Influence of Metal Precursors and Reduction Protocols on the Chloride-Free Preparation of Catalysts for the Direct Synthesis of Hydrogen Peroxide without Selectivity Enhancers

Stefano Sterchele,^[a, b] Pierdomenico Biasi,^[b, c] Paolo Centomo,^[a] Andrey Shchukarev,^[d] Krisztián Kordás,^[c, d] Anne-Riikka Rautio,^[d] Jyri-Pekka Mikkola,^[b, c] Tapio Salmi,^[b] Patrizia Canton,^[e] and Marco Zecca^{*[a]}

In memory of Professor Benedetto Corain (July 8th 1941–September 24th 2014), a catalyst for our research activities and ideas.

Different metal precursors and reducing agents were applied in the preparation of 1 wt% Pd catalysts supported on commercial ion-exchange resin (Lewatit K2621) and used in the direct synthesis of H_2O_2 . The catalysts were characterized by using TEM and their performance was evaluated in the direct synthesis of H_2O_2 (in a batch and semi-batch reactor) to investigate the relationship between the catalyst preparation methods, morphology, and catalytic performance. As expected, both the choice of the Pd precursor and the reduction conditions had a strong influence on the size and size distribution of the resulting supported nanostructured metal nanoparticles and, consequently, on the catalytic performance. The best combination of metal precursor and reduction agent was $[Pd(NH_3)_4]SO_4$ reduced with hydrogen. This catalyst had the largest average size of the Pd nanoparticles and the broadest size distribution.

Introduction

Hydrogen peroxide is a versatile and green commodity chemical used, for example, as a bleaching agent in the pulp and paper industry and in wastewater treatment.^[1] Its worldwide

	— to laborious wastev
 [a] Dr. S. Sterchele, Dr. P. Centomo, Prof. M. Zecca Dipartimento di Scienze Chimiche Università degli Studi di Padova via Marzolo 8, I35131 Padova (Italy) E-mail: marco.zecca@unipd.it 	direct synthesis of small-scale, on-site, tions, which are oft The fundamenta
[b] Dr. S. Sterchele, Dr. P. Biasi, Prof. JP. Mikkola, Prof. T. Salmi Department of Chemical Engineering Laboratory of Industrial Chemistry and Reaction Engineering Johan Gadolin Process Chemistry Centre Åbo Akademi University Biskopsgatan 8, FI-20500 Åbo-Turku (Finland)	viewed recently, ^[1-5] mechanism still re the three-phase (Scheme 1). Metallio tion ^[1-3, 12, 15] and is
[c] Dr. P. Biasi, Dr. K. Kordás, Prof. JP. Mikkola Department of Chemistry Chemical-Biochemical Centre (KBC), Technical Chemistry Umeå University SE-90187 Umeå (Sweden)	most studies, the o typically by the im In general, the im a subsequent redu
 [d] Dr. A. Shchukarev, Dr. K. Kordás, Dr. AR. Rautio Faculty of Technology, Microelectronics and Materials Physics Laboratories EMPART Research Group of Infotech Oulu University of Oulu FI-90014 Oulu (Finland) 	temperature (473– though this is a sin catalysts, both in a
 [e] Dr. P. Canton Department of Molecular Sciences and Nanosystems Università Ca' Foscari di Venezia via Torino 155/b, 30170 Venezia-Mestre (Italy) Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/ 	$H_2 + O_2 \rightarrow H$ $H_2 + \frac{1}{2}O_2 \rightarrow H_2 + H_2O_2 \rightarrow H_2O_$
CCTC.201600021.	Scheme 1. Reaction net

demand is increasing, and for some applications a process alternative to the auto oxidation process is desirable. It has a number of shortcomings: the capital expenditure (CAPEX) is high, it is affordable only for large-scale operation, and leads to laborious wastewater treatment. Consequently, the catalytic direct synthesis of H_2O_2 (CDS) could be a viable route for small-scale, on-site, and on-demand production of dilute solutions, which are often required.^[1]

The fundamental aspects of the CDS process have been reviewed recently,^[1–5] but many issues that concern the reaction mechanism still remain unclear because of the complexity of the three-phase system^[6–14] and the reaction network (Scheme 1). Metallic Pd is the most active catalyst for this reaction^[1–3,12,15] and is applied generally in a supported form. In most studies, the catalysts utilized in the CDS were prepared typically by the impregnated solids are typically subjected to a subsequent reduction/calcination step at medium to high temperature (473–773 K) often under a hydrogen flow. Although this is a simple way to produce supported noble-metal catalysts, both in academia and industry, catalysts for the CDS

$H_2 + O_2 \rightarrow H_2O_2$	ΔH° = -187.8 Kj·mol ⁻¹	(1)
$H_2 + \frac{1}{2} O_2 \rightarrow H_2 O$	ΔH° = -285.8 Kj·mol ⁻¹	(2)
$H_2 + H_2O_2 \rightarrow 2 H_2O$	ΔH° = -98.2 Kj·mol ⁻¹	(3)
$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$	ΔH° = -379.4 Kj·mol⁻¹	(4)

Scheme 1. Reaction network of H₂O₂ direct synthesis (side-reactions shaded).

ChemCatChem 2016, 8, 1564-1574



often give rise to a moderate activity or modest selectivity towards $H_2O_2^{\,\,[2]}$

If crosslinked ion-exchange resins such as sulfonated polystyrene/divinylbenzene (S-PS/DVB) are applied as the catalyst support, a different approach is possible. The ion-exchange ability and hydrophilicity of S-PS/DVB resins such as Lewatit K2621 make the introduction of cationic metal precursors into the support straightforward. The procedure entails a simple ion-exchange step,^[15-22] in which a precursor such as $[Pd(NH_3)_4]^{2+}$ in water or $[Pd(OAc)_2]$ (AcO⁻ = CH₃COO⁻) in a (preferably polar) organic solvent replaces the counterions (H⁺ or Na⁺) of the sulfonic groups of the resin. A remarkable advantage of S-PS/DVB as an ion-exchanger is that the concentration and the distribution of the sulfonic groups inside the polymer can be controlled,^[19,20] and they are optimized for continuous operation. To expand the scope of this method, the ion-exchange step can be replaced by a ligand-exchange reaction, in which functional groups that are good ligands for the metal to be introduced enter its coordination sphere.^[23,24] However, the commercial availability, the relatively low cost of S-PS/DVB resins, their good properties, and their full compatibility^[25] with the working conditions for CDS make them particularly attractive as heterogeneous catalytic materials. Moreover, a number of industrial processes based on these materials as either acid $\mathsf{catalysts}^{\scriptscriptstyle[23,24,26,27]}$ or catalytic $\mathsf{supports}^{\scriptscriptstyle[26,27]}$ have already been implemented (e.g., methylisobutylketone and methyl-tert-butylether processes, Bisphenol A synthesis, direct synthesis of alcohol from olefins and syn-gas, and the hydrogenation of different substrates).

Although the open literature on CDS is pretty extensive, the problem of the role of the different metal precursors and reduction protocols on the catalytic performance has not yet been addressed systematically. Only recently, Sankar et al.^[28] demonstrated that an excess of chloride ions during the impregnation stage produced a stable bimetallic Au/Pd catalyst with a smaller size distribution and better productivity in CDS than that prepared using the more traditional and established routes. The performance of the materials depended strongly on the type of Pd and Au precursors used and, in particular, the use of a tetrahalide complex seemed to be the key factor that influenced the size of the nanoparticles marked-

ly and, consequently, the catalytic behavior of the resulting material.

