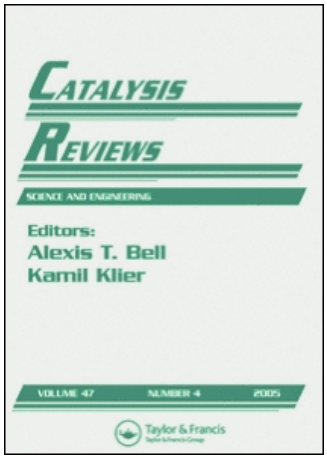

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Alkylation, Hydrogenation and Oxidation Catalyzed by Mesoporous Materials

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Alkylation, Hydrogenation and Oxidation Catalyzed by Mesoporous Materials

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The potentialities of mesoporous materials both as catalysts and catalytic supports in reactions like alkylation, hydrogenation, and oxidation of various substrates are reviewed. Much of our current research effort is devoted to exploring the mechanistic aspects of the reactions, the role of the catalyst structure, and to characterizing the active sites.

Keywords Mesoporous materials, Catalysts, Alkylation, Hydrogenation, Oxidation

1. INTRODUCTION

The increasing demand for new and selective catalysts with larger molecular dimensions led to the discovery of mesoporous catalytic materials. Unlike in the case of microporous and macroporous solids, catalysts with a mesoporous structure can achieve an optimum compromise of high site density and good transport characteristics. Acidic and redox functionalities were generated in these materials by the incorporation of transition metals or by the encapsulation of well-defined homogeneous complexes inside the pores. Also, they opened up many new strategies for shape-selective, enantioselective, and regioselective, conversions.

Since their first description in 1992 (1), the mesoporous materials have attracted much interest as catalysts for various organic transformations. Quite a few reviews are available in open literature (2–7) based on different aspects like synthesis and catalytic activity of mesoporous materials. In this critical approach, we have pointed out the potentialities of these materials both as catalysts and catalytic supports in reactions including alkylation,

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hydrogenation, and oxidation of various substrates. Much of our current effort is devoted to exploring the mechanistic aspects of the reactions, the role of the catalyst structure, and characterizing the active sites.

II. ALKYLATION OVER MESOPOROUS CATALYSTS

The catalytic alkylations of aromatic hydrocarbons are of significant fundamental and practical importance and have been intensively investigated in recent years. Although current homogeneous catalysts are efficient, their corrosive and toxic nature provide potential environmental hazards and their operational problems, including difficulty in separation, recovery, and reutilization result in higher capital costs. A review covering the various aspects of the shape-selective catalysts in alkylation recently was published (8).

A. Alkylation of Benzene

About 70% of the 29.3 million tonnes accounting for the world benzene demand in 1999, were expected to be consumed by acid-catalyzed alkylation of benzene for the production of ethylbenzene and cumene (4). Starting from the mid 1960s different zeolite-based catalysts were extensively evaluated for benzene alkylation using various alkylating agents (9–12). The available literature data on benzene alkylation over mesoporous catalysts are assembled in Table 1.

1. With Alcohols

Alkylation of benzene using benzyl alcohol over $AlCl_3$/mesoporous molecular sieves (MCM-41) was reported by Shinae and Ryoo (13). The disordered KIT-1 exhibited significantly higher catalytic activity than MCM catalysts. Among the various synthesis routes used, post-synthesis impregnation of aqueous $AlCl_3$ turned out to be the most effective means for increasing the catalytic activity.

Valtierra et al. (14) reported the selective formation of cumene as the main product in the isopropylation of benzene by isopropanol over MCM-41/γ-Al_2O_3 catalyst. High temperature ($>350^\circ$C) favors the selective formation of toluene + ethyl benzene, which is formed by cumene disproportionation. In addition, other side reactions such as polyalkylation as well as cracking took place at even higher temperatures.

- It is interesting to note that the primary product of isopropylation is cumene on MCM-41. This may be because of the lower number of acid sites in MCM-41, which may prevent further reaction probabilities unlike in the case of microporous zeolites.

Table 1: Alkylation of benzene over mesoporous catalysts.

Reactant	Reagent	L/V	Catalyst	Product	Ref.
With alcohols					
Benzene	Isopropanol	V	MCM-41/γ Al_2O_3	Cumene, Toluene + ethylbenzene Xylenes	(14)
Benzene	Benzyl alcohol	V	MCM-41, MCM-48		(13)
With alkalihalides					
Benzene	Benzyl chloride	V	Ga-MCM-41	Diphenyl methane	(15)
Benzene	Benzyl chloride	L	Fe-MCM-41	Diphenyl methane	(16)
Benzene	Benzyl chloride	L	$AlCl_3$-, $GaCl_3$, $InCl_3$-MCM-41	Diphenyl methane	(19)
With alkenes					
Benzene	Isobutene		(Si,Al)-MMM	ter-butyl Benzene	(30)
Benzene	Linear long chain olefines	L	$AlCl_3$ immobilized on MCM-41	Linear alkyl benzene	(29)
Substituted benzenes					
Bromobenzene	Benzyl chloride	L	H-Al-MCM-41	Isomeric, bromo substituted DPM	(34)
Difluorobenzene	Propene, isopropanol, 2-chloropropane	V	$AlCl_3$ immobilized on MCM-41	2- (2,4) Difluoro phenyl propane	(32)
Trimethylbenzene	Cyclohexene	L	Cs-TPA-MS	2,4 Dimethyl phenyl cyclohexane	(41)
Ph-X (X = Br, Cl, CH_3)	Benzyl chloride	L	$AlCl_3$, $FeCl_3$, $CuCl_2$-$ZnCl_2$-MCM-41	Diphenyl methane	(33)

