Highly Chemoselective Hydrogenation of 2-Ethylanthraquinone to 2-Ethylanthrahydroquinone Catalyzed by Palladium Metal Dispersed inside Highly Lipophilic Functional Resins

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Abstract: Most hydrogen peroxide is currently produced by the selective hydrogenation of 2-ethylanthraquinone (EAQ) to 2-ethylanthrahydroquinone (EAHQ), followed by treatment with dioxygen; this produces hydrogen peroxide and regenerates 2-ethylanthraquinone. We have developed novel catalysts for this process that are based on palladium supported on very lipophilic functional resins and that are able to promote a chemoselectivity for EAHQ slightly but definitely superior to that provided by an industrial catalyst under identical conditions. This finding demonstrates the potential of variations of the lipophilic/hydrophilic character of the support as a tool for the improvement of the chemoselectivity of resin-based metal catalysts.

Keywords: functional resins · heterogeneous catalysis · hydrogen peroxide · palladium · quinones

Introduction

Functional resins are cross-linked organic polymers widely used in the field of ion-exchange,[1] but are also employed as industrial catalysts in about eighteen commercial processes.[2, 3] In a few of these processes, they actually act as supports of catalytically active metal particles.[3–5]

Catalysis by supported metals has enabled enormous progress in modern industrial chemistry, especially in the area of commodity synthesis. Furthermore, the increasingly strict demand for cleaner processes ("green chemistry") is currently promoting the replacement of well-established, albeit environmentally expensive, fully stoichiometric processes with synthetic routes that include one or more catalytic steps. As a consequence, considerable expansion of supported metal catalysis to the realm of fine chemistry has recently been predicted by authoritative scientists and technologists.[6–8] Up to now, the metal catalysts that have been developed in order to meet this demand are still mainly based on conventional inorganic supports or on active carbon.[9] However, these materials do not represent the only possible solution to new operational needs, and innovative strategies based on designed functional resins might become a fruitful approach.

A schematic comparison of metal catalysts supported on classical inorganic supports or dispersed inside organic functional resins is shown in Figure 1.

Supported metal particles inside the pore system of an inorganic support are in *direct* contact with a surrounding liquid phase. In contrast to this situation, the resin-supported metal particles are located inside a polymer matrix where their contact with molecules from the liquid phase is *mediated* by the swelling of the polymer network in the liquid phase itself. Reagents involved in a given metal-catalyzed reaction must be able to enter the swollen portion of the resin, where the reaction proceeds in an environment quite different from that of the bulk liquid phase. As a consequence, the physicochemical features of the polymer support can be designed and controlled in such a way as to induce steric restrictions and reagent-concentration effects inside the swollen resin.[3, 10, 11] Therefore, resin-supported metal catalysts should be consid-

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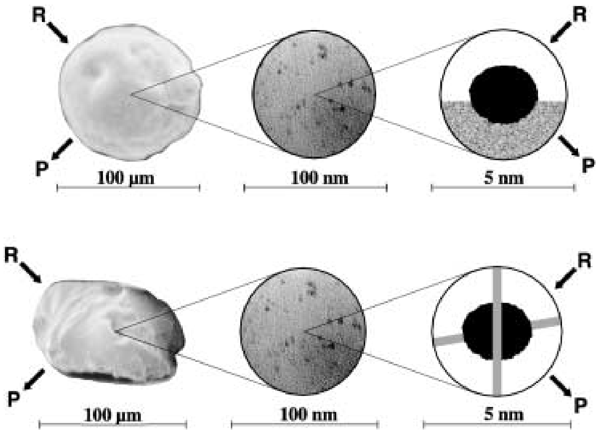
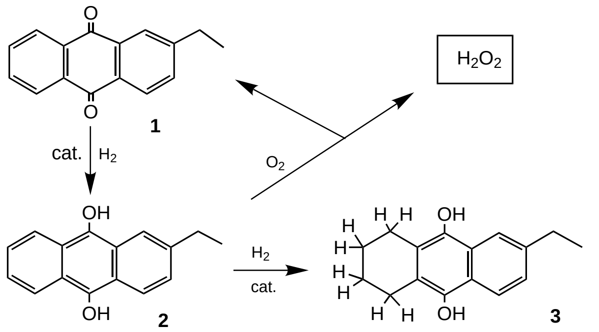


Figure 1. Different locations of catalytically active metal particles supported on inorganic supports (above) or in organic resins (below).

ered to be innovative materials offering possibilities for performance optimization that are unavailable for catalysts based on inorganic supports.

