

Iron and copper immobilised on mesoporous MCM-41 molecular sieves as catalysts for the oxidation of cyclohexane

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Abstract

A pure silica mesoporous molecular sieve analogous to MCM-41 (Si-MCM-41) was organofunctionalised with 3-aminopropyltrimethoxysilane. The resulting organofunctionalised Si-MCM-41 ((NC₃)Si-MCM-41) was suspended in alcoholic solutions of iron and copper salts to form the respective metal complexes (M(NC₃)Si-MCM-41). Iron and copper were also incorporated into the framework of mesoporous MCM-41 metallosilicates (M-MCM-41) by hydrothermal synthesis. All these catalysts were employed in the liquid phase oxidation of cyclohexane with aqueous H₂O₂ (30%). The results show that the M(NC₃)Si-MCM-41 are more active than the corresponding M-MCM-41. The activity of the catalysts decreases in the following order: Fe(NC₃)Si-MCM-41 ≫ Fe-MCM-41 ≫ Cu(NC₃)Si-MCM-41 ≫ Cu-MCM-41. However, when the catalysts are recycled, leaching of the metals is observed. The good catalytic activity found for Fe(NC₃)Si-MCM-41 can be attributed to the heterogenised iron complex. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: MCM-41 molecular sieves; Organofunctionalisation; Iron catalyst; Copper catalyst; Cyclohexane oxidation

1. Introduction

Metal complexes with nitrogen containing molecules are widely used as model compounds for mimicking the catalytic properties of monooxygenases, which catalyse the selective hydroxylation of alkanes and other substrates [1]. It was shown that especially iron and copper complexes are active catalysts for the mimick-

ing of monooxygenases [2]. Also Gif-systems [3–5], which use iron and copper salts in a mixture of pyridine and acetic acid are good biomimetic catalytic systems. We studied the Gif-systems as catalysts for the oxidation of cyclohexane and could show that they are active at room temperature [6]. However, due to the formation of metal–oxygen–metal bonds, these catalysts deactivate rapidly.

It was already suggested that the immobilisation of transition metals in the stable matrix of zeolites and zeotypes would allow the preparation of stable catalysts for the liquid phase oxidation of organic compounds [7]. Since the

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first description of the microporous zeotype TS-1 [8] as catalyst for the liquid phase oxidation of organic compounds and its successful application as catalyst in large-scale processes such as the hydroxylation of phenol [9] and the ammoxidation of cyclohexanone [10], large efforts have been done to study the catalytic properties of other so-called redox molecular sieves [11]. In general there are three different possibilities to create redox active sites in molecular sieves [11]: the encapsulation of organic metal complexes into the zeolite pores and cavities [12], the exchange of the charge-compensating cations like Na^+ by redox active cations like transition metals [13] and rare earth metals [14,15], or the substitution of the structure building atoms like Si and Al, by redox active metals such as Ti, V, Cr, Mn, Fe and Co [16–23].

The mesoporous molecular sieves of the M41S family [24,25] can be prepared with pore diameters between 15 and 100 Å. It was shown that the incorporation of transition metals into the framework of MCM-41 [26–29], one of the members of the M41S family, allows the preparation of active catalysts for the oxidative transformation of molecules too bulky to enter the channels of TS-1 and other microporous redox molecular sieves with pore diameters in the range between 4 and 13 Å [11,30]. Also the incorporation of metal phthalocyanine complexes in the pores of MCM-41 molecular sieves and its application as catalyst in the liquid phase oxidation were described [31].

Mesoporous MCM-41 molecular sieves whose properties resemble that of amorphous silica [25], contain a large number of silanol groups at the surface of their channels, which enable its organofunctionalisation by the reaction with $\text{SiR}(\text{OCH}_3)_3$ compounds where R is a functionalised organic group.

