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Catalytic oxidation of cyclohexene over metalloporphyrin supported on mesoporous molecular sieves of FSM-16 type—Steric effects induced by nanospace constraints

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Abstract

Aluminated mesoporous molecular sieves of FSM-16 type were functionalized by cation exchange with MnTMPyP metalloporphyrin species. Textural analysis showed that the method of alumination determines the distribution of metalloporphyrin cations between the internal mesopore system and the external support surface. Direct alumination leads to the preferential accumulation of MnTMPyP within the internal channels, while impregnation of the purely siliceous FSM-16 with aluminium results in the immobilization of a large part of metalloporphyrin at the outer surface of the support. This conclusion is supported by the selectivity patterns observed in the oxidation of cyclohexene with iodosylbenzene. The nanospace constraints experienced by MnTMPyP centres located in the channels of the directly aluminated supports suppress the epoxidation pathway leaving way for the allylic oxidation. The metalloporphyrin species abundant at the external surface of FSM-16 supports aluminated by impregnation of purely siliceous material are free of steric hindrances and yield predominantly epoxide. The results point to the crucial role of the alumination procedure in tailoring the catalytic properties of FSM-16 supported metalloporphyrins.

Keywords: FSM-16; Alumination; Metalloporphyrin; MnTMPyP; Cyclohexene oxidation

1. Introduction

Metalloporphyrins are well-known catalysts for homogeneous oxidation and hydroxylation processes. An important aspect of research into their catalytic action is associated with immobilization of the porphyrin species onto a solid support, in order to facilitate handling of the catalyst, as well as possibly stabilize and/or modify the catalytic performance [1,2]. Our recent works demonstrated that Al,Si-mesoporous molecular sieves represent an extremely interesting class of supports for cationic metalloporphyrins, allowing for a strong, electrostatic binding of the metalloporphyrin species and, in many cases, for tailoring of the catalyst selectivity [3–7]. In particular, the oxidation of cyclohexene with iodosylbenzene as an oxygen donor over cationic metalloporphyrin supported on mesoporous aluminosilicates of HMS (MMS) and MCM-41 types was shown to proceed along two different pathways: epoxidation or allylic oxidation, depending on the metalloporphyrin location within the mesoporous framework [3,4]. It has been demonstrated that the porphyrin species anchored exclusively on the internal pore wall surface, as opposed to the external surface, of the aluminosilicate supports impose selectivity which favours allylic oxidation over epoxidation. The effect is related to steric restrictions within the pore channels, which prohibit the favourable mutual orientation of the cyclohexene molecule and the metalloporphyrin required for the formation of an intermediate leading to epoxide [3,4,8]. On the other hand, porphyrins anchored on external surfaces, free from any steric hindrances, behave similarly to free metalloporphyrin catalyst, yielding predominantly epoxidation products. We have shown that the selectivity pattern in the oxidation of cyclohexene over metalloporphyrin was different for directly aluminated MCM-41 and HMS(MMS) types of supports, indicating different distribution of metalloporphyrin within the support lattice [3].

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The effect was interpreted in terms of different spatial distribution of Al sites in both types of solids, and related to the different assembly mechanism operating during the formation of both types of supports. While the formation of MCM-41 depends on the cooperative assembly of anionic inorganic precursor species and the cationic surfactant head groups, the synthesis of HMS solids is based on a neutral assembly mechanism, involving hydrogen bonding between the neutral amine surfactant and neutral inorganic precursor. The present work reports the results of catalytic oxidation of cyclohexene with iodosylbenzene over metalloporphyrin supported on aluminated mesoporous silicas of FSM-16 type, which are materials obtained from synthetic layered mineral kanemite [9]. It has been demonstrated that the kanemite-derived materials are formed via mechanism essentially different from that of MCM-41, despite the use in both cases of cationic surfactants as structure directing agents [10–13]. It has been proposed that, after intercalation of the surfactant cations between the silicate layers, a transformation occurs to a layered mesophase containing fragmented silicate sheets, which is the actual precursor of the FSM-16 structure. This suggests that also aluminated FSM-16 materials may display unique features. In view of the fact that the oxidation of cyclohexene with iodobenzene has proved to be a simple but effective tool for probing the Al distribution within aluminated MCM-41 and HMS matrices, we decided to check on the behaviour of aluminated FSM-16 solids when used as supports for catalytically active metalloporphyrin species in this reaction.

