

Letter

Metal palladium dispersed inside macroporous ion-exchange resins: the issue of the accessibility to gaseous reactants

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Abstract

Commercial macroporous ion-exchange resins (Lewatit SPC 118 and UCP 118) were used to support Pd metal by a two step ion-exchange and reduction procedure. The textural features of the resins were determined by Inverse Steric Exclusion Chromatography (ISEC) measurements. TEM characterization of the obtained Pd/resin composite showed the presence of uniformly sized Pd crystallites located at the macropore “surface”. Pulse chemisorption analysis gave evidence for the lack of accessibility of the crystallites when the resin composite is in the dry state. This suggests that the metal particles are in fact embedded in a gel-type resin layer at the “surface” of the macropores and therefore practically inaccessible to the molecules of a gaseous phase unless the support is in the swollen state. © 2000 Elsevier Science B.V. All rights reserved.

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Macroporous ion-exchange resins are well known as efficient acid catalysts for numerous industrial processes, the most important being the large scale synthesis of MTBE from methanol and isobutene (20 million tons estimated for 1997) [1]. In addition, they are used as active supports of metal palladium in the preparation of bifunctional catalysts comprising acid as well as hydrogenation-active centers.

Such catalysts are employed, for example, in the industrial synthesis of methyl-isobutyl ketone (MIBK) (Bayer catalyst OC 1038) [2], where the acid centers catalyze the dimerization of acetone to diacetone alcohol and its dehydration to mesityloxide, which is then hydrogenated on the metal surface to the end product. Similar catalysts based on anion exchange resins (Bayer catalysts K 6333 and VP OC 1063) [3] are employed in industrial heat-exchange units for the reduction of dioxygen level in water from ppm to ppb. Other applications include an alternative route to MTBE (EC Erdölchemie process) [2] and the etherification–hydrogenation of mixtures of unsaturated hydrocarbons to give

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blends of alkanes and branched ethers for the manufacture of unleaded petrol (BP Etherol Process) [4]. In spite of these valuable applications, information on the preparation and the textural features of these catalysts is lacking, even in the patent literature.

In the frame of our ongoing interest in the synthesis and characterization at the molecular level of metal catalysts based on synthetic resins [5–13], we wish to report here on the preparation and characterization of a Pd/resin composite prepared from Bayer acidic resin catalysts UCP 118 or Lewatit SPC 118. Both are macroreticular-type resins possessing nearly identical exchange capacity (4.75 meq/g) and BET surface area (45 m²/g), and differing only in the bead size distribution. In this respect, SPC 118 is a conventional product whereas UCP 118 is a polymer produced by an innovative suspension polymerization technology resulting in an exceptionally narrow bead size distribution. Beside the textural characterization of the polymer support, we have determined the location and size of metal crystallites and we have addressed the question of their accessibility to reactive gases able to diffuse within the macropores of the support in the dry state.

An important feature of polymer supported catalysts swollen by a suitable liquid medium is the availability of functional groups *within* the swollen polymer mass for interaction with reactant molecules diffusing from the bulk liquid phase. Due to the swelling phenomenon, morphological parameters determined on dry samples, like, e.g., the BET surface area, have little relevance to the actual performance of the polymer-supported catalyst under the liquid-phase conditions employed in the commercial processes listed above. In this connection, Inverse Steric Exclusion Chromatography (ISEC) [14,15] is a useful technique providing information on the swollen state morphology of these materials. The method makes it possible to obtain data both on macroporous and gel-type (nanoporous) domains of the swollen polymer mass.

The results of the ISEC characterization of the resin Lewatit SPC 118 in 0.2 M aqueous Na₂SO₄ are reported in Table 1. The macropore morphology is interpreted in terms of the model of cylindrical pores [14,15]. A bidisperse distribution of pore diameters is observed: one population of wider pores with diameter from 30 to 60 nm and another of narrower ones with diameters from 8 to 20 nm. Comparison of these data with the BET surface area determined on a dry sample suggests that the bigger pores remain open after drying while the smaller ones collapse when the solvent is removed. This picture is in agreement with the morphology proposed for macroporous resins by Guyot and coworkers [16,17] on the basis of scanning electron microscopy for resins obtained by suspension polymerization in the presence of a bad solvent for the polymer chains.