In this paper we describe the organofunctionalisation of MCM-41 silicate (Si-MCM-41) with 3-aminopropyltrimethoxysilane ($\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$), and the complexation of iron and copper on the organofunctionalised Si-MCM-41

($(\text{NC}_3)_3\text{Si-MCM-41}$) to give active metal catalysts ($\text{M}(\text{NC}_3)_3\text{Si-MCM-41}$, with $\text{M} = \text{Fe}$ or Cu). We will also describe the hydrothermal synthesis of MCM-41 molecular sieves in the presence of iron and copper salts in order to incorporate the metals in the framework of MCM-41. The catalytic activity of these catalysts (M-MCM-41 , with $\text{M} = \text{Fe}$ or Cu) for the oxidation of cyclohexane with aqueous H_2O_2 (30%) in the liquid phase is compared to that of the $\text{M}(\text{NC}_3)_3\text{Si-MCM-41}$.

2. Experimental

2.1. Materials

For the synthesis of the MCM-41 molecular sieves, Aerosil-200 (Degussa) or silicium(IV) ethoxide (TEOS, Aldrich) as silica sources, cetyltrimethylammonium bromide (CTMABr, Aldrich) as template, tetraethylammonium hydroxide (TMAOH, Aldrich) and sodium hydroxide (Aldrich) as hydroxyl ion sources, iron(III) nitrate (Aldrich) and copper(II) acetate (Aldrich) as metal sources were used. The organofunctionalisation with 3-aminopropyltrimethoxysilane ($\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$, Aldrich) was carried out in toluene (Aldrich). For the oxidation of cyclohexane, acetone (Aldrich) and aqueous hydrogen peroxide (H_2O_2 (30%), Merck) as oxidant were used. All these reagents were employed without further purification.

Cyclohexane was supplied by Nitrocarbonyl and purified by stirring a volumetric mixture (1:1) of cyclohexane and concentrated sulphuric acid for 12 h at room temperature in a one-neck flask equipped with a reflux condenser [32]. After separation, the organic phase was washed with water, with an aqueous solution of sodium carbonate (5%) and with water until its pH was neutral. Finally, the cyclohexane was dried over calcium chloride, filtered and distilled.

2.2. Synthesis

Metal-free Si-MCM-41 was synthesised by a method given by Corma et al. [33]. A reaction gel with the molar composition: 1 SiO₂:0.18 CTMABr:0.26 TMAOH:27 H₂O was prepared by suspending Aerosil 200 in an aqueous solution of TMAOH and subsequent addition of a suspension of CTMABr in water. The final mixture was transferred into an autoclave and heated at 140°C for 16 h. The resulting solid was separated, washed with water and dried in an oven at 120°C. The occluded template molecules were removed by calcination at 540°C for 1 h under a stream of nitrogen (100 ml/min) and for 6 h under a stream of air.

For the organofunctionalisation, the calcined Si-MCM-41 (5 g) was dried under vacuum at 300°C for 24 h and subsequently suspended in 180 ml of toluene. To the stirred suspension, 2 ml (11 mmol) of H₂NC₃H₆Si(OCH₃)₃ was added at room temperature and the stirred mixture was refluxed at 100°C for 2 days. After filtering off, the functionalised (NC₃)Si-MCM-41 was washed with water and ethyl ether and dried at 100°C under vacuum.

The complexation of iron and copper ions at (NC₃)Si-MCM-41 was carried out at room temperature by stirring a suspension of 0.5 g of the organofunctionalised material in 100 ml of a 0.01 M alcoholic solution of Fe(NO₃)₃ or of Cu(OOC₂H₃)₂, respectively, for 3 h. After separation by filtration, the catalysts (M(NC₃)Si-MCM-41) were washed with ethanol and acetone and dried at 100°C under vacuum.

For the incorporation of iron and copper into the MCM-41 molecular sieve framework, a synthesis similar to that described by Huo et al. [34] was used. Reaction gels with the following molar composition: 1 SiO₂:0.20 CTMABr:0.50 NaOH:0.018 Mⁿ⁺:150 H₂O (with Mⁿ⁺ = Fe³⁺ or Cu²⁺) were prepared by adding TEOS and the respective metal source into a stirred solution of CTMABr and NaOH. The final mixture was stirred at room temperature for 2 h. Subsequently, the precipitated solid was separated by

filtration, washed with water and transferred into an autoclave, which was placed for 12 days in an oven preheated to 100°C. After filtration and washing, the M-MCM-41 was dried in an oven and the occluded template was removed by calcination as described above for Si-MCM-41.

