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Oxidation of cyclooctane over Mn(TMPyP) porphyrin-exchanged Al,Si-mesoporous molecular sieves of MCM-41 and SBA-15 type

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Abstract

Mn(TMPyP) metalloporphyrin catalysts supported on aluminated MCM-41 and SBA-15 mesoporous silicas were investigated in the liquid phase oxidation of cyclooctane with molecular oxygen (as air) without the use of sacrificial co-reductant. Cyclooctanone and cyclooctanol were the only reaction products, the first one appearing in overwhelming majority. The activity of the catalysts increased with the increasing pore size of the support, which pointed to the existence of diffusion limitations within the pore inner space. An exceptionally high selectivity to cyclooctanone observed for the MCM-41-derived catalysts, as opposed to SBA-15-based ones and to homogeneous oxidation process, is tentatively interpreted in terms of steric effect due to the suppression of the hydroperoxide intermediate formation in relatively narrow channels of MCM-41. Catalysts show good stability in the reaction conditions.

Keywords: Metalloporphyrins; Mesoporous molecular sieves; Hydrocarbon oxidation; Cyclooctane

1. Introduction

Metalloporphyrins are the most widely studied catalysts for homogeneous selective oxidation and hydroxylation of hydrocarbons. An important area of research into their catalytic properties is associated with immobilization of the porphyrin onto a solid support, in order to make the catalyst easier to handle and to separate from the reaction medium, as well as possibly stabilize and/or modify the catalytic performance [1]. 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 the case of cyclohexene oxidation with iodosylbenzene, for tailoring of the catalyst selectivity [1–4]. In the present work we investigate the potential of metalloporphyrin-exchanged aluminated MCM-41 and SBA-15 mesoporous molecular sieves in the oxidation of cyclooctane with molecular oxygen (as air). This type of reaction, in which an inexpensive, abundant and readily available oxidant such as oxygen from air is used for oxidation of a fairly inert saturated hydrocarbon, without the prohibitive requirement of sacrificial co-reductant, represents one of the most challenging aspects in oxidation processes catalyzed by metalloporphyrins [5–16].

2. Experimental

2.1. Materials

Al-MCM-41 materials were prepared via two different and well established synthesis routes, either by direct addition of Al source to the synthesis gel, or by post-synthesis alumination of purely siliceous MCM-41. In the first case the Al-MCM-41 material was obtained according to the hydrothermal procedure described in detail by Mokaya [17], using tetramethylammonium hydroxide, cetyltrimethylammonium bromide (CTAB) as template, fumed silica as Si source, and aluminium isopropoxide as Al source. The samples prepared this way are denoted Al-MCM-41/D1 and Al-MCM-41/D2, where numbers 1 or 2

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describe materials with different Si/Al ratios. The post-synthesis alumination was carried out following the method of Mokaya and Jones [18], by grafting of aluminium onto purely siliceous MCM-41, using appropriate amounts of aluminium chlorhydrol as the source of Al. The resulting materials are referred to as Al-MCM-41/G1, Al-MCM-41/G2, Al-MCM-41/G3. Alumination of SBA-15 mesoporous silicas was also performed either by direct or by post-synthesis routes. Direct alumination was carried out following the hydrothermal method of Yue et al. [19], using triblock copolymer poly(ethylene glycol)-block-poly(-propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$) as a structure directing agent, tetraethyl orthosilicate (TEOS) as a source of Si and aluminium isopropoxide as a source of Al. The resulting samples are referred to as Al-SBA-15/D1 and Al-SBA-15/D2. Post-synthesis alumination was carried out by grafting of aluminium onto purely siliceous SBA-15 obtained according to the procedure proposed by Zhao et al. [20]. The employed method of grafting, described in detail elsewhere [21,22], involved using a solution of aluminium isopropoxide in dry *n*-hexane. The sample prepared this way is denoted Al-SBA-15/G1.