2. With Alkali Halides

Okumura et al. (15) studied alkylation of benzene over Ga-MCM-41 (as synthesized) and Ga/MCM-41 (impregnated) at 313 K using benzyl chloride as the alkylating agent. Independent of the method of introduction of Ga, the activity increases considerably until 0.4 mol/Kg of Ga loading and then decreases, which may be due to the generation of agglomerated Ga_2O_3 species above this concentration. The authors found the presence of weak acid sites generated from Ga_2O_3 species evidenced by NH_3 TPD. The impregnated catalyst exhibited a higher activity than did the as-synthesized catalyst in the formation of diphenyl methane. Calcination at higher temperature in direct synthesis causes the formation of extra-framework aggregates, which in turn decreases the activity in the latter case.

Benzylation of benzene over Fe-containing zeolite molecular sieve materials prepared by different methods and exhibiting different pore sizes was studied by He et al. (16). These catalysts gave 100% monoalkylated product selectively under the employed experimental conditions and showed better stability than did the previously reported Fe-pillard clays (17). But Fe-containing mesoporous molecular sieves cannot catalyze the reaction at $<$313K. The reaction can be explained following Choudhari's Redox mechanism (18), according to which, catalysts containing reducible cations exhibit high activities in spite of their low number of Lewis acid sites, when benzyl chloride is the alkylating agent.

$$\text{Ph-CH}_2\text{Cl} \longrightarrow \text{Ph-CH}_2 + \text{Cl} \tag{1}$$

$$\text{Ph-CH}_2 + \text{Fe}^{3+} \longrightarrow \text{Ph-CH}_2^{+} + \text{Fe}^{2+} \tag{2}$$

$$\text{Fe}^{2+} + \text{Cl} \longrightarrow \text{Fe}^{3+} + \text{Cl}^{-} \tag{3}$$

The energy of rupture of C-Cl bond Eq. (1) will prevent the reaction from taking place at 313 K or below.

Choudary's group (19) have studied the alkylation of benzene by benzyl chloride on various supported trivalent metal chloride catalysts, $InCl_3$ and $GaCl_3$ supported on montmorillonite K-10 and mesoporous MCM-41 show high activity for the reaction at 353 K. Among the catalysts, $InCl_3$/K-10 showed the best performance while supported $AlCl_3$ showed poor activity. The Lewis acid character of these catalysts is in the order, supported $InCl_3$ $<$ supported $AlCl_3$ $<$ supported $GaCl_3$.

- This trend can be explained on the basis of the higher electronegativity of Ga. But in the case of supported $InCl_3$ catalyst, redox property, rather than acidic property seems to play an important role (19).
- However, understanding the mechanism of benzylation over these catalysts may require further studies.

Miller and coworkers (20a) compared the superior activity of $ZnCl_2$ incorporated mesoporous silica with that of Clayzic, the commercially available supported reagent, in the Friedel–Crafts alkylation of benzene using benzyl chloride. These catalysts gave 41% and 24% conversion of benzyl chloride respectively under identical conditions.

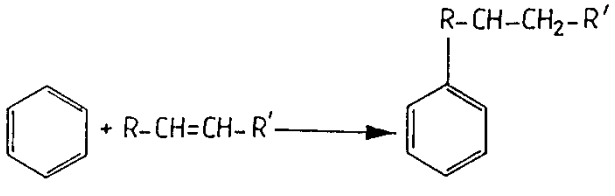
Bachari et al. (20b), in a recent report, discussed the catalytic activity of Fe-containing mesoporous molecular sieve materials in the alkylation of benzene by benzyl chloride at 333 K. The authors suggested a mechanism that involves a redox step at the reaction initiation as reported earlier by Choudary et al. (19). The catalytic compounds showed an activity that increased with their iron content. However, the selectivity to diphenylmethane at complete conversion of benzylchloride decreased while the Fe content increased.

3. *With Olefins*

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry (21). Linear alkyl benzene (LAB) is the primary raw material used to produce LAB sulfonate (LAS), a surfactant detergent intermediate.

The key step in the synthesis of LAB is the alkylation of benzene with linear long chain olefins. The main reaction (Scheme 1) is usually accompanied by other side reactions with coproduction of undesired compounds. Various solid acids like zeolites (22), clays (23), sulfated zirconia (24) and immobilized ionic liquids were tested. However, so far these results have not been industrially exploited. MCM-41 has been used successfully for transformations of bigger molecules (25–27). Lewis acid catalysts can be obtained by immobilizing $AlCl_3$ or other Lewis acids on MCM-41 (28).

Stephan Jaenicke et al. (29) investigated $AlCl_3$ supported on MCM-41[n], (the qualifier 'n' corresponds to the number of C atoms in the main chain of the alkyltrimethylammonium ions used as the micelle-forming agent in the synthesis of the material), for its capability to catalyze the Friedel–Crafts alkylation of benzene with linear 1-alkenes. An increase in selectivity to the mono-substituted product with the length of the olefin molecule for a given MCM-41[n] as well as with the decrease in pore size of the support was apparent in the reaction.