2.3. Characterisation

The X-ray diffractograms of the solids were recorded on a Shimadzu XD-2A diffractometer with Cu-K α radiation between 2 and 10° (2 θ) with a scanning rate of 2°/min.

The SEM micrographies of the calcined solids were obtained in a Jeol JSM T-300 Scanning Electron Microscopy operated at 20 kV.

The metal contents of the solids were determined by X-ray fluorescence analysis with a Spectrace TX-5000 spectrometer, using mechanical mixtures of the corresponding metal oxide and SiO₂ for the calibration curves. The carbon, hydrogen and nitrogen contents of the uncalcined Si-MCM-41, M-MCM-41 and the (NC₃)Si-MCM-41 were determined with a Perkin-Elmer 2401 C/H/N analyser.

The specific surface areas of the calcined solids were determined by the BET method using the adsorption of nitrogen measured with a Micromeritics Flowsorb II 2300 equipment.

The solid state ²⁹Si and ¹³C MAS NMR spectra were recorded on a Bruker AC 300/P spectrometer at 59.6 and 75.4 MHz, respectively, using zirconium oxide rotors, a rotation frequency of 4000 Hz, and tetramethyl silane as external standard. For the ²⁹Si MAS NMR spectra, 1200 scans with 5 s between each scan were accumulated. The ¹H, ²⁹Si CP MAS NMR spectra were recorded at the following conditions: 90° pulse for 10.6 μ s, contact time 3 ms and accumulation of 300 to 6000 scans with 3 s between each scan. The ¹³C MAS NMR spectra were obtained by accumulation of 300 scans with 5 s between each scan.

The ESR spectra of the Fe(NC₃)Si-, and Fe-MCM-41 were obtained at room temperature

in the X band at 9 GHz with DPPH as reference recorded on a Bruker ESP 300E spectrometer.

2.4. Oxidation of cyclohexane

The oxidation of cyclohexane was carried out in a 30 ml Teflon lined and magnetically stirred autoclave heated in an oil bath to 373 K for 12 h. A total volume of 19 ml with a volumetric ratio acetone:cyclohexane:H₂O₂ (30%) = 15:2:2 and 100 mg of the catalyst were used. After 12 h the reaction mixture was quenched to room temperature and the catalyst was separated by filtration. The products were analysed with an HP 5890 series II gas chromatograph equipped with a packed column (4 m × 1/8 in.) of Carbowax 20M (15%) on Chromosorb W-HP and a flame ionisation detector. The temperature was raised at a rate of 10 K/min from 313 to 443 K and kept there for 10 min. Cyclohexane, cyclohexanol and cyclohexanone were quantified using calibration curves and cyclooctane as internal standard. The oxidation products were identified using an HP 5980 series II gas chromatograph equipped with a 25 m HP-1 capillary column coupled to an HP 5970B mass spectrometer. The temperature was kept at 313 K for 10 min and subsequently raised at a rate of 10 K/min up to 523 K. In the leaching experiments, the catalyst and the liquid phase were separated at reaction temperature by filtration after reaction, the liquid phase was transferred into the autoclave together with new portions of cyclohexane and H₂O₂ and heated to 373 K for another 12 h.

3. Results and discussion

The X-ray diffractograms of the uncalcined Si-, Fe- and Cu-MCM-41 and the organofunctionalised (NC₃)Si-MCM-41 are shown in Fig. 1. For Si- and Fe-MCM-41 and for (NC₃)Si-MCM-41, four well resolved Bragg reflexes are observed, which can be indexed in a pseudo-hexagonal symmetry with *hkl* triplets of 100, 110, 200 and 210. The presence of these four

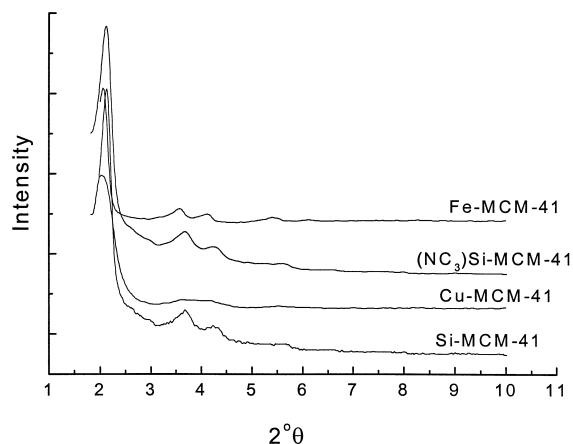


Fig. 1. X-ray diffractograms of Si-, (NC₃)Si-, Fe- and Cu-MCM-41.