Mn(TMPyP) porphyrin cation has been 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 amount of the metalloporphyrin was twice the expected CEC of the mesoporous supports, assuming that all incorporated Al produced the exchange sites. 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

The contents of Al and Si were determined from X-ray fluorescence using a Philips PW1400 XRF spectrometer. Specific surface areas and porosity were determined from nitrogen adsorption at 77 K on an ASAP 2020 apparatus (Micromeritics). Prior to measurement the samples were outgassed at 180 °C. Solid state MAS-NMR spectra were measured on a home-made pulse NMR spectrometer at the magnetic field of 7.05 T. A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to record the MAS spectra at 8 kHz spinning speed. The ^{27}Al MAS-NMR spectra were measured at 78 MHz, using a single 2 μs rf pulse, corresponding to $\pi/6$ flipping angle. The acquisition delay used in accumulation was 1 s, and the number of acquisitions was equal to 4000. The frequency scale in ppm was referenced to the ^{27}Al resonance of 1 M aqueous solution of $Al(NO_3)_3$. UV–vis absorbance spectra of Mn(TMPyP) solutions were recorded on a Shimadzu UV 160A spectrophotometer.

2.3. Catalysis

The oxidation of cyclooctane was performed in a stainless steel batch reactor system at 120 °C, under an air pressure of 10 atm, using 60 ml of cyclooctane, with the molar ratio of cyclooctane to oxygen set at 6.5. A 1 l (1000 cm^3) Teflon lined reactor equipped with magnetic stirrer was used. In each experiment the amount of catalyst was adjusted in such a way that the net content of the active MnTMPyP phase corresponded to 0.001 g. After 6 h of reaction the oxidation was stopped by immersing the hot reactor in a cold water bath. The products were recovered and analyzed with a SRI 8610B gas chromatograph equipped with MXT-200 (15 m) column. The catalytic test with finely ground unsupported Mn(TMPyP) powder was carried out for reference purposes.

3. Results and discussion

3.1. Physicochemical characterization of the catalysts

The use of two groups of mesoporous supports, one based on the MCM-41, the other on the SBA-15 structure, aluminated to a different degree either by the direct synthesis route or by the post-synthesis treatment, ensured that the study materials covered a wide range of mesoporous matrices differing by the cation exchange properties and textural characteristics. XRD analysis of the synthesized supports (not shown) confirmed that the materials possessed the expected MCM-41 or SBA-15 structures with characteristic hexagonal mesopore ordering described in earlier works [17–23]. The nitrogen sorption isotherms for some of the mesoporous aluminosilicate supports are shown in Fig. 1. All the supports show type IV isotherms typical of well ordered mesoporous materials. All the isotherms exhibit a sharp capillary condensation (mesopore filling) step; the position of this step varies depending on the pore size of the mesoporous aluminosilicates. The isotherms therefore indicate that all the aluminosilicate supports possess good mesostructural ordering and a narrow pore size distribution. All SBA-15 materials show only very small contribution from microporosity, not exceeding 10% of total, both in terms of the specific surface area and the pore volume.

The elemental composition and the textural properties of the supports are given in Table 1. The average pore sizes range from 2.7 to 3.9 nm within the MCM-41 family, and from 8.2–12.0 nm within the SBA-15 group. Table 1 contains also the data on the amount of metalloporphyrin anchored at the surface of the supports. In principle, for a given family of mesoporous silicas, a higher Al content should result in a higher capacity for trapping the metalloporphyrin cations at the support surface. This, however, is not observed, and in fact, an opposite trend seems to prevail. This is particularly pronounced in the case of grafted samples, where an important loss of the exchange capacity for Mn(TMPyP) cations is observed at higher amounts of incorporated Al. Obviously, an ever increasing fraction of aluminium retained by the solids does not contribute to the exchange process. Past works have demonstrated that the ''inactive'' Al sites may be either buried within the wall of the