Scheme 1: Reaction network for alkylation of benzene with linear olefins (4).

The catalytic activity of highly ordered mesoporous mesophase materials (MMM), like C16-(Si,Al)-MMM with different Al concentrations was studied by Kodenev et al. (30) in the alkylation of benzene using iso-butene. Even though the activity of these materials was found to increase with increase in Al content, the value is five to six times lower as compared to that of beta zeolite unlike the conclusion published by Perego et al. recently (31).

B. Substituted Benzene

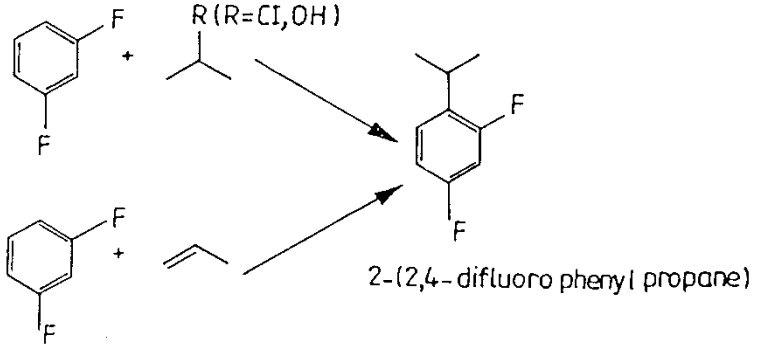
It is clear that the acid strength requirements of an organic reaction are going to be strongly influenced by the presence of electron donor or electron withdrawing substituents on the functional group undergoing chemical transformation.

In principle, electron donor group will facilitate protonation by stabilizing the positively charged reaction intermediate, thus lowering the strength needed to promote the chemical transformation. The reverse applies for electron withdrawing substituents (7).

Alkylation of difluorobenzene (32), Ph-X (X = Br, Cl, CH_3) (33), and bromobenzene (34) by various alkylating agents over $AlCl_3$ immobilized on MCM-41[n] was studied by Stephan Jaenicke and coworkers.

Difluorobenzene (32) was alkylated using three different alkylating agents like isopropanol, propene, and 2-chloropropane (Scheme 2) and the activity of $AlCl_3$/MCM-41[n] was compared with various homogeneous catalysts like $AlCl_3$, H_2SO_4, solid acids like Nafion, Amberlyst, clayzic ZrO_2/SO_4^{2-}, etc.

It was found that $AlCl_3$/MCM-41[n] initially showed some activity, but it was quickly poisoned by H_2O that formed during the reaction. Similarly, in the reaction of difluorobenzene and propene (32), a fast deactivation of the catalyst was observed due to the formation of an organic deposit, which, in turn, is formed by the polymerization of propene on the surface of the catalyst.

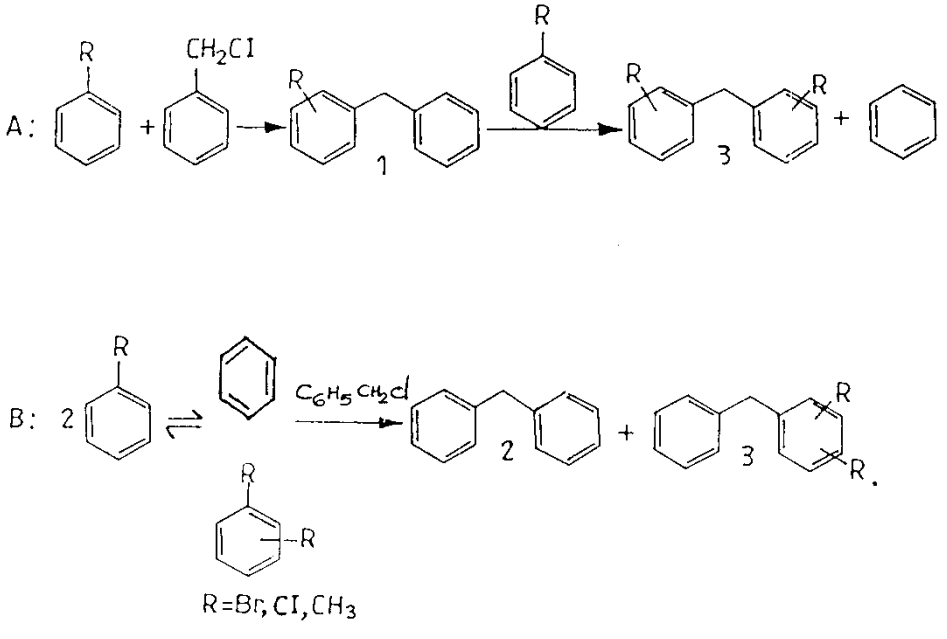


Scheme 2: Catalytic synthesis of 2-(2,4-difluorophenyl)propane over solid acid (32).

$AlCl_3$ immobilized on MCM-41 showed high activity (equal to that of $AlCl_3$ in the homogeneous phase) and good stability at room temperature when 2-chloropropane (32) was used as the alkylating agent. The selectivity for the monoalkylated product was found to be 78.2 and 75.8 for $AlCl_3$ and $AlCl_3$/MCM-41, respectively, at a conversion of 100%.