During the past years, we have been engaged in an extensive research project on resin-supported metal catalysts,[11, 12] in the frame of which we have set up clear protocols for i) the dispersion of metal centers inside functional resins, ii) the subsequent reduction of the metal centers to the zerovalent state, iii) the control of the size of the consequently formed metal nanoparticles,[13] and iv) the quantitative description of the nanomorphology and molecular accessibility of swollen polymer networks.[14–16] In this paper we report on the successful use of tailor-made resin supports in the chemoselective hydrogenation of 2-ethylanthraquinone (EAQ) to 2-ethylanthrahydroquinone (EAHQ) (Scheme 1). This reaction is the crucial step in the industrial synthesis of hydrogen peroxide (AO-process).[17]



Scheme 1. Production of hydrogen peroxide by the anthraquinone route (AO processs).

In industrial practice, catalysts containing palladium metal supported on inorganic carriers are currently employed. However, the process is plagued by undesired consecutive reactions occurring at the surface of the palladium particles (e.g. the formation of **3** in Scheme 1), which subtract precious substrate from the overall mass balance. The aim of our strategy is to develop tailor-made resin supports able to improve the selectivity of the process without adversely affecting the activity of the metal catalyst.

Our approach is based on the utilization of the "microenvironmental effect" exerted by a resin support, that is, its influence on the properties of the environment surrounding the metal particles under liquid-phase conditions. The desired hydrogenation product—EAHQ—is clearly less lipophilic than the starting compound. Therefore, it can be assumed that an increase in the lipophilic character of the environment surrounding the metal centers provided by a lipophilic resin would facilitate the removal of the product from the vicinity of the catalytic surface, and consequently decrease the probability of further hydrogenation to give undesired consecutive reactions.

Gel-type resin supports, which lack permanent pores so that the particle interior is accessible exclusively through the swelling of the polymer mass, are likely to be excellent candidates for this application as they offer the possibility of building up a more homogeneous microenvironment around the metal particles. We have prepared and tested lipophilic gel-type resins based on styrene or dodecyl methacrylate as the major comonomer. Furthermore, we have followed a parallel approach based on surface functionalization of a commercial catalyst, supported on an inorganic material (Pd/Al_2O_3) by attachment of lipophilic groups, in order to critically compare the activity and chemoselectivity provided by the lipophilicity of the swollen resin support with that offered by the lipophilicity of a surface layer on a conventional Pd-catalyst particle.

Results and Discussion

Preparation of the resin-supported catalysts: The gel-type resin supports were prepared by batch polymerization of a monomer mixture containing i) styrene or dodecyl methacrylate as the major comonomer; ii) a functional monomer (sulfoethyl methacrylate, methacrylic acid or 4-vinylpyridine), useful for anchoring the inorganic precursors of the metal particles; iii) a crosslinker, namely ethylene dimethacrylate or divinylbenzene; iv) methyl methacrylate as an auxiliary comonomer useful for tuning the lipophilic character of the resin. The compositions of the individual resins are reported in Table 1. In the case of resins PDMA-MMA and PS-DVB, a solvent, such as *N*,*N*-dimethylformamide or dimethylsulfoxide, respectively, was added to the reaction mixture in order to achieve complete miscibility of the monomers (see Experimental Section). In all cases, the polymerization was initiated by γ-ray irradiation from a ^{60}Co source, and quantitative conversion of the monomers was achieved.[11, 18, 19]

Table 1. Composition of the functional resins [mol].

Polymer	S	DMA	MMA	SEMA	MAA	VP	DVB	EDMA
PDMA-MMA	–	0.46	0.46	0.04	–	–	–	0.04
PDMA-MAA	–	0.92	–	–	0.04	–	–	0.04
PDMA-VP	–	0.92	–	–	–	0.04	–	0.04
PS-DVB	0.92	–	–	0.04	–	–	0.04	–

S = styrene, DMA = dodecyl methacrylate, MMA = methyl methacrylate, SEMA = sulfoethyl methacrylate, MAA = methacrylic acid, VP = 4-vinylpyridine, DVB = divinylbenzene, EDMA = ethylene dimethacrylate.