2. Experimental

2.1. Materials

Kanemite was synthesized from the aqueous solution of sodium silicate prepared by addition of 0.05 M SiO_2 to 0.05 M of NaOH dissolved in a small amount of water [14]. The reaction was carried out under vigorous stirring, at room temperature, for 15 min. The mixture was dried in air at 100 °C and calcined at 700 °C for 5 h. The obtained solid was ground, suspended in water and stirred for 10 min. The kanemite product was filtered, washed and air dried. The FSM-16 solids were obtained according to the procedure originally proposed by Inagaki et al. [9], by mixing the kanemite powder with the 0.1 M aqueous solution of hexadecyltrimethylammonium bromide and adjusting pH to 11.5–12 by addition of NaOH. The mixture was heated to 70 °C and stirred for 3 h. Afterwards the pH was adjusted to 8.5 by drop wise addition of 1 M HCl and the mixture stirred for further 3 h. The FSM-16 product was filtered, washed and dried in air. The template was removed by calcination at 550 °C for 6 h. In the present study two types of alumination procedures were employed: direct, at the stage of the kanemite synthesis, and a post-synthesis treatment applied to the purely siliceous FSM-16. In the first case an appropriate amount of $Al(NO_3)_3 \cdot 9H_2O$ was added to the mixture of NaOH and SiO_2 used in the preparation of kanemite. Post-synthesis alumination consisted in impregnation of purely siliceous FSM with a required amount of $Al(NO_3)_3 \cdot 9H_2O$ dissolved in a small quantity of water, followed by drying at 80 °C and calcination for 1.5 h at 550 °C. The directly and the post-synthesis aluminated samples are referred to as Al-FSM-16(Si/Al = x)/D and Al-FSM-16(Si/Al = x)/P, respectively ($x = 20$, 40). The purely siliceous FSM-16 sample is denoted FSM-16(Si/Al = ∞). Mn(TMPyP) porphyrin cations, which can be regarded as squares with dimensions 1.4 nm × 1.4 nm, were incorporated into aluminated mesoporous silicas by means of cationic exchange. The exchange experiments were carried out for 24 h at 70 °C in aqueous medium, using commercially available chloro[meso-tetra(4-*N*-methylopyridynio)-porphirynato] manganese(III) tetrachloride (midcentury) as a source of the Mn(TMPyP) cations. The products were filtered, washed with distilled water in a Soxhlet apparatus for 24 h and dried in air at 70 °C. The amount of the adsorbed metalloporphyrin was determined by means of UV–vis spectroscopy, as a difference between the quantity used for the exchange experiment and that remaining in the solution after filtering and washing.

2.2. Methods

X-ray diffraction patterns were recorded with a Philips 1710 powder diffractometer using Ni-filtered Cu Kα radiation. UV–vis absorbance spectra were recorded on a Shimadzu UV 160 A spectrophotometer. Nitrogen adsorption isotherms were recorded at −196 °C using Quantachrome Autosorb 1 apparatus. Prior to the measurement the samples were outgassed at 150 °C. Specific surface area measurement was based on BET formalism. Pore size distribution analysis was carried out for the adsorption branch of the isotherm using the BJH model.

2.3. Catalysis

Oxidation of cyclohexene with iodosylbenzene (C_6H_5IO) was carried out in an argon atmosphere for 16 h in 3 ml of solvent. CH_2Cl_2 and CH_3OH mixture (1:2) was used as a solvent. The molar ratio of cyclohexene:iodosylbenzene:metalloporphyrin was 800:20:1 (in each experiment the amount of metalloporphyrin corresponded to the concentration of 0.67 mmol/dm^3). Products were analysed with an Agilent 6890N GC equipped with FID, using 30 m column filled with Innowax.