The catalytic properties of MCM-41 activated with $AlCl_3$, $ZnCl_2$, and other Lewis acids, such as $FeCl_3$, $NiCl_2$, and $CuCl_2$ were investigated by the same research group (33), in the liquid phase at room temperature Friedel–Crafts alkylation of substituted benzenes. $AlCl_3$/MCM-41 showed higher activity than $ZnCl_2$/MCM-41, while other catalysts were inactive under identical conditions. However, in the benzylation of substituted aromatics, $AlCl_3$/MCM-41 was found to catalyze some alkyl transfer reactions also (Scheme 3).

Large pore zeolites, particularly H-beta were active and regioselective for the para-substituted products in the benzylation of arenes. With deactivated aromatics, such as bromo benzene (34), the selectivity towards the para-substituted products decreased with reaction time, which is due to the blockage of zeolite channels by high molecular weight deposits formed by self condensation of benzyl chloride. Mesoporous materials, such as montmorillonite K-10 and H-Al-MCM-41, were active but not regioselective for the reaction because the pores of these materials are too large to impose restraints on the geometry of the products or the transition state.



Scheme 3: Simplified reaction network for benzylation and side chain transfer of substituted benzenes over $AlCl_3$/MCM-41 (33).

Tungstophosphoric acid (TPA) is the most extensively studied of the various heteropoly acids due to its high Bronsted acidity (5, 35), which results from minimized charge on the anion surface. But the major drawbacks in using them as catalysts are low surface area, rapid deactivation, and relatively poor stability. Attempts to improve the efficiency of these materials were made by supporting TPA on various high surface area supports (36–40).

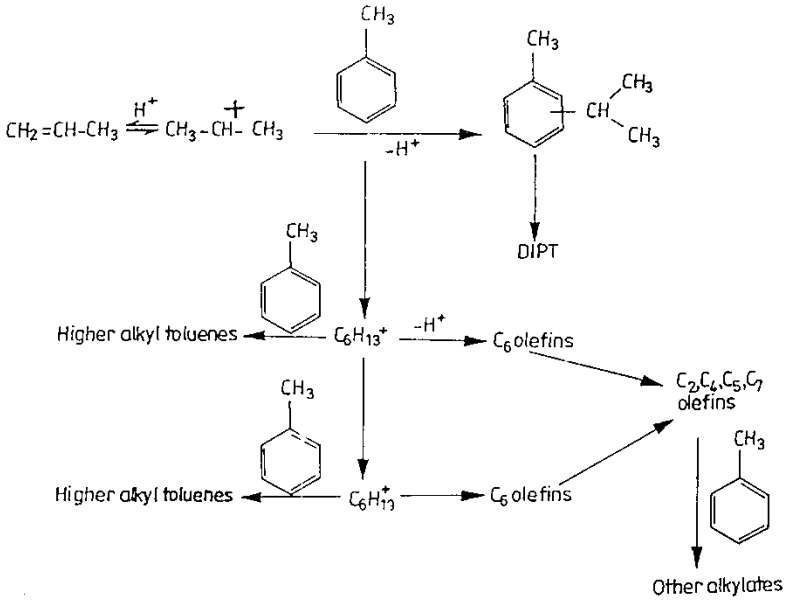
Choi et al. (41) reported the catalytic properties of highly dispersed Cs-TPA supported on MCM-41 in the alkylation of 1,3,5-trimethyl benzene by cyclohexene and these catalysts demonstrated superior activity than those prepared by previously published method (42).

Likewise, as in the case of benzene, toluene alkylation using various alkylating agents over a few mesoporous catalysts was investigated (31, 43, 46).

C. Alkylation of Toluene

The alkylation of toluene with propylene is an electrophilic substitution on the aromatic ring. Acid-catalyzed alkylations are commonly considered as proceeding through carbenium ion type mechanism (Scheme 4).

Perego et al. (31) compared the activity of two amorphous mesoporous silica aluminas (MSA and MCM-41) with amorphous microporous silica alumina (ERS-8) and zeolite beta in the liquid phase alkylation of toluene by propylene to produce cymenes. The mesoporous catalysts showed a comparable catalytic activity but lower cymene selectivity than that of zeolite beta, because of the



Scheme 4: Reaction network for alkylation of toluene with propylene (31).

larger formation of polyalkylates, which in turn is due to the presence of larger pores and lower transalkylation activity. Also, MSA, MCM-41, and ERS-8 produced a large amount of o-cymene due to their lower isomerization ability.

In the case of toluene, the substitution of electrophile on the aromatic ring is activated on o- and p-positions by the presence of the methyl group. The meta isomer is thermodynamically more stable (4) and can be obtained by either direct isopropylation or isomerization. Hence, the final isomer distribution depends on the combination of alkylation-isomerization rates, which in turn depends on the substrate and catalyst features (acidity and pore structure). But the relative rates of alkylation and isomerization reactions are important parameters, which have to be truly evaluated.

The acid strength of Al-MCM-41 was found to be sufficient for the activation of propylene in toluene alkylation leading to cymenes with selectivity over 96% as reported by Cejka et al. (43). Also, siliceous MCM-41 modified by heteropoly acid (HPA) exhibited a higher cymene selectivity and a lower rate of cymene isomerization compared to Al-MCM-41, even though HPA-MCM-41 are strongly acidic catalysts (44).

