Stacked phthalocyanines in VPI-5 pores as evidenced by CPDOR ^{1}H–^{27}Al NMR

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Abstract

Stacks of phthalocyanine complexes were synthesized in the pores of the extra large pore molecular sieve VPI-5, as evidenced by the new CPDOR NMR technique, thus enabling the stabilization of the open structure in absence of the triple helix structure of adsorbed water and affording the system with exceptional catalytic properties. It was found that the stacks of Pc piles in the pores of VPI-5 very much enhance the redox properties of those FePc complexes that protrude from the surface.

Catalytic activity and adsorption properties of molecular sieves were, until very recently, limited by their pore dimensions. New molecular sieves with extra large pore dimensions, such as VPI-5, now exist [1,2]. VPI-5 however lacks thermal stability, tends to collapse into a more dense and stable microporous material, and as such does not contain active catalytic sites. Stabilization and functionalization of the structure are key issues [2–9]. We report now that encapsulated and catalytically active iron phthalocyanine complexes synthesized in situ in the channels prop up the VPI-5 structure. The material catalyses alkane oxidation at high rates. Encapsulation is proven by stabilization of the structure and by cross-polarization double rotation (CP/DOR) solid

state ^{27}Al-NMR [10], which shows a very pronounced enhancement of the NMR signal caused by the tight fit between arrays of stacked phthalocyanine ligands and the VPI-5 pore walls. The system was also characterized by XRD, FTIR, ^{13}C-, ^{27}Al- and ^{31}P-MAS NMR, thermogravimetry, nitrogen sorption measurements, molecular modelling and catalytic tests.

Our material was prepared by heating a mixture of the starting products (1,2-dicyanobenzene, ferrocene and VPI-5), and purified by Soxhlet extractions (full procedure is described in [9]). FTIR and ^{13}C-MAS NMR [6] shows the integrity of encapsulated phthalocyanines (Pc), and that they are the only organic species present in the material, 40% being in the metallated form, as generally observed with this synthesis. XRD shows that the VPI-5 structure is for at least 90%

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preserved. In absence of Pc precursors, the treatment we apply always leads to transformation of the VPI-5 to molecular sieve $AlPO_4$-8, in agreement with literature [11]. Preservation of the structure is the first proof of occupation and propping of the channels by the encapsulated complexes.

Thermogravimetric analysis shows that structural water is replaced by ferrocene dissolved in dicyanobenzene (DCB). Pc's formed in situ prevent the structural transformation of VPI-5. Al/8N atomic ratios of 10 and 8 ± 1 measured chemically and with XPS, respectively, Thermogravimetric analyses show that dicyanobenzene (DCB) melts and dissolves ferrocene just before structural water is removed. The liquid solution can then replace outgoing water, and form Pc's in situ for the stabilization of the structure.

The concentration of Pc's in the molecular sieve can be measured by chemical analysis, or by the surface technique XPS. Al/8N atomic ratios of 10 (chemical analysis) and 8 ± 1 (XPS) point to an almost quantitative encapsulation of Pc in the channels of VPI-5. The loss of the nitrogen sorption capacity after encapsulation points to the absence of micropores.

Proof of the pillaring of the VPI-5 pores by Pc is obtained from MAS NMR (Fig. 1) as the introduction of FePc in the VPI-5 structure has a strong broadening effect on the line width of the ^{27}Al line and results in resolution loss in the ^{31}P spectrum. Introduction of FePc in the VPI-5 structure has a strong broadening effect on ^{31}P- and ^{27}Al-MAS NMR signals (Fig. 1). As the XRD data indicate that at least 90% of the structure remains intact, the NMR line broadening is mainly attributed to an enhanced dispersion on the NMR line positions, caused by local deformation of the framework, which can be the result of a tight fit between encapsulated Pc and the walls of the VPI-5 channels.

The reduction of intensity upon encapsulation of the Al NMR spectrum signal at -18 ppm, assigned to framework aluminum sites in VPI-5 linked to two molecules of chemisorbed water

[6,8] points to a decreased complexing effect with water, compared to hydrated VPI-5.

^1H–^{27}Al CPDOR NMR was used to demonstrate the strong interaction between encapsulated Pc and the VPI-5 structure through the proximity between protons and quadrupolar nuclei.