3. Results and discussion

XRD analysis of aluminated FSM-16 supports reveals structural differences between the materials prepared by different alumination procedures (Fig. 1). Although XRD diagrams of all samples show clear Bragg peaks assignable to the (1 0 0) reflection of the hexagonal mesostructure at $2\Theta \approx 2.5^\circ$, the patterns obtained for materials prepared by post-synthesis impregnation show poorer resolution than those recorded for directly aluminated samples of comparable degree of Al doping. The effect indicates that the former method of Al incorporation affects the parent, undoped lattice of FSM-16(Si/

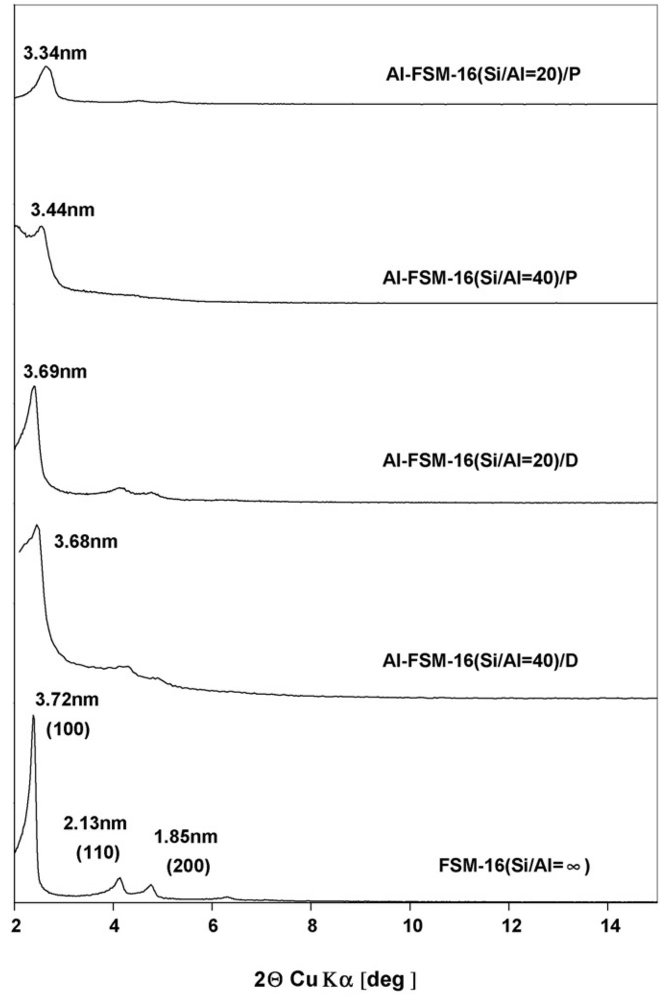

Fig. 1. XRD patterns of purely siliceous and aluminated FSM-16 solids.

Al = ∞) to a higher extent and leads to a less ordered hexagonal structure. The structural deterioration is accompanied by a shift of the (0 0 1) reflection towards slightly higher 2Θ values, which implies a shrinking of the hexagonal lattice parameter a_0 (Table 1). Both effects are most likely associated with the hydrothermal treatment experienced by the parent purely siliceous FSM-16 during impregnation procedure. The ^{27}Al MAS NMR spectra of the solids, published elsewhere [15], confirmed that in both types of materials Al is incorporated in tetrahedral sites of silica framework, the post-synthesis aluminated samples showing additionally a small contribution from extraframework octahedral Al.

Insertion of metalloporphyrin affects the textural properties of the directly and the post-synthesis aluminated FSM supports in a different manner, although both types of carriers retain similar amount of metalloporphyrin for the same nominal Al content (Table 1). Fig. 2 shows, as an example, the nitrogen adsorption/desorption isotherms for Al-FSM-16(Si/Al = 40)/D and Al-FSM-16(Si/Al = 40)/P solids before and after metalloporphyrin incorporation. The data show that the MnTMPyP immobilization onto directly aluminated FSM-16 is accompanied by a significant decrease of the specific surface area and the cumulative pore volume and causes a large downward shift of the isotherm. In the case of post-synthesis aluminated FSM-16 materials, the downward shift of the isotherm is much smaller and the drop in the specific surface area and cumulative pore volume less pronounced. Bearing in mind that in the case of mesoporous solids both the specific surface area and the cumulative pore volume depend primarily on the characteristics of the internal mesopore system, it appears that the mesoporous channels in the post-synthesis aluminated materials are much less affected by loading with metalloporphyrin than the mesopore network in directly aluminated solids. This is also visible in the way the pore size distribution (PSD) curves of the supports are influenced by the loading with metalloporphyrin. Fig. 3 compares the PSD profiles obtained for the Al-FSM-16(Si/Al = 20)/D and Al-FSM-16(Si/Al = 20)/P samples before and after deposition of metalloporphyrin. In the case of directly aluminated support, the loading with MnTMPyP causes a significant shift of the curve maximum from ca. 2.7 to 1.7 nm. The effect is accompanied by the downward shift of the maximum, which is consistent with filling of the mesopore volume with MnTMPyP species. Similar behaviour is also observed in the MnTMPyP/Al-FSM-16(Si/Al = 20)/P sample, but to a much lesser extent, both with the respect to the pore size maximum (shift from ca. 2.3 to 1.9 nm) and the maximum height, which implies that in the materials prepared by post-synthesis alumination the pore filling by MnTMPyP is less effective. The observed result indicates that alumination via impregnation from aqueous solution of Al salt is not very effective as far as the internal pore walls are concerned, most likely due to the diffusion limitations known to play an important role in liquid phase/mesoporous solid systems [6,7,16].

