A new and easy method for anchoring manganese salen on MCM-41

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This work reports a new method to covalently attach manganese salophen complex onto MCM-41, using a diisocyanate as a binder. The prepared catalyst was tested on the liquid phase limonene oxidation reaction. Diluted *t*-Butyl hydroperoxide was used as oxygen supplier. Limonene oxide, carveol and carvone are formed, but the main product obtained was a polymer. The preservation of the MCM-41 channel system was checked by X-ray diffraction and nitrogen adsorption analysis. The use of the same catalyst sample in four consecutive experiments, without loss of activity, is a confirmation of the success of the anchoring process.

KEY WORDS: manganese Schiff base; MCM-41; epoxidation; limonene; diisocyanate.

1. Introduction

Oxyfunctionalization of unfunctional terpenes is of great importance in synthesis of fine chemicals, pharmaceuticals and flavours [1]. Manganese Schiff base materials have been widely described as good epoxidation catalysts with different oxidants [2–4]. However, these catalysts easily deactivate, in homogeneous liquid solution, due to ligand oxidation and/or to the formation of μ-oxo dimmers and other polymeric species [5,6]. Immobilization of the homogeneous Schiff bases onto a solid support may be a strategy to combine its high activity and selectivity with the advantages of the heterogeneous catalysis [5,7–9]. The MCM-41 materials are very attractive supports since they have very high surface areas and a regular array of large pore channels. Furthermore, the high concentration of silanol groups allows the development of different approaches to covalently attach metal complexes. Many published works report salen complexes anchoring on the MCM-41 surface. The reported methods usually start with the grafting of appropriate organosilane species on the MCM-41 surface silanol groups. These coupling agents bear specific functional groups such as chloride, carboxylic acid, thiol, amine, etc., which are available for binding to the complex ligand or to the central metal itself [10–12]. Zhang *et al.* [13] have also reported a different strategy for the immobilization of chiral Mn(salen) complexes into MCM-41, via a phenoxy group.

Isocyanates are known to be very reactive with –OH groups to give urethane bonds [14,15]. Depending on the isocyanate used, the binding strengths to the surface of the support can be higher or at least equal to those obtained for the organosilane binders [15]. In recent works, Kumar *et al.* [16] report the anchoring of a Schiff base complex on a carbamate modified silica gel, consisting of a three steps procedure: in the first step the isocyanate coupling agent is attached to the silica surface, being chemically modified in a second step in order to introduce a chloride function to which the complex is bound in a third step.

In the present work, we describe a two steps method for the anchoring of Schiff base complexes bearing hydroxyl groups in the salen ligand (OHsalen). By this simple method a diisocyanate is used as coupling agent, being one of the isocyanate endings attached to the silica surface, while the other remains available for reaction with the complex.

The catalyst obtained by this method was tested in the limonene liquid phase oxidation, using *t*-Butyl hydroperoxide (t-BHP) as oxidant.

2. Experimental

2.1. Materials

Aerosil 200 was obtained from Degussa. Tetramethylammonium hydroxide pentahydrate (97%) (TMAOH), cetylmethylammonium bromide (C_{16}TMABr) and Diethylenetriamine were purchased from Aldrich. Limonene, 1,2-phenylenediamine, 2,4-dihydroxybenzaldehyde and 1,4-diisocyanatobutane (DIC-4) were obtained from

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Fluka. Manganese chloride tetrahydrate and acetonitrile were from Merck. Diethylether and ethanol were supplied by Panreac. Toluene and dichloromethane were purchased from Riedel-de-Haën. All solvents were distilled and dried with molecular sieves (3A) prior to use. Diethylether was passed through an alumina column in order to eliminate peroxides.

2.2. MCM-41 synthesis

The synthesis of the parent MCM-41 was carried out according to the method reported by Corma *et al.* [17]. Aerosil 200 (2.6 g) was suspended in a solution of TMAOH (28 mmol) in 12.6 ml of water. After 2 h stirring the mixture was added to 100 ml of a CTMABr (10 mmol) aqueous solution. This final mixture was stirred for 1 h, and heated at 140 °C, for 16 h. The resulting solid was filtered and washed with deionised water. The occluded templates were removed by calcination at 540 °C for 1 h under a stream of dry nitrogen (heating ramp of 1 °C/min) and for 6 h under a stream of dry air.