Para-cymene is an important intermediate used in pharmaceutical industries and for the production of fungicides, pesticides, as flavoring agent, and as a heat transfer medium (45). Isopropylation of toluene using isopropanol as alkylating agent over two different Al-MCM-41 catalysts with Si/Al ratios of 93 and 104 respectively was carried out by Selvaraj et al. (46). The Al-MCM-41 (Si/Al ratio 93) gave a high selectivity of p-cymene (75.3%), which is higher than the earlier reports by Perego et al. (31) and Cejka et al. (43) where the selectivity of p-cymene was only (37%–47%) and 38% respectively.

D. Alkylation of Naphthalene

Alkylation of naphthalene by zeolites was studied extensively (47–52) and found to be governed simultaneously by several mechanisms. In the alkylation of naphthalene with conventional Friedel–Crafts catalysts, it is very difficult to obtain good yields of dialkylated product selectivity, since tri- and tetrasubstitution occur rapidly.

In naphthalene, both α and β positions are likely to be alkylated. Kinetic factors favor α-alkylation while thermodynamic factors favor β-alkylation. The rearrangement of α to β and vice versa are governed by the nature of the catalyst and the reaction conditions employed (8).

The available information on the alkylation of naphthalene over mesoporous catalysts is given in Table 2.

Liquid phase Friedel–Crafts isopropylation of naphthalene is a process currently used in the chemical industry to produce 2,6-DIPN (2,6-diisopropyl naphthalene), an important chemical intermediate for manufacturing advanced polymers (53). Zhao et al. (54) recently reported the isopropylation

Table 2: Alkylation of naphthalene over mesoporous materials.

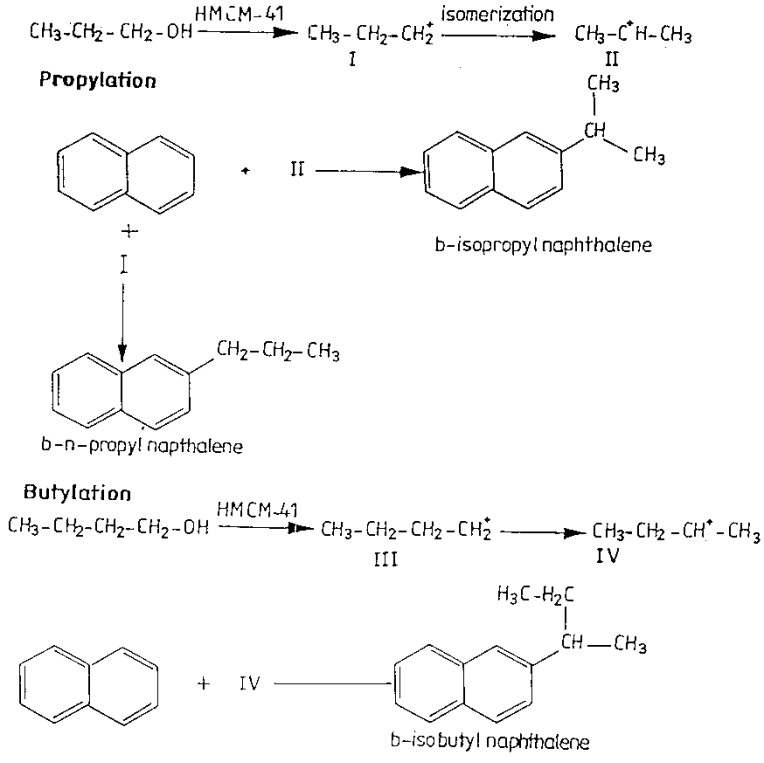
Sl. No.	Substrate	Alkylating agent	Catalyst	Reference
1	Naphthalene	Isopropanol	$AlCl_3$/MCM-41	(54)
2	Naphthalene	Isopropanol	HAl-MCM-41 Pt/ AlMCM-41	(50)
3	Propylation	n-Propanol	MCM-41	(55)
4	Naphthalene	Ethanol	ModifiedY, MCM-41, SAPO-5	(56)
5	Naphthalene	Isopropyl alcohol	″	(57)
6	Naphthalene	ter-Butanol	″	(58)
7	Naphthalene	ter-butyl Alcohol	H-Y,MCM-41, H-beta	(59)
8	Anthracene	″	″	(59)
9	Thianthrene	″	″	(59)

of naphthalene by isopropyl alcohol in liquid phase over $AlCl_3$ immobilized on silylated mesoporous MCM-41, and they found it a promising catalyst for the previous reaction. The catalyst produced more diisopropyl naphthalene (DIPN) with a higher selectivity of 2,6-DIPN than did homogeneous $AlCl_3$ catalyst.

Formation of mono-, di-, tri-, and tetraisopropyl naphthalene over H-AlMCM-41 and Pt/Al MCM-41 was reported by Reddy and Song (50). In both the catalysts, α-substitution preceded in preference to β-substitution and they showed almost the same activity. Also, formation of tri- and tetra-IPN in large quantities is a clear indication of easy diffusion of large molecules in MCM-41 catalysts.

Chakraborthy et al. (55) compared the activity of HMCM-41 with H-Y and H-ZSM-5 in the vapor phase propylation of naphthalene using n-propanol. Under the reaction conditions employed, H-Y zeolite yields 100% β-IPN, whereas in the case of H-MCM-41, although the same β-isomer is observed, there seems also to be the formation of β-substituted n-propyl naphthalene (Scheme 5). In the case of butylation of naphthalene by n-butanol, isobutyl naphthalene was exclusively formed on H-MCM-41 while H-Y and H-ZSM-5 were not found to catalyze the reaction due to size restrictions.