In this study, we examined the dependence of the catalytic performance on the synthesis conditions and, in particular, on the nature of the metal precursor applied in the ion-exchange step as well as the reducing agent applied in the subsequent reduction step. We screened three different metal precursors and five different reduction protocols. The three metal precursors, [Pd(NH₃)₄]SO₄, Pd(NO₃)₂, and [Pd(AcO)₂], were introduced into the K2621 resin and subsequently reduced under a continuous hydrogen flow in which the catalyst was immersed in a THF suspension of the ion-exchanged materials. It is well known^[1,2,8,29] that bromide or chloride ions, in combination with an acid, are able to enhance the selectivi-

CHEMCATCHEM Full Papers

ty of the catalysts. To avoid the unintentional presence of these promoters that could hinder the real catalytic behavior of the pristine catalyst, we used halide-free conditions in both the preparation of the catalysts and the catalytic runs. K2621 ion-exchanged with [Pd(NH₃)₄]SO₄ was employed to screen the different reducing agents, which included hydrogen flowing in a suspension of the precatalyst (either at room temperature and atmospheric pressure or 333 K and 0.5 MPa); an aqueous solution of formaldehyde (37 wt%);^[21] a solution of methanol in water (50% v/v);^[15] and an aqueous solution of sodium borohydride.^[30] The different conditions applied to prepare the two sets of catalysts (different precursor and same reducing agent; same precursor and different reducing agents) were expected to lead to different morphologies of the supported nanostructured phase, which was investigated by using TEM. After the screening of the catalysts under batch conditions, a few selected nanocomposites were tested in semi-batch experiments at 283 K and 50 bar to mimic conditions of CDS feasible for industrial operation.

Results and Discussion

The fresh metal-polymer nanocomposites were characterized by using TEM and elemental analysis (Table 1). A commercial 1 wt% Pd/C catalyst was applied as the benchmark catalyst and was also characterized by TEM (Table 1). The size distribution of the Pd nanoparticles in the fresh catalysts were assessed by TEM, for which at least 250 particles were counted for each sample.

This showed that, for all the samples, most of the individual aggregates had a spherical shape and were well dispersed in the polymeric support. They generally have a lognormal size distribution,^[31] with moderate statistical dispersions (Figure 1 and Table 1). The Pd aggregates in the samples 1PdK/N/H and 1PdK/A/H (Figure 2A–B and C–D, respectively) feature broad distributions centered at 4.4 and 6.7 nm, respectively. 1PdK/S/H has a broader size distribution with an average diameter of 12.2 nm (Figure 1). The commercial 1 wt% Pd/C used as the benchmark showed the narrowest size distribution centered at 3.8 nm.

Table 1. Analytical data for the 1 wt% Pd catalysts supported on K2621.							
Sample	Reductant	Metal precursor	Pd found [wt%]	Fresh d [nm] ^[c] SC ^[d]		Spent d [nm] ^[c] SC ^[d]	
1PdK/S/H	$H_{2}^{[a]}$	[Pd(NH ₃) ₄]SO ₄	1.01	12.2	1.06	10.2	1.06
1PdK/N/H	$H_{2}^{[a]}$	Pd(NO ₃) ₂	1.03	4.4	1.46	4.18	0.81
1PdK/A/H	$H_{2}^{[a]}$	Pd(OAc) ₂	1.03	6.7	1.40	n.d.	n.d.
1PdK/S/F ^[e]	HCHO	[Pd(NH ₃) ₄]SO ₄	1.00	8.1	1.44	n.d.	n.d.
1PdK/S/M	MeOH	$[Pd(NH_3)_4]SO_4$	1.00	5.5	1.61	n.d.	n.d.
1PdK/S/B	$NaBH_4$	$[Pd(NH_3)_4]SO_4$	1.02	3.83	0.88	n.d.	n.d.
1PdK/S/H _{PT} ^[f]	H ₂ ^[b]	$[Pd(NH_3)_4]SO_4$	1.02	4.80	0.91	n.d.	n.d.
1Pd/C	-	-	-	3.68	0.83	4.03	1.21

[a] Reduction as described in Supporting Information Section 1.3.1; [b] Reduction as described in Supporting Information Section 1.3.5; [c] Diameter estimated by lognormal fit on size distribution data; [d] Skewness coefficient (SC) calculated by lognormal parameters on size distribution data as reported in Ref. [36]; [e] From Ref. [21]; [f] From Ref. [22].





Figure 1. Nanoparticle size and size distribution of the fresh catalysts in the first set (different metal precursors, reduction with hydrogen) and of benchmark catalyst. 1Pd/C: commercial catalyst 1% Pd on carbon (benchmark); 1PdK/N/H: 1% Pd on K2621 from $Pd(NO_3)_2$ precursor reduced with hydrogen; 1PdK/S/H: 1% Pd on K2621 from $[Pd(NH_3)_4]SO_4$ precursor reduced with hydrogen; 1PdK/A/H: 1% Pd on K2621 from $[Pd(OAc)_2]$ precursor reduced with hydrogen.



Figure 2. TEM images of A, B) fresh 1PdK/N/H material (both the scale bars are 50 nm); C, D) fresh 1PdK/A/H material (the scale bars are 100 and 50 nm, respectively); E, F) fresh 1PdK/S/H material (both the scale bars are 100 nm).

In general, a poor relationship was observed between the average size of Pd nanoparticles in the hydrogen-reduced catalysts 1PdK/S/H, 1PdK/N/H, and 1PdK/A/H and the pore size in K2621 swollen in THF, which is the solvent employed in the reduction stage. This is different from what is usually observed with gel-type resins and hyper-cross-linked resins, in which the reduction of the metal precursors and the formation of the nanoparticles takes place inside the swollen polymer framework or in permanent, very small mesopores so that the size

of the nanoparticles is strictly comparable with the pore diameters in the polymer mass.^[32-39] Apparently, the polymer framework of K2621 did not swell in THF: no gel phase was detected by inverse size-exclusion chromatography (ISEC; Table S2). This suggests that the reduction of Pd^{II} occurred on the surface of the mesopores of the resin, which had diameters of 13 and 43 nm. These sizes are too large to give the effective control of the nanoparticle size observed with swollen gel-type resins^[34-35] or hyper-cross-linked resins.^[37,39] Hence, the final size of the metal nanoparticles is expected to be controlled only by the kinetics of their formation.^[40] In this case, the ratio between their growth rate and the reduction-nucleation rate should increase as the nanoparticles size and size distribution become larger and broader.^[40] This ratio should, therefore, increase in the following order of the metal precursor: $Pd(NO_3)_2 < [Pd(OAc)_2] < [Pd(NH_3)_4]SO_4$. Although it is clear that different morphologies of the nanostructured Pd phase ensue from different precursors, it is not trivial to understand how this occurs.^[41] The speciation of Pd^{II} to be reduced is expected to affect the rate of reduction directly. For instance, the $[Pd(NH_3)_4]^{2+}$ ion, which is a stable complex of Pd^{II}, is also likely more difficult to reduce, and the relevant 1PdK/S/H catalyst contained clusters with a much larger size and size distribution of metal nanoparticles than that of 1PdK/N/H and 1PdK/A/H. In the synthesis of Pt nanoparticles, the final size and morphology were affected by the presence of methylamine, a good ligand for the metal to be reduced, which stabilized the most defective facets of the growing nanoparticles.^[41] It cannot be ruled out that NH₃ played a similar role when [Pd(NH₃)₄]SO₄ was used as the precursor in the preparation of our catalysts.