The results of catalytic performance of the MnTMPyP supported on aluminated FSM-16 in the oxidation of cyclohexene with iodosylbenzene are presented in Table 2. No oxidation products have been observed in blank experiment

Table 1
Hexagonal lattice parameter a_0 of aluminated FSM-16 solids, content of incorporated metalloporphyrin, specific surface areas and cumulative pore volumes of supports before and after loading with MnTMPyP

Sample	a_0 (nm)	MnTMPyP content (wt.%)	S_{BET} (m^2/g)		Cumulative pore volume (cm^3)	
			As prepared	After MnTMPyP deposition	As prepared	After MnTMPyP deposition
FSM-16(Si/Al = ∞)	4.29	–	1003	–	1.011	–
FSM-16(Si/Al = 40)/D	4.25	7.7	903	490	1.286	0.604
FSM-16(Si/Al = 20)/D	4.26	9.2	823	349	1.378	0.549
FSM-16(Si/Al = 40)/P	3.97	8.8	866	834	0.702	0.595
FSM-16(Si/Al = 20)/P	3.86	9.4	855	821	1.071	0.891

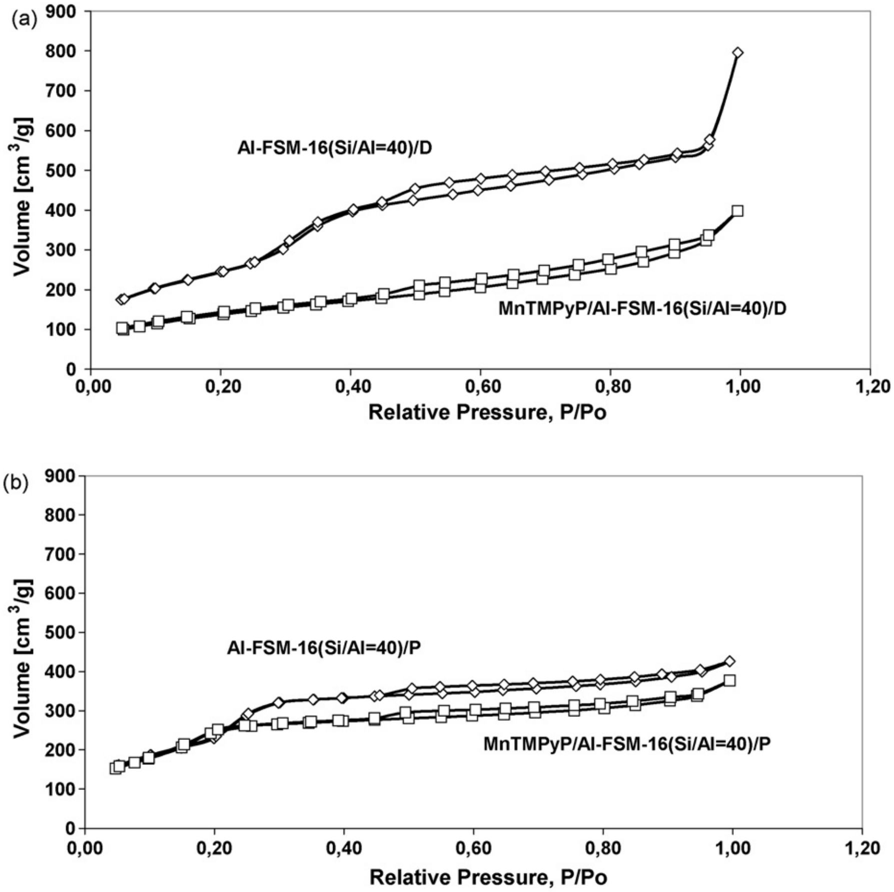

Fig. 2. Nitrogen adsorption/desorption isotherms for Al-FSM-16(Si/Al = 40)/D and Al-FSM-16(Si/Al = 40)/P before and after MnTMPyP deposition.

