Metal Catalysis inside Polymer Frameworks: Evaluation of Catalyst Stability and Reusability

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Abstract: The polymer framework of a resin-based catalyst built up with Pd nanoclusters (ca. 3 nm) dispersed inside the nanoporous domains of a thermally stable gel-type polyacrylic resin exhibits a good chemical stability under 5 bar H_2 at 40 °C for reasonable contact times. Chemical and physico-chemical integrity of the polymer framework are checked with a variety of instrumental analytical methods. Catalyst reusability turns out to be quite good.

Keywords: cluster compounds · gel-type resins · metal catalysis · palladium · polymers

Introduction

Metal catalysts built up with metal nanoclusters supported on functional resins are currently used in a few industrial processes, which originated from Bayer technology developed in the Eighties.[1–3]

In spite of the scientific novelty and of potential further technological breakthroughs, the pertinent scientific and patent literature appeared to be almost nonexistent at the beginning of the Nineties. This observation prompted us to start a long-term project aimed at discovering the scientific bases of these most promising catalysts.[4–12]

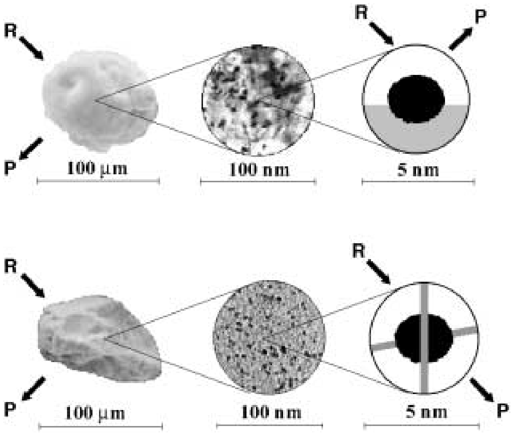

Figure 1. Metal catalysis on inorganic supports (top) versus metal catalysis inside organic polymer frameworks (below).

In conventional supported metal catalysts (Figure 1), the support is typically a "microstone" with defined physical and physico-chemical features, and its chemical ones are controllable to some extent. In the case of resin-supported metal nanoclusters, the support particles are "microsponges", the physical, physico-chemical, and chemical features of which can be designed and are controllable in nature.[13, 14]

Thus, reagents involved in a given metal-catalyzed reaction must be able to enter the microreactor (size selectivity), in which they will meet a liquid medium (e.g. a mixture of two different solvents). The composition of the reagents and solvents may be quite different from that which they exhibit in the bulk of the reaction medium. Moreover, the kinetics and the thermodynamics of the catalyzed reaction might be quite different from those existing in the bulk medium itself,[15] and even the concentration of the reagents inside the microreactors may be quite different from that existing in the bulk medium. Consequently, functional resin-supported metal

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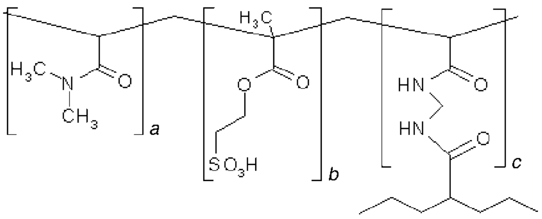
catalysts have to be considered as innovative catalysts, in which the support is able to exert promotion or cocatalytic actions that are inconceivable in the case of conventional metal catalysts supported by metal oxides and amorphous carbon under gas–liquid conditions. A clear illustration of this reasoning was recently offered by the highly chemoselective hydrogenation of 2-ethylanthraquinone to 2-ethylanthrahydroquinone performed with palladium metal supported on very lipophilic resins in these laboratories.[16]

In view of the reasonable assumption that metal catalysts based on functional resins will be useful in the realm of fine and specialty chemicals[17–22] and that hydrogenation processes will be their first working arena, overall thermal and chemical stability under dihydrogen as well as reusability under operational conditions are to be carefully evaluated.