In line with the arguments above, the use of different reducing agents should lead to metal nanoparticles of different sizes and morphologies. To gather information on the reducing agent, a second set of catalysts was prepared upon the ion-exchange of K2621 with [Pd(NH₃)₄]SO₄ and its subsequent reduction with aqueous solutions of either methanol (1:1, v/v; reflux temperature),^[8] formaldehyde (37%; reflux temperature),^[21] or sodium borohydride ($\approx 1 \text{ M}$; room temperature).^[30] These treatments produced 1PdK/S/M, 1PdK/S/F, and 1PdK/S/B, respectively. It is well known that noble metals can be produced upon reduction of their compounds with alcohols and aldehydes under mild conditions,^[42] which can be applied for the preparation of Pd catalysts supported on resins.^[16,34,43] However, it is difficult to compare published data because different precursors and resins have been used so far.^[30,44] For comparison, a second batch of 1PdK/S/H was produced upon reduction with H₂ and in THF at a high temperature (333 K) and pressure (0.5 MPa).^[22] It will be hereafter referred to as 1PdK/S/ H_{PT} The size distributions of the metal nanoparticles in this second set are reported in Figure 3.

In this second set of catalysts the relationship between the average values of the nanoparticle diameter and of the resin mesopores was poor. 1PdK/S/B, 1PdK/S/F, and 1PdK/S/M were prepared from suspensions of ion-exchanged K2621 in an aqueous environment. ISEC analysis of K2621 in a sodium sulfate solution in water showed clearly that a gel phase was formed in the resin (Table S2). This suggests that some of the

ChemPubSoc Europe



Figure 3. Nanoparticle size and size distribution of the fresh catalysts of the second set (same metal precursor, different reduction agents). 1PdK/S/F: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with formaldehyde; 1PdK/S/B: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with sodium borohydride; 1PdK/S/M: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with methanol; 1PdK/S/H_{PT}: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with hydrogen; 1PdK/S/H: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with hydrogen at 333 K and 0.5 MPa.

nanoparticles were formed in the swollen polymer framework, although this did not lead to the full control of the metal nanoparticle morphology. This is in line with previous findings on the reduction of Pd^{II} loaded onto K2621 from $[Pd(OAc)_2]$ and reduced with aqueous methanol or ethanol.^[16]

In the set of catalysts prepared from [Pd(NH₃)₄]SO₄, the smallest nanoparticles were achieved in 1PdK/S/B (NaBH₄ reduction), and the largest ones were observed in 1PdK/S/F (formaldehyde reduction^[22]). In the latter case, the assessment of the nanoparticle size was difficult, mainly because of the relatively small number of nanoparticles detected.[22] The size distribution of nanoparticles of $1PdK2621S/H_{\mbox{\scriptsize PT}}$ (obtained from [Pd(NH₃)₄]SO₄ and reduction with H₂/THF in an autoclave at 0.5 MPa and 333 K) has a lognormal shape (Figure 3). The nanoparticle size was much smaller and distributed more narrowly in comparison with 1PdK/S/H (and generally smaller and less dispersed in comparison with all the other catalysts too). At a relatively high temperature and pressure, the reduction rate was expected to be comparatively high and this could again allow for the comparatively small nanoparticle size.[40] Moreover, the total number of counted Pd aggregates was remarkably high for 1PdK/S/HPT, which indicates that this reduction protocol generated a large number of nanoparticles in the outer portion of the polymer matrix (Figure 4).

Catalytic performance under batch conditions

The catalytic performance of our catalysts depended on the metal precursor used in the preparation of materials and is illustrated in Figures S3–S6. The concentrations of products (H_2O_2 and water), as well as the H_2 conversion and H_2O_2 selectivity data are presented as a function of time. The commercial catalyst, 1 wt % Pd/C, is included as the benchmark.

CHEMCATCHEM Full Papers



Figure 4. TEM images of A, B) fresh 1PdK/S/F material (the scale bars are 50 and 10 nm, respectively); C, D) fresh 1PdK/S/B material (both the scale bars are 100 nm); E, F) fresh 1PdK/S/M material (the scale bars are 50 and 5 nm, respectively); G, H) fresh 1PdK/S/H_{PT} material (both the scale bars are 100 nm).

The concentration profiles of the products (Figures S4 and S6) illustrate that there are two reaction stages for almost all the catalysts. In the first stage, the concentration of the products increased relatively quickly and linearly (at least in the first 10–30 min after the reaction onset). The slopes of these initial linear portions of the kinetic plots represent the initial rates of H_2O_2 and H_2O production, respectively. Their values were used to calculate the initial selectivity as described in the Experimental Section. The two catalysts obtained with hydrogen as the reducing agent (1PdK/S/H and 1PdK/S/H_{PT}) showed a long induction time in the production of water. The changes in the product concentrations were much smaller, if any, in the



second stage (Figures S4 and S6): the amount of H_2O_2 either decreased slowly or not at all and the amount of water increased slowly. H_2 was always consumed completely in the first stage so that the consumption of H_2O_2 in the second stage can be attributed only to its dismutation [Scheme 1, Eq. (4)]. Notably, the H_2 mass balance had an error of 3% only, hence the induction time is real and must depend on features of the catalysts.

From the initial rates of cumulative production $(H_2O+H_2O_2)$ and of H_2O_2 production, it is possible to calculate the initial productivities (Table 2).

The analysis of the initial rates of formation of the individual products also allowed us to estimate the initial selectivity values towards H_2O_2 (Table 2). This method, however, is not feasible if there is an induction period in the formation of one of the products, which was observed in the production of water over 1PdK/S/H_{PT} and 1PdK/S/H. In these cases, the catalysts seemed to undergo a transformation from a poorly active form into a much more active one for the production of water.

To circumvent this problem, the catalytic performance can be also evaluated in terms of $t_{1/2}$ (the time required to convert 50% of H₂) and selectivity at $t_{1/2}$ (S_{1/2}; Table 2). This approach is applicable to all the catalysts and will be used hereafter.

In the set of the catalysts reduced with hydrogen, at relatively low pressures and temperatures, the activity decreased generally (increasing t_{γ_2}) as the Pd nanoparticles increased in size (Figure 5). However, the selectivity increased with the increasing nanoparticle size. As the result, although t_{γ_2} was around eight times higher for 1PdK/S/H than for 1Pd/C, its S_{γ_2} increased almost fourfold. In general, all the polymer-supported catalysts were more selective than 1 wt% Pd/C and the two best ones gave selectivities comparable to those achieved with selectivity enhancers in other systems.^[1-5,25]

If the same reducing conditions with different precursors were applied in the catalyst preparation, the catalytic performance was apparently controlled by the particle size. The selectivity increased more or less linearly with the increasing nanoparticle size and the activity decreased steadily (Figure 5). Interestingly, the benchmark catalyst (1Pd/C) fits the correlation, which suggests that in this set of catalysts the interaction of the metal with the support does not play a significant role.

CHEMCATCHEM Full Papers



Figure 5. t_{h_2} [min] and selectivity at t_{h_2} [%] for 1Pd/C, 1PdK/N/H, 1PdK/A/H, and 1PdK/S/H. 1Pd/C: commercial catalyst 1% Pd on carbon (benchmark); 1PdK/N/H: 1% Pd on K2621 from Pd(NO₃)₂ precursor reduced with hydrogen; 1PdK/S/H: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with hydrogen; 1PdK/A/H: 1% Pd on K2621 from [Pd(OAc)₂] precursor reduced with hydrogen.