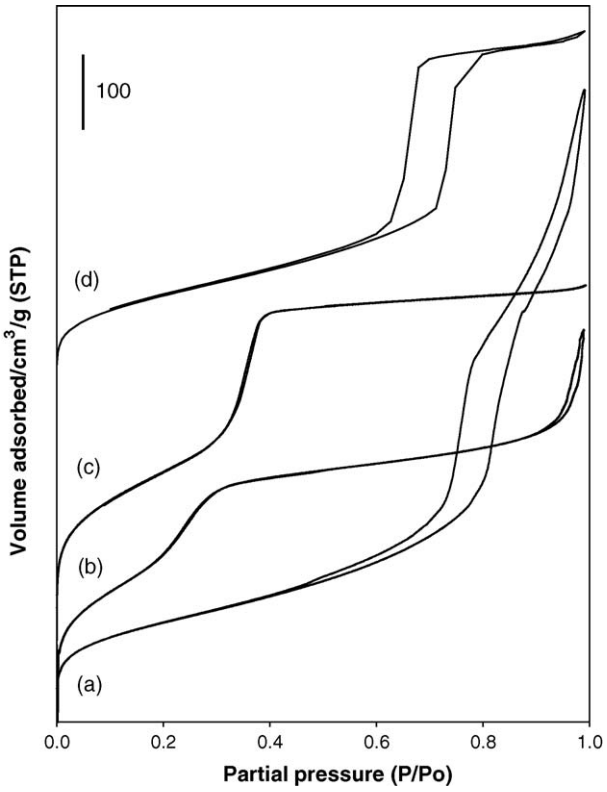

Fig. 1. Nitrogen sorption isotherms over aluminosilica supports: (a) Al-SBA-15/D1, (b) Al-MCM-41/D2, (c) Al-MCM-41/G2 and (d) Al-SBA-15/G1. See Section 2 and Table 1 for sample details. For clarity the isotherms of Al-MCM-41/G2 and Al-SBA-15/G1 are offset (*y*-axis) by 100 and 400, respectively.

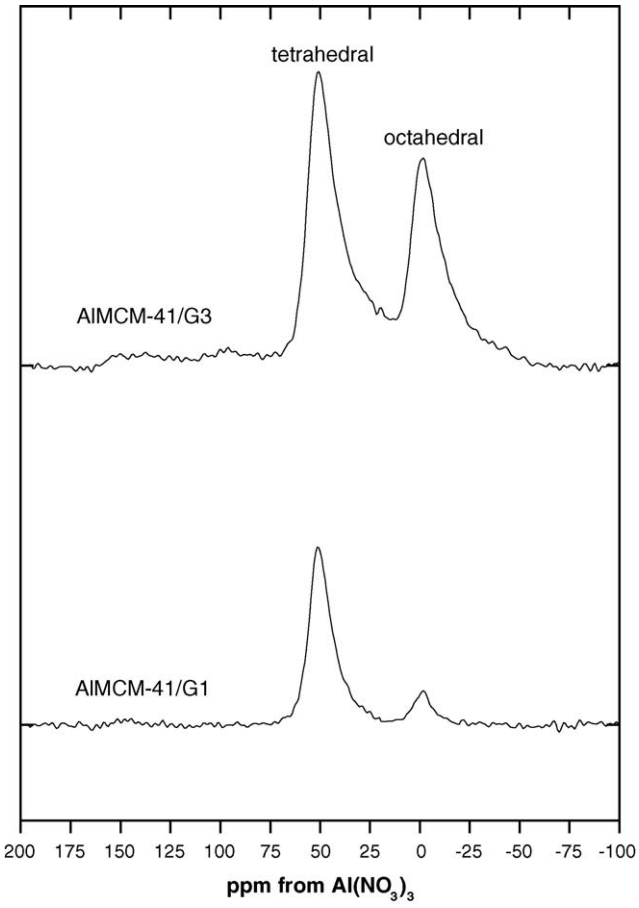

Fig. 2. ^{27}Al NMR spectra of Al-MCM-41/G1 and Al-MCM-41/G3 supports.

mesoporous solid, away from its surface, or may exist as extra-framework species [17,18,23]. The occurrence of the latter is particularly likely in the Al-grafted, heavily Al-doped samples. Fig. 2 shows as an example the ^{27}Al MAS-NMR spectra of Al-MCM-41/G1 (Si/Al = 10) and Al-MCM-41/G3 (Si/Al = 4) supports. Indeed, the material with lower sorption capacity towards MnTMPyP (despite its higher overall Al content) shows much larger contribution from the octahedrally coordinated extra-framework Al (at 0 ppm). The observed lower capacity for Mn(TMPyP) cations in mesoporous silica solids with lower Si/Al ratios may be thus understood as due to the presence of patches of extra-framework Al species which, beside being inactive in the exchange experiment, may additionally block the access of metalloporphyrin cation to the surface exchange sites.