The supports were obtained as stiff rods, which were crushed and sieved to a particle size $<180\ \mu m$. Scanning electron microscopic (SEM) analyses of the obtained powders showed the expected glassy morphology in the dry state for all materials. The swelling properties of the resins were assayed in ethanol and in THF, which are the solvents of choice for the subsequent incorporation of the metal. As is apparent from Figure 2, all the resins showed poor swelling in ethanol, whereas swelling was much more appreciable in THF. The swellability of the resins is expressed as V_s/V_o, where V_s is the volume of a given mass of the swollen resin in a given solvent and V_o is its dry volume.

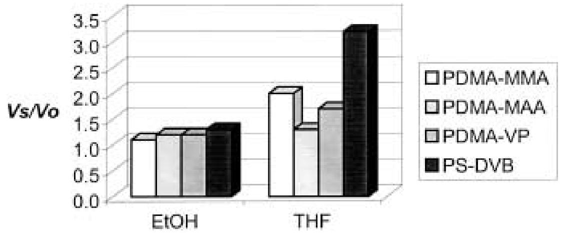


Figure 2. Swelling capacity of the investigated supports.

The morphological features of the resins swollen in THF were evaluated with Inverse Steric Exclusion Chromatography (ISEC).[11] Figure 3 shows the relevant results, expressed as fractions of swollen volume featured by a given value of polymer-chain concentration. It is evident that all the investigated supports are characterized by a fairly homogeneous chain concentration centered around $0.4-0.8\ nm^{-2}$. This means that the resins possess a homogeneous degree of "porosity" as required by our approach.

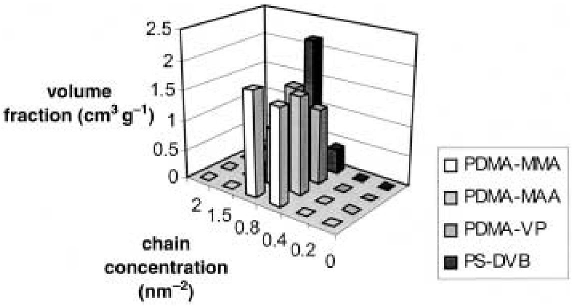


Figure 3. ISEC characterization of the investigated supports in THF.

The organic supports were conveniently loaded with palladium(II) ions by using a methodology extensively developed and optimized in these laboratories.[12] The resins were pre-swollen in THF and treated with a solution of palladium(II) acetate in THF. The amount of metal complex was calibrated in order to reach a metal content of 1% by weight in the polymer by quantitative incorporation. The palladium was incorporated into the resins by an acid–base reaction between the polymer-bound functional groups and the acetate ligands ("forced" ion-exchange[12]) or by simple coordination of the palladium(II) complexes (in the case of the pyridine moieties). The metal was usually quantitatively incorporated. Only in the case of resin PDMA-MAA, did the incorporation yield turn out to be 90%.

The resin-bound palladium(II) was subsequently reduced in order to form Pd nanoparticles inside the polymer framework.[12, 13] Two different reduction procedures were employed, utilizing either H_2 or $NaBH_4$ as the reducing agent. The reduction with $NaBH_4$ was performed in EtOH/THF to ensure both a good solubility of the reducing agent and a good swelling of the polymer support. The reaction conditions were chosen in order to favour the formation of an homogeneous distribution of Pd nanoparticles throughout the polymer support.[11] Reduction with hydrogen gas was performed in situ at room temperature and pressure, prior to the catalytic tests, in the presence of the solvent mixture employed for the reaction. The same two reduction protocols were employed to reduce an industrial catalyst precursor (1% *w/w* Pd^{II} on a silicoalluminate) currently used by the company Ausimont (Bussi sul Tirino, Pescara, Italy), which served as the benchmark catalyst for our studies.