In line with previous discoveries,^[18,45] the best results are achieved with relatively large nanoparticles and a poor performance is correlated to the small nanoparticles. The selectivity towards H_2O_2 in CDS is expected to depend on the topology of the metal surface, which dictates the number and the nature of the catalytic sites.^[46] The largest nanoparticles, which have a flattened surface that may be more favorable to achieve high selectivity in CDS,^[54,47] were found in 1PdK/S/H. In general the size was modulated by the nature of the Pd precursor, likely because of the different kinetics of the nanoparticle formation.^[40]

The catalysts obtained upon the reduction of the precursors with hydrogen were analyzed by using X-ray photoelectron spectroscopy (XPS) to evaluate the atomic ratio between Pd^{II} and Pd^{0} . Indeed, the $Pd^{0}/Pd^{II}+Pd^{0}$ value depends on the reduction procedure and can affect the catalytic performance.^[18,45] The proportion of Pd^{0} is generally around 25% and not much different in 1Pd/C, 1PdK/N/H, and 1PdK/A/H (Table S3). In 1PdK/S/H it is around 37%, which could contribute to some

Catalyst	Pd amount ^(a)	Initial cumulative rate ^(b)	lnitial cumulative productivity ^(c)	Initial H ₂ O ₂ productivity ^(d)	Initial selectivity ^(e)	<i>t</i> ¹ / ₂ ^[f]	Selectivity at $t_{1/2}^{[e]}$
1Pd/C	1.41	235	6801	1401	21	6	18
1PdK/N/H	1.43	135.0	3792	877	23	10	23
1PdK/A/H	1.43	143.3	4032	1605	40	10	40
1PdK/S/H	1.42	40.9	1160	760	66	33	64
1PdK/S/M	1.42	83.8	2460	977	40	19	41
1PdK/S/F ^[g]	1.45	83.6	2343	792	34	17	34
1PdK/S/B	1.44	48.3	1388	313	23	29	24
1PdK/S/H _{PT} ^[h]	1.45	29.3	n.d.	n.d.	n.d.	38	50

ChemCatChem 2016, 8, 1564-1574



extent to the better selectivity of this catalyst, in line with the beneficial effect of Pd^0 for the direct synthesis.^[18]

However, the effect of the oxidation state, if any, here is minor, probably because the differences from one catalyst to another are not so great. Hence, the most important morphological parameter was apparently the nanoparticle size when hydrogen was the reducing agent.

Some changes of the nanoparticle size distributions were observed in the spent catalysts compared to the pristine materials (Figure S5). In the case of the 1Pd/C sample, a slightly broader distribution with an average size shifted to 4.0 nm (from 3.8 nm) was observed, which indicates moderate sintering as reported by Abate et al.^[48] and Chinta and Lunsford.^[49] In the case of 1PdK/N/H and 1PdK/S/H, no changes in the average nanoparticle size were observed, although the size distribution was somewhat narrower than that in the fresh catalyst for 1PdK/N/H.

The use of different reducing agents with $[Pd(NH_3)_4]SO_4$ as the metal precursor led to catalysts with Pd nanoparticles of different sizes. The smallest nanoparticles were obtained with NaBH₄, which is the most reactive of the reducing agents used and led to a fast reduction at room temperature. Methanol and formaldehyde are more sluggish and their water solutions were used at reflux temperature and for relatively long time. Moreover, to achieve with hydrogen a faster reduction of Pd^{II}, it was used at 333 K and 0.5 MPa. The performance of this set of catalysts (Figures S3 and S4) was then evaluated under experimental conditions similar to those employed for the first set. The experimental data were also treated in the same way (Table 2) using t_{V_2} and S_{V_3} .

Apparently, the catalysts obtained by using reducing agents other than hydrogen, are less active (higher $t_{1/2}$) and selective. At variance from the previous set of catalysts, in this one no relation between the nanoparticle size and the catalytic performance was found (Figure 6). Differently from the catalysts prepared by the reduction of the Pd precursor with hydrogen, this second set was prepared upon reduction in an aqueous environment. Under these conditions, K2621 formed a swollen gel phase and the Pd nanoparticles, or at least some of them, were likely formed inside this phase. One of the possible reasons for the apparent lack of any relationship between the catalytic performance and the nanoparticle size could be a different balance between the number of nanoparticles inside the gel phase and those on the surface of the mesopores. These two kinds of particles are expected to interact differently with the support and, therefore, to show different catalytic behaviors. Gas adsorption techniques could be helpful to assess their balance. For instance, these techniques were employed recently for the characterization of the Pd surface of CDS catalysts.^[50] However, if flexible materials, such as ion-exchange resins, are used as the catalyst support, the metal surface can be inaccessible to the gas to be adsorbed,^[51] and therefore, in our case these methods do not seem feasible. Another possible explanation for the lack of any relationship between the catalytic performance and the nanoparticle size could be a different balance between the areas of the exposed crystallographic faces if different reducing agents are employed. Recently, Kim et al.



CHEMCATCHEM

Full Papers

Figure 6. $t_{V_{2}}$ [min] and selectivity at $t_{V_{2}}$ [%] for 1Pd/C, 1PdK/S/B, 1PdK/S/M, 1PdK/S/F, 1PdK/S/H, and 1PdK/S/H_{PP} 1Pd/C: commercial catalyst 1% Pd on carbon (benchmark); 1PdK/S/F: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with formaldehyde; 1PdK/S/B: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with sodium borohydride; 1PdK/S/M: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with methanol; 1PdK/S/ H: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with hydrogen; 1PdK/S/H_{PT}: 1% Pd on K2621 from [Pd(NH₃)₄]SO₄ precursor reduced with hydrogen at 333 K and 0.5 MPa.

showed that the Pd{111} face was more selective in CDS than the Pd{100} face.^[47] Moreover, it was observed that different reduction agents affect the morphology of Pd nanoclusters.^[52] In this case, gas adsorption techniques, such as CO chemisorption monitored by diffuse reflectance infrared Fourier transform spectroscopy could be helpful in principle,^[50] but for the reasons illustrated above, they are not applicable for polymersupported catalysts.

The catalyst obtained by reduction with hydrogen at a relatively high pressure and temperature, $1\text{PdK/S/H}_{\text{PT}}$ was included in this second set of catalysts (the reduction conditions are anyway different from those used for the previous set). The increase in the H₂ pressure and in the reduction temperature led to a remarkable decrease in the nanoparticle size and to a much narrower size distribution (Figure 3). In spite of this, 1PdK/S/H_{PT} is not only appreciably less selective than 1PdK/S/H but also slightly less active. This was the result of a shorter induction time in the production of water for $1\mbox{PdK/S/H}_{\mbox{PT}}$ and a slower initial production of H_2O_2 (Figure S4). In line with the above reasoning, the worse catalytic performance in comparison with 1PdK/S/H could be the result of a different balance of the exposed crystallographic faces of Pd. In addition, the amount of Pd^{II} , which is detrimental for the reaction,^[18] is higher in 1PdK/S/H_{PT} than in 1PdK/S/H.

In any case, it is clear that any catalyst supported by K2621 is much better than Pd/C. This could arise from the acidity of the sulfonic groups contained in the resin.^[25] However, our data do not support this hypothesis.^[16] In the first place, the presence of CO_2 as the diluent of the reacting gases made the reaction medium acidic and this could have hindered the influence of the acidic groups of the resin. Moreover, even if this was not true, 1PdK/N/H was practically as selective as 1Pd/C,



although it contained sulfonic groups in the acidic form (in the absence of bases during the reduction step, the oxidation of H_2 produces H^+ , which should replace the metal ions that are reduced).

These results are of extremely high value as it was demonstrated that the size of the Pd nanoparticles^[53] is not the only parameter that affects the direct synthesis.

Catalytic results under semi-batch conditions

The best catalysts found in the batch experiments were tested by using a semi-batch reactor under conditions similar to those reported by Lunsford et al.^[12,49] The results were obtained under a total pressure up to 50 bar and without any selectivity enhancers. The catalytic results are reported in Table 3 and Figures S6 and S7.

Table 3. Results of the catalytic runs under semi-batch conditions over the Pd catalysts supported on K2621.						
Sample	H_2O_2 Rates [mol _{H2O2} mol _{Pd} ⁻¹ h ⁻¹] formation hydrogenation dismutation				S ^[a] [%]	H ₂ O ₂ [wt %]
1Pd/C	185	10754	254	66	3	0.1
1PdK/S/H 1PdK/S/H _{PT}	594 499	269 298	197 180	43 21	25 36	0.5 0.4
[a] Conversion of H_2 and selectivity towards H_2O_2 after 5 h.						

