Letter

Metal palladium dispersed inside macroporous ion-exchange resins: rotational and translational mobility inside the polymer network

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Abstract

Commercial macroporous strongly acidic ion-exchange resin (Bayer UCP 118) in its acidic and Na^+ forms and a resin/Pd composite were investigated by means of electron spin resonance (ESR) and pulse field gradient spin echo-nuclear magnetic resonance (PGSE-NMR) techniques, to determine their molecular accessibility to 2,2,6,6-tetramethyl-4-oxo-1-oxypiperidine (TEMPONE) dissolved in water and the molecular mobility of both TEMPONE and water inside their accessible domains. The paramagnetic probe and water itself occupy both the micro- and macroporous domains of the resin particles, among which a rapid exchange is observed. © 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 (22.6 million tons in 1996) [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) [1–4], 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 give the end product. In spite of this and other valuable applications [1–4], information on the preparation, the textural features and the molecular accessibility of the macroporous and gel domains of these materials 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* [5–14], we have recently reported [15] on a thorough characterization of the textural properties of a Pd/resin composite prepared from Bayer acidic resin catalysts UCP 118 or Lewatit SPC 118. Both materials are macroreticular-type

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resins possessing nearly identical exchange capacity (ca. 4.7 meq/g) and BET surface area (45 m^2/g), differing only in beads 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. Besides 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.

The main feature of resins-based catalysts is their ability to be swollen by suitable liquid media, under which conditions their functional groups become available to reacting molecules *within* the swollen polymer mass. For this reason, morphological parameters determined on dry samples, like e.g. the BET surface area, have little relevance to their operational conditions pertinent to the commercial processes listed above and to this end, we have employed inverse steric exclusion chromatography (ISEC) [16,17] to obtain *quantitative* data both on the macroporous and gel-type (nanoporous) domains of the swollen polymer mass. These data are of paramount importance in that they define the physical sites of the swollen supports where in fact *catalysis can take place*. In this specific case, 0.85 and 0.71 ml/g of macroporous (pore sizes from 30 to 60 nm and from 8 to 20 nm) and gel-type (pore sizes less than 2 nm) domains, respectively, were quantitatively determined in water.

In this letter, we report on other important physico-chemical features of swollen UCP 118 both in its acidic form and as UCP 118/Pd composite in which H$^+$ ions are replaced by Na$^+$ ones [15].

Three physico-chemical analytical technologies were employed: (i) standard SEM (Cambridge Stereoscan 250 EDX PW 9800) on dry samples, (ii) electron spin resonance (ESR) of 2,2,6,6-tetramethyl-4-oxo-1-oxypiperidine (TEMPONE) in water (JEOL JES-RE1X apparatus at 9.2 GHz (modulation 100 kHz) over the temperature range 2–40°C at variable temperature controlled by a unit Stelar VTC91) and (iii) pulse field gradient spin echo-nuclear magnetic resonance (PGSE-NMR; Stelar Spinmaster) 4–100 MHz apparatus operating at 21 MHz for protons, over the temperature range 5–35°C at 5° intervals, controlled by a unit BRUKER-VT 100 to an accuracy of within ±0.25°C. ESR provides information on the rotational mobility of TEMPONE inside the investigated resins [16] as well as on the molecular accessibility of the interiors of the swollen resins to the paramagnetic probe itself and PGSE-NMR informs on the translational mobility of a selected solvent inside the polymer network [18,19].

The whole of the information reported in Ref. [15] and in this paper provide an unprecedented comprehensive picture of the nanomorphology and molecular accessibility of a paradigmatic example of a macroreticular functional resin, both in the dry and in the swollen state.

The dry state morphology of the investigated resins is illustrated in Fig. 1 at medium–high (Fig. 1a) and high (Fig. 1b) magnification.

It can be appreciated that the macroporosity (pore diameter larger than 20 nm [20] results from the ''glueing'' (vide infra) of a myriad of polymer mass nodules [21,22] and that the pore walls are in fact built up with tiny portions of the nodules surface.