2.3. Catalysts preparation

2.3.1. Schiff base synthesis

The complexing agent N,N′-bis(4-hydroxysalicylaldehyde)phenylenediimine(4-HOsalophen) was prepared according literature [18–20], by condensing 1,2-phenylenediamine (37 mmol) and 2,4-dihydroxybenzaldehyde (75 mmol), in ethanol, for 1–2 h. Upon reaction completion a yellow-orange precipitate appeared, which was filtrated and dried under vacuum. The obtained solid was characterized by FTIR and seems to be in good agreement with the literature data [20]: 1640, 1608, 1575, 1543, 1468, 1435, 1383, 1325, 1209, 1160, 1124, 995, 849, 803, 645 (cm^{-1}).

2.3.2. Manganese salen complex

The manganese(III) complex [Mn(4-HOsalophen)Cl] was prepared as described in literature [19,20], by refluxing ethanolic solutions of 3 mmol of ligand and 3.3 mmol of manganese(II) chloride tetrahydrate, for 1–2 h. During the reflux it was observed a change in the solution colour from yellow-orange to dark-brown. The manganese complexes were recrystallised by using a mixture of ethanol:acetonitrile (1:1) and dried under vacuum, overnight . The so obtained solid was characterized by FTIR and compared with the literature data [20]: 1619, 1599, 1541, 1500, 1437, 1375, 1330, 1258, 1210, 1194, 1130, 990, 850, 800, 750, 661 (cm^{-1}).

2.3.3. Complex anchoring

The manganese complex was grafted on the MCM-41 surface, by using DIC-4 as a binder (see scheme 1). The catalyst was prepared by refluxing the unmodified MCM-41 and DIC-4, in dry toluene, for 3 h [15]. After cooling down, Mn(4-OHsalophen)Cl was added and the mixture was again refluxed for another 6 h. The obtained modified materials were soxhlet extracted with ethanol, for 24 h and dried under vacuum. The obtained material was denoted as [Mn(4-OHsalophen)DIC]@MCM-41.

2.4. Catalyst characterization

The specific surface areas of the MCM-41 samples were determined by the BET method, by using the N$_2$ adsorption isotherms obtained at 77 K in a Micrometrics ASAP 2010 V1.01 B instrument. The BET surface area was calculated by using the relative pressure data in the range 0.04–0.2. The pore size distributions were obtained from the adsorption branches of the isotherms, using the BJH method with the modified Kelvin equation and a correction for the statistical film thickness of the pore walls. The Harkins-Jura equation was used to calculate the statistical film thickness in the p/p$_0$ range of 0.1–0.95 [21].

The manganese loading was determined by inductively coupled plasma atomic emission spectroscopy (ICP), carried out on a Jobin-Yvon (Ultima) instrument. Elemental analysis of C, H, N and S was performed in an Automatic CHNS-O Elemental Analyser Flash EATM. Infrared spectra were obtained on a BIO-RAD FTS 155 spectrometer, by using KBr pellets. The spectra were taken with a resolution of 4 cm^{-1}, by running 500 scans.

XPS analyses were carried out on a XSAM800 (KRATOS) X-ray spectrometer operated in the fixed analyzer transmission (FAT) mode with a pass energy of 20 eV, by using a non-monochromatic radiation from Mg anode (main hυ = 1253.6 eV). Pressure in the
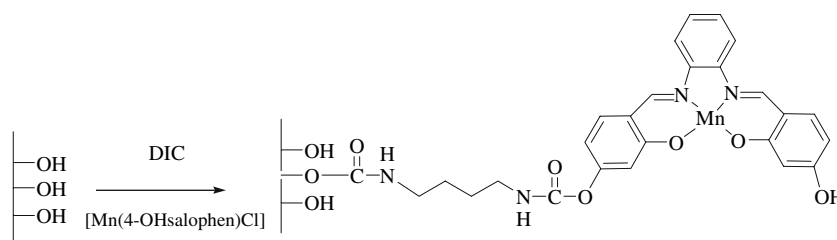
Scheme 1.

analysis chamber: in the range of 1×10^{-7} Pa; power: 130 W.

