

## Experimental

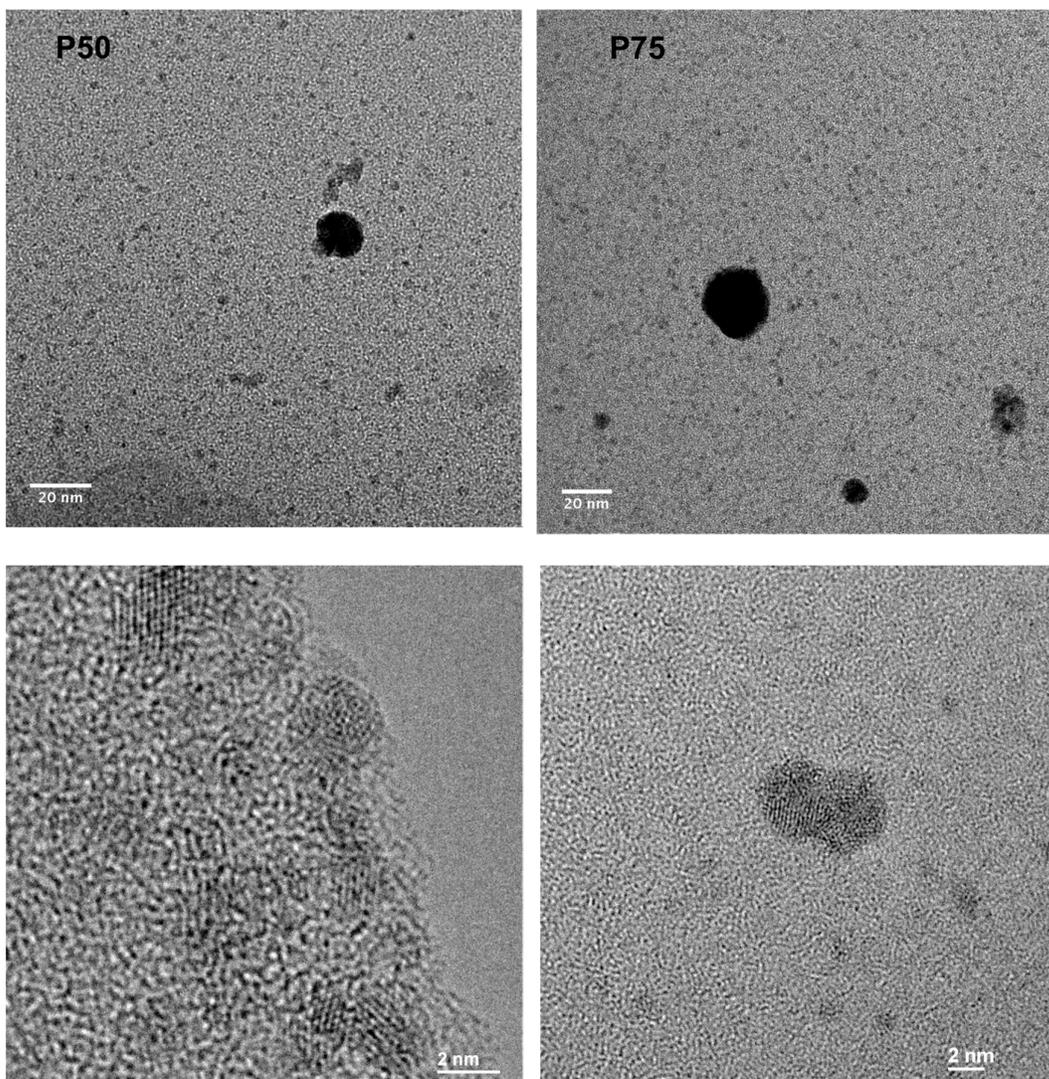
**Materials and apparatus.** All reagents and solvents (reagent grade) were purchased from commercial suppliers sources and used as received.

MD10-4 resin is a poly-2-(methylthio)ethyl methacrylate-*N,N*-dimethylacrylamide-*N,N*-methylenebisacrylamide, 4, 8, 88 mol%, respectively. The material was prepared upon free radical polymerization of the monomer mixture, promoted by  $\gamma$ -irradiation. The procedure is reported in [Corain, B.; Burato, C.; Centomo, P.; Lora, S.; Meyer-Zaika, W.; Schmid, G. Generation of size-controlled gold(0) and palladium(0) nanoclusters inside the nanoporous domains of gel-type functional resins: Part I: Synthetic aspects and first catalytic data in the liquid phase. *J. Mol. Catal. A-Chem.* **2005**, *225*, 189–195.], along with the details of a thorough characterization of the swollen state morphology of the material. The resin was dried at 60°C, and 6 mm Hg overnight, and stored in a closed glass vessel under ambient conditions.

