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Synthesis, Characterization and Catalytic Activity of a New Chromium Catalyst Supported on Nanoporous MCM-41 for Oxidation of Olefins and Alkyl Aromatics

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Abstract

The mesoporous molecular sieve MCM-41 was covalently grafted with 3-chloropropyl trimethoxylsilane and then was reacted with [Cr(salpr)(H_2O)]Cl, (salpr = N,N'-bis(3-salicylidenaminopropyl)amine) to afford MCM-41 containing Cr(salpr) moiety, Cr(salpr)MCM-41. Powder X-ray diffraction and nitrogen adsorption-desorption analyses revealed that not only the textural characteristics of the support were preserved during the grafting experiments but also the channels remained accessible despite sequential reduction in surface area, pore volume and pore size. The chromium content of the prepared catalyst was 0.57 mmol.g^{-1}. The chromium-containing MCM-41 was shown to successfully catalyze the epoxidation of 1-hexene, 1-octene, cyclohexene, cyclooctene, trans-stilbene and norbornene and also benzylic oxidation of toluene and ethyl benzene with tert-butylhydroperoxide (TBHP).

Keywords: Chromium; Oxidation; Heterogeneous; Catalysis

Introduction

Selective oxidation of organic compounds catalyzed by transition metal compounds is one of the most common techniques for the oxo functionalization of organic substrates. In this context, chromium-catalyzed oxidations of organic compounds are of great interest in chemical researches since chromium compounds, in general, oxidize many of the organic functional groups in homogeneous medium. Chromium compounds from its simple salts i.e. acetates, halides and oxides to complexes with porphyrin and salen ligands were used for a variety of oxidations in organic syntheses [1-3]. Among them chromium (III)-salen catalyzed epoxidation of olefins started with Kochi and co-workers in the mid-1980s has been interested in recent years [4]. These types of catalysts also catalyze oxygenation of heteroatom containing organic compounds such as sulfides, sulfoxides and aromatic amines [5]. The catalytic activities of these complexes can be finely tuned by introducing substituents in the 3- and 5-positions of the salen ligands [6,7]. Chromium (III)-salen complexes also catalyze the ring opening reactions of epoxides by a variety of different nucleophiles [8,9]. It is known that the mechanisms of epoxidation and epoxide ring opening are not similar. In

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epoxidation, the catalyst serves as an oxo-transfer agent, whereas in epoxide ring opening, it plays a dual role, serving both as a lewis acid to activate the epoxide and as a counter ion for the nucleophile. Despite the extensive researches performed on homogeneous catalysts of chromium [1-9, 10], there are limited works on preparation and investigation of catalytic activity of heterogeneous chromium catalysts. Garcia and co-workers prepared two series of solid chromium catalysts in which a chiral chromium salen complex has been anchored on aminopropyl-functionalized SiO_2, ITQ-2 or MCM-41 [9]. The catalytic activities of these catalysts were investigated in asymmetric ring opening of epoxides. On the other hand, Che and co-workers investigated catalytic activity of chromium (III)-binaphthyl Schiff base complex immobilized on modified MCM-41 in asymmetric epoxidation of unfunctionalized olefins and gave significantly higher enantioselectivity than the free complex [11]. Immobilization of $[Cr^{III}(salen)]^+$ complex in MCM-41 molecular sieve with impregnation method gave a new heterogeneous catalytic system that was active in oxidation of norbornene and 1-naphthol [3]. Chromium containing mesoporous MCM-41 and MCM-48 molecular sieves are another class of heterogeneous chromium catalysts that show significant activity for the liquid phase oxidation of alkyl aromatics with tert-BuOOH [12-14].

In this work we attempt to prepare a new heterogeneous catalyst of chromium with covalent attachment of a chromium complex i.e. $[Cr(salpr)(H_2O)]Cl$ onto chloropropyl modified MCM-41(ClpMCM-41). The catalytic activity of the prepared catalyst in the epoxidation of olefins and benzylic oxidation of alkyl aromatics was investigated.

Materials and Methods

Infrared spectra of the materials were recorded using Shimadzu 4300 FT-IR spectrometer. X-ray diffraction (XRD) data were collected with a SIEFERT XRD 3003 PTS diffractometer using Cu Kα radiation. Chemical analyses of the samples were carried out with VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer. Nitrogen sorption studies were performed at liquid nitrogen temperature using Quanta chrome Nova 2200, Version 7.11 Analyzer. Gas chromatograms were recorded using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a FID detector. GC-MS of products were recorded using a HP Agilent 6890N gas chromatograph fitted with a capillary column HP-5.