Kulkarni et al. reported vapor phase alkylation of naphthalene using aliphatic alcohols like ethanol (56), isopropanol (57), and ter-butanol (58) as alkylating agents over various catalysts like modified zeolite Y (alkali, alkaline earth metal, and transition metal exchanged), SAPO-5, and MCM-41. It was observed that medium or weak Bronsted acidic centers are required for selective formation of 2,6- and 2,7-dialkyl naphthalenes under the conditions studied. An increase in selectivity of 2,6 and 2,7-isomers with a great decrease in polyalkylated products is observed in ter-butylation in comparison with ethylation and isopropylation reactions. This can be attributed to the



Scheme 5: Reaction scheme for alkylation of naphthalene with n-propanol and butanol (55).

steric hindrance caused by ter-butylated products when compared to the other two alkylating agents.

Armengol et al. (59) reported ter-butylation of polynuclear aromatic compounds (naphthalene, anthracene, and thianthrene) at 373 K using iso-octane as the solvent. Highest conversion and product yield were obtained using iso-octane as the alkylating agent in the absence of ter-butanol. Also it was observed that the reactivity of anthracene is considerably higher than that of naphthalene over MCM-41, while thianthrene showed a lower activity under analogous conditions.

Although catalysis by mesoporous MCM-41 materials is applicable in principle to reactions involving large molecules, there are numerous examples showing that it suffers from the limitation of weak acid strength of its sites that may not be strong enough to meet the requirements of a reaction.

E. Alkylation of Phenol

Alkylphenols are valuable industrial chemicals. Both C- and O-alkylation of phenol is possible depending on reaction conditions such as temperature,

source of reagent, and type of catalyst. C-alkylated phenols, in particular, *tert*-butyl-, *iso*-octyl-, and *iso*-decyl phenols, are widely used in the chemical industry as drilling oil additives, antioxidants, and polymer stabilizers. The isomeric O-alkylated phenols also have numerous industrial applications, particularly in the production of dyes and agrochemicals.

Alkylation of phenols is generally carried out using a liquid acid catalyst, giving wide product distribution. The use of highly corrosive and polluting liquid acids is a major environmental problem and, therefore, later heterogeneous solid acids like anion exchange resins, NaX and Y zeolites, heteropoly acids, acid-treated clays, and titania-supported $AlPO_4$ have replaced them.

In this section the potentialities of mesostructured materials in the alkylation of phenol and substituted phenols are discussed (Table 3).

Alkylation of phenol, in general, leads to thermodynamically favorable m-isomer rather than the o- and/or p-isomers. However, the presence of a phenolic group in the reactant under consideration kinetically favors the latter. Although the o-isomer is kinetically more favorable than the p-isomer, the former isomerizes easily into stable p-isomer owing to steric hindrance at the ortho position. Further, the selectivity of the products depends mainly on the nature of the acidic sites present on the catalyst as well as the reaction temperature. A schematic representation of alkylation of phenol with ter-butyl alcohol proposed by Sakthivel et al. (60, 61) is given in (Scheme 6).

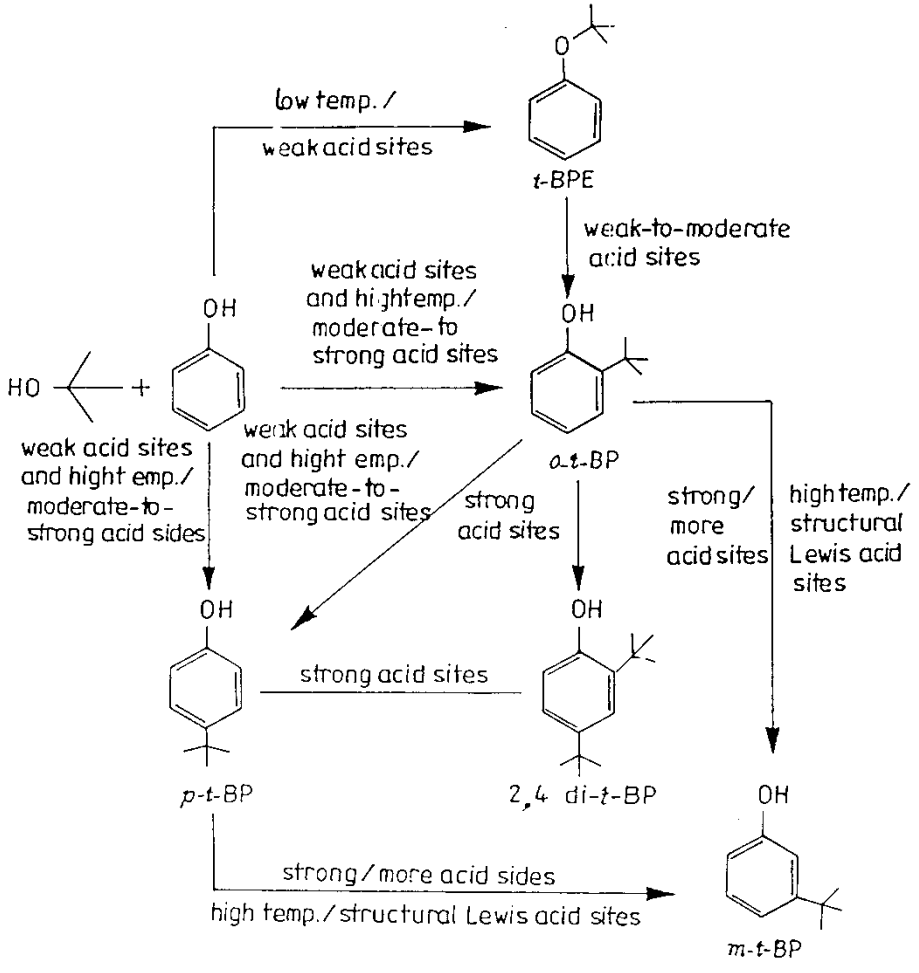
Sakthivel and Selvam (62a) summarized the effect of various trivalent ions in the vapor phase ter-butylation of phenol with ter-butyl alcohol. The comparison of the results using various mesoporous metallosilicate molecular sieves is given in Table 4. They explained the results on the basis of the nature of the acid sites present in the catalysts. The relative number of various types of acid sites in the catalysts studied are given in Table 5.