We designed a set of experiments aimed at relevant evaluations to be carried out under relatively severe conditions (5 atm H_2 at 40 °C for a contact time ca. *50* times longer than that required for 98 % conversion of cyclohexene 1м into cyclohexane (hereafter referred to as "heavy-duty" conditions), $[Pd_{analytical}] = 4-5$ mм).

Results

Synthesis and first-level characterization of the catalyst: We selected as paradigmatic catalyst a resin–metal composite from previous work in our laboratories.[23] The selected resin is a copolymer of *N*,*N*-dimethylacrylamide (92 mol %), sulfoethyl methacrylate (4 mol %), and *N*,*N*′-methylenebisacrylamide (4 mol %) as the cross-linker (SPIM(H)) (Scheme 1) and was obtained upon γ-ray irradiation of the reacting comonomers at room temperature.[23]



Scheme 1. Sketch showing the primary structure of resin SPIM(H); *a* = 92, *b* = 4; *c* = 4 in mol %.

Two batches of the resin were synthesized, both able to incorporate a maximum (theoretical) 2 % Pd metal. Polymerization yields are very high, as expected from all previous work.[23] SPIM(H) undergoes facile ion-exchange of protons for Pd^{2+} by using $Pd(OAc)_2$ in methanol to give a brown resin that can be easily transformed into a dark black material $SPIM^-Na^+/Pd^0$ upon reduction with $NaBH_4$ in methanol (Pd = 1.67 %) [Eq. (1)].

$$SPIM(H) + 0.5\,Pd(OAc)_2 \xrightarrow{-AcOH} SPIM^-Pd^{2+}/2 \xrightarrow{+NaBH_4} SPIM^-Na^+/Pd^0/2 \quad (1)$$

The resin appears to be swellable in *n*-hexane, toluene, dichloromethane, methanol, and water (Figure 2); thus it appears to be somewhat amphiphilic in nature, as expected from previous literature[24] and previous experience in our laboratories.[14] The good swellability in methanol and the employment of a relatively high BH_4^- concentration let one predict an even distribution of metal centers in the body of each resin particle and, consequently, of the metal nanoclusters.[11, 23] A good semiquantitative confirmation of this prediction is provided by XRMA analysis (X-ray Microprobe Analysis) (Figure 3). Notice that metal distribution is substantially homogeneous, within the limits of an estimated resolution power of approximately 5 μm. SEM (Scanning Electron Microscopy) analysis confirms the expected purely gel-type, nanoporous, nature of SPIM(H) as revealed by high magnification pictures (the estimated resolution power is ca. 200 nm).

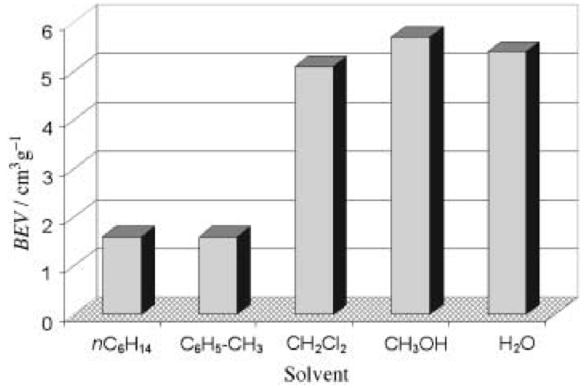


Figure 2. Bulk expanded volume (*BEV*) of SPIM(H) in various solvents.