Cyclohexene, cyclooctene, 1-hexene, 1-octene, norbornene, trans-stilbene, toluene, ethyl benzene and tert-butyl hydroperoxide (TBHP, 80% in di-tertiary butyl peroxide) were purchased from Merck Chemical Company.

Preparation of the Support

Preparation of MCM-41 was performed according to the literature method [15]. After calcination and removing of the template, the resulting material was modified with chloropropyl trimethoxy silane according to literature method [16] to afford chloropropyl modified MCM-41 (ClpMCM-41).

Preparation of the Chromium Catalyst

For preparation of the catalyst excess of $[Cr(salpr)(H_2O)]Cl$ complex (700 mg, prepared according to the literature method [17]) and 1 ml of triethylamine were suspended in 60 ml of toluene and after half hour to the mixture was added ClpMCM-41 (1.5 g, dried in vacuum oven at 423 K). The resulted suspension was refluxed for 24 hours. After filtration the solid was dried and then soxhlet extracted with mixture of dichloromethane and methanol for 24 hours.

Catalytic Oxidation of Organic Compounds

Epoxidation of olefins such as cyclohexene, cyclooctene, 1-hexene, 1-octene, norbornene and trans-stilbene purchased from Merck was carried out in a 25 ml round bottomed flask equipped with a condenser and a magnetic stirrer. Tert-butylhydroperoxide (TBHP) (obtained from Merck as 80% in di-tertiary butyl peroxide) was used as oxidant. In a typical procedure, to a mixture of catalyst (100 mg) and olefin (8 mmol) in chloroform (20 ml) was added TBHP (1.6 ml, 14.4 mmol) under nitrogen atmosphere and the mixture was refluxed for appropriate time. Analyses of the products were performed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a FID detector. Products were quantified using isooctane (1 g, 8.75 mmol, Merck) as internal standard.

Oxidation of toluene and ethyl benzene was performed as above procedure. 8 mmol of toluene or ethyl benzene, 100 mg of catalyst and 1.6 ml of TBHP in 20 ml solvent (chloroform or the substrate itself) was refluxed under nitrogen atmosphere for appropriate times.

The chromium content of the recycled catalyst was measured with VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer after dissolution of the solid in hydrogen fluoride solution.

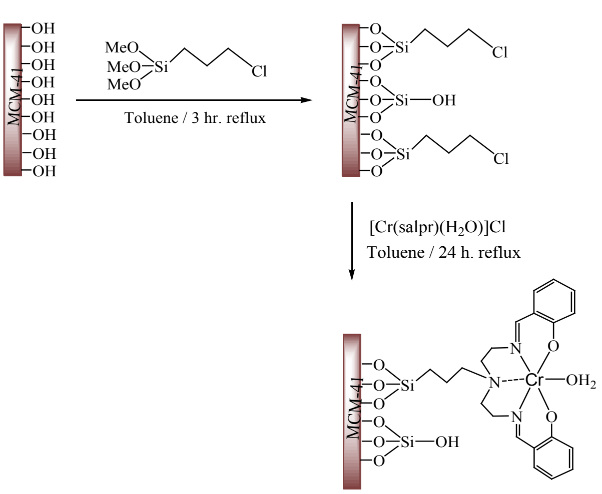
Results and Discussion

Preparation of the Cr(salpr)MCM-41

Synthesis of the chromium complex [Cr(salpr)(H_2O)]Cl was performed as described previously [17]. The immobilization of the complex was carried out as depicted in Scheme 1. In this process secondary amine group of salpr ligand replaced the chloro groups of the ClpMCM-41 which prepared from the reaction of silanol groups of MCM-41 with chloropropyl trimethoxy silane. Excess of chromium complex has been employed and small amount of trimethylamine was added to assure of performance of the substitution reaction. The resulted solid product was then soxhlet extracted with mixture of dichloromethane and methanol to remove unreacted chromium complexes from the prepared catalyst.

The FT-IR spectrum of the Cr(salpr)MCM-41 material has been shown in Figure 1. The band at 1629 cm^{-1} assigned to C=N stretching vibration in this compound. The same band for free chromium complex was also observed in this wavenumber. The bands in the range 1318-1470 cm^{-1} have been assigned to aromatic ring vibrations. On the other hands, there is a peak at 900 cm^{-1} assigned to Cr-O stretching vibration. The free chromium complex has also a similar band in this region. These observations are evidences for immobilization of chromium compound onto the MCM-41.