The powder X-ray patterns were obtained on a Rigaku D/max III C diffractometer with a Cu Kα ($\lambda = 1.5418$ Å) radiation source (50 kV, 30 mA). Measurements were performed for 2θ in the 2–40° range. The unit cell parameter, a_0, was determined by using the d_{100} () reflection of the MCM-41 type materials.

2.5. Catalytic experiments

The catalytic experiments were carried out at 60 °C, in a batch reactor, under atmospheric pressure and magnetic stirring, using an excess of diluted oxidant, i.e., t-butyl hydroperoxide (t-BHP) 3% wt/wt in a solution of acetone and t-butanol (100:1.2 volume ratio). Typically, the reactor was loaded with 14.5 mmol of limonene and the oxygen donor, in a 1:8 molar ratio along with 50 mg of catalyst and 425 ml of solvent.

A hot-filtration experiment was carried out by using the above described reaction conditions and by removing the catalyst when 12% limonene conversion was achieved.

Stability tests were carried out by running four consecutive experiments with the same catalyst sample, which was recovered by filtration, washed and dried before use in the next experiment.

In order to check the support activity, limonene oxidation was also carried out over the parent material MCM-41, under similar experimental conditions. Samples were taken periodically and analysed by GC and GC-MS on a 30 m × 0.25 mm DB-1 column, from J&W, using n-nonane as internal standard.

3. Results and discussion

3.1. Catalyst preparation

The manganese salen complex was covalently attached to the MCM-41 support by using a diisocyanate as linking agent. Urethane links are formed between the hydroxyl groups present on the surface of MCM-41 and one of the terminal isocyanate groups of the binder (DIC-4) [15]. The other terminal isocyanate group remains available to react with the free hydroxyl groups present in the salen ligand (scheme 1). 1,4-Diisocyanatobutane (DIC-4) was chosen, since its small carbon chain is likely to self-assemble vertically on the MCM-41 surface, thus avoiding the undesirable folding in a U-shape and the attachment of both isocyanate ends to the MCM-41 surface [15].

3.2. Catalyst characterization

3.2.1. ICP and XPS analyses

The XPS signal in the Mn 2p region, obtained for the [Mn(4-OHsalophen)DIC]@MCM-41 material, is barely

Table 1
Textural characteristics obtained from nitrogen adsorption/desorption data: BET surface area, S_{BET}, and average pore diameter, d_p (BJH). Manganese loading as determined by ICP analysis.

Sample	$S_{BET}(m^2g^{-1})$	d_p(nm)	%Mn_{ICP}
MCM-41	1238	28.0	–
[Mn(4-OHsalophen)DIC]@MCM-41	858	18.0	0.2

distinguishable from noise. Although a correct quantification is not possible, the Mn amount seems to be less than 1% of the C amount. This observation is in agreement with the low metal loading determined by ICP analysis (0.2%–table 1).

3.2.2. XRD diffraction

Figure 1 shows the low angle range XRD patterns of the parent MCM-41 (A), and the catalyst sample (B). The calcined MCM-41 starting material exhibits the peak patterns characteristic of mesopourous silica materials with hexagonal symmetry [22]: three well resolved Bragg reflections for 2θ values between 2° and 6,5°, one very intense due to the (100) reflection and two weaker peaks due to (110) and (200) reflections. The presence of these Bragg reflections is a first indication that the obtained catalyst has a highly ordered pore system with a high porosity [23]. The found d value of the (100) reflection was 34.5 Å leading to a lattice parameter, a_0, of 39.8 Å. Upon complex immobilization, no change was observed in the XRD pattern.
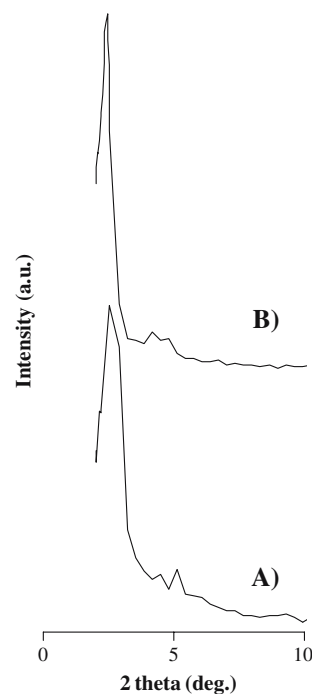