The production rates of H_2O_2 and H_2O were more or less constant up to 5 h (Figure S9), but the selectivity changed during the catalytic tests. As expected from the results obtained under batch conditions, the benchmark catalyst, 1PdC, was the most active with 66% of H_2 conversion, but gave the poorest selectivity. The 1PdK/S/H sample gave a moderate initial selectivity (\approx 50%), but it decreased almost linearly with time to 25%, and the conversion was almost constant (40–43%). This catalyst gave the highest final concentration of H_2O_2 (\approx 0.5 wt%). However, in this case the least active and most selective catalyst was 1PdK/S/H_{PT}. It had an initial selectivity towards H_2O_2 of around 70%, which decreased to 35% after 5 h, but in spite of a final conversion as low as 20%, the final concentration of H_2O_2 was \approx 0.4 wt% (almost as high as with 1PdK/S/H).

In these tests it was possible to estimate the H_2O_2 formation rate (Table 3). In addition, the estimated rates of H_2O_2 hydrogenation and dismutation were obtained by experiments using a methanol solution of 2 wt% H_2O_2 (Table 3). Compared to the catalysts supported on K2621, Pd/C had the lowest rate of H_2O_2 formation and the highest rate for its dismutation and hydrogenation. The hydrogenation of the product is particularly high (two orders of magnitude larger than all the others), which was apparently responsible for its very poor selectivity. However, the rates of the side-reactions for the resin-supported catalysts were all close to each other so that the main difference in the catalytic performance arose from the relative rates of H_2O_2 and H_2O formation. In particular the H_2O_2 formation rates obtained under both batch and semi-batch conditions were relatively similar, although the operational temperature was not the same and the H_2O_2 profile changed after \approx 90 min, as a consequence of the side-reactions.

In conclusion, the catalysts supported by K2621 prepared using [Pd(NH₃)₄]SO₄ and H₂ as the reducing agent gave a better performance in the CDS than the benchmark catalyst because they showed the best balance between the rates of H₂O₂ and H₂O formation and the rates of the side-reactions. In this way it was possible to achieve a final H₂O₂ concentration of 0.5 wt% without the use of any selectivity enhancers, such as acids or halides. These promising results confirm the hypothesis that the reaction conditions play an important role in the direct synthesis of H₂O₂ and that the catalyst has to be optimized to the reaction conditions used.^[54]

Conclusions

The aim of the present study was to understand how different conditions for the preparation of new, advanced polymer-supported monometallic Pd catalysts can affect the direct synthesis of H_2O_2 . For this purpose, we prepared two sets of catalysts, one using different metal precursors and the same reduction procedure and the other using the same metal precursor but different reduction procedures. The catalysts thus obtained were characterized by TEM to assess the morphological differences that arose from the different preparation conditions and to disclose

the existence of a relationship, if any, with the catalytic performance (activity, selectivity).

When different precursors were reduced with the same agent (hydrogen flowing through a THF suspension of the material to be reduced) were used, the activity decreased and the selectivity increased with the increasing size of the metal nanoparticles; in particular, the selectivity correlated very well with the nanoparticle size. The Pd^{II}/Pd⁰ ratio played only a minor role, if any. Apparently, the morphological changes, which controlled the nature and the relative number of the catalytic sites on the surface, depended only on the nanoparticle size. This indicates that the number of relatively poorly active and highly selective sites would increase at the expense of exceedingly highly active and poorly selective sites with the increasing nanoparticle size. The simple change of their relative numbers, and not of their intrinsic nature, is enough to explain this result. Therefore, the morphology of the metal surface apart from its curvature could be even the same in all these catalysts and the simple flattening of the active surface is desirable as far as the selectivity is concerned.

This is not the case if different reduction conditions (reducing agent and reaction medium or pressure and temperature) were applied for a single Pd precursor ($[Pd(NH_3)_4]SO_4$). In this case, there must be differences that depend on the reduction conditions. Our results demonstrate clearly that in the direct synthesis of H_2O_2 , the control of the dimensions of the nanoclusters is not always enough. Morphological features different from the curvature of the surface can also be important. An in-



spection of the literature suggests that the balance of the areas of the exposed crystal faces could play an important role. Moreover, with flexible supports such as ion-exchange resins (such as K2621), conditions that favor the swelling of the polymer framework during the preparation of the catalyst could lead to different results in comparison to conditions under which swelling is negligible. In this context, the balance between the number of active nanoparticles formed in the swellable domains of the support and the nanoparticles formed on the surface of permanent pores is expected to change and to lead to different catalytic performances. However, further work is needed to provide a stronger experimental support to these hypotheses.

The best combination of metal precursor and reduction conditions was [Pd(NH₃)₄]SO₄ for the ion-exchange step and hydrogen flowing through a THF suspension of Pd-exchanged K2621 at room temperature and atmospheric pressure. This gave a catalyst that featured the largest average size of the Pd nanoparticles and the broadest distribution thereof. This catalyst showed an initial rate of H_2O_2 production of 760 and 594 $mol_{H_2O_2}$ $mol_{Pd}^{-1}h^{-1}$ under batch and semi-batch conditions, respectively. It was, therefore, the most selective catalyst: the average initial selectivity was 66% (considering both experiments) and the instant value topped 70% shortly after 50% conversion under batch-wise operation. This catalyst, as well as most of the catalysts supported on K2621, outperformed the benchmark 1 wt % Pd/C catalyst under the reaction conditions employed in this work. Moreover, no selectivity enhancers in the form of acids or halide ions were present.

Experimental Section

Catalyst Synthesis

Unless otherwise stated, all the reagents and the materials were used as received. A batch of Lewatit K2621 (sulfonated polystyrene-divinylbenzene macroreticular, ion-exchange resin (SPS); exchange capacity = 1.92 mmol g⁻¹) was kindly provided by Lanxess; it was used after washing carefully with water and methanol. $[Pd(NH_3)_4]SO_4$ and $Pd(NO_3)_2$ were purchased from Alfa Aesar, and [Pd(OAc)₂] was purchased from Sigma Aldrich; sodium thiosulfate pentahydrate (99.5%), potassium iodide, starch, concentrated sulfuric acid, 37 wt% aqueous formaldehyde, sodium borohydride, and methanol were purchased from Sigma-Aldrich; THF was supplied by Sigma-Aldrich and used after distillation. HPLC-grade methanol (99.99%) was obtained from J.T. Baker; H₂, O₂, and CO₂ (99.999% mol/mol purity) and were provided by AGA gas (Linde group). Methanol for Karl Fischer titration, Hydranal composite 2, and ammonium molybdate tetrahydrate were purchased from Fluka. The reference catalyst was a standard, reduced 1 wt% Pd/C (Alfa Aesar), which was used as received.

Pd ion exchange

All the samples were prepared with a Pd loading of 1 wt%. Although $[Pd(NH_3)_4]SO_4$ and $Pd(NO_3)_2$ are soluble in water, $[Pd(OAc)_2]$ is soluble only in less polar solvents, and therefore, two protocols of metalation were employed, the former in water, the latter in THF.

Typically, K2621 (2.0 g) was suspended in distilled water (10 mL) and left to stand for 2 h. An aqueous solutions prepared with Pd precursor (0.188 mmol) was added (Table 1). The suspension was left to react overnight under mechanical stirring, and then the product was recovered by filtration and washed carefully with distilled water (3×10 mL) on the filter (water was always replaced with THF if [Pd(OAc)₂] was used). The mother liquor (filtrate and water from washing) was analyzed for the unreacted metal by ICP-MS. In the case of THF, the mother liquor was evaporated by using a rotavapor, and the dry residue was dissolved in a few milliliters of aqua regia. This solution was then analyzed for the metal by ICP-MS. The amount of unreacted metal after the ion-exchange step was less than 0.1 wt % of the respective precursor amounts. The mass balance of the metal showed that their uptakes were always complete and the experimental metal loading was equal to the nominal value for each sample.