The resin-supported catalysts in the reduced form were characterized by evaluating their swelling in solvents that are suitable for carrying out the AO process. Generally, the reaction is carried out in a solvent mixture composed of a strongly lipophilic and a moderately lipophilic solvent, in order to guarantee the solubilization of both the reagent EAQ (more lipophilic) and the product EAHQ (less lipophilic) throughout the process. To this end, we tested the swelling of the resin-supported catalysts in definitely lipophilic (*n*-heptane, toluene) and in comparatively less lipophilic (octan-2-ol, cyclohexyl acetate) solvents, as well as in 1:1 cyclohexyl acetate/xylenes, which is a reasonable mimic of the solvent mixture currently utilized in industry (Figure 4). It may be appreciated that all polymer supports swell preferably in cyclohexyl acetate and in aromatics. Therefore, the model cyclohexyl acetate/xylenes mixture appears to be the best choice as the reaction solvent. A particularly high degree of swelling in this mixture is exhibited by the styrene-based copolymer PS-DVB.

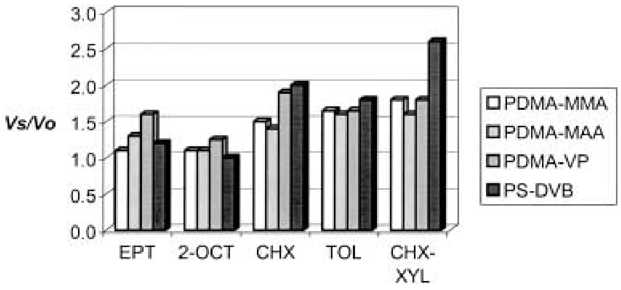


Figure 4. Swelling capacity of the investigated polymer-supported catalysts; EPT = *n*-heptane, 2-OCT = octan-2-ol, CHX = cyclohexyl acetate, TOL = toluene, XYL = xylenes.

Preparation of the surface-functionalized catalysts: In order to evaluate an alternative strategy for the construction of a hydrophobic microenvironment around the metal particles, we also prepared a set of catalysts based on surface functionalization with hydrophobic groups of a commercial 1% *w/w* Pd/Al_2O_3 catalyst. This catalyst was functionalized by treatment with trialkoxysilane-bearing ethyl (AlPdE), octyl (AlPdO) or hexadecyl (AlPdH) chains, respectively. The reaction was accomplished by simply heating the catalyst at reflux with a solution of the trialkoxysilane in dry toluene. Elemental analyses of the recovered functionalized catalysts revealed the successful incorporation of the organic modifier (Table 2).

Table 2. Elemental analysis of the surface functionalized catalysts

Catalyst	C [%]	H [%]
AlPdE	3.92	1.85
AlPdO	8.31	2.71
AlPdH	12.05	3.05

Catalytic tests: All the prepared catalysts were checked for their activity and selectivity in the hydrogenation of EAQ to EAHQ. The catalytic tests were run at 20 °C and 100 kPa in a magnetically stirred glass reactor connected with a gas burette through a septum inlet immersed in the liquid phase. The resin-supported catalysts were allowed to swell for at least 1 hour in the reaction mixture before starting the reaction, in order to ensure that the swelling equilibrium had been reached.

The reaction progress was monitored by measuring the time dependence of dihydrogen consumption (Figure 5). The end of the main hydrogenation process (i.e. the hydrogenation of EAQ to EAHQ) at a consumption of dihydrogen close to the stoichiometric one for the formation of 2-EAHQ was generally clearly seen by a sharp decrease in the dihydrogen consumption rate (Figure 6); the reaction time corresponding to this point was defined for each catalyst as t_f. Stirring of the reaction mixture under dihydrogen was continued after this point up to a time corresponding to a constant multiple of t_f (usually $40 \times t_f$), intentionally identical for all the catalysts. After reaching this "normalized reaction time" (NRT), the reaction was stopped. The resulting mixture was oxidized with dioxygen, and its composition was determined by gas chromatography. This procedure allowed the concentration of the overhydrogenated products to be increased up to a level at which they could be quantified with sufficient accuracy. Furthermore, this procedure made it possible to take into account the different activities of the various catalysts.