with pure supports, showing that the catalytic activity is associated with the metalloporphyrin component. In all catalytic experiments with supported MnTMPyP the reaction mixtures remain colourless. The UV–vis spectra of the liquid decanted after the reaction show no presence of the Soret band typical of metalloporphyrin species. Furthermore, upon addition of a fresh dose of iodosylbenzene to the decanted liquid no catalytic effect is observed. These facts indicate that the catalytic activity is associated with metalloporphyrin centres trapped within the mesoporous support. Analysis of the data presented in Table 2 shows that both types of aluminated FSM-16 carriers modify the catalytic performance as compared to that of free metalloporphyrin. However, depending on the mode of support alumination different types of selectivity patterns can be observed. Deposition of metalloporphyrin onto directly aluminated supports results in catalysts, which behave in a completely different way than free MnTMPyP and yield over 90% allylic oxidation products. As demonstrated previously [4], the selectivity pattern in the oxidation of cyclohexene with iodosylbenzene is a sensitive probe of the distribution of metalloporphyrin cations and the Al sites at which they are anchored between the internal pore spaces and the external support surface. Thus, the observed dramatic suppression of epoxidation pathway implies that the catalytically active porphyrins are confined predominantly to the internal pore system of the mesoporous supports [3,4]. When post-synthesis aluminated FSM-16 solids are used as supports, the product distribution changes—the catalysts yield epoxide as the major product, albeit in a lesser quantity than the unbound metalloporphyrin. This means that a substantial part of anchored metalloporphyrin cations are free of steric hindrances imposed by internal pore geometry and are located at the external surface of mesoporous solid. Obviously, both types of alumination procedures result in different spatial distribution of Al sites: direct alumination leads to the preferential accumulation of Al dopant at the internal pore walls, while impregnation of the purely siliceous FSM-16 with aluminium allows for the incorporation of a significant amount of Al sites into the framework positions exposed at the outer surface of the support. This result is consistent with the previously discussed textural characteristics of the investigated materials. Directly aluminated FSM-16 samples, in which framework Al sites and, consequently, metalloporphyrin cations, are located predominantly within the internal channel system, after loading with metalloporphyrin show large reduction of specific surface area, pore size and pore volume, which confirms that the inner pore system is the main reservoir of catalytically active MnTMPyP species. In contrast, in the post-synthesis aluminated FSM-16 supports the textural parameters are much less affected by cation exchange with MnTMPyP. This agrees well with the model, in which only part of the deposited metalloporphyrin enters the inner pore system, the rest remaining anchored at the