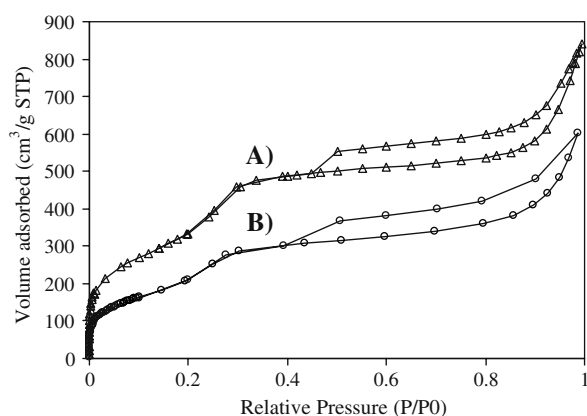Figure 1. XRD spectra of (A) MCM-41, (B) [Mn(4-OHsalophen) DIC]@MCM-41.

Figure 2. Nitrogen adsorption/desorption isotherms obtained for MCM-41 (**A**) and [Mn(4-OHsalophen)DIC]@MCM-41 (**B**).

3.2.3. Nitrogen adsorption

Figure 2 shows the isotherm profiles for MCM-41 (A) and [Mn(4-OHsalophen)DIC]@MCM-41 (B). The calcined MCM-41 material exhibits a type IV isotherm typical of mesoporous materials, according to IUPAC classification. No change in the isotherm profile was observed after complex immobilization, indicating that the mesoporous structure was retained. However, nitrogen uptake decreases, which is an indication of the presence of bulky material inside the support channels [24]. The values of BET area and pore diameter of the prepared materials are reported on table 1. The decreases observed for both parameters are also clear indications that the catalyst anchoring took place mainly inside the support porous system [25,26].

3.2.4. Fourier transform infrared spectra (FTIR)

Figure 3 shows the spectra of MCM-41 (a), [Mn(4-OHsalophen)DIC]@MCM-41 (b), Mn(4-OHsalophen) (c) and DIC-4 (d).

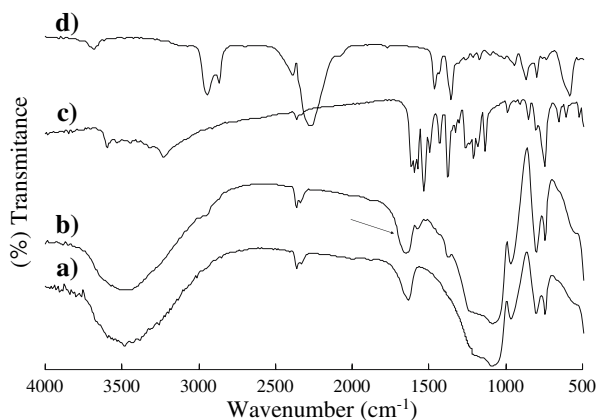The spectra of MCM-41 and Mn(4-OHsalophen)DIC@MCM-41 are dominated by strong bands

Figure 3. FTIR spectra of (**a**) calcined MCM-41, (**b**) [Mn(4-OHsalophen)DIC]@MCM-41, (**c**) Mn(4-OHsalophen)Cl and (**d**) 1,4-diisocyanatobutane.

characteristic of the support matrix. These bands are due to the surface hydroxyl groups, in the range of 3770–3300 cm^{-1}, and to lattice vibrations, in the range 1300–750 cm^{-1}. Two strong bands are present at about 1085 cm^{-1} and 801 cm^{-1}, which can be assigned to the v_{as}(Si–O–Si) and v_s(Si–O–Si), respectively. The band present at about 970 cm^{-1} is attributable to v(Si-OH) vibrations [27–29]. No significant changes are observed in these MCM-41 structure sensitive vibrations, after complex anchoring, which is another indication that the support framework remained unchanged.