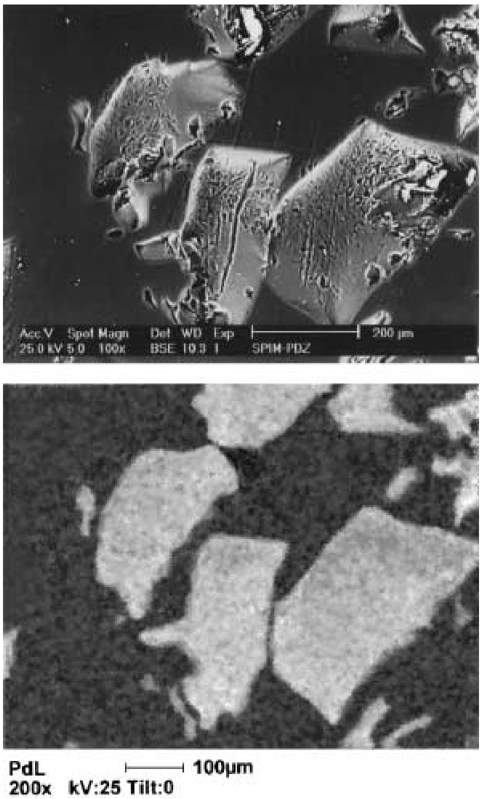


Figure 3. SEM image (top) and XRMA Pd scanning picture (below) showing palladium distribution through sections of $SPIM^-Na^+/Pd^0$ particles.

Second-level characterization of the catalyst: ISEC, ESR, TGA: The framework nanostructure of resin SPIM(H) and of composite SPIM⁻Na⁺/Pd⁰ was evaluated with ISEC (Inverse Steric Exclusion Chromatography)[25, 26] in dichloromethane, the potency of which analytical technique was often illustrated in our work with both gel-type,[6] and macroreticular resins.[27] The nanomorphology of the gel polymer mass is depicted either as polymer chain concentration, nm^{-2} (length of polymer chain in a unit volume of resin = nm/nm^3),[28] or as “cylindrical pores”, nm,[28] referring to a chosen number of gel domains (generally four to six, Figures 4 and Figure 5). It can be seen that the protonated resin displays an almost monomodal nanomorphology characterized by 0.8 nm^{-2} polymer chain concentration or 1.5–2.8 nm “cylindrical pores”. SPIM⁻Na⁺/Pd⁰ exhibits an almost perfect monomodal porosity, corresponding to 1.5 nm^{-2} polymer chain concentration or 1.4 nm “cylindrical pores”.

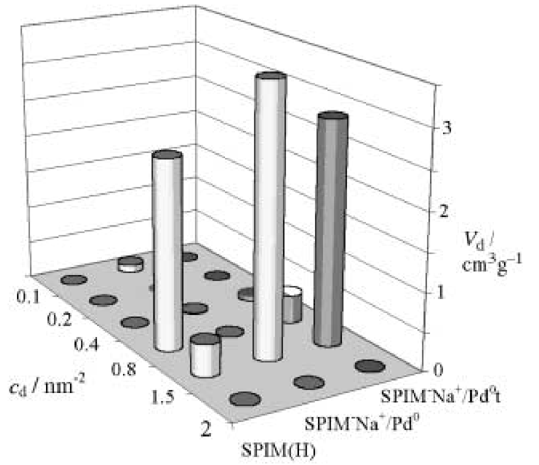


Figure 4. Specific volume (V_d) of resin domains with a certain concentration (c_d) of polymer chains; SPIM⁻Na⁺/Pd⁰t denotes the catalyst after “heavy-duty” tests.

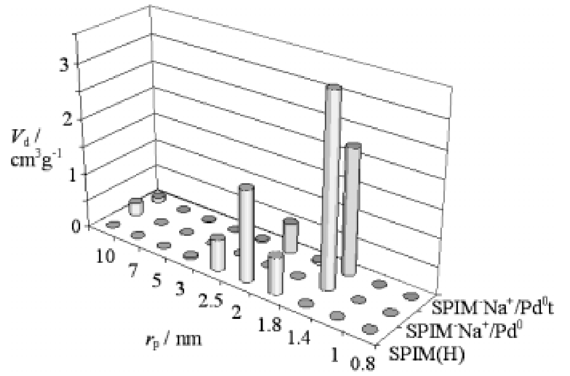


Figure 5. Nanomorphology of resin domains expressed as cylindrical pore gel volumes.