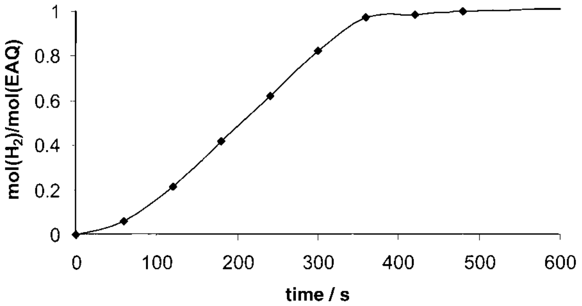


Figure 5. Dihydrogen consumption curve obtained from the industrial catalyst reduced with H_2.

The results obtained with the benchmark industrial catalyst are reported in Table 3. It may be appreciated that reduction with hydrogen affords a catalyst which is significantly more active, but slightly less selective than that obtained with $NaBH_4$ as reducing agent.

Table 3. Activity and selectivity of the industrial catalyst

Catalyst	Activity[a] [$mol_{H_2} g_{Pd}^{-1} s^{-1}$]	t_f [s]	Selectivity[b] [%]
Ausimont ($NaBH_4$)	0.13	1080	95
Ausimont (H_2)	0.39	360	93

[a] Activity determined at 50 % stoichiometric dihydrogen consumption. [b] Selectivity after NRT = $40 \times t_f$

We then turned to the evaluation of the catalytic properties of the surface-functionalized commercial catalysts. The results are reported in Table 4. It is clear from the presented data that the surface modification procedure has a detrimental effect on the performance of the catalyst both in terms of activity and selectivity. While the unfunctionalized catalyst exhibits a catalytic behaviour rather close to that of the benchmark catalyst, the activity decreases considerably with increasing length of the alkyl chains (i.e. increasing thickness of the hydrophobic shell). A possible explanation, at least as far as the activity is concerned, may lie in the increased difficulty for the dissolved hydrogen to diffuse towards the metal particles. A similar decrease of activity with this series of catalysts is seen in the direct synthesis of hydrogen peroxide from hydrogen and oxygen.[20]

Table 4. Activity and selectivity of the surface-functionalized catalysts.

Catalyst	Activity[a] [$mol_{H_2} g_{Pd}^{-1} s^{-1}$]	t_f [s]	Selectivity[b] [%]
AlPd	0.17	840	92
AlPdE	0.046	4200	88
AlPdO	0.021	9600	n.d.[c]
AlPdH	0.016	n.d.[c]	n.d.[c]

[a] Activity determined at 50 % stoichiometric dihydrogen consumption. [b] Selectivity after NRT = $40 \times t_f$; [c] Not determined

The subsequent step was the evaluation of the performance of the resin-supported palladium catalysts. We started to investigate the catalyst based on the styrene-divinylbenzene support, which exhibited the best swelling in the reaction solvent mixture (Figure 4). Surprisingly, the performance of this catalyst was very unsatisfactory (Table 5). The catalyst based on PS-DVB was much less active and remarkably less selective than the benchmark catalyst, despite the presumably

Table 5. Activity and selectivity of the resin-supported metal catalysts based on styrene

Catalyst	Activity[a] [$mol_{H_2} g_{Pd}^{-1} s^{-1}$]	t_f [s]	Selectivity[b] [%]
PS-DVB ($NaBH_4$)	0.024	8400	65
PS-DVB (H_2)	0.023	8400	50

[a] Activity determined at 50 % stoichiometric dihydrogen consumption. [b] Selectivity after NRT = $10 \times t_f$.

good accessibility of the particle interior due to the higher degree of swelling of the polymer framework in the solvent mixture employed. Moreover, whereas the loss in selectivity in all the other catalysts employed is almost exclusively due to the formation of 2-ethyl-5,6,7,8-tetrahydroanthrahydroquinone—that is, to ring hydrogenation at the unsubstituted phenyl ring of the hydroquinone—in this case a substantial amount of product hydrogenated at the substituted ring is formed.