Reduction protocols

Different reduction protocols were performed after the metalation of the K2621 with the $[Pd(NH_3)_4]SO_4$ precursor.

Reduction with hydrogen

The ion-exchanged resin (generally a beige-colored solid) was suspended in THF (50 mL) in a vessel, which was then flushed with H_2 , directly bubbled into the suspension at RT and ambient pressure, for 5 h. The resulting solid was collected by filtration and washed carefully with THF. Finally, the solid (dark gray color) precipitate was dried in an oven at 383 K overnight and then ground with pestle and mortar. Data on the catalysts obtained in this way (1PdK/A/H, 1PdK/N/H, 1PdK/S/H, where A stands for acetate, N for nitrate, and S for sulfate) are collected in Table 1.

Reduction with formaldehyde

The details are reported in Ref. [21]. Briefly, the beige material, already swollen in distilled water, was suspended in 37% aqueous formaldehyde solution (50 mL) and left to react under reflux for 3 h. The black product was recovered by vacuum filtration and washed carefully on the filter with distilled water (3×10 mL). The solid was dried in an oven at 383 K overnight.

Data on the catalysts obtained in this way (1PdK/S/F, where S stands for sulfate and F for formaldehyde) are collected in Table 1.

Reduction with methanol

The details are reported in Ref. [15]. The (beige) solid, already swollen in distilled water, was suspended in 1:1 (v:v) methanol/water solution (20 mL) and left to react under reflux conditions for 3 h. The black product was recovered by vacuum filtration and washed carefully over a filter with distilled water (3×10 mL). The solid (dark gray-black), was dried in an oven at 383 K overnight and then ground with a pestle and mortar. Data on the catalysts obtained in this way (1PdK/S/M, S stands for sulfate and M for methanol) are collected in Table 1.

Reduction with sodium borohydride

The beige material, already swollen in distilled water, was suspended in water (10 mL). A solution of $NaBH_4$ (0.58 g) in water (15 mL)



was added to the beige suspension under moderate stirring. The color of the solid immediately turned to dark gray. After 2 h, the solid became black, and the product was recovered by vacuum filtration and washed carefully on the filter with distilled water ($5 \times 10 \text{ mL}$). The solid was dried in an oven at 383 K overnight and then ground with a pestle and mortar. Data on the catalysts obtained in this way (1PdK/S/B, where S stands for sulfate and B for borohydride) are collected in Table 1.

Reduction in autoclave with 0.5 MPa of hydrogen at 333 K

The details are reported in Ref. [22]. Briefly, the beige solid recovered from the ion-exchange reaction was suspended in THF (50 mL) in a glass vessel inserted into an autoclave. After flushing three times with H₂, the autoclave was filled with H₂ and the reduction was performed at 0.5 MPa H₂ at 333 K for 5 h. After the autoclave was cooled and vented, the catalyst was recovered by vacuum filtration and washed carefully on the filter with distilled water (5×10 mL). The solid was dried in an oven at 383 K overnight and then ground with a pestle and mortar.

Data on the catalysts obtained in this way (1PdK/S/H_{PT} where S stands for sulfate and H_{PT} for hydrogen at high temperature and high pressure) are collected in Table 1.

Characterization

ICP-MS measurements were performed by using a Perkin Elmer Sciex ICP Mass Spectrometer 6100 DRC Plus. The analysis was performed in the quantitative standard mode. Consequently, the samples were prepared upon diluting the mother liquor from the metalation experiments (aqueous solutions of the unreacted metal precursor) to a known fixed volume.

Karl Fisher titrations were performed by using a Titrino GP 736 from Metrohm.

TEM analyses were performed by using an energy-filtered transmission electron microscope (EFTEM, LEO 912 OMEGA, LaB6 filament, 120 kV). Samples were prepared by suspending a few milligrams of the powder in high-purity isopropyl alcohol (or ethanol). After sonication (30 s), a small droplet (5 μ L) of the suspension was transferred onto a holey-carbon film coated Cu grid, which was introduced into the microscope.

XPS spectra were recorded by using a Kratos Axis Ultra electron spectrometer equipped with a delay line detector. A monochromated AlK_{α} source operated at 150 W, hybrid lens system with magnetic lens, an analysis area of 0.3×0.7 mm², and charge neutralizer were used for the measurements. The binding energy (BE) scale was referenced to the C1s line of aliphatic carbon, set at BE = 285.0 eV. The spectra were processed with the Kratos software.

Batch experiments

Catalytic tests were performed as reported previously.^[6,18,22] Briefly, the catalyst (0.15 g) was loaded into the reactor (600 mL). The reactor was then closed, CO₂ (1.84 MPa) and O₂ (0.6 MPa) were fed directly from cylinders at 296 K. After stabilization of the gas pressure, 420 mL (V_L) of methanol was fed by using a HP pump at 4 mLmin⁻¹. Then the reactor was cooled to 275 K. The equilibrium between the liquid and the gas phase was reached upon starting the stirrer, which operated at 1000 rpm. After the stabilization of

pressure and temperature (275 K), the stirrer was switched off, and H₂ was fed up to the desired amount. The number of moles of hydrogen introduced into the reactor $(n_{\rm H_2,0})$ was calculated from the pressure drop of hydrogen in the precylinder.^[7] The final composition of the gases was 2.5% H₂, 25.5% O₂, and 72% CO₂. When the delivery of the desired amount of H₂ was complete, the stirrer and the pump (in recirculation mode) were switched on again. This was taken as start of the reaction. Unless otherwise stated, the reaction was stopped after 3 h. Portions of the liquid phase were withdrawn periodically from a six-way valve placed in the recirculation line of the reactor for H₂O₂ and water analysis; their volume (V_{taken}) was small enough to ensure that the amount of the catalyst per unit volume of the liquid phase was practically constant throughout the whole test. The concentration of the products, in the samples ($[H_2O_2]$, $[H_2O]'$ [mM]) were determined by iodometric and Karl Fischer titrations. The initial concentration of water, [H₂O]₀, was also determined by Karl Fischer titration of the solvent and used to calculate the concentration of water effectively produced by the reaction, [H₂O] [Eq. (5)]:

$$[H_2O] = [H_2O]' - [H_2O]_0$$
(5)

These data were used to monitor the progress of the reaction and its selectivity. Finally, the cumulative yield (*C*) was calculated [Eq. (6)]:

$$C \ [\%] = 100 \cdot \{ [H_2O_2]_t + [H_2O]_t \} \cdot V_L / n_{H_{2,0}}$$
(6)

The selectivity towards H_2O_2 at time t ($S_{H_2O_2,t}$) was calculated as [Eq. (7)]:

$$S_{H_2O_2,t} \ [\%] = 100 \cdot [H_2O_2]_t / \{[H_2O_2]_t + [H_2O]_t\}$$
(7)

The initial productivities (rates of H₂O and H₂O₂ production per mol of metal) were calculated in a similar way as described in Ref. [21]. The initial (up to 10–30 min from the onset of the reaction, which depends on the activity of the catalyst) sections of the kinetic plots were linear and their slopes were provided by linear interpolation. The division of the slope values by Pd moles yielded the apparent rates of water and H₂O₂ formation for each catalyst ($r_{H_2O}^i$, $r_{H_2O_2}^i$ [mmol_{product/s} dm⁻³ h⁻¹]. Their sum is the initial cumulative rate (r_{cumul}^i). The initial selectivity towards H₂O₂ was calculated as [Eq. (8)]:

Initial H₂O₂ selectivity
$$[\%] = 100 \cdot r^{i}_{H_2O_2} / r^{i}_{cumul.}$$
 (8)

The initial rates were transformed into the respective initial productivity (cumulative and of H_2O_2 ; $mmol_{product/s}mmol_{Pd}^{-3}h^{-1}$) as follows [Eqs. (9) and (10)]:

Initial cumulative productivity = $r_{\text{cumul.}}^{i} \cdot V_{\text{L}} / \{10^{-3} \cdot \text{mol}_{\text{Pd}}\}$ (9)

Initial H₂O₂ productivity =
$$r^{i}_{H_2O_2} \cdot V_L / \{10^{-3} \cdot mol_{Pd}\}$$
 (10)

in which $V_{\rm L}$ is the volume of the liquid phase.