An indirect, but quite reliable and ISEC-related illustration of nanomorphology and molecular accessibility of SPIM⁻Na⁺/Pd⁰ is provided by the rotational mobility of TEMPONE (2,2,6,6-tetramethyl-4-oxo-1-oxypiperidine, Table 1) inside the swollen polymer framework. It can be seen that TEMPONE rotates freely in water or methanol located inside the swollen polymer framework, and the rotational correlation time figures fit the known values observed in the bulk solvent. The τ figures 61 ps (in water) and 38 ps (in methanol) reveal only a moderate reduction of rotational correlation time due to a cavity effect, and the trend is as expected.[9]

Table 1. Rotational mobility of TEMPONE in water and methanol[9] measured in the fresh and treated SPIM⁻Na⁺/Pd⁰ catalyst.

Sample	Medium	$\tau_{25^\circ C} \pm 5\%$ [ps][a]	a_N ($G \pm 0.05$)[b]	$E_a \pm 0.5$ [kJ mol^{-1}][c]
SPIM⁻Na⁺/Pd⁰	water	61	15.73	21.8
SPIM⁻Na⁺/Pd⁰	methanol	38	14.93	20.1
SPIM⁻Na⁺/Pd⁰t	water	63	15.75	23.1
SPIM⁻Na⁺/Pd⁰t	methanol	38	14.94	19.8

[a] Rotational correlation time. [b] Hyperfine coupling constant. [c] Activation energy in the Arhenius type relationship $\tau = A\exp(-E_a/(RT))$.

The overall thermal stability of SPIM⁻Na⁺/Pd⁰ was also checked with a standard TGA (Thermo Gravimetric Analysis) apparatus under dinitrogen (Figure 6).

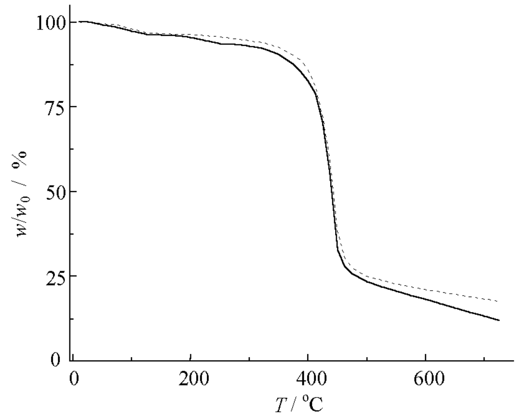


Figure 6. Relative weight (w/w_0) versus temperature (T) of SPIM⁻Na⁺/Pd⁰ catalysts before and after “heavy duty” (solid and dashed lines, repectively).

The polymer framework is thermally stable up to approximately 350 °C after a likely gradual loss of absorbed methanol from room temperature to approximately 150 °C. A moderate loss of weight from 200 to 350 °C is likely to be due to gradual depolymerization.

Catalytic runs: Conditions and data are given in the legends of Figure 7, Figure 8 and Figure 9. The conversion curves make possible the clear evaluation of the time needed by the system to consume 98 % of the substrate. At first, a simple recycling of the catalyst was investigated at a pressure of 1.7 bar (Figure 7). These tests reveal a full reusability of the catalyst. Then, we carried out experiments aimed at a longer exposure of the catalyst to a reaction environment under more severe conditions, that is, higher hydrogen pressure (5 bar, Figure 8) and higher temperature (40 °C, Figure 9). The reaction time for achieving 98 % conversion was multiplied by 50, and the consequent time range was considered suitable for an evaluation of physical and chemical stability of the catalyst. Three batches (500 mg each) of SPIM⁻Na⁺/Pd⁰ were submitted to this test and subsequently analyzed with the same instrumental methods employed for characterizing the fresh catalyst.