Bragg reflexes is a first indication that the obtained molecular sieves have a highly ordered pore system with a high porosity [35]. The presence of four Bragg reflexes for (NC₃)Si-MCM-41 shows that the organofunctionalisation did not affect the order of the pore structure of the parent Si-MCM-41 molecular sieve. On the other hand, for Cu-MCM-41 only the peak attributed to *hkl* = 100 can be observed, which indicates that its pore system is less ordered and that its porosity is low.

The unit cell parameter a_0 of the different MCM-41 molecular sieves, calculated from the peak with *hkl* = 100 by the formula $a_0 = 2d_{100}/\sqrt{3}$, are given in Table 1. The increase of a_0 for Fe- and Cu-MCM-41 compared with a_0 of Si-MCM-41 might be taken as an indication of the incorporation of the metals in the MCM-41 framework. The organofunctionalisation of Si-MCM-41 reduces the a_0 from 44.3 to 39.2 Å. We believe that the H₂N(C₃H₆)Si groups were immobilised on the surface of MCM-41 channels by reaction with SiOH groups of defect sites. This process reduces the defect sites of the material, resulting in a more dense structure with a lower a_0 value and a reduction of the pore size by the immobilised H₂N(C₃H₆)Si groups.

The results of the elemental analysis and the specific surface area (BET) of the calcined ma-

Table 1

Unit cell parameter a_0 and results of the elemental analysis and specific surface area (BET) of Si-, $(\text{NC}_3)\text{Si}$ -, $\text{M}(\text{NC}_3)\text{Si}$ and M-MCM-41

MCM-41	a_0 (Å)	Metal content (%)	C content (%)	N content (%)	C:N	(NC_3) : metal	BET (m^2/g)
Si-	44.3	–	33.6	1.9	20.2	–	1296 ^a
$(\text{NC}_3)\text{Si}$ -	39.2	–	6.1	2.2	3.2	–	n.d.
$\text{Fe}(\text{NC}_3)\text{Si}$ -	n.d.	2.3	6.1	2.2	3.2	3.8	582
$\text{Cu}(\text{NC}_3)\text{Si}$ -	n.d.	2.9	6.1	2.2	3.2	3.5	n.d.
Fe	46.3	1.0	33.5	2.0	19.1	–	1164 ^a
Cu	48.5	0.8	16.8	1.0	19.2	–	350 ^a

^aDetermined after calcination; n.d. = not determined.

terial which are given in Table 1 show that Cu-MCM-41 possesses a lower content of occluded organic material and a lower specific surface area than the Si- and Fe-MCM-41, thus confirming its lower porosity. The decrease of the BET surface area for $\text{Fe}(\text{NC}_3)\text{Si}$ -MCM-41 shows that the pore volume of the molecular sieve is reduced by the immobilised complex.

Scanning electron microscopy shows the presence of large amounts of amorphous material in Cu-MCM-41 indicating that the presence of copper ions hampers the formation of the MCM-41 mesophase, thus resulting in the low porosity of this material.

A C:N ratio around 19, observed for the uncalcined Si- and M-MCM-41, demonstrates that the template molecules are occluded during the synthesis without decomposition as it was already observed for other MCM-41 materials [24–26].