3.2. Catalysis

The UV–vis analysis of the reaction medium after the catalytic oxidation of cyclooctane with dioxygen shows no evidence of MnTMPyP species leached to the solution, which may be taken as an indication that the observed catalytic effect is due to metalloporphyrin anchored at the support. However, bearing in mind that after cooling the leached metalloporphyrin could readsorb at the surface of the catalyst [24], an experiment has been carried out, in which the reaction mixture extracted

Table 1
Composition (Si/Al ratio), textural properties, and metalloporphyrin content of aluminated mesoporous silica supports

Support	Si/Al	S_{BET} (m^2/g)	Average pore size (nm)	Mn(TMPyP) content (mg/g support)
Al-MCM-41/D1	23.0	856	3.9	93.6
Al-MCM-41/D2	8.5	922	2.7	79.3
Al-MCM-41/G1	10	907	3.4	111.0
Al-MCM-41/G2	4.3	771	3.1	74.5
Al-MCM-41/G3	4.0	714	2.9	64.5
Al-SBA-15/D1	6.1	544	10.8	82.7
Al-SBA-15/D2	3.0	484	12.0	78.7
Al-SBA-15/G1	6.3	681	8.2	71.3

from the reactor has been brought to the boiling point and then filtered. Also in this case the UV–vis analysis of the filtered solution showed no presence of MnTMPyP species, which provides strong support for the true heterogeneity of the oxidation process under study. The results of catalytic tests are presented in Table 2. The activity of the samples, indicated by the degree of cyclooctane conversion, ranges from 1.5 to 13.6%. All supported catalysts show better performance than the unsupported metalloporphyrin, with the best one, Mn(TMPyP)/Al-SBA-15/D2, being more efficient by an order of magnitude. The data show that all SBA-15-based catalysts are much more active than any of the MCM-41-derived materials. Since the major textural difference between both types of the catalysts consists in the dimensions of pore size, the effect points to the importance of this parameter in determining the catalyst activity. Indeed, the diagram in Fig. 3 shows that there is a general trend linking the pore size of the mesoporous supports with the catalytic performance of the supported metalloporphyrin. Such an effect strongly suggests that the efficiency of the process is controlled primarily by diffusion phenomena. It is likely that the catalytically active zone is limited to the pore area near the pore mouth, where an efficient transport of substrates and products in and out of the pore may take place, the depth of penetration depending on the pore size.

Analysis of the product distribution shows that cyclooctanone is the main reaction product, cyclooctanol being produced in only small quantities. The cyclooctanone selectivities observed for the MCM-41 type catalysts are exceptionally high (≥95%). For comparison, the selectivities for homogeneous catalytic systems obtained in our laboratory under similar conditions never exceeded 90% [15,16], and such level of selectivity is observed in the present study for the unsupported catalyst and the catalysts derived from SBA-15 mesoporous solids. Table 2 shows that the essence of the change in the selectivity pattern, when passing from one group of supports to the other, consists thus in an unprecedented suppression of the cyclooctanol yield over the MCM-41 type catalysts, where it is several times smaller. The effect may be