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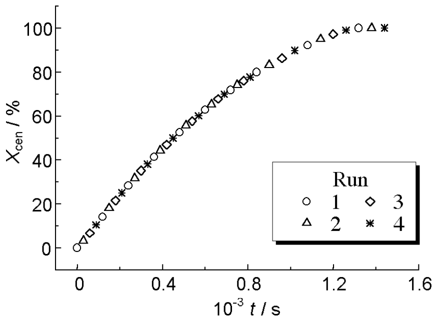

Figure 7. Conversion (X_{cen}) of cyclohexene versus time in four consecutive runs over SPIM$^-$Na$^+$/Pd^0 catalysts at 1.7 ± 0.05 bar, 40 °C; 1 M cyclohexene and 1 M cyclohexane in solution in methanol yielding 2 M cyclohexane solution at 100 % conversion of cyclohexene. [$Pd_{analytical}$] = 5 mol m^{-3}. 250 mg catalyst in 8 mL of the reaction mixture. Catalyst particles size 180–400 μm.

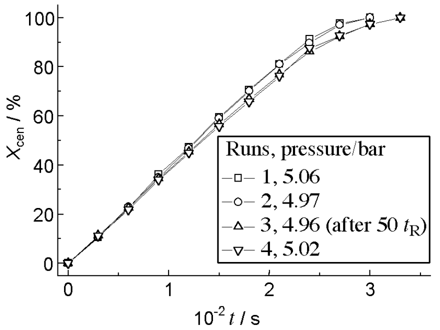

Figure 8. Conversion (X_{cen}) of cyclohexene versus time in four consecutive runs over SPIM$^-$Na$^+$/Pd^0 catalysts at 5 ± 0.1 bar, 27 °C; 1 M cyclohexene and 1 M cyclohexane in solution in methanol yielding 2 M cyclohexane solution at 100 % conversion of cyclohexene; [$Pd_{analytical}$] = 4 mol m^{-3}. 129.4 mg catalyst, in 6 mL of the reaction mixture. Catalyst particles size 180–400 μm.

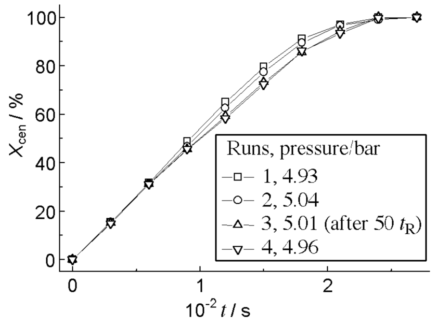

Figure 9. Conversion (X_{cen}) of cyclohexene versus time in four consecutive runs over SPIM$^-$Na$^+$/Pd^0 catalysts at 5 ± 0.1 bar, 40 °C; 1 M cyclohexene and 1 M cyclohexane in solution in methanol yielding 2 M cyclohexane solution at 100 % conversion of cyclohexene; [$Pd_{analytical}$] = 5 mol m^{-3}. Particles size 180–400 μm.

Evaluation of framework stability of catalyst SPIM$^-$Na$^+$/Pd^0: The comparison was carried out on the basis of the following:
a) TGA (Figure 6).
b) ISEC (Figure 4 and Figure 5).
c) ESR (Table 1).

TGA: No noticeable degradation effect can be deduced from the relevant thermograms.

ISEC: A moderate effect is evident from the slight decrease of polymer chain concentration due to the increase of 0.37 mL g^{-1} of 0.8 nm^{-2} domains and a comparable decrease of 1.5 nm^{-2} ones. (Less concentrated domains contribute less to the average polymer-chain concentration.[26])

ESR: The spectra recorded in methanol and water are typical of a fast rotation mode of the molecular probe, with no evidence of TEMPONE absorption by the molecular framework of the catalyst before and after the long hydrogenation test. Differences in τ, E_a, and a_N values are very small, if any (Table 1).

The combination of these techniques strongly suggests that no marked hydrogenolytic effect has occurred, after a reasonably long period of time spent by the catalyst under reasonably severe conditions.