The gel-type porosity of the swollen polymer mass can be advantageously described in terms of the Ogston model [18,19]. In this model, pores are treated as spaces between randomly oriented rigid cylindrical rods representing the polymer chains; instead of the pore diameter, the polymer concentration in units of chain length per unit volume is used to characterize the porosity. It is important to remark that the

Table 1
Swollen state morphology of Lewatit SPC 118 in 0.2 M aqueous Na₂SO₄ as determined by ISEC

Macroporous domains		
Macropores	Volume (cm ³ /g)	Surface area (m ² /g)
Pore diameter 30–60 nm	0.44	50
Pore diameter 8–13 nm	0.41	142
Swollen polymer mass		
Polymer chains concentration (nm/nm ³)	Volume of the polymer mass fraction (cm ³ /g)	
0.1	0.00	
0.2	0.08	
0.4	0.00	
0.8	0.00	
1.5	0.19	
2	0.51	

considered volume is not the volume of empty spaces only but the total volume of the gel. The investigated nanopore structure is modelled as a set of discrete fractions, each composed of a homogeneous gel characterized by a single value of polymer concentration. A polymer concentration of $0.1 \text{ nm}^3/\text{nm}^3$ corresponds to a very expanded gel, whose density approaches that of the polymer coils of a soluble polymer dissolved in a “good” solvent. At the opposite end of the set of gel volume fractions, the polymer concentration $2 \text{ nm}^3/\text{nm}^3$ corresponds to a very dense polymer mass, poorly accessible even to small molecules. The data of Table 1 reveal that the polymer mass of Lewatit SPC 118 is largely made out of such dense fractions. This observation is not surprising and is in agreement with the relatively high crosslinking degree of the investigated resin (nominal content of divinylbenzene 18 mol.%). In this specific case, we attribute the $0.08 \text{ nm}^3/\text{nm}^3$ domain to gel-type domains reasonably located as a surface layer on the highly crosslinked polymer nodules [16,17] which define the resin macropores [19] (Fig. 1).

The resin UCP 118 was palladiated with $\text{Pd}(\text{OAc})_2$ in a THF/water mixture and then reduced with NaBH_4 , according to a protocol stemming from our laboratories [5],¹ applied to give a material with 2% w/w Pd content. TEM analysis of the resulting polymer-supported metal catalyst reveals a remarkably heterogeneous distribution of Pd crystallites throughout the polymer network, which appear clearly concentrated at or near the macropore surface (Fig. 1). This can be interpreted on the basis of the

following rationale. The palladiation of the macroporous resin readily occurs at the macropore “surface”, and also to some extent inside the highly cross-linked nodules of the resin. However, the reduction with NaBH_4 is expected to be relatively fast at the macropore surface but considerably slower inside the nodules; this difference can promote a concentration gradient-driven migration of “ Pd^{2+} ” ions from the interior of the nodules to their periphery, i.e., towards the macropore “surface” [20,21]. The very final consequence of this physico-chemical situation is the generation of Pd nanocrystallites in well defined volume elements of the resin network, as it is experimentally observed (Fig. 1). Most remarkably, the generation of Pd nanoparticles inside (fully) gel-type networks is found to produce a totally different scenario, i.e., 3–4 nm crystallites homogeneously dispersed throughout the whole of the polymer mass [22].

The TEM analysis leaves the question open, whether the Pd crystallites are embedded in the gel-type surface layer covering the polymer nodules or truly located at the macropore surface (Fig. 1). In the first case, the gel-type domains are expected to become a glassy, non-porous medium in the dry state, not allowing the metal crystallites to be reached by gaseous reagents, whereas in the second case they should be accessible even in the dry state. In this connection, pulse chemisorption measurements [23] offer an unambiguous answer. We measured the chemisorption of CO on our resin–Pd composite; a sample of 1.2% Pd on silica, prepared by ion-exchange and subsequent reduction with H_2 , was also investigated for comparison.² The results are reported in Fig. 2.

¹ Resin UCP 118 (3 g) was soaked for 1 week under occasional stirring in 75 ml THF/water (2/1) with 131 mg of $\text{Pd}(\text{OAc})_2$ (2% w/w Pd). The brown material was separated from the colourless supernatant solution upon filtration. Pd incorporation was practically quantitative, as confirmed by Pd determination on the supernatant. The palladiated resin was treated with 751 mg NaBH_4 in 200 ml ethanol; evident evolution of hydrogen was observed and at the end of gas evolution the dark-gray resin/Pd composite was isolated upon filtration, washed with ethanol and dried under vacuum at 60°C . In the final material, hydrogen ions are replaced by sodium ones.

² The samples were evacuated for 2 h and then reduced in H_2 for 1 h at room temperature prior to the measurement. An H_2 flow of 25 ml/min was passed over the sample. In this gas flow pulses of 75 ml CO were given. After having passed the sample, the amount of unadsorbed CO was measured (TCD). The palladiated resin was measured twice. For the first one, 150.1 mg of resin were used and a CO/Pd ratio of 0.03 was measured; in the second one, 247.5 mg for a CO/Pd ratio of 0.01.