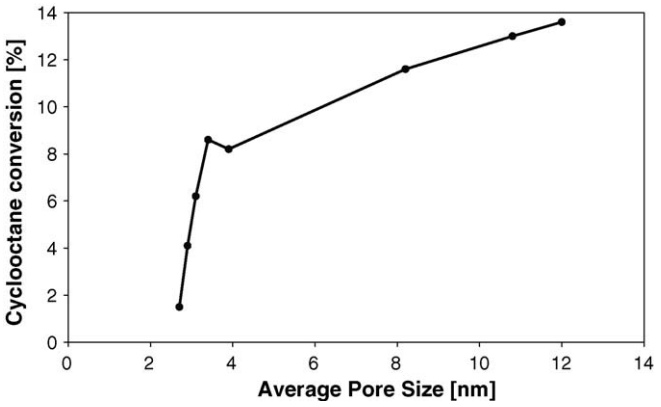

Fig. 3. Dependence of the cyclooctane conversion on the average pore size of mesoporous supports.

discussed in terms of the mechanism, proposed recently for the oxidation of cyclooctane by Haber et al. [16] (Fig. 4). According to these authors, the oxidation of cyclic hydrocarbons is a radical-chain reaction, whose initiation step consists in formation of cycloalkyl radicals $R^{\bullet}$ by reaction of hydrocarbon with the axial ligand of M(III)PorX porphyrin. The radical remains trapped in the neighbourhood of metalloporphyrin by the solvent cage and the subsequent reaction with molecular oxygen leads to the formation of an intermediate metalloporphyrin-cycloalkylperoxo M(II)Por–OOR complex, which decomposes to yield ketone. The part of $R^{\bullet}$ radicals that escape from the solvent cage may react in a parallel reaction with dioxygen to give the cycloalkylperoxo radicals $ROO^{\bullet}$. $ROO^{\bullet}$ transforms further yielding first cycloalkylhydroperoxide ROOH, which, in turn, upon interaction with M(II)Por undergoes a homolytic splitting forming $RO^{\bullet}$ The latter picks up a hydrogen from another hydrocarbon molecule and produces alcohol. The observed reduction in the cyclooctanol yield over MCM-41-type catalysts suggests that the reaction pathway described above is suppressed. Since the effect is not observed in the large pore SBA-15 systems, we tentatively associate its occurrence to the stereoselective action

Table 2
Catalytic performance of different Al-MCM-41- and Al-SBA-15-supported Mn(TMPyP) catalysts in the oxidation of cyclooctane with air[a]

Catalyst	Cyclooctane conversion (%)	Cyclooctanone yield (%)	Cyclooctanol yield (%)	Cyclooctanone selectivity (%)
None	0	–	–	–
AlMCM-41/G1	0	–	–	–
Al-SBA-15/D2	0	–	–	–
Unsupported Mn(TMPyP)	1.5	1.3	0.2	87
Mn(TMPyP)/Al-MCM-41/D1	8.2	7.9	0.3	96
Mn(TMPyP)/Al-MCM-41/D2	1.6	1.5	0.1	94
Mn(TMPyP)/Al-MCM-41/G1	8.6	8.4	0.2	98
Mn(TMPyP)/Al-MCM-41/G2	6.2	6.0	0.2	97
Mn(TMPyP)/Al-MCM-41/G3	4.1	4.0	0.1	97
Mn(TMPyP)/Al-SBA-15/D1	13.0	11.7	1.3	90
Mn(TMPyP)/Al-SBA-15/D2	13.6	11.8	1.8	87
Mn(TMPyP)/Al-SBA-15/G1	11.6	10.4	1.2	90
Mn(TMPyP)/Al-MCM-41/G1 recycled	7.8	7.5	0.3	96
Mn(TMPyP)/Al-SBA-15/D2 recycled	11.7	10.2	1.5	87

[a] Reaction conditions: 60 ml cyclooctane, cyclooctane/oxygen molar ratio = 6.5, 120 °C, 10 atm, 6 h. In each experiment with metalloporphyrin the MnTMPyP content was 0.001 g.