Semi-batch experiments

The semi-batch experiments were performed in a 300 mL stainlesssteel reactor (Parr) in the absence of any selectivity enhancers.^[13] The catalyst (70 mg) was loaded into the injection system of the reactor with 2–3 mL of methanol and left to stand overnight.



Methanol (180 mL; HPLC grade) was placed in the reactor, and the injection system was connected (t_0 is the injection of catalyst slurry). H₂, O₂, and N₂ were bubbled through a stainless-steel frit (2 µm) into the reaction medium under vigorous stirring (1000 rpm) and cooled to 275 K with a O₂/H₂/N₂ 20:4:76 gas mixture and a total flow rate of 300 std mLmin⁻¹, in which the molar ratio of H₂ to O₂ in the feed stream was fixed at 0.2. The methanol was presaturated with the gas mixture before the introduction of catalyst slurry through the injector (t_0). The catalytic run went on for 5 h.

Portions of the liquid phase were withdrawn periodically from a six-way valve placed in the recirculation line of the reactor for H_2O_2 and water analysis; their volume (V_{taken}) was small enough to ensure that the amount of the catalyst per unit volume of the liquid phase was practically constant during the whole test cycle. The concentration of H_2O_2 and water was determined by iodometric titration and the Karl Fisher method, respectively.

The gas mixture that flowed out the autoclave was analyzed for unreacted H_2 by using GC (Agilent 6890GC) equipped with a thermal conductivity detector (TCD) and a capillary column (HP MOLSIV, 30 m, ID 0.53 mm, film 25 μ m). The conversion of H_2 and selectivity to H_2O_2 were calculated according to Equations (11) and (12):

$$H_2 \text{ conversion } (\%) = 100 \cdot \frac{\text{moles of } H_2 \text{ unreacted}}{\text{moles of } H_2 \text{ supplied}}$$
(11)

$$H_2O_2 \ \text{selectivity} \ (\%) = 100 \cdot \frac{\text{moles of } H_2O_2 \ \text{formed}}{\text{moles of hydrogen reacted}} \ (12)$$

in which the moles of H_2 reacted is the sum of the moles of H_2O_2 and H_2O formed.

To estimate the activity of catalysts, in terms of the side-reactions such as hydrogenation or dismutation of H_2O_2 , the same equipment was used in additional experiments. H_2O_2 hydrogenation experiments were performed in a similar way as the H_2O_2 synthesis experiments by simply replacing O_2 with N_2 and introducing a 30 wt% H_2O_2 commercial solution to give a reaction mixture that contained 2 wt% H_2O_2 . Dismutation experiments were performed in the same way with a gas flow composed only of N_2 . No consumption of H_2O_2 was detected up to 10 h.

The H_2O_2 productivity, hydrogenation rate, and dismutation rate were estimated as follows [Eqs. (13)–(15)]:

$$H_2O_2 \text{ productivity} = r^{ds}_{H_2O_2} \cdot V / \{10^{-3} \cdot \text{mol}_{Pd}\}$$
(13)

 $H_2O_2 \text{ hydrogenation rate} = r^h_{H_2O_2} \cdot V / \{10^{-3} \cdot \text{mol}_{Pd}\}$ (14)

$$H_2O_2 \text{ dismutation rate} = r^d_{H_2O_2} \cdot V / \{10^{-3} \cdot \text{mol}_{Pd}\}$$
(15)

in which $r_{H_2O_2}^{X}$ [mmol_{H_2O_2} dm⁻³ h⁻¹] is the rate of reaction that produces (ds) or consumes (h and d) H₂O₂ in the medium, respectively, and V is the volume of the liquid phase.

Acknowledgements

Lanxess is acknowledged for kindly providing the K2621 resin. This work is part of the activities of Johan Gadolin Process Chemistry Centre (PCC), financed by the Åbo Akademi University (ÅA). S.S. is grateful to the Johan Gadolin scholarship 2013–14 (ÅA). Financial support from the Academy of Finland is gratefully acknowledged. P.B. gratefully acknowledges the Kempe Foundations (Kempe Stiftelserna) for support. In Sweden, also the Bio4-Energy program and Wallenberg Wood Science Center under the auspices of the Knut and Alice Wallenberg Foundation are acknowledged. We are indebted to Dr. K. Jeřábek (Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic) for providing the ISEC data of K2621.

Keywords: hydrogen peroxide • nanoparticles • palladium • reduction • supported catalysts

- J. M. Campos-Martin, G. Blanck-Brieva, J. L. G. Fierro, Angew. Chem. Int. Ed. 2006, 45, 6962–6984; Angew. Chem. 2006, 118, 7116–7139.
- [2] C. Samanta, Appl. Catal. A 2008, 350, 133-149.
- [3] J. García-Serna, T. Moreno Rueda, P. Biasi, M. J. Cocero, J. P. Mikkola, T. Salmi, Green Chem. 2014, 16, 2320–2343.
- [4] J. K. Edwards, S. J. Freakley, R. J. Lewis, J. C. Pritchard, G. J. Hutchings, *Catal. Today* 2015, 248, 3–9.
- [5] R. Dittmeyer, J. D. Grunwaldt, A. Pashkova, *Catal. Today* 2015, 248, 149– 159.
- [6] P. Biasi, N. Gemo, J. R. Hernandez Carucci, K. Eranen, P. Canu, T. O. Salmi, Ind. Eng. Chem. Res. 2012, 51, 8903–8912.
- [7] N. M. Wilson, D. W. Flaherty, J. Am. Chem. Soc. 2016, 138, 574-586.
- [8] P. Biasi, J. Garcia-Serna, A. Bittante, T. Salmi, Green Chem. 2013, 15, 2502-2513.
- [9] I. Huerta, P. Biasi, J. Garcia-Serna, Cocero, M. J. Cocero, J. P. Mikkola, T. Salmi, *Catal. Today* 2015, 248, 91–100.
- [10] P. Biasi, F. Menegazzo, F, Pinna, K. Eranen, P. Canu, T. O. Salmi, Ind. Eng. Chem. Res. 2010, 49, 10627–10632.
- [11] M. Piccinini, E. N. Ntainjua, J. K. Edwards, A. F. Carley, J. A. Moulijn, G. J. Hutchings, Phys. Chem. Chem. Phys. 2010, 12, 2488-2492.
- [12] a) Q. Liu, J. H. Lunsford, *Appl. Catal. A* **2006**, *314*, 94–100; b) N. Gemo, P. Biasi, P. Canu, F. Menegazzo, F. Pinna, A. Samikannu, K. Kordàs, T. O. Salmi, J.-P. Mikkola, *Top. Catal.* **2013**, *56*, 540–549.
- [13] a) A. Bernardini, N. Gemo, P. Biasi, P. Canu, J. P. Mikkola, T. Salmi, R. Lanza, *Catal. Today* **2015**, *256*, 294–301; b) P. Biasi, S. Sterchele, F. Bizzotto, S. Lindholm, P. Ek, J. Bobacka, J.-P. Mikkola, T. Salmi, *Catal. Today* **2015**, *246*, 207–215.
- [14] a) T. Salmi, N. Gemo, P. Biasi, J. Garcia-Serna, *Catal. Today* 2015, *248*, 108–114; b) N. Gemo, P. Biasi, T. O. Salmi, P. Canu, *J. Chem. Thermodyn.* 2012, *54*, 1–9; c) N. Gemo, P. Biasi, P. Canu, T. O. Salmi, *Chem. Eng. J.* 2012, *207–208*, 539–551.
- [15] C. Burato, P. Centomo, M. Rizzoli, A. Biffis, S. Campestrini, B. Corain, Adv. Synth. Catal. 2006, 348, 255–259.
- [16] C. Burato, S. Campestrini, Y.-F. Han, P. Canton, P. Centomo, B. Corain, *Appl. Catal. A* 2009, 358, 224–231.
- [17] P. Biasi, F. Menegazzo, P. Canu, F. Pinna, T. O. Salmi, *Ind. Eng. Chem. Res.* 2013, *52*, 15472–15480.
- [18] N. Gemo, S. Sterchele, P. Biasi, P. Centomo, P. Canu, M. Zecca, A. Shchukarev, K. Kordas, T. Salmi, J. P. Mikkola, *Catal. Sci. Technol.* 2015, *5*, 3545– 3555.
- [19] A. Guyot in Synthesis and Separations using Functional Polymer (Eds.: D. C. Sherrington, P. Hodge), Wiley, New York, 1988.
- [20] R. L. Albright, I. J. Jakovac, *Catalysis by Functionalized Porous Organic Polymers*, Bulletin IE-287, Rohm&Haas Company, Philadelphia, **1985**, pp. 4–6.
- [21] S. Sterchele, P. Biasi, P. Centomo, P. Canton, S. Campestrini, T. Salmi, M. Zecca, Appl. Catal. A 2013, 468, 160–174.
- [22] S. Sterchele, P. Biasi, P. Centomo, P. Canton, S. Campestrini, A. Shchukarev, A. R. Rautio, J. P. Mikkola, T. Salmi, M. Zecca, *Catal. Today* 2015, 248, 40-47.
- [23] B. Corain, M. Basato, M. Zecca, G. Braca, A. M. Galletti, S. Lora, G. Palma, E. Guglielminotti, J. Mol. Catal. 1992, 73, 23–41.
- [24] W. Keim, P. Mastrorilli, C. Nobile, N. Ravasio, B. Corain, M. Zecca, J. Mol. Catal. 1993, 81, 167–184.