In Fig. 2 are given the ^1H , ^{29}Si CP MAS NMR spectra of (a) Si-MCM-41 and (b) $(\text{NC}_3)\text{Si}$ -MCM-41. The peaks around $\delta = -90$, -99 and -109 ppm are attributed to $(\text{Si}-\text{O}-)_2\text{Si}(\text{OH})_2$ groups (Q_2) with two OH groups attached to the silicon atom, $(\text{Si}-\text{O}-)_3\text{Si}(\text{OH})$ groups (Q_3) with one OH group attached to the silicon atom and $(\text{Si}-\text{O}-)_4\text{Si}$ groups (Q_4) with no OH attached to the silicon atom, respectively [36]. The high intensities of the Q_2 and Q_3 peaks show the large number of OH groups present at the surface of the non-crystalline Si-MCM-41 framework. The successful anchoring of $\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$ at the channel sur-

face is demonstrated by Fig. 2b. Here the decreased intensity of the Q_3 and Q_2 peaks, relative to the Q_4 peak, indicates the esterification of the free hydroxyl groups by the trimethoxy silylester. The additional peaks around $\delta = -65$ and -55 ppm can be attributed to $(\text{Si}-\text{O}-)_3\text{Si}(\text{C}_3\text{H}_6\text{NH}_2)$ groups with no OH group attached to the silicon atom and to $(\text{Si}-\text{O}-)_2\text{Si}(\text{OH})(\text{C}_3\text{H}_6\text{NH}_2)$ with one OH group attached to the silicon atom [36], respectively, as it is schematised in Fig. 2b.

It can be calculated from the elemental analysis of $(\text{NC}_3)\text{Si}$ -MCM-41, which is given in Table 1, that approximately 1.6 mmol of $\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$ was anchored per 1 g of Si-MCM-41, which corresponds to approximately 73% of the $\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$ used for the organofunctionalisation. This is only slightly less than the maximum amount of approximately 76% of the used $\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$, calculated considering that approximately 30% of the silicon atoms in calcined Si-MCM-41 have silanol groups [25]. That not all silanol groups, originally present in the Si-MCM-41, are esterified. This is confirmed by the ^1H , ^{29}Si CP MAS NMR spectrum of $(\text{NC}_3)\text{Si}$ -MCM-41 (Fig. 2b) as after the organofunctionalisation Q_3 groups are still present.

From the elemental analysis of $(\text{NC}_3)\text{Si}$ -MCM-41 given in Table 1, a C:N ratio around 3 can be calculated, thus demonstrating that the $\text{H}_2\text{NC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$ is incorporated into the molecular sieve without decomposition of the

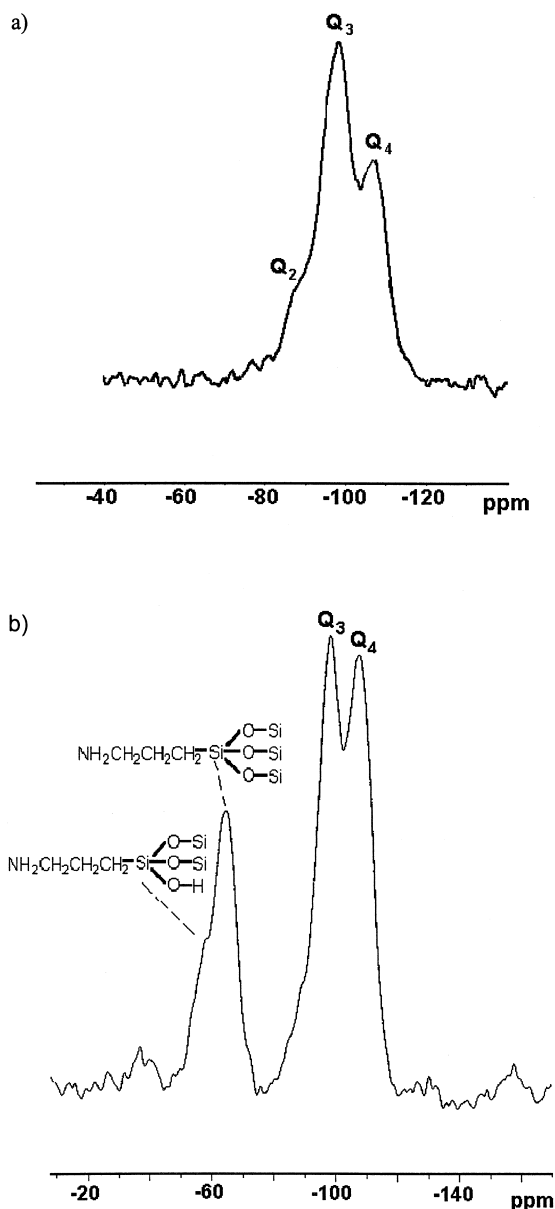


Fig. 2. ^1H , ^{29}Si CP MAS NMR spectra of Si-MCM-41 (a) and $(\text{NC}_3)\text{Si}$ -MCM-41 (b).

functional 3-aminopropyl group. The preservation of the 3-aminopropyl unit after the organofunctionalisation is confirmed by the ^{13}C MAS NMR spectrum, given in Fig. 3. Three peaks with equal intensity at around $\delta = 10$, 22 and 43 ppm can be attributed to the three different C-atoms of the 3-aminopropyl group.