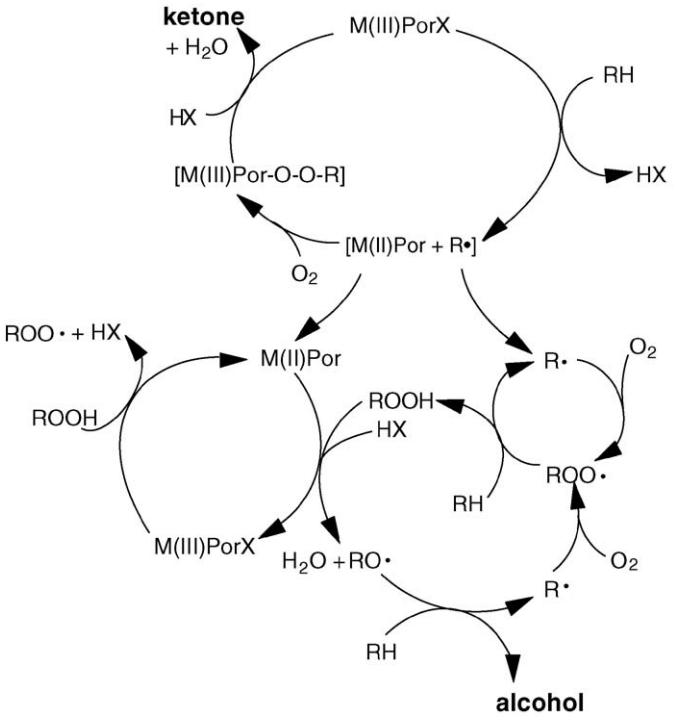

Fig. 4. Scheme of the oxidation of hydrocarbons with dioxygen without the use of sacrificial co-reductant (after Ref. [16]). In the present case M = Mn, Por = TMPyP, X = Cl, R = C_8H_{15}.

of smaller pore MCM-41 supports. Apparently, in the confined space of smaller mesopores, the escape of free radicals $R^{\bullet}$ from the solvent cage is hindered, which favours the reaction chain leading to cyclooctanone and results in the observed high selectivities of this product. The effects of stereoselectivity displayed by catalytic systems based on metalloporphyrins located within the pores of MCM-41 type materials have been already reported by us for the reaction of cyclohexene oxidation with iodosylbenzene [3].

Results presented in this work may be also taken as a contribution to the discussion on the mechanism of the hydroxylation process in the homogeneous catalytic systems. Beside the reaction pathway based on the alkyl hydroperoxide decomposition chain described above, and originally proposed by Gray and colleagues [12,14], a pathway involving activation of dioxygen through binding to the reduced metalloporphyrin and formation of the peroxo-bridged MPor–O–O–MPor dimer, followed by its decomposition to MPor=O complexes, has been proposed by Lyons et al. [8] as a key step of the hydroxylation reaction. The fact that in the present work the metalloporphyrin species are immobilized at the surface of the support and thus held apart from each other makes the formation of dimer species unlikely. For this reason, the reaction mechanism proposed by Gray et al. seems to be more appropriate for description of the oxidation of alkanes with dioxygen over heterogenized metalloporphyrin catalysts.

An important feature of the catalyst is its stability in the conditions of the catalytic reaction. To check on this, the solid residue remaining after the first catalytic run over Al-MCM-41/G1 and Al-SBA-15/D2 catalyst have been separated by filtration from the reaction medium and returned to the reactor with a fresh portion of cyclooctane. The catalytic activity of the recycled materials corresponds to ca. 90 and 85%, respectively, of the values observed in the first run, with the selectivity to cyclooctanone remaining in both cases at the same level as in the first run (Table 2). Both effects point to a quite good resistance of the metalloporphyrin species supported on mesoporous MCM-41 and SBA-15 aluminosilicates.

4. Conclusions

The catalytic activity of Mn(TMPyP) metalloporphyrin is enhanced by its dispersion on the surface of aluminated mesoporous silicas. The activity increases with the increasing pore size of the support, hence large pore SBA-15 type materials produce most active catalysts. The effect indicates that the reaction is primarily controlled by the reactants diffusion within the pore inner space. An exceptionally high selectivity to cyclooctanone observed for the MCM-41-derived catalysts, as opposed to SBA-15-based ones and homogeneous oxidation process, is tentatively interpreted in terms of steric effect due to the suppression of alkyl radical escape from the solvent cage in relatively narrow channels of MCM-41. Catalysts show quite good stability in the reaction conditions.

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