Evaluation of the stability of the metal component: TEM control of possible sintering effects: Low-resolution TEM (Transmission Electron Microscopy) pictures are shown in

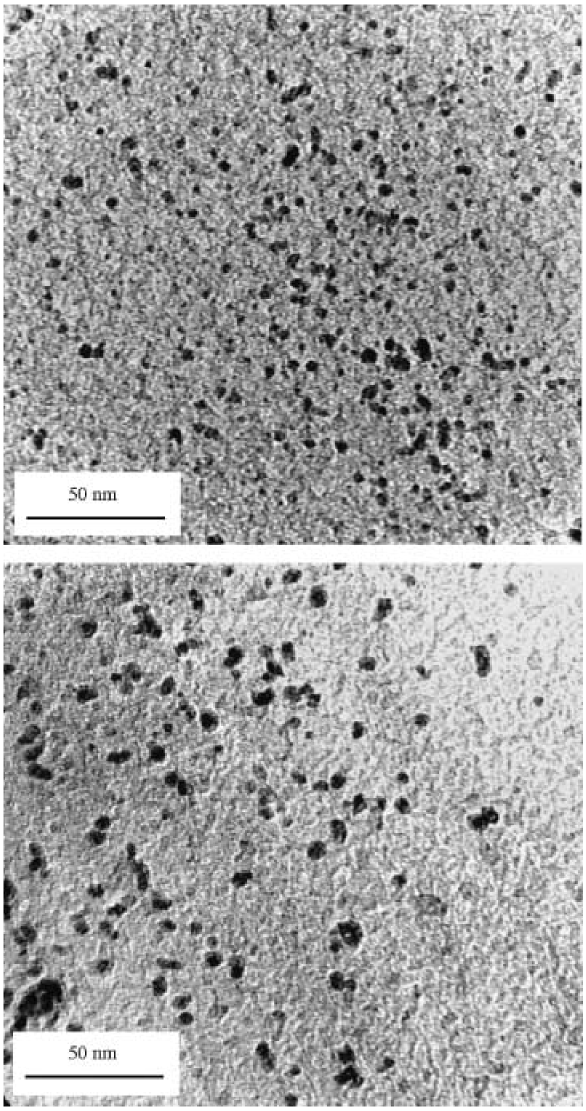

Figure 10. TEM micrographs of the SPIM$^-$Na$^+$/Pd^0 catalysts before (top) and after "heavy-duty" catalytic tests (below).

Figure 10. Pd nanoclusters in the used catalyst are apparently somewhat larger than those in the fresh catalyst (ca. 3 nm) but they appear still well spaced in the polymer framework. The appreciable increase of the size and an increase of the size dispersion are well evident in Figures 10 and 11.

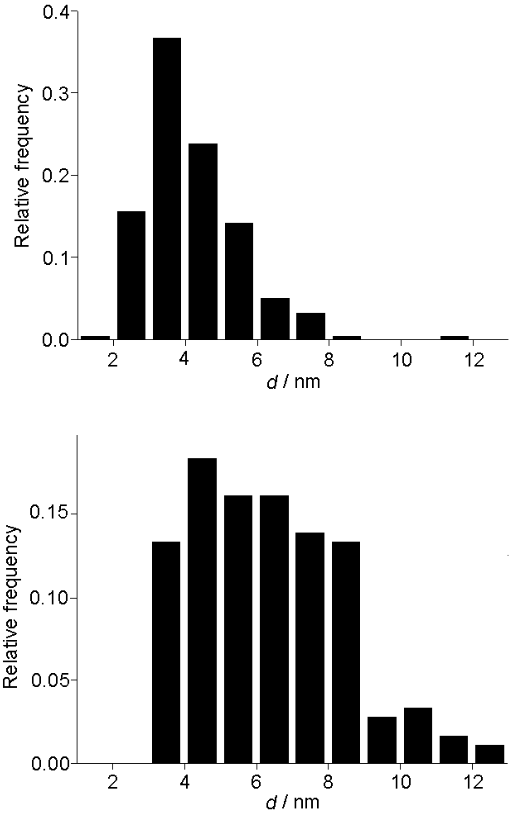

Figure 11. Size distribution of palladium particles before (top) and after "heavy-duty" catalytic tests (below).