After the complexation of the metals $\text{Fe}(\text{NC}_3)\text{Si}$ -MCM-41 and $\text{Cu}(\text{NC}_3)\text{Si}$ -MCM-41 show a orange and blue coloration, respectively, which indicates the formation of a complex of the metals with the immobilised 3-aminopropyl units. The successful complexation of the metals is also supported by the 3-aminopropyl:metal ratio which can be calculated from the nitrogen and metal content of the $\text{M}(\text{NC}_3)\text{Si}$ -MCM-41, and which indicates a coordination number of 4 for iron as well as for copper. The incorporation of iron into the MCM-41 framework is confirmed by the white colour of the 'as made' Fe-MCM-41, which indicates the absence of extra-framework iron oxide species. On the other hand, Cu-MCM-41 presents a grey colour, indicating the presence of extra-framework copper oxide species.

The ESR spectrum of $\text{Fe}(\text{NC}_3)\text{Si}$ -MCM-41, given in Fig. 4a, shows signals at $g = 2.0$ and $g = 4.3$. The signal at $g = 2.0$ is attributed to Fe(III) in octahedral coordination with a high symmetry [37], suggesting that the Fe(III) cations are complexed by four 3-aminopropyl units and two water molecules as it is schematised in Fig. 5. As described by Bordiga et al. [38], the strong hydrogen bonds of the water molecules ensure the symmetry of the ferric ions surrounded by the nitrogen atoms of the 3-aminopropyl units. The weak signal at $g = 4.3$ might be attributed to iron cations compensating negative framework charges [38], which are due

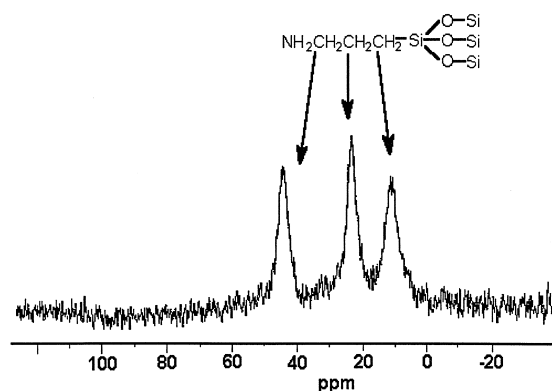


Fig. 3. ^{13}C MAS NMR spectrum of $(\text{NC}_3)\text{Si}$ -MCM-41.