The chromium content of the prepared material was found to be 0.57 $mmol.g^{-1}$ on the basis of ICP-AES chemical analysis.



Scheme 1. Schematic illustration of Cr(salpr)MCM-41 catalyst preparation.

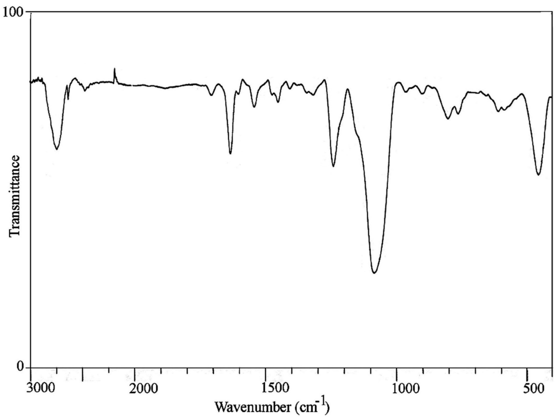


Figure 1. FT-IR spectrum of the Cr(salpr)MCM-41 material.

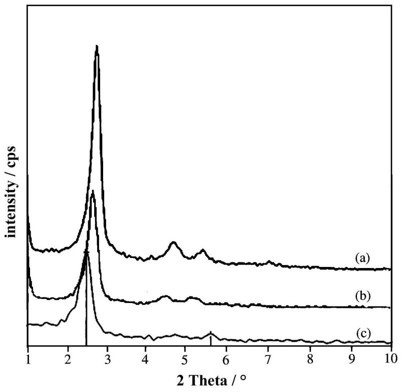


Figure 2. The XRD patterns of (a) MCM-41, (b) ClpMCM-41, and (c) Cr(salpr)MCM-41 materials.

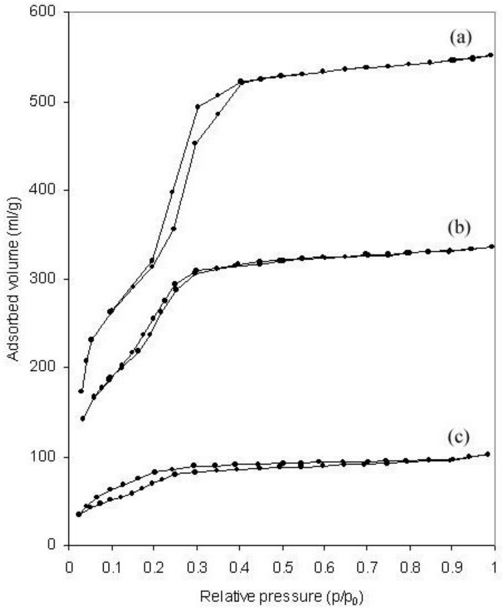


Figure 3. Nitrogen sorption isotherms of (a) MCM-41, (b) ClpMCM-41, and (c) Cr(salpr)MCM-41 materials.

Textural Properties of the Catalyst

In order to investigate the effect of incorporating chromium complex on the texture properties of the materials powder X-ray diffraction and nitrogen adsorption/desorption analyses were performed. The XRD pattern of the MCM-41, ClpMCM-41 and Cr(salpr)MCM-41 materials are shown in Figures 2a-c. In the XRD pattern of the chromium complex grafted on MCM-41 only a single peak at $2\theta = 2.48$ is present, which is corresponding to the <1 0 0> plane of the hexagonal unit cell. This peak shifts to a lower angle with respect to MCM-41 and ClpMCM-41 and has lower intensity. As a result of the contrast matching of silicate framework and organic moieties located inside the MCM-41channels, the higher angle peak (corresponding to <1 10>, <2 0 0> and <2 1 0>) are absent in this material. Compared to MCM-41 the increase in lattice parameter of this material (Table 1) indicates the unit cell expansion due to the incorporation of organic moieties and chromium complex within MCM-41.