- Although para-ter-butyl phenol selectivity over these catalysts remains nearly the same, the phenol conversion is slightly higher in the case of Ga-MCM-41, which may be due to the presence of higher numbers of both moderate and strong acid sites in the catalyst.
- For Fe-MCM-41, no formation of meta-ter-butylphenol and 2,4 di-ter-butylphenol is observed due to the fewer number of strong Lewis acidic sites. Also, a higher amount of ortho-ter-butylphenol is observed due to the lack of isomerization of this isomer to meta-ter-butylphenol.

The same reaction was carried out to study the influence of different Al sources on the framework substitution of aluminium. Among the various aluminium sources employed, sodium aluminate was found to be a promising source for incorporation of Al(III) in the tetrahedral framework. This catalyst, with high aluminium content shows higher conversion, but lesser selectivity for

Table 3: Alkylation of phenol and substituted phenols over mesoporous catalysts.

Substrate	Alkylating agent	Catalyst	Product	Reference
Phenol	methanol	Al_2O_3 multilayer grafted WPMCM-41	Anisole(major) o-,m-,p- cresols	(64)
Phenol	ter-butyl alcohol	Al-MCM-41	p-ter-BP(major) o-,m-,ter-BP, 2,4-Di-ter-BP	(60, 61)
Phenol	ter-butyl alcohol	Ga-MCM-41	p-ter-BP(major) o-,m-,ter-BP, 2,4-Di-ter-BP	(62)
SUBSTITUTED PHENOLS				
2,4-di-ter-BP	Cinnamyl alcohol	MCM-41	6-ter-butyl-2-phenyl-2,3-dihydro(4H)benzopyran	(66)
2,4-di-ter-BP	Cinnamyl alcohol	Th-MCM-41, U-MCM-41	6-ter-butyl-2-phenyl-2,3-dihydro(4H)benzopyran and 4-ter-butyl phenol	(66)
m-Cresol	*ter*-Butyl alcohol	Al-MCM-41	2-ter-butyl-5-methyl phenol	(68)
4-*ter*-BP	Styrene	PW/MCM	2-(1-phenylethyl)-4-ter-BP and 2,6-bis-(1-phenylethyl)-4-ter-BP	(67)
Naphthol	*ter*-Butanol	Al-MCM-41	B-naphthyl methyl ether	(69)



Scheme 6: Effect of experimental conditions and acidic sites on the ter-butylation of phenol. (J. App. Catal. *in press*).

the major product, p-ter-butylphenols. This is because, the presence of more aluminium in the framework sites leads to an increase in acid sites, which initiate the formation of the m-isomer through isomerization of o- and p-isomers (Scheme 6).

A comparative study on the catalytic activity of Zn and Fe containing Al-MCM-41 molecular sieves on the vapor phase tertiary butylation of phenol using ter-butyl acetate as the alkylating agent, was carried out by Savidha et al. (62b). These materials always showed a higher phenol conversion than Al-MCM-41 due to stronger acidity generated by Zn and Fe incorporation in the tetrahedral coordination site of the latter. The major products obtained were o- and p-ter-butyl phenols.

Table 4: Effect of MCM catalysts with various trivalent ions in the ter-Butylation of phenol (60–62).

Reactant/products	H-GaMCM-41	H-AlMCM-41	H-FeMCM-41
Phenol Conv (wt %)	37.0	31.0	8.4
Selectivity (%)			
o-ter-BP	8.7	8.1	16.2
m-ter-BP	4.3	6.4	–
p-ter-BP	84.6	84.2	83.8
2,4-di-*ter*-BP	2.4	1.3	–

Reaction conditions: T = 448 K, WHSV = 4.8h-1, cat.wt. = 0.75 mg, *t*-BA : phenol = 1 : 2.

Alkylation of substituted aromatic substrates can either give rise to substitution at the ring position or at the side chain. It is generally believed that both strong acidity and basicity favor ring alkylation while basic catalysts promote preferentially O-alkylation.