The swelling of the polymer network of a macroreticular resin is known to produce an overall moderate expansion of the dry polymer mass and to make chemically accessible both the pore walls and (partially) the relevant nodule volumes [15,23]. Our previous paper [15] has revealed in quantitative terms (see above) that 0.85 ml/g of macroporous and 0.71 ml/g of microporous volumes are available in water to probe molecules of convenient hydrodynamic radii. However, ISEC data are relevant in fact to a thermodynamically defined situation and they cannot provide ''kinetic'' information dealing with the mobility of hosted molecules inside the
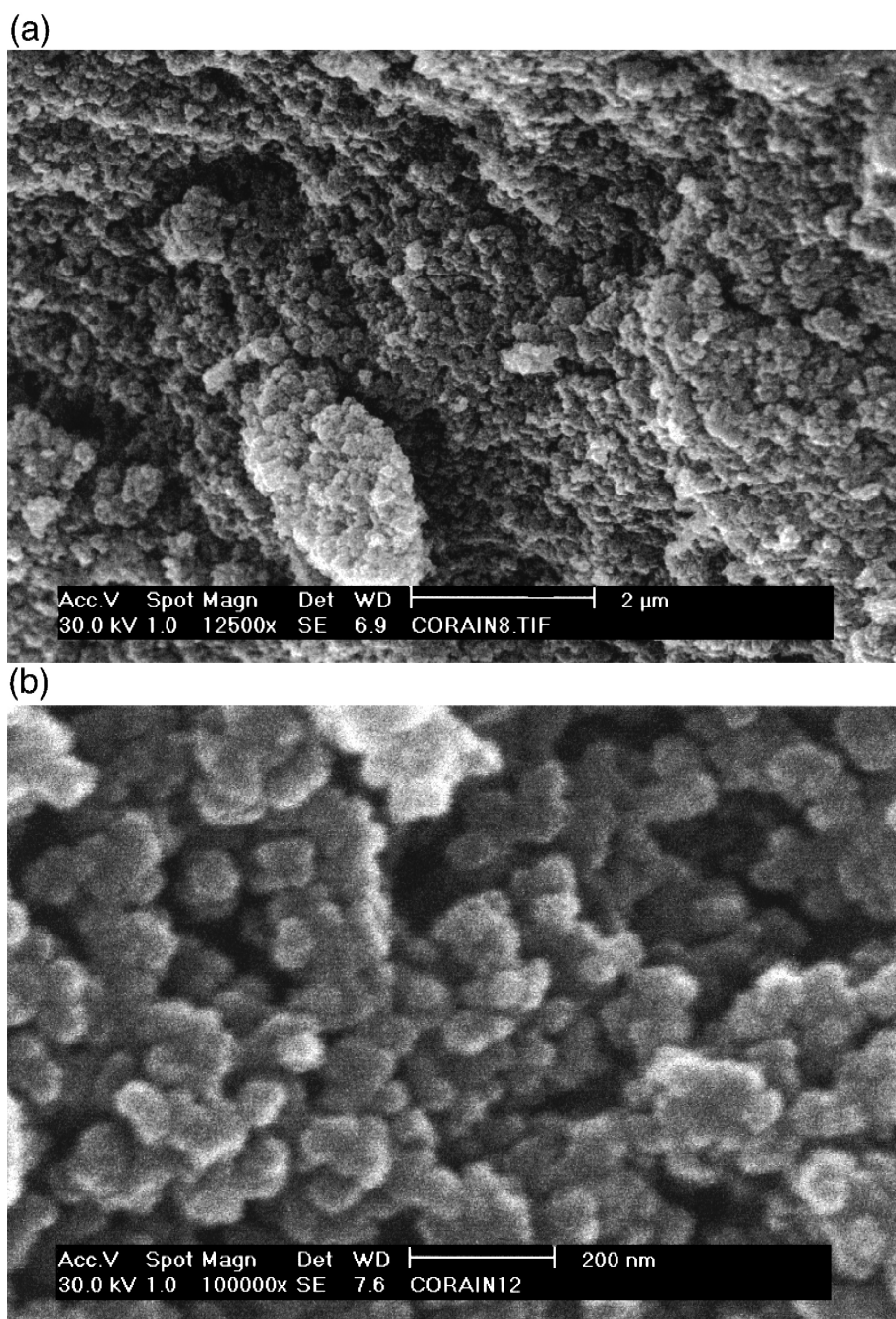
(a)

(b)

Fig. 1. SEM picture of UCP 118/Pd at (a) medium–high and (b) high magnifications.

solvent-filled porous domains. In this connection, ESR [16,17] and PGSE-NMR [18,19] spectroscopies offer excellent possibilities.