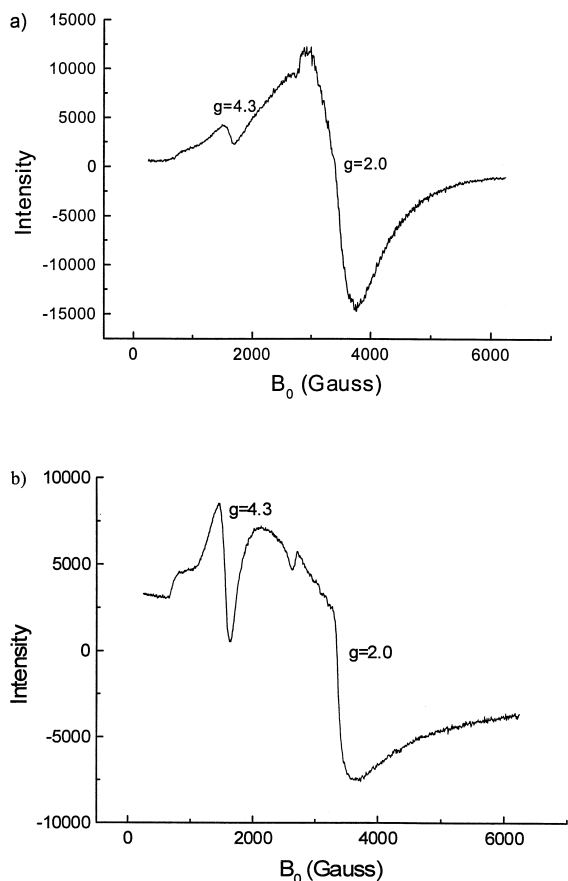


Fig. 4. ESR spectra of (a) $\text{Fe}(\text{NC}_3)\text{Si-MCM-41}$ and (b) calcined Fe-MCM-41 .

to the incorporation of traces of aluminium present in the used chemicals. The presence of such charge compensating iron cations would also explain why the 3-aminopropyl:metal ratio, given in Table 1, is lower than 4.

The ESR spectrum of the calcined Fe-MCM-41 (Fig. 4b), where the iron is incorporated in the framework, shows signals at $g = 4.3$ and 2.0, which can be attributed to $\text{Fe}(\text{III})$ in tetrahedral coordination with strong rhombic distortion and $\text{Fe}(\text{III})$ in octahedral coordination, respectively [38]. A comparison of the ESR spectrum of the calcined Fe-MCM-41 (Fig. 4b) with that of the uncalcined Fe-MCM-41 (not shown) reveals an increase of $\text{Fe}(\text{III})$ in octahedral coordination after calcination. This indicates that during the calcination, which is necessary to

remove the occluded template molecules, tetrahedral $\text{Fe}(\text{III})$ is transformed in extra-framework iron oxide. The demetallation of the Fe-MCM-41 by the calcination process is also confirmed by the change of colour from white for the uncalcined Fe-MCM-41 to brown for the calcined Fe-MCM-41 which is characteristic for the presence of extra-framework iron oxide species [39].

The results of the oxidation of cyclohexane with aqueous H_2O_2 (30%) catalysed by iron and copper immobilised on mesoporous MCM-41 molecular sieves are given in Table 2. It can be seen that the $\text{M}(\text{NC}_3)\text{Si-MCM-41}$ are, in contrast to iron and copper salts, used as homogeneous catalysts [6], inactive at room temperature and even at 70°C . On the other hand, Ernst et al. [31] observed that iron phthalocyanine complexes immobilised on mesoporous MCM-41 are more active than the free complex, while the immobilised copper phthalocyanine was also inactive at room temperature.

Table 2 reveals that at 100°C all catalysts prepared in this study are, with exception of Cu-MCM-41 , active for the oxidation of cyclohexane. The negligible conversion observed for Cu-MCM-41 and the very high metal loss indicate that the Cu is not incorporated in the MCM-41 structure but present as catalytically

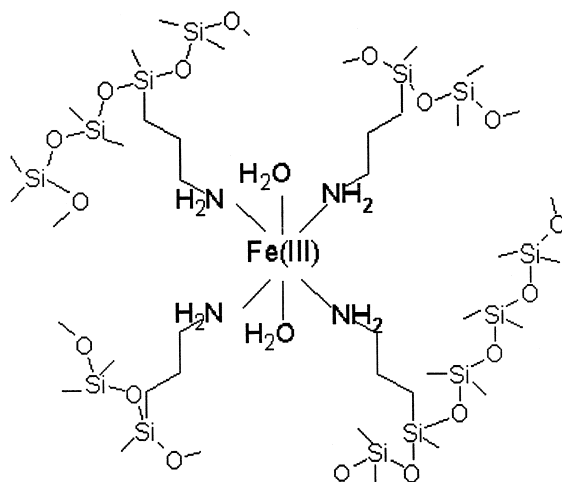


Fig. 5. Proposed structure of the active site of $\text{Fe}(\text{NC}_3)\text{Si-MCM-41}$.