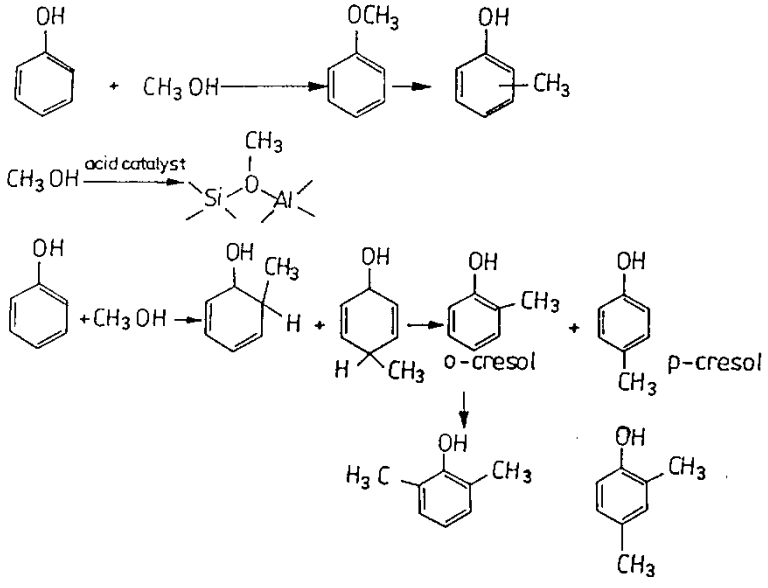
- Alkylation of phenol with methanol is catalyzed by both Bronsted and Lewis acid sites as well as by basic sites. Phenol adsorbs both on acidic and basic sites.

Mesoporous Al-MCM-41 molecular sieve materials with three different SiO_2/Al_2O_3 ratios were used by Bhattacharyya et al. (63) as catalysts for phenol methylation with methanol as the alkylating agent. The formation of the predominant product *o*-cresol was enhanced by lower temperature, less amount of alkylating agent in the feed, and lower acidity of the catalyst. Higher acidity favored the formation of C-alkylated products, while O-alkylation required lower acid strength of the catalyst. The presence of substantial amounts of anisole in the products and a value of nearly 2.0 for the cresols to anisole ratio, indicate that in the mechanism, both the schemes (Scheme 7 and Scheme 8) are operating simultaneously with (Scheme 7) being the predominant one.

Phenol methylation on a new type of catalytic material (alumina grafted on wide pore MCM) was examined by Landau et al. (64). The main products

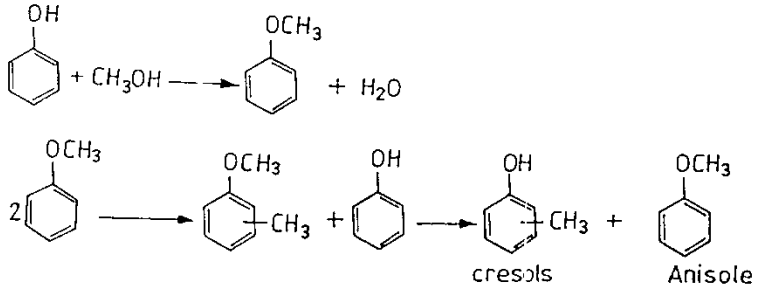
Table 5: Relative number of various types of acid sites in the catalysts. (Calculated manually from TPD profile of Ref. (60,62).)

Catalyst	Weak/mild Bronsted sites	Moderate Bronsted sites	Strong Bronsted sites	Weak Lewis sites	Strong Lewis sites
Ga-MCM-41	8.74	25.74	41.25	9.33	10.06
Fe-MCM-41	34.53	34.02	22.79	5.03	0.98
Al-MCM-41	20.67	27.09	28.05	0.08	10.42



Schemes 7: Reaction scheme for methylation of phenol with methanol over Al-MCM-41 catalyst (63).

obtained were anisole and isomeric cresols. The catalytic sites on the alumina are acid-base pair sites that facilitate the adsorption of the substrate. The TPD studies of alumina-grafted wide-pore MCM (WPMCM) shows Lewis sites of medium strength, which is found to be responsible for the formation of o-alkylated product. Anisole formation requires sites with lower acid strength compared to those necessary for cresol formation. This material displayed the highest acivity (2–3 times the activity of the reference alumina and an o-/p-cresol ratio comparable to that reported for zeolite catalysts) in the previous reaction. This higher activity is attributed to the clusters of grafted alumina with hexa and penta coordinated Al atoms located in the WPMCM pores.



Schemes 8: Reaction scheme for methylation of phenol with methanol over Al-MCM-41 catalyst (63).

- In the case of alkylation with alcohols, the relationship between acid strength and isomer selectivity is well established. Hence, it is possible to predict the isomer selectivity from the knowledge of acid strength.

F. Substituted Phenols

Highly acidic Al-MCM-41 was reported by Armengol et al. (65) as an effective catalyst for the Friedel–Craft alkylation reaction involving the substrate 2,4-di-ter-butylphenol with cinnamyl alcohol to yield flavan [6,8-di-ter-butyl 2-pheny-2,3 dihydro (4H) benzopyran] **1** (arising from intramolecular cyclization of the 1°-cinnamyl phenol) with the concomitant formation of 4-ter-butyl phenol **2** and corresponding substituted benzopyran **3.** The reaction scheme is shown in Scheme 9.

Recently new types of actinide materials, Th-MCM-41 and U-MCM-41, were found to be active for the previously-mentioned reaction (66) and the observed catalytic properties are summarized in Table 6.