ESR spectra of TEMPONE dissolved in water appear uncomplicated in nature, i.e. a single relatively sharp triplet is observed, which circumstance reveals that the probe rotates freely in the domains accessible to it. The moderate, but quite appreciable, reduction of rotational mobility (Table 1) compared to that recorded in

Table 1
Rotational mobility of TEMPONE and translational mobility of water inside UCP 118 (H^+), UCP 118 (Na^+) and UCP 118 (Na^+)/Pd

Material	τ (ps)[a]	E_a (KJ/mol)[b]	D^c ($\times 10^6$) cm^2 s^{-1}	E_a (KJ/mol)[d]
Bulk water	13	18.0 ± 0.5	23.0	18 ± 1
UCP 118 (H^+)	70	5.2 ± 0.5	9.5	12 ± 1
UCP 118 (Na^+)	47	6.1 ± 0.5	9.7	10 ± 1
UCP 118 (Na^+)/Pd	46	6.4 ± 0.5	8.4	12 ± 1

[a] Rotational correlation time of TEMPONE.
[b] Obtained in the 2–40°C temperature range.
[c] Self-diffusion coefficient.
[d] Obtained in the 5–35°C temperature range.

bulk water leaves little doubts on the fact that TEMPONE penetrates into the gel ''nanophases'' of the resin nodules. In fact, the rotation of the paramagnetic probe only inside the comparatively very large macropores would lead to rotational correlation time values, τ [24], indistinguishable from those seen in bulk water [24] and the apparent reduction of τ's reveals that in water, both pore walls and at least portions of the denser nodule volumes are accessible to the paramagnetic probe.

Similar overall considerations are suggested by the PGSE-NMR data of Table 1. Thus, the moderate reduction of the water self-diffusion coefficient D associated with the diffusion inside the resin macro- and microporosity leaves little doubts about the effective penetration of water inside the macroporous domains of the resins nodules revealed by ISEC analysis.

Apparently, TEMPONE experiences a defined cavity effect in that its rotational diffusion decreases appreciably from the bulk solvent state to the state created by its dispersion inside the polymer networks. The effect appears to be greater (albeit still moderate) inside the resin in acid form and somewhat smaller inside both resins in Na^+ form, independently of the presence of Pd nanoclusters. It is worth noting that the invariance of the hyperfine coupling constant (15.85 G in water vs. 15.85 G in swollen resins) clearly reveals that no detectable polarity change at the paramagnetic site turns out to be associated with its confinement inside the investigated materials.

Quite similar considerations are suggested by PGSE-NMR data. Water mobility is affected by its dispersion inside the resin particles for all investigated materials. The dispersion inside the macroreticular network reduces significantly the relevant self-diffusion coefficients to a quantitative relative extent quite similar to that detected for the rotational mobility of TEMPONE.

The close agreement of the rotational mobility and the self-diffusion translational mobility patterns observed on the basis of two quite independent analytical technologies and their overall agreement with the ISEC results confirm previous observations [16,17] on *the ability of these techniques to provide concomitant and convergent information on the nanomorphology and molecular accessibility of both gel-type and macroreticular polymer networks.*

A rather remarkable observation remains to be discussed. The data of Table 1 reveal a marked *reduction of activation energy*, compared to the bulk solvent state, both for the rotation of TEMPONE and for the translation of water inside all three investigated materials. We believe that this remarkable observation can be rationalized in the following terms.

Water and TEMPONE do diffuse inside these relatively accessible materials, i.e. both inside macroporous domains (ISEC and SEM analyses) and microporous ones, a significant fraction of which is built up with a relatively little dense polymer network (ISEC analysis). Consequently, diffusion mechanism [16,17] and E_a values for bulk and confined liquid medium are

expected to be the same. In case, possible inter-actions of the diffusants with the polymer chains or, and shearing effects [25,26] should lead to higher E_a's.

The observed unexpected dependence of τ and D has to be related to essentially experimental circumstances. If we assume that the populations of the two diffusants do ''slowly'' exchange between macroporous domains (in which the microviscosity is expected to be that of bulk solvent) and microporous domains (where an appreciable, but not dramatic increase of microviscosity is expected [16,17]), the resulting observed spectral features have to be considered the result of the superimposition of two components that may be so similar to give rise to a single signal in the ESR experiment and to a single spin echo decay in the PGSE-NMR one. Keeping this in mind, an increase of temperature will (i) increase the overall rotational diffusion of TEMPONE, (ii) increase the diffusion of water molecules and (iii) increase the exchange rates between the micro- and macroporous domains. This last circumstance causes both a broadening of the ESR lines [27,28] and an increase of the contribution of the slower diffusing water fraction to the total echo signal. In fact, this contribution that is in principle underestimated owing to the lower transversal relaxation time of this fraction, turns out to be gradually less underestimated thanks to the gradual increase of the exchange rate. Consequently, τ and D values are experimentally superestimated and underestimated respectively and an overall underestimate of the temperature effect on the rotational and translational diffusion phenomena is produced. On the basis of the above, the final consequence could well be an apparent reduction of overall activation energy.