A visual impression suggests that some nanoclusters in the used catalyst are in fact aggregates of smaller ones, but HRTEM (High-Resolution Transmission Microscopy) pictures (Figure 12) reveal that this is not the case. Nanoclusters in the used catalyst are well built up nanocrystals, in which the easily measurable inter-row distance (0.21 nm, Figure 13) does not change in spite of "disintegration" and reformation of metal nanoclusters. The value 2.15 nm for ten layers of atoms is in perfect agreement with that determined by Yacaman et al.[29] for the hexagonally shaped FCC structure and ⟨200⟩ planes.

Evaluation of catalyst reusability: As described above, catalyst SPIM$^-$Na$^+$/Pd^0 was subjected to recycling tests (Figures 7–9) at conditions given in the legends. The catalyst, after recovery under dihydrogen, appears to be perfectly reusable in at least four consecutive tests. Since the hydrogenation process applied for testing of the catalyst's overall features appears to be diffusion controlled, the kinetic data suggest a substantial stability of the polymer framework. Moreover, the moderate sintering of palladium-metal particles does not affect the hydrogenation rate that result to be in fact the same in the fresh and in the "after heavy-duty" catalysts.

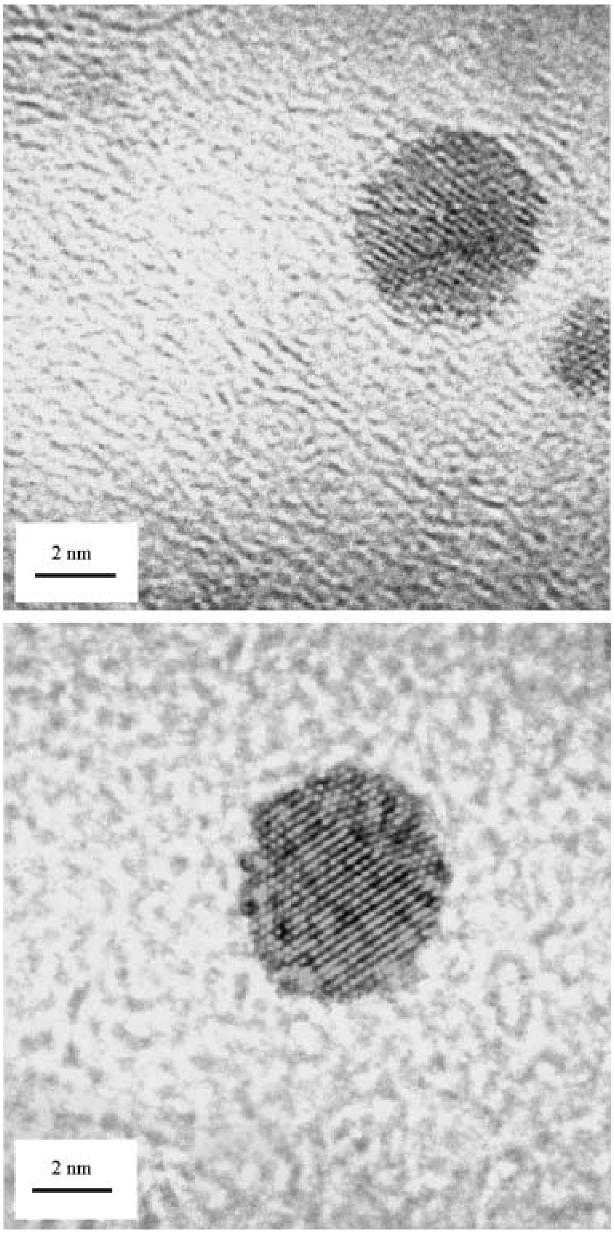

Figure 12. HRTEM of relatively large Pd nanoclusters before (top) and after "heavy-duty" test (below).

Conclusion

A paradigmatic example of a palladium-metal catalyst supported on a cross-linked gel-type resin reveals that the polymer framework is well resistant to hydrogenolysis under conditions corresponding to several consecutive catalytic experiments with the recycled catalyst. However, an appreciable sintering effect is observed also under moderate gas/liquid phase conditions. The catalyst appears to be, in practice, very reusable after ambient-conditions runs.