CHEMCATCHEM Full Papers

- [25] G. Blanco-Brieva, E. Cano-Serrano, J. M. Campos-Martin, J. L. G. Fierro, Chem. Commun. 2004, 1184–1185.
- [26] R. Wagner, P. M. Lange, Erdoel Kohle Erdgas 1989, 105, 414.
- [27] K. Weissermel, H. P. Arpe, Industrial Organic Chemistry, Vol. 11, 3rd ed., Wiley-VCH, Weinheim, 1997, p. 281.
- [28] M. Sankar, Q. He, M. Morad, J. Pritchard, S. J. Freakley, J. K. Edwards, S. H. Taylor, D. J. Morgan, A. F. Carley, D. W. Knight, C. J. Kiely, G. J. Hutchings, ACS Nano 2012, 6, 6600–6613.
- [29] E. N. Ntainjua, M. Piccinini, J. C. Pritchard, J. K. Edwards, A. F. Carley, J. A. Moulijn, G. J. Hutchings, *ChemSusChem* 2009, 2, 575–580.
- [30] M. Kralik, M. Hronec, V. Jorik, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, J. Mol. Catal. A 1995, 101, 143–152.
- [31] J. Aitchison, J. A. C. Brown, *The LogNormal Distribution*, Cambridge University Press, **1957**.
- [32] B. Corain, K. Jeřàbek, P. Centomo, P. Canton, Angew. Chem. Int. Ed. 2004, 43, 959–962; Angew. Chem. 2004, 116, 977–980.
- [33] P. Centomo, P. Canton, D.; Canova, M.; Zecca, J. Nanosci. Nanotechnol. 2013, 13, 6872-6879.
- [34] P. Centomo, M. Zecca, B. Corain, J. Cluster Sci. 2007, 18, 947-962.
- [35] P. Centomo, P. Canton, M. Ferroni, M. Zecca, New J. Chem. 2010, 34, 2956–2961.
- [36] P. Centomo, K. Jeřàbek, D. Canova, A. Zoleo, A. L. Maniero, A. Sassi, P. Canton, B. Corain, M. Zecca, Chem. Eur. J. 2012, 18, 6632-6643.
- [37] K. Jeřàbek, M. Zecca, P. Centomo, F. Marchionda, L. Peruzzo, P. Canton, E. Negro, V. Di Noto, B. Corain, *Chem. Eur. J.* 2013, *19*, 9381–9387.
- [38] R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'Horo, B. N. Ganguly, V. Mehrotra, M. W. Russel, D. R. Huffman, *Science* **1992**, *257*, 219–223.
- [39] E. Sulman, V. Matveeva, V. Doluda, L. Nikoshvili, A. Bykov, G. Demidenko, L. Bronstein, Stud. Surf. Sci. Catal. 2010, 175, 153–160.
- [40] H. Bönnemann, K. S. Nagabhushana in Metal nanoclusters in catalysis and materials science: the issue of size control (Eds.: B. Corain, G. Schmid, N. Toshima), Elsevier, Amsterdam, 2008, p. 21.

- [41] X. Huang, Z. Zhao, J. Fan, Y. Tan, N. Zheng, J. Am. Chem. Soc. 2011, 133, 4718–4721.
- [42] D. J. Lockwood, Nanotechnology in Catalysis (Eds.: B. Zhou, S. Hermans, G. A. Somorjai), Kluwer Academic, New York, 2004.
- [43] P. Centomo, M. Zecca, M. Kralik, D. Gasparovicova, K. Jeřàbek, P. Canton, B. Corain, J. Mol. Catal. A 2009, 300, 48–58.
- [44] M. Králik, M. Zecca, P. Bianchin, A. A. D'Archivio, L. Galantini, B. Corain, J. Mol. Catal. A 1998, 130, 85–93.
- [45] L. Ouyang, P.-f. Tian, G.-j. Da, X.-C. Xu, C. Ao, T.-y. Chen, R. Si, J. Xu, Y. F. Han, J. Catal. 2015, 321, 70–80.
- [46] F. Menegazzo, M. Signoretto, G. Frison, F. Pinna, G. Strukul, M. Manzoli, F. Boccuzzi, J. Catal. 2012, 290, 143–150.
- [47] S. Kim, D. W. Lee, K. Y. Lee, J. Mol. Catal. A 2014, 391, 48-54.
- [48] S. Abate, S. Perathoner, G. Centi, Catal. Today 2012, 179, 170-177.
- [49] S. Chinta, J. H. Lunsford, J. Catal. 2004, 225, 249-255.
- [50] S. Abate, K. Barbera, G. Centi, G. Giorgianni, S. Perathoner, J. Energy Chem. 2016, 25, 297–305.
- [51] A. Biffis, H. Landes, K. Jeřábek, B. Corain, J. Mol. Catal. A 2000, 151, 283–288.
- [52] S. C. Kim, S. C. Jung, Y. K. H. G. Park, S. G. Ahn Seo, J. Nanosci. Nanotechnol. 2013, 13, 1966–1969.
- [53] S. Cheong, J. D. Watt, R. D. Tilley, Nanoscale 2010, 2, 2045-2053.
- [54] N. Gemo, T. Salmi, P. Biasi, *React. Chem. Eng.* 2016, DOI: 10.1039/ C5RE00073D.

Received: January 8, 2016 Revised: February 19, 2016 Published online on April 9, 2016