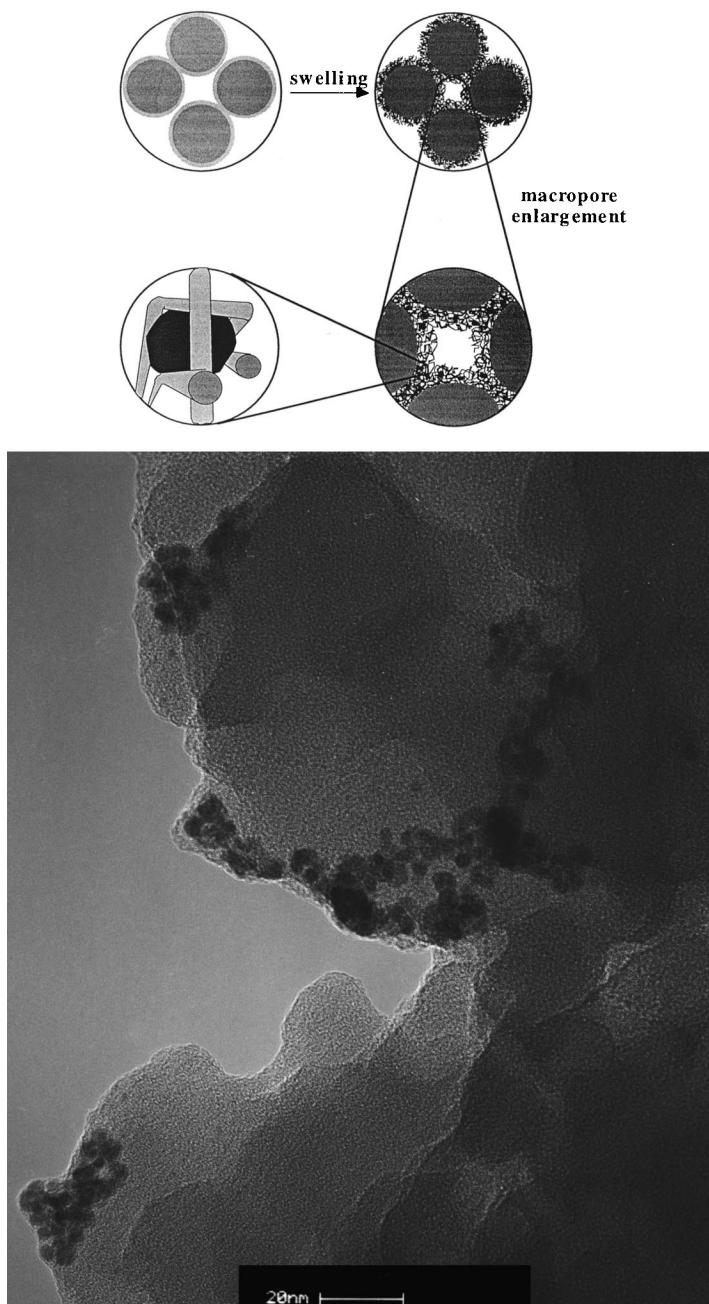


Fig. 1. Graphical model of a macropore of a palladiated resin, with nanocrystallites located at or near the macropore “surface”, and related TEM picture of the UCP 118 Pd composite.

It is quite apparent that the CO uptake by our material is very small (0.02 CO/Pd on average), in spite of the accessibility of its interior guaran-

teed a priori by the permanent macroporosity. This clearly indicates that under gas–solid conditions the metal crystallites are not accessible

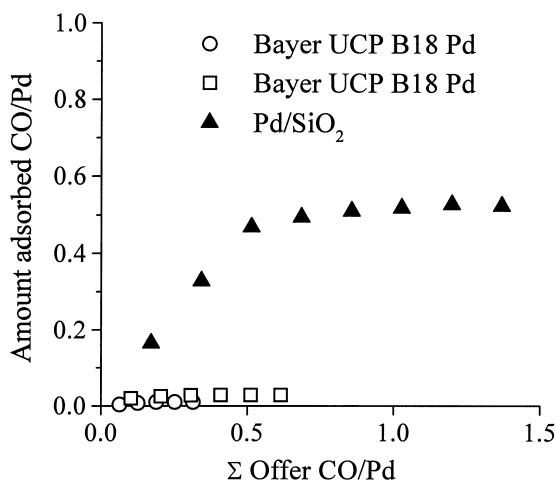


Fig. 2. Pulse chemisorption profiles referring to two samples of UCP 118 Pd composite and to a conventional Pd/SiO₂ material. For experimental details, see Footnote 2.

from the gas phase; they appear to be buried inside the relatively thin gel-type layer covering the macropore surface. By contrast, under proper liquid–solid conditions the gel-type layer swells and becomes permeable, thus making the metal available for chemical transformations [21,22].

The results depicted in this paper uncover an interesting feature of technologically relevant catalysts based on metal crystallites dispersed inside macroporous resins. It has been demonstrated that the crystallites are located in well defined gel-type domains at the macropore surface, which do become accessible only in the swollen state. Therefore, it can be inferred that the catalytic performance of these materials will be affected by the macromolecular structure of the gel-type domains under the employed reaction conditions, an aspect to be borne in mind in the design of catalysts of this kind and for the rational interpretation of their performance.

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