The reasons for this peculiar behaviour are not readily apparent at the moment. Possibly, both the anthraquinone reagent and especially the hydroquinone product have sufficient affinity to the pendant phenyl groups of the polymer backbone to contrast the expulsion of EAHQ from the catalyst particles. This may cause both a decrease in the overall activity due to increased transport difficulties through the polymer support, and an increased rate of quinone overreduction. A similar effect was observed in our study dealing with the selective hydrogenation of benzene to cyclohexene over resin-supported ruthenium catalysts.[21] Indeed, changing from a polymer support based on styrene to one based on dodecyl methacrylate results in a much better performance in terms of both activity and chemoselectivity (Table 6). In particular, the catalyst based on PDMA-MAA and reduced with $NaBH_4$ shows a slightly higher selectivity than the corresponding benchmark industrial catalyst while maintaining a satisfactory catalytic activity. Furthermore, it is interesting to note that, with this support, the reduction with $NaBH_4$ affords far more active catalysts than with molecular hydrogen. Potentially faster reduction with the borohydride may lead to smaller palladium particles than those produced by reduction with hydrogen, hence to a higher metal surface area. A TEM investigation able to confirm this hypothesis is currently underway.

Table 6. Activity and selectivity of the resin-supported metal catalysts based on dodecyl methacrylate.

Catalyst	Activity[a] [$mol_{H_2} g_{Pd}^{-1} s^{-1}$]	t_f [s]	Selectivity[b] [%]
PDMA-MMA ($NaBH_4$)	0.085	1800	93[b]
PDMA-MMA (H_2)	0.041	5100	94[b]
PDMA-VP ($NaBH_4$)	0.086	1800	93[b]
PDMA-VP (H_2)	0.052	3600	83[b]
PDMA-MAA ($NaBH_4$)	0.070	2400	96[b]
PDMA-MAA (H_2)	0.005	16200	98[c]

[a] Activity determined at 50% stoichiometric dihydrogen consumption. [b] Selectivity after NRT $= 40 \times t_f$. [c] Selectivity after NRT $= 16 \times t_f$.

All the reported reactions were repeated at least once with different samples of the same catalyst batch, and in some cases also with samples from different batches of the same catalyst; the results were in all cases fully reproducible.

Finally, we have made a preliminary attempt to recycle the catalyst PDMA-MAA reduced with $NaBH_4$ (i.e. the one which gave the best selectivity). The catalyst was collected by simple filtration in air, dried and reused. We could obtain exactly the same activity and selectivity as in the first cycle. In contrast, recycling of the benchmark industrial catalyst reduced with H_2 (i.e. the most active catalyst) resulted in a significant drop in catalytic activity (0.18 $mol_{H_2} g_{Pd}^{-1} s^{-1}$ intead of 0.39 in the first cycle).

Conclusion

The results presented in this paper point out the effectiveness of suitable tailor-made resin supports in providing lipophilic microenvironments around catalytically active metal particles that are able to improve the chemoselectivity of the latter in the reduction of EAQ. It is important to note that the peculiar three-dimensional structure of the swollen resin support is of chief importance in order to achieve this effect. Simple surface lipophilization of conventional catalysts on inorganic supports turns out to be detrimental both in terms of activity and chemoselectivity. It must also be stressed that the chemical structure of the investigated resin supports was not optimized; we are confident that their finer tuning should lead to chemoselectivities approaching 100%. Finally, the optimization of this new generation of catalyst also implies the maximization of their catalytic activity and long-term mechanical stability. Both these issues can, in principle, be achieved by switching to suitably designed resins containing permanent pores. Work is in progress along this direction.

Experimental Section

Materials: All solvents and chemicals were of reagent grade unless otherwise stated. All monomers were from Aldrich apart from SEMA, which was from Polyscience. Commercial $Pd(OAc)_2$ (Aldrich) was used without further purification. Commercial 1% *w*/*w* Pd/Al_2O_3 catalyst was from Alfa (serial 89112, lot 1969000). Industrial Pd/silicoaluminate catalyst and technical EAQ were a gift from Ausimont (Bussi sul Tirino, Pescara, Italy).

Apparatus: SEM micrographs were taken with a Cambridge Stereoscan 250EDXPW9800 instrument. ISEC measurements were carried out by using an established procedure and a standard chromatographic set-up described elsewhere.[14, 15] GC analyses were performed with a Shimadzu GC-8A gas chromatograph equipped with an Agilent HP-FFAP capillary column.