Fig. 2 depicts the ^{27}Al DOR and ^1H–^{27}Al CPDOR NMR spectra of hydrated and intercalated VPI-5. Despite the application of the DOR technique the Al lines in the NMR spectrum remain broad (Fig. 2c) compared to those in hydrated VPI-5 (Fig. 2a). This is in line with an increased dispersion of the Al sites in an intercalated and locally deformed VPI-5 lattice. The CP enhancement of the line intensity in the Pc intercalated VPI-5 is very high compared to that in hydrated VPI-5. This difference can only be explained by the presence of immobilized protons caused by close contact between the Al atoms in the pore walls of VPI-5 and the protons of encapsulated Pc. By contrast, the Al sites of hydrated VPI-5 show weak interactions with protons of adsorbed water molecules due to the motion of water complexes [8].

Split FTIR bands show that the encapsulate is a mixture of H_2Pc with D_{2h} symmetry and FePc with D_{4h} symmetry. A previous publication for-
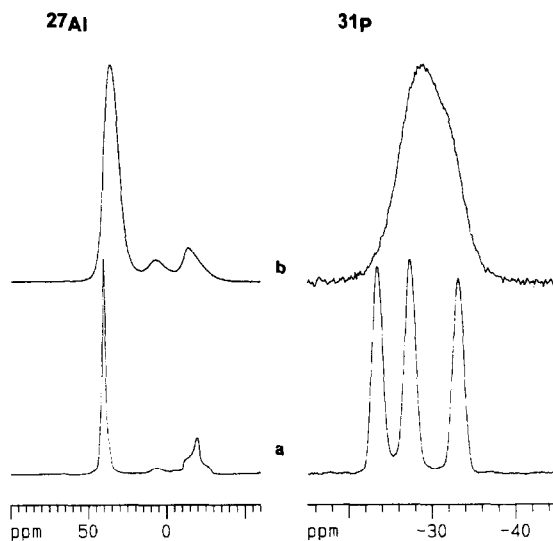

Fig. 1. ^{27}Al and ^{31}P NMR spectrum of VPI-5: (a) as synthesized, (b) after incorporation of FePc. The ^{27}Al line at $+6$ ppm is due to a boehmite impurity. The spectra are referenced to dilute aqueous $Al(NO_3)_3$ and 85% H_3PO_4 respectively.
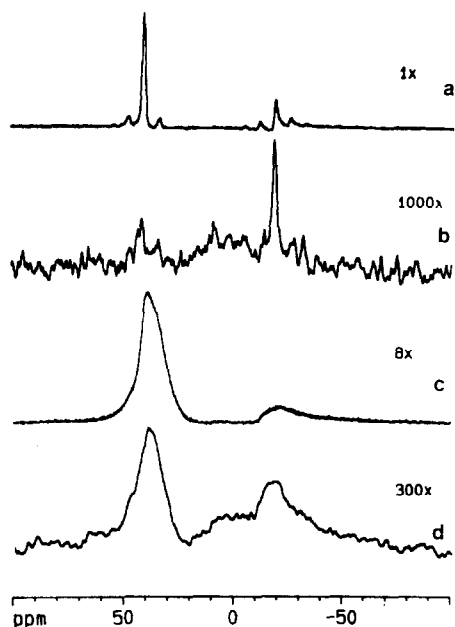
Fig. 2. ^{27}Al DOR NMR spectra of (a) VPI-5 and (c) FePc–VPI-5, and ^{27}Al–^{1}H CPDOR NMR spectra of (b) VPI-5 and (d) FePc–VPI-5. The outer rotor spinning frequency was 730 Hz, the inner 6 kHz. Contact time: 300 ms, radiofrequency amplitude: 15 kHz for the proton channel, 5 kHz for the aluminum channel.

mally presented the organic complex with only two benzene rings touching the walls of the channel [4]. The impossibility for small molecules to diffuse through the channels, the strong enhancement of the CPDOR lines, the average distance of 0.81 nm between the complexes (as derived from the encapsulate loading), and the structure stabilizing effect of the encapsulate point to the presence of stacks of Pc with the molecular plane in a position perpendicular to the channel direction. Molecular modelling gives a minimum adsorption energy for an angle of 53° between the Pc molecule and the channel axis. A strict perpendicular position is not impossible, as NMR results suggest a deformation of the lattice by Pc. In a position perpendicular to the channel direction, encapsulated Pc will push with the 4 benzene rings against the walls (Fig. 3), thus preventing transformation of VPI-5 into AlPO$_4$-8.