Further evidence of mesoporous nature of the prepared materials was obtained by nitrogen sorption isotherms. Al three samples exhibit type IV isotherms (according to IUPAC definition) and hysteresis loop resulted from capillary condensation of N_2 gas inside the mesopores (Figures 3a-c). Table 2 give the specific surface area, total pore volume and pore diameter (calculated with BJH method) of the materials. Compared to parent mesoporous samples the Cr(salpr)MCM-41 material exhibit a drastic decrease in N_2 uptake due to the presence of the comparatively bulky compound on the surface of the mesoporous channels. On the other hands, the average pore diameter of this material is smaller than that of MCM-41 and ClpMCM-41.

Catalytic activity of the prepared catalyst was investigated in epoxidation of some olefins such as cyclooctene, cyclohexene, 1-octene, 1-hexene, trans-stilbene and norbornene as well as benzylic oxidation of toluene and ethyl benzene with tert-BuOOH. The results of the epoxidation of olefins are given in Table 3. Considering the results revealed two points in this Table. First, norbornene and trans-stilbene which have high electronic density on the C=C double bond are more reactive in epoxidation reaction. Secondly, in the other substrates cyclohexene and 1-hexene which have lower steric hindrance are more reactive than bulkier homologues i.e. cyclooctene and 1-octene. This observations accounts for involvement of an electrophilic mechanism in which a peroxidic oxygen atom transfer to the olefin occurred from alkylperoxo chromium intermediate, produced from attack of tert-BuOOH to chromium center of catalyst. The main product of this reaction is an epoxide that in side reaction may undergo ring opening to yield other by-products. The results of catalytic benzylic oxidation of toluene and ethylbenzene with tert-BuOOH are given in Table 4. As seen, the major product of toluene and ethylbenzene in presence of Cr(salpr)MCM-41 is benzaldehyde and acetophenone, respectively. Changing the solvent from low boiling point chloroform to higher boiling point solvents i.e. toluene, ethylbenzene and chlorobenezene increase the reaction rate. This can be explained by more activating the alkylperoxo chromium intermediate in higher reaction temperature and fast oxygen atom transfer.

Table 1. Texture parameters of samples taken from XRD analyses

Material	XRD d value (Å)	Lattice parameter[a] (Å)
MCM-41	32.6	37.6
ClpMCM-41	33	38.1
Cr(salpr)MCM-41	35.6	41.1

[a] Determined by equation: $a_0 = d_{100}\,(2/\sqrt{3})$

Table 2. Texture parameters of samples taken from nitrogen sorption studies

Material	Specific surface area ($m^2.g^{-1}$)	Total pore volume ($ml.g^{-1}$)	Pore diameter (Å)
MCM-41	1211	0.851	28.2
ClpMCM-41	1060	0.51	19.2
Cr(salpr)MCM-41	286.2	0.16	11

Table 3. Results of catalytic epoxidation of some olefins with TBHP in presence of Cr(salpr)MCM-41

Olefin	Time(hours)	Conversion (%)	Selectivity(%)[a]
Cyclooctene	10	7	77
Cyclohexene	10	56	83
1-octene	10	5	65
1-hexene	10	19	79

Reaction conditions: catalyst (100 mg), olefin (8 mmol), TBHP (1.6 ml, 14.4 mmol), refluxing chloroform (20 ml).

[a] Selectivity toward formation of the corresponding epoxide.

Table 4. Results of catalytic oxidation of toluene and ethyl benzene with TBHP in presence of Cr (salpr) MCM-41

Substrate	Solvent	Time (hour)	Conversion (%)	Selectivity (%)
Toluene	Chloroform	7	19[a]	71[d]
Toluene	Toluene	7	98[b]	70[d]
Ethyl benzene	Chloroform	7	25[c]	67[e]
Ethyl benzene	Ethyl benzene	7	98[b]	89[e]
Ethyl benzene	Chlorobenzene	7	99[b]	81[e]

Reaction conditions: catalyst (100 mg), olefin (8mmol), TBHP (1.6 ml, 14.4 mmol), refluxing chloroform (20 ml).
[a] Conversion based on consumption of toluene, [b] based on based on consumption of TBHP, [c] based on consumption of ethyl benzene, [d] Selectivity toward formation of benzaldehyde, [e] Selectivity toward formation of acetophenone.

In summary, we have shown that functionalization of MCM-41 with chloropropylsilyl group and subsequent reaction of the prepared material with [Cr(salpr)(H_2O)]Cl complex afforded a new heterogeneous catalyst of chromium which successfully catalyzed epoxidation of olefins and benzylic oxidation of alkyl aromatics in presence of tert-BuOOH.

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