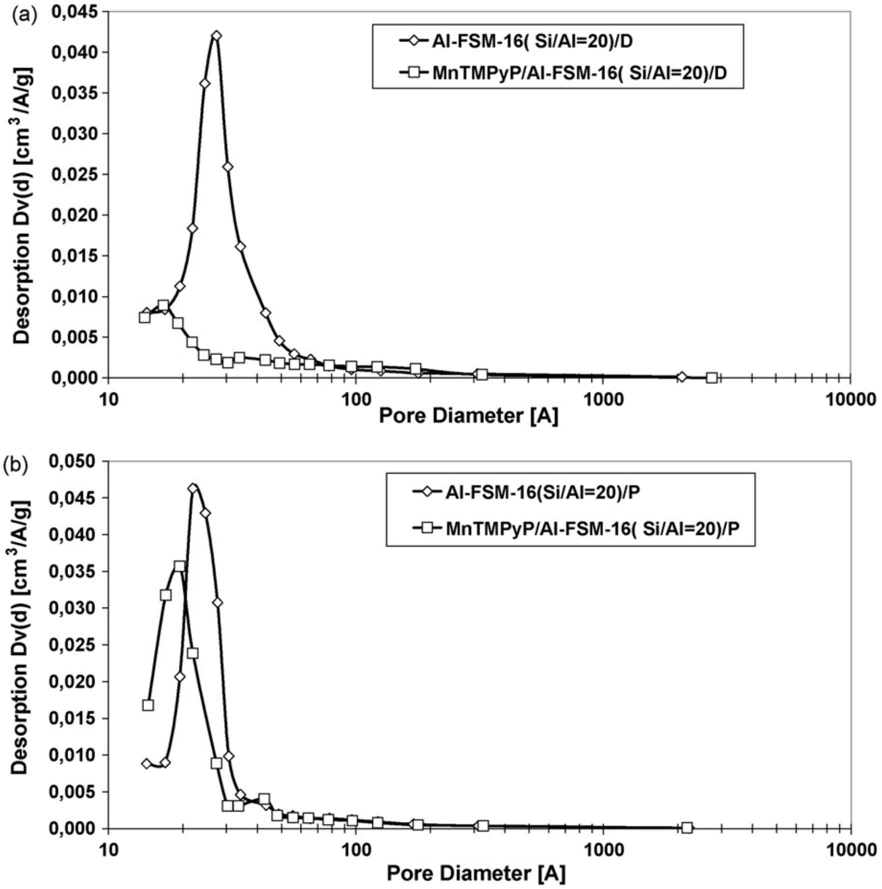

Fig. 3. Pore size distribution curves for Al-FSM-16(Si/Al = 20)/D and Al-FSM-16(Si/Al = 20)/P before and after MnTMPyP deposition.

Table 2
Catalytic oxidation of cyclohexene with iodosylbenzene using unsupported and supported metalloporphyrins[a]

Catalyst	Activity (%)[b]	Epoxidation selectivity (%)	Allylic oxidation selectivity[c] (%)
Al-FSM-16 supports	0	0	0
MnTMPyP unsupported	28.0	85.9	14.1
MnTMPyP/FSM-16(Si/Al = 40)/D	21.1	5.7	94.3
MnTMPyP/FSM-16(Si/Al = 20)/D	25.8	8.4	91.6
MnTMPyP/FSM-16(Si/Al = 40)/P	19.4	69.5	30.5
MnTMPyP/FSM-16(Si/Al = 20)/P	23.9	70.3	29.7

[a] Room temperature, argon atmosphere, 16 h, cyclohexene:iodosylbenzene:metalloporphyrin = 800:20:1, solvent: 3 ml of dichloromethane and methanol (1:2), MnTMPyP concentration 0.67 mmol/dm^3.

[b] Mols cyclohexene consumed/maximum possible cyclohexene consumption (mols) based on the iodosylbenzene added × 100%.

[c] Cyclohexenol and cyclohexenone.

outer surface of the support. It should be stressed that both the nitrogen adsorption/desorption and the catalytic data allow only for qualitative assessment of metalloporphyrin distribution between the surface and the interior of the pore system, because several important factors, including the mode of metalloporphyrin anchoring at either location, the pore volume actively participating in catalysis or the turnover frequencies of differently sited metalloporphyrin species, remain unknown.

It is worthwhile to note that the reported catalytic results and the conclusions concerning the distribution of Al in FSM-16 solids have important implications for understanding the mechanism of FSM-16 formation. In particular, they represent an indirect evidence for the postulated occurrence of fragmentation of kanemite layers [10–13], since only then a preferential accumulation of Al at the inner pore walls of directly aluminated solids is conceivable. This issue will be discussed in detail in our forthcoming paper.

4. Conclusions

Textural analysis of aluminated mesoporous FSM-16 solids before and after exchange with MnTMPyP cations points to the different distribution of metalloporphyrin species within the support lattice, depending on the applied method of alumination. Direct alumination leads to the preferential accumulation of metalloporphyrin species within the internal pore system, while impregnation of the purely siliceous FSM-16 with aluminium results in the immobilization of a large part of metalloprphyrin onto the outer surface of the support. Catalytic oxidation of cyclohexene with iodosylbenzene, known to be a sensitive probe for the distribution of metalloporphyrin (and of the adjacent Al sites) within the mesoporous aluminosilicate framework, confirms these findings. The nanospace constraints experienced by metalloporphyrin centres located within the channels of the directly aluminated FSM-16 supports suppress the epoxidation pathway and favour allylic oxidation. The metalloporphyrin species abundant at the external surface of FSM-16 supports aluminated by impregnation of purely siliceous material are free of steric hindrances and contribute to the high yields of epoxide. Thus, the method of alumination is a powerful tool in tailoring the catalytic properties of metalloporphyrin deposited on FSM-16 carriers.

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