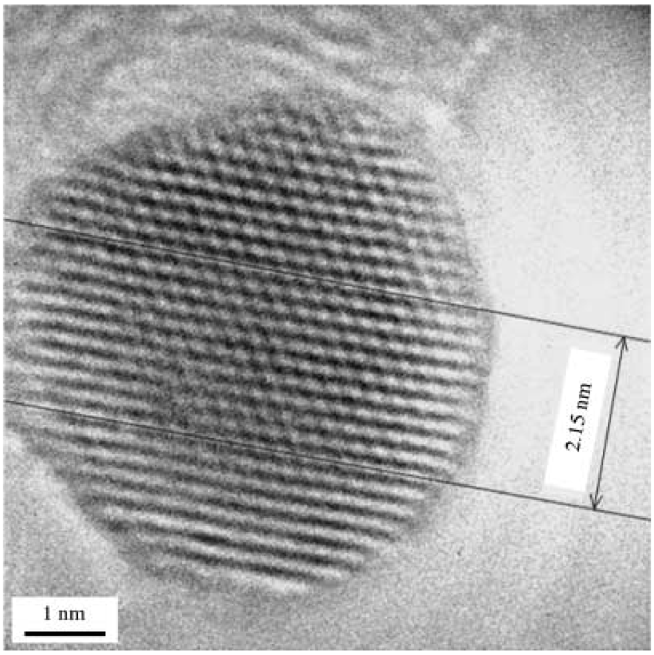

Figure 13. HRTEM of a Pd nanocluster with indication of distance between ten layers of atoms in the SPIM$^-$Na$^+$/Pd^0 catalyst after "heavy-duty" test.

Experimental Section

Apparatus: SEM and XRMA: Cambridge Stereoscan 250 EDX PW 9800; ESR: X-band JEOL JES-RE1X apparatus at 9.2 GHz (modulation 100 KHz) equipped with a variable temperature unit Steler; TGA: Thermogravimetric System Perkin Elmer VTC91; ISEC: home-assembled apparatus made available by Dr. K. Jerabek, Institute of Chemical Process Foundamentals, Czech Academy of Sciences (Prague-Suchdol); TEM: Jeol 2010 with GIF; BEV: 5 mL standard burette fitted with a G3 frit.

Solvents and chemicals: Solvents and chemicals, from various commercial sources, were of reagent grade and used as received. Methacryloylethylenesulfonate (H^+ form) (also called 2-sulfoethyl methacrylate, SEMA), *N*,*N*-dimethylacrylamide (DMAA), and *N*,*N*′-methylene bisacrylamide (MBAA) were from Polysciences.

Resins synthesis: In a typical experiment, DMAA (21.31 g, 0.215 mol), SEMA (1.80 g, 0.00927 mol), and MBAA (1.40 g, 0.00908 mol) were mixed in a cylindrical glass vessel to give a clear colorless solution that, after oxygen removal by means of nitrogen bubbling, was subjected to γ-irradiation (^{60}Co) for 18 h, at a distance of 17.1 cm from the source (total dose was ca. 10 KGy) at room temperature. The solution was transformed into a transparent pale yellow cylindrical block that was triturated in methanol, washed with 3 × 50 mL methanol, and dried at 70 °C under approximately 5 mbar pressure. Polymerization yield was 92%. The resin was fully ground with an IKA A 10 impact grinder, sieved to 180–400 µm, rewashed with 3 × 50 mL methanol, and redried as above. Volumetric acid–base titration gave approximately 0.42 meq H^+/g. Elemental analysis was quite consistent with the expected composition. Addition of palladium and reduction of Pd^{II} to Pd^0 were carried out as described in previous papers.[5–8] Pd content was found to be 1.67%.

Catalytic tests: They were performed with a homemade pressostatic reactor described in ref. [5].

Acknowledgements

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