The spectrum of 1,4-diisocyanatobutane exhibits a very intense band, due to the -NCO group, at about 2275 cm^{-1}. The absence of this band in the catalyst spectrum (b) indicates that both functional groups of 1,4-diisocyanatobutane have reacted [30]. A new band arising at 1670 cm^{-1}, assignable to the carbamate amide group [16,30], confirms that reaction. Another band also arises at about 1600 cm^{-1} characteristic of the metal complex [31]. Also, new additional weak bands appear at about 2960, 1549, 1482 and 1446 cm^{-1}, which can be assigned to stretching vibrations of the aliphatic (–CH$_2$) groups present in the tether [26,32].

3.3. Catalytic experiments

Similarly to the previously reported experiments of limonene oxidation over heterogeneously supported transition metal Schiff base complexes [12,33,34], the limonene oxidation reaction carried out over [Mn(4-OHsalophen)DIC]@MCM-41, using diluted t-BHP as oxidant, yields a polymer as main product. Limonene oxide, carveol and carvone are also formed in small amounts, under the reaction conditions. A number of other products such as perillaldehyde, *p*-mentha-1(7),8-dien-2-ol, *p*-mentha-2,8-dien-1-ol as well as several unidentified substances are also formed. The similarity of the mass spectra of these unidentified products with that of carvone, suggests that they are carbonyl compounds with a *p*-menthene skeleton. All these products, which are likely to be formed by limonene autoxidation, were lumped as "others".

Also similarly to the previous observations [12], the absence of any induction period in the kinetic curves (Figure 4A) along with the high carbon content observed for the polymer (analysis: C–84.42%; H–13.68%) suggests that the main reaction products, limonene oxide and polymer, are primary products directly formed from limonene through a parallel reaction network. This hypothesis is also supported by the constant selectivity observed in a wide limonene conversion range (Figure 4B).

The MCM-41 support material does not show significant catalytic activity, since the concentration profile of limonene obtained for the blank oxidation reaction carried out over that material, is an almost horizontal line (Figure 5).
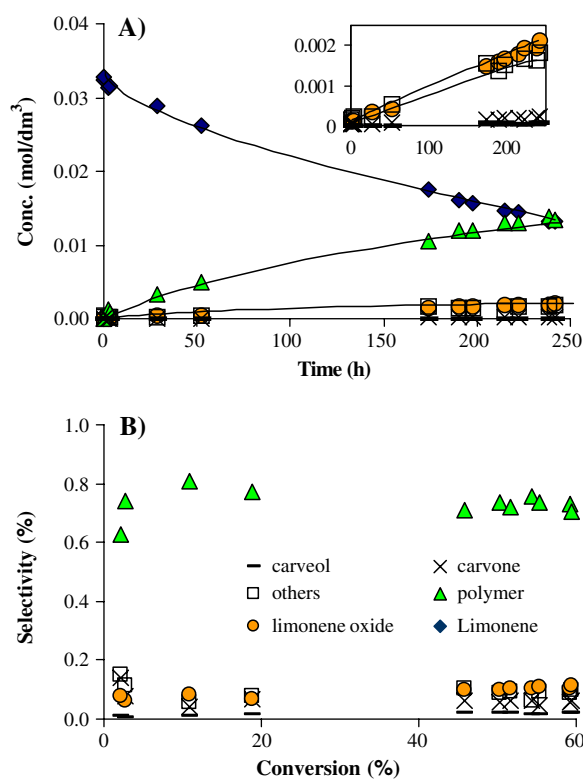
Figure 4. Limonene oxidation carried out over [Mn(4-OHsalophen)DIC]@MCM-41. Concentration profiles of limonene, limonene oxide, carveol, carvone, "others" and polymer (**A**) and selectivities to the main products (**B**).
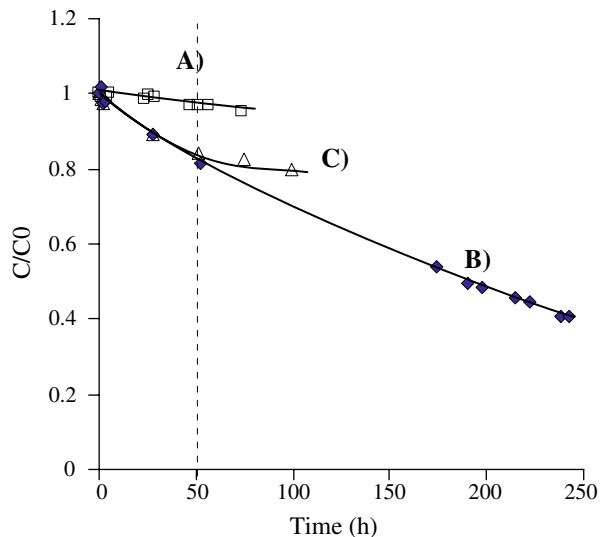
In fact, small amounts of metal leaching can have a significant effect on the observed catalytic results in such a way that, in some cases, the leached metal ions can be responsible by all the catalysis [35].