As reported previously [4,9], FePc–VPI-5 is a catalyst of alkane oxidation by tertiary butylhydroperoxide (TBHP) at room temperature. The catalytic oxidations were performed using 0.25 g

of FePc–VPI-5, 25 mmol of substrate, 15 ml of acetone as solvent and TBHP (70% in water) added to a batch reactor at a rate of 0.3 ml h^{-1}. Typical selectivities in the oxidation of cycloalkanes, up to 20% conversion, are 15% for the mono-alcohol and 85% for the mono-ketone. In
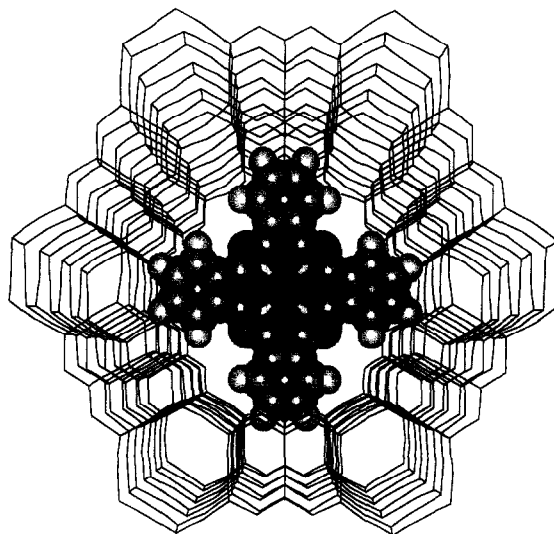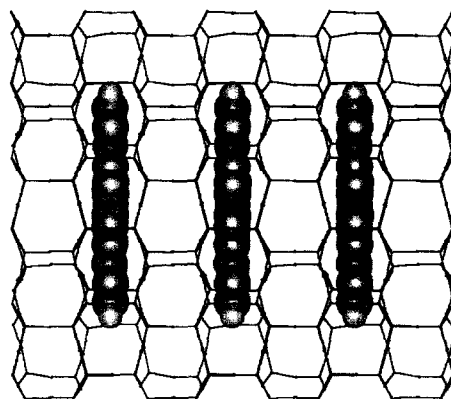

Fig. 3. Molecular model of FePc–VPI-5 (Hyperchem V 3.0 for Windows, using a completed version of the MM+ force field, i.e. of Allinger's MM2(91) [13]). Top: view perpendicular to the main axis of the molecular sieve channel, and bottom: along the channel axis. VPI-5 structure was retrieved from crystallographic data [8] and the metal complex was modelled using a fixed geometry and covalent bonding between the central iron atom and the nitrogens of the ligand. Distance between complexes (8.1 Å) is deduced from the loading and average size of VPI-5 crystals (the amount of phthalocyanines in the VPI-5 was determined by Vis–NIR spectroscopy after dissolution of the VPI-5 in concentrated sulfuric acid and by IR spectroscopy in KBr pellets, as we already described in [9]). This inter-complex distance is an average and more compact stacking alternating with channel sections filled with water is possible. VPI-5 is represented by bonding between atoms.

new experiments, we have measured turnover numbers (TON) of 125 and 313, for cyclododecane and cyclohexane, respectively, assuming that every FePc is accessible. However, as in a sequence of stacked Pc in the monodimensional pores of VPI-5, only those at channel ends are accessible, we estimate, for 30–50 μm crystals, TON to be in the range of a few 100,000. This corresponds to rates of a few hundred turnovers per minute, a value that surpasses all literature data [12].

It is clear that stacks of Pc piles in the pores of VPI-5 very much enhance the redox properties of those FePc complexes that protrude from the surface. How this mechanistically happens requires further research.

We have synthesized stacks of phthalocyanine complexes in the pores of the extra large pore molecular sieve VPI-5 as evidenced by the new CPDOR NMR technique, thus enabling the stabilization of the open structure in absence of the triple helix structure of adsorbed water and attributing to the system exceptional catalytic properties.

Acknowledgements

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