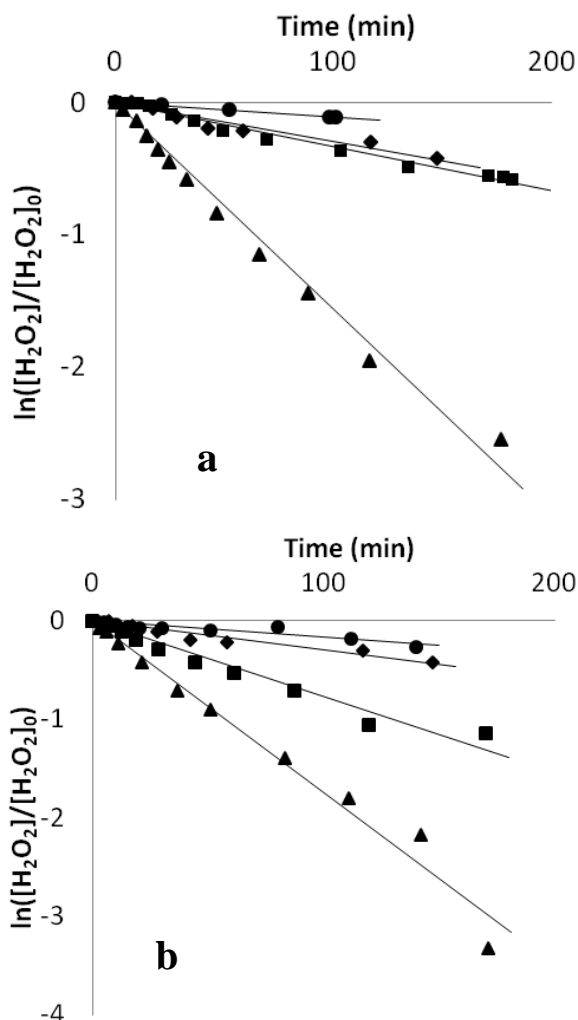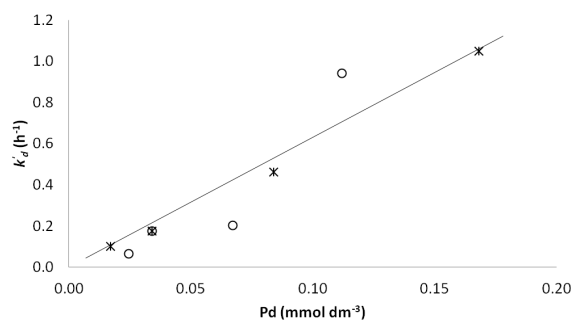

Supplementary Figure 5. Fitting of the disproportionation data (collected after H_2 complete conversion) according to Equation 3 from the experiments with different amounts of the 1.0- Pd/K2621 (a; 0.110 g ●, 0.150 g ♦, 0.300 g ■, 0.500 g ▲) and fixed amount (0.150 g) of X-Pd/K2621 (X=0.5 ●, 1.0 ♦, 2.5 ■ and 5.0 ▲).

$$ln\left(\frac{[H_2O_2]_t}{[H_2O_2]_0}\right) = -(k'_d)t \qquad 3$$

A linear decrease of $\ln[H_2O_2]$ with time was observed in both sets of experiments, as shown in Supplementary Figure 5. This confirmed that the disproportionation was first order in hydrogen peroxide. k'_d values were evaluated as the slopes of the lines fitting the experimental data.

Interestingly, when k'_d values from both sets of experiments were represented together as a function of catalyst concentration (molar amount of active metal over the volume of the liquid phase) a linear plot was obtained (Supplementary Figure 6) if the same amount of catalyst with different loading is used. Varying the total catalyst amount somehow deviates from linearity. This shows that the disproportionation constant was directly proportional to metal concentration, the activity of Pd being the same also when different catalysts were used. In other words the disproportionation reaction was first order in palladium, with an intrinsic kinetic constant of 6.3 dm^3 $mmol_{Pd}^{-1}$ h^{-1}, extrapolated from the linear fitting of k'_d. This value is comparable with values reported in our previous paper[2], for a different catalyst.

Supplementary Figure 6. Apparent disproportionation constant as a function of Pd concentration in the liquid phase: ○, different amounts of the 1.0- Pd/K2621; *, fixed amount of X-Pd/K2621.

References

1 P. Biasi, N. Gemo, J. R. Hernández Carucci, K. Eränen, P. Canu and T. O. Salmi, *Industrial and Engineering Chemistry Research,* 2012, **51**, 8903-8912 (DOI:10.1021/ie2021398).

2 N. Gemo, P. Biasi, P. Canu, F. Menegazzo, F. Pinna, A. Samikannu, K. Kordás, T. Salmi and J. Mikkola, *Topics in Catalysis,* 2013, **56**, 540-549 (DOI:10.1007/s11244-013-0009-2).