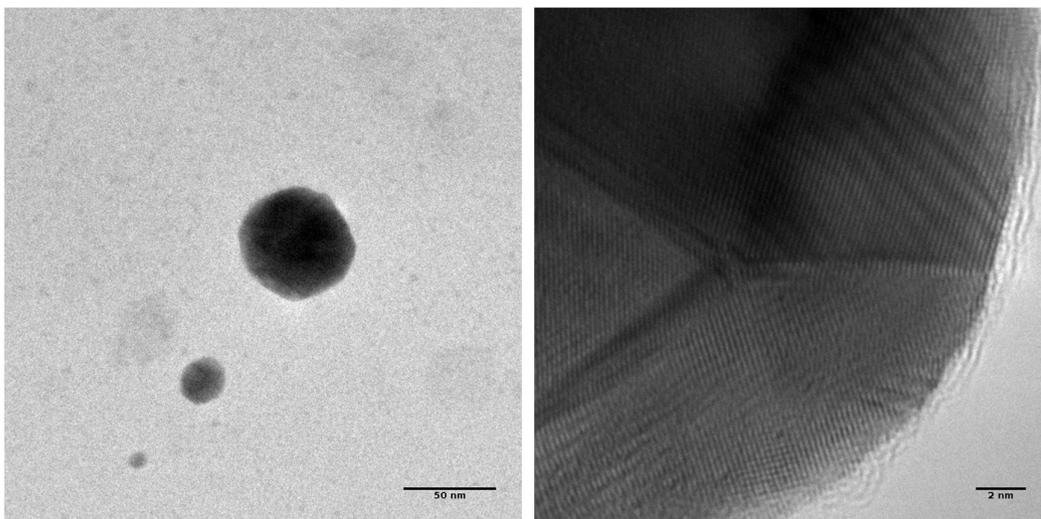
**Metallation of functional resins and reduction to resin/Au<sup>0</sup>-Pd<sup>0</sup> composite (typical procedure).** 29 mg of PdCl<sub>2</sub> were suspended in 25 ml of an aqueous solution of NaCl (103 mg) in a round bottomed flask and heated to 70°C. After ca. 6 hours, an orange transparent solution was obtained. 97 mg of HAuCl<sub>4</sub> were dissolved in 5 ml of deionized water. 1.8 g of MD10-4 resin was swollen in a beaker in ca. 5 ml of distilled water for 2 hours. The resin suspension was added under mild mechanic stirring to the Pd(II) solution. After 1 minute also the Au(III) solution was added and the supernatant phase appeared yellow colored. After 15 minutes the liquid phase was almost completely colorless. The round-bottomed flask was wrapped with an aluminum foil and let to stir overnight. After 17 hours the supernatant solution was completely colorless and the solid appeared yellow-orange. The material is filtered and washed with deionized water (10 ml, four times). The metallated resin (ca. 1 g) is suspended in ca. 250 ml water and left under moderate stirring for 2 h. 300 mg of NaBH<sub>4</sub> dissolved in 70 ml water are added under manual stirring with consequent vigorous gas evolution, and left under moderate mechanic stirring for ca. 180 min, after which time the supernatant phase appears to be colorless and the resins have become dark gray. Reduced resins are filtered, washed with deionized water (10 ml, four times) and dried under vacuum (6 mmHg) at 60 °C to constant weight.

**Catalytic tests.** The catalytic reactions were carried out in a jacketed stainless steel reactor of 17.4-mL total available volume, including dead volumes due to connection lines, gauges and digital manometer, kept at -10°C by an external liquid circulation thermostat. The vessel contains a glass beaker with an external diameter very close to the internal one of the reactor, which was loaded with the solvent (normally water:methanol 1:2.4, 5.0 mL), catalyst (50.0 mg) and a magnetic bar for stirring. In the absence of stirring, the reactor was pressurized first with a 25% O<sub>2</sub>/CO<sub>2</sub> mixture (15.0 bar) and then with a 5% H<sub>2</sub>/CO<sub>2</sub> mixture (5.0 bar) thus yielding a mixture of 2.98·10<sup>-3</sup> O<sub>2</sub> and 1.99·10<sup>-4</sup> H<sub>2</sub> moles. The catalytic process was triggered by stirring which allows the gases to rapidly dissolve in the liquid phase. Once the desired reaction time has elapsed, the vessel was vented off, the catalyst isolated by filtering and washed with water. The re-united aqueous layers were then analysed by iodometric titration in order to determine the amount of hydrogen peroxide formed. Scout experiments were carried out to check the effect of reaction time (30, 60, 90, 120 minutes) on the amount of hydrogen peroxide formed. The best yields were usually obtained after 90 minutes and this reaction time was maintained for all the experiments. Indeed, in view of the fact that with the apparatus exploited the determination of H<sub>2</sub> conversion is not feasible, the hydrogen peroxide molar yields were measured supposing a complete hydrogen conversion. Therefore, the molar yields represent, as a matter of fact, a lower limit of the hydrogen conversion to hydrogen peroxide. From a practical point of view, the concentration of the hydrogen peroxide solutions thus obtained ranges from 3.83·10<sup>-3</sup> M to 1.83·10<sup>-2</sup> M.

**TEM analysis** was carried out with JEM 3010 (JEOL) electron microscope operating at 300 kV, point-to-point resolution at Scherzer defocus of 0.17 nm. Samples for TEM analysis were suspended in isopropanol, sonicated and transferred as a suspension to a copper grid covered with a lacey carbon film.



**Figure S1.** Representative TEM images of P50 (left) and P75 (right) samples. Both the samples depict bimodal distribution with small (1–2nm) and few large (10–20 nm) particles. The NPs appear well crystallized in fcc structure. The lower panel reports the HREM for the two specimens taken at 1M and 600k, respectively.



**Figure S2.** TEM images of P75 specimen. The left side is a low magnification micrograph while the right side is the corresponding High Resolution image; the left and the right micrographs are taken at a magnification of 60k and 800k respectively. The multi-twinned structure of the biggest particle (red box) present in the low-resolution image is evident from HREM image showing lattice fringes belonging to different crystalline domains.