A strong reduction in the slope of the limonene kinetic curve is observed for the hot-filtration experiment after catalyst removal, when compared with the corresponding kinetic curve obtained for the normal oxidation experiment (Figure 5). This result shows clearly that the reaction rate is strongly reduced upon catalyst removal and that there is no significant catalytic activity attributable to metal ions or complexes leached out to the homogeneous liquid phase.

Figure 5. Limonene concentration profiles obtained for the experiments carried out over MCM-41 (**A**) and [Mn(4-OHsalophen)DIC]@MCM-41 (**B**), as well as for the hot-filtration experiment (**C**). The dashed line shows the time at which the catalyst was removed by hot-filtration.

The catalyst stability was checked not only by performing a hot-filtration experiment, in which the catalyst was removed after 50 h reaction (12% limonene conversion), but also by carrying out four consecutive oxidation experiments with the same catalyst sample.

Table 2
Limonene oxidation catalysed by [Mn(4-OHsalophen)DIC]@ MCM-41, using diluted t-BHP as oxygen donor in a t-butanol/acetone solution. Conversion, selectivity and initial turnover frequency (TOF).

Run	Product selectivity (%)[a]					TOF[b]
	Limonene oxide	Carveol	Carvone	Polymer	Others	
1st	10.0	2.1	6.3	71	10.6	17.1
2nd	5.8	–	1.3	64	28.9	17.4
3rd	5.9	0.5	1.4	62	30.0	17.2
4th	8.1	2.0	6.6	70	13.3	17.3

[a] Selectivity obtained at 40% conversion.
[b] Initial turnover frequency.

Table 2 shows the initial turnover frequency (TOF) and selectivity for the main products obtained for four consecutive oxidation experiments carried out with the same catalyst sample. Not only TOF remains practically unchanged but also selectivities remain within a narrow range of values, attesting to the high stability of [Mn(4-OHsalophen)DIC]@MCM-41.

4. Conclusions

The anchoring of Mn(4-OHsalophen) on MCM-41 was successfully achieved by a new post-synthetic method, using DIC-4 as a linking agent. Different characterization techniques such as XPS, ICP, FTIR, XRD and textural analysis showed evidences that the metal complex was covalently attached to the MCM-41 surface and that its channel structure remained unchanged.

The prepared catalyst seems to be very stable since it kept its activity (TOF) when used in four consecutive runs. Also the rate of limonene consumption is strongly reduced upon catalyst removal in a hot-filtration experiment.

Acknowledgments

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