References

[1] K. Weissermel, H.-P. Arpe, Industrial Organic Chemistry, 3rd edn., VCH, Weinheim, 1997, Chap. 11, p. 281 (MIBK), Chap. 3, p. 71 (MTBE).

[2] PM. Lange, F. Martinola, S. Oeckel, Hydrocarbon Processing, December 1985.

[3] A. Mitschker, R. Wagner, P.M. Lange, in: M. Guisnet (Ed.), Heterogeneous Catalysis and Fine Chemicals, Elsevier, Amsterdam, 1988, p. 61.

[4] R. Wagner, P.M. Lange, Erdöl, Erdgas, Kohle 105 (1989) 414.

[5] M. Kralik, M. Hronec, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain et al., J. Mol. Catal. A: Chem. 97 (1995) 145.

[6] M. Kralik, M. Hronec, V. Jorik, S. Lora, G. Palma, M. Zecca, A. Biffis, B. Corain, J. Mol. Catal. A: Chem. 101 (1995) 143.

[7] A. Biffis, B. Corain, Z. Cvengrosova, M. Hronec, K. Jeřabek, M. Králik, Appl. Catal. A: Chem. 124 (1995) 355.

[8] A. Biffis, B. Corain, Z. Cvengrosova, M. Hronec, K. Jeřabek, M. Králik, Appl. Catal. A: Chem. 142 (1996) 327.

[9] M. Králik, M. Zecca, P. Bianchin, A.A. D'Archivio, L. Galantini, B. Corain, J. Mol. Catal. A: Chem. 130 (1998) 85.

[10] M. Zecca, M. Kralik, M. Boaro, G. Palma, S. Lora, M. Zancato, B. Corain, J. Mol. Catal. A: Chem. 129 (1998) 27.

[11] R. Fisera, M. Kralik, J. Annus, V. Kratky, M. Zecca, M. Hronec, Collect. Czech. Chem. Commun. 62 (1997) 1763.

[12] M. Kralik, R. Fisera, M. Zecca, A.A. D'Archivio, L. Galantini, K. Jeřabek, B. Corain, Collect. Czech. Chem. Commun. 63 (1998) 1074.

[13] D. Gasparovicova, M. Králik, M. Hronec, Collect. Czech. Chem. Commun. 64 (1999) 502.

[14] A.A. D'Archivio, L. Galantini, A. Biffis, K. Jeřabek, B. Corain, Chem. Eur. J. 6 (2000) 794.

[15] A. Biffis, H. Landes, K. Jeřabek, B. Corain, J. Mol. Catal. A: Chem. 151 (1999) 283.

[16] A. Biffis, B. Corain, M. Zecca, C. Corvaja, K. Jeřabek, J. Am Chem. Soc. 117 (1995) 1603, and references therein.

[17] A.A. D'Archivio, L. Galantini, A. Panatta, E. Tettamanti, B. Corain, J. Phys. Chem. B 102 (1998) 6779, and references therein.

[18] P. Stilbs, Prog. NMR Spect. 19 (1987) 1, and references therein.

[19] S. Pickup, F.D. Blum, W.T. Ford, M. Periyasamy, J. Am. Chem. Soc. 108 (1986) 3987.

[20] D. Sherrington, Chem. Commun. (1998) 2275, and references therein.

[21] A. Guyot, in: D.C. Sherrington, P. Hodge (Eds.), Synthesis and Separations using Functional Polymers, Wiley, New York, 1988, p. 1.

[22] A. Guyot, Pure Appl. Chem. 60 (1988) 365.

[23] R.L. Albright, React. Polym. 4 (1986) 155–174.

[24] P.L. Nordio, in: L.J. Berliner (Ed.), Spin Labeling-Theory and Applications vol. I Academic Press, New York, 1976, pp. 5–52.

[25] A.H. Muhr, J.M.V. Blanshard, Polymer 23 (1982) 1012.

[26] S. Pickup, F.D. Blum, Macromolecules 22 (1989) 3961.

[27] L.H. Horvath, P.J. Brophy, D. Marsh, Biochemistry 27 (1988) 46.

[28] D.M. Harryvan, Y.K. Levine, Spectrochim. Acta, Part A 54 (1998) 535.