Table 2

Results of the oxidation of cyclohexane with aqueous H₂O₂ catalysed by M(NC₃)Si-MCM-41 and M-MCM-41

MCM-41	Metal content (%)	Temperature (°C)	Products (mmol)		Turnover number	H ₂ O ₂ efficiency (%)	Leaching (%)
			one	ol			
Fe(NC ₃)Si- ^a	2.3	25	0.1	0.1	5	2	n.d.
Fe(NC ₃)Si- ^a	2.3	70	0.2	0.1	7	3	39
Fe(NC ₃)Si- ^a	2.3	100	3.2	0.4	88	34	35
Fe(NC ₃)Si- ^b	1.5	100	1.7	0.5	83	20	30
Fe(NC ₃)Si- ^c	1.0	100	1.1	0.5	86	14	n.d.
Liquid phase ^d	–	100	0.2	0.2	–	4	–
Cu(NC ₃)Si- ^a	2.9	25	0.1	0.1	4	2	n.d.
Cu(NC ₃)Si- ^a	2.9	100	0.6	0.3	20	8	27
Fe- ^a	1.0	100	0.7	0.3	55	9	22
Cu- ^a	0.8	100	0.2	0.1	3	3	74

Reaction conditions: acetone/cyclohexane/H₂O₂ (30%) = 15/2/2/ (v/v/v); 100 mg catalyst; 12 h; one = cyclohexanone; ol = cyclohexanol.

^aFirst reaction cycle; ^bsecond reaction cycle; ^cthird reaction cycle; ^dliquid phase from the first reaction cycle; n.d. = not determined.

inactive copper oxide which is simply washed out of the solid under the reaction conditions.

It should be remarked that at 100°C the Fe(NC₃)Si-MCM-41 is more active than the microporous zeotype TS-1 under the same conditions [40], as it is demonstrated by the amount of products 3.6 and 2.8 mmol, the turnover numbers of 88 and 76 and the peroxide efficiencies of 34% and 22% for Fe(NC₃)Si-MCM-41 and TS-1 [40], respectively. However, if Fe(NC₃)Si-MCM-41 is recycled, leaching of the metal is observed (the liquid phase which is separated at reaction temperature is lightly brown) and the catalyst deactivates progressively, although the turnover number remains constant and the observed loss of activity is proportional to the amount of leached iron, thus demonstrating that the complexed iron keeps its activity. In contrast Cu(NC₃)Si-MCM-41 deactivates after the first reaction cycle. The relative stability of the Fe(NC₃)Si-MCM-41 is in contrast with the results described by Ernst et al. [31], who observed a complete and irreversible loss of the activity of the iron phthalocyanine immobilised on MCM-41 after 2 h of reaction time. The leaching of Fe(NC₃)Si-MCM-41 is probably caused by complexation of the iron by the polar product molecules. This would explain why the leached iron is no longer active for cyclohexane oxidation under our reac-

tion conditions (Table 2). Homogeneous iron complexes were less active under these conditions as the nitrogen ligands are necessary to stabilise the activated complex [41]. Therefore, the catalytic activity can be attributed to iron complexed by the organofunctionalised MCM-41.

Iron complexed on amorphous silica organofunctionalised by the same method showed a much lower activity for cyclohexane oxidation under similar conditions. Only 0.3 mmol of one and 0.2 mmol of ol (turnover number 20) were obtained after 12 h at 100°C [42]. We, therefore, believe that the ordered pore system supplied by the MCM-41 is responsible for the observed activity. This pore system favours the formation of an octahedral structure, with the iron and the four nitrogen atoms in the same plane (Fig. 5), as observed in porphyrins. In amorphous silica it seems to be more difficult to form such a complex.

4. Conclusions

Mesoporous Si-MCM-41 can be easily organofunctionalised by anchoring (H₂NC₃H₆-Si(OCH₃)₃) at the surface of the Si-MCM-41 channels. The resulting (NC₃)Si-MCM-41 forms stable complexes with iron and copper. Iron can

also be incorporated in the MCM-41 framework by hydrothermal synthesis. However, copper ions in the synthesis gel lead to an almost amorphous silica phase with precipitated copper oxide on it. Fe(NC₃)Si-MCM-41 shows a good activity for oxidising cyclohexane with H₂O₂ at 100°C, however approximately 30% of the iron leach from the catalyst in each reaction cycle. The leached iron is complexed by the reaction products and shows nearly no activity. The good catalytic activity of Fe(NC₃)Si-MCM-41 is explained by an octahedral coordination with four nitrogen ligands in the same plane.

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