Resin preparation: Monomers were mixed in the desired ratios (Table 1) and the resulting mixtures (20 g) were poured in screw-cap vials. In two cases, the monomer mixtures were diluted with *N*,*N*-dimethylformamide (40% *w*/*w*) (PDMA-MMA) or dimethylsulfoxide (PS-DVB) in order to ensure complete miscibility of the monomers. The vials were exposed to the γ-rays from a ^{60}Co source at 0.5 $Gy s^{-1}$ at room temperature and at a distance of 21 cm for 72 h. The resulting clear transparent rods were crushed, extensively washed with methanol, acetone and diethyl ether, vacuum dried and sieved to a particle size <0.18 mm.

Metallation with palladium(II): Resin samples were pre-swollen in THF (50 mL) for 1 h. A solution of $Pd(OAc)_2$ (1% by weight of Pd with respect to the polymer) in THF (50 mL) was then added. The suspension was allowed to stand with occasional stirring for 24–72 h, after which time the orange colour of the liquid phase had almost vanished, whereas the resin became reddish brown; this indicated the coordination of the Pd salt to the polymer. The polymer was filtered off, washed thoroughly with THF and diethyl ether and allowed to dry in air. The metallation yield was calculated by determining the palladium content in the supernatant solution by atomic absorption spectroscopy.

Palladium(II) reduction with $NaBH_4$: The resins loaded with Pd (2 g) were pre-swollen in THF (20 mL) for 1 h. A solution of $NaBH_4$ (0.29 g) in ethanol (90 mL) was added, and the resulting suspension was allowed to stand with occasional stirring for 24–48 h. The resulting dark brown material was filtered off, washed with ethanol and dried under vacuum at room temperature to constant weight.

Preparation of catalysts AlPdE, AlPdO and AlPdH: Commercial Pd/Al_2O_3 (1% *w*/*w*, 2 g) was suspended in dry toluene (50 mL) under a nitrogen atmosphere. According to the catalyst to be prepared, ethyltriethoxysilane (4 mL), octyltriethoxysilane (4 mL) or hexadecyltrimethoxysilane (5.5 mL) was then added, and the suspension was heated at reflux for 12 h. The catalyst was filtered off, washed with toluene and dried under vacuum at room temperature to constant weight.

Catalytic tests: Catalytic tests were performed in a glass reactor thermostated at 20 °C and equipped with a magnetic stirrer and a gas burette to monitor the gas consumption. In a typical test, the catalyst (0.5 g) was placed into the reactor, and a solution of EAQ (50 mL, 25 $g L^{-1}$) in cyclohexyl acetate/xylenes (1:1) was added. In the case of resin-supported catalysts, the resin was left to swell in the reaction mixture for 1 h before continuing the experiment. The gas burette was filled with dihydrogen. The reactor was evacuated and filled with dihydrogen, the gas burette was connected to the reactor, and the reaction was started by switching the stirring on. The reaction progress was monitored by measuring the dihydrogen consumption. The reaction rate was evaluated at 50% dihydrogen conversion by determining the slope of the tangent to the dihydrogen conversion curve. After the given normalized reaction time (NRT, see above), the reactor was opened and the reaction mixture was rapidly filtered. Water (25 mL) was added to the filtrate, and dioxygen was bubbled through the resulting mixture for 10 min. The two phases were then separated, and the content of EAQ and of its decomposition products in the organic phase was determined by GC.

Catalytic tests with in situ reduced catalysts were run as follows. The precatalyst (0.5 g) was placed into the reactor and cyclohexyl acetate/xylenes (1:1, 25 mL) were added. In the case of the resin-supported precatalysts, the resin was left to swell in the reaction mixture for 1 h before continuing the experiment. The gas burette was filled with dihydrogen. The reactor was evacuated and filled with dihydrogen, the gas burette was connected to the reactor, and the reduction was started by switching the stirring on. The catalyst was reduced for 16 h, after which the reactor was opened and a solution of EAQ (25 mL, 50 $g mL^{-}$) in cyclohexyl acetate/xylenes (1:1) was added. The reactor was again evacuated and filled with dihydrogen, the gas burette was connected to the reactor, and the reaction was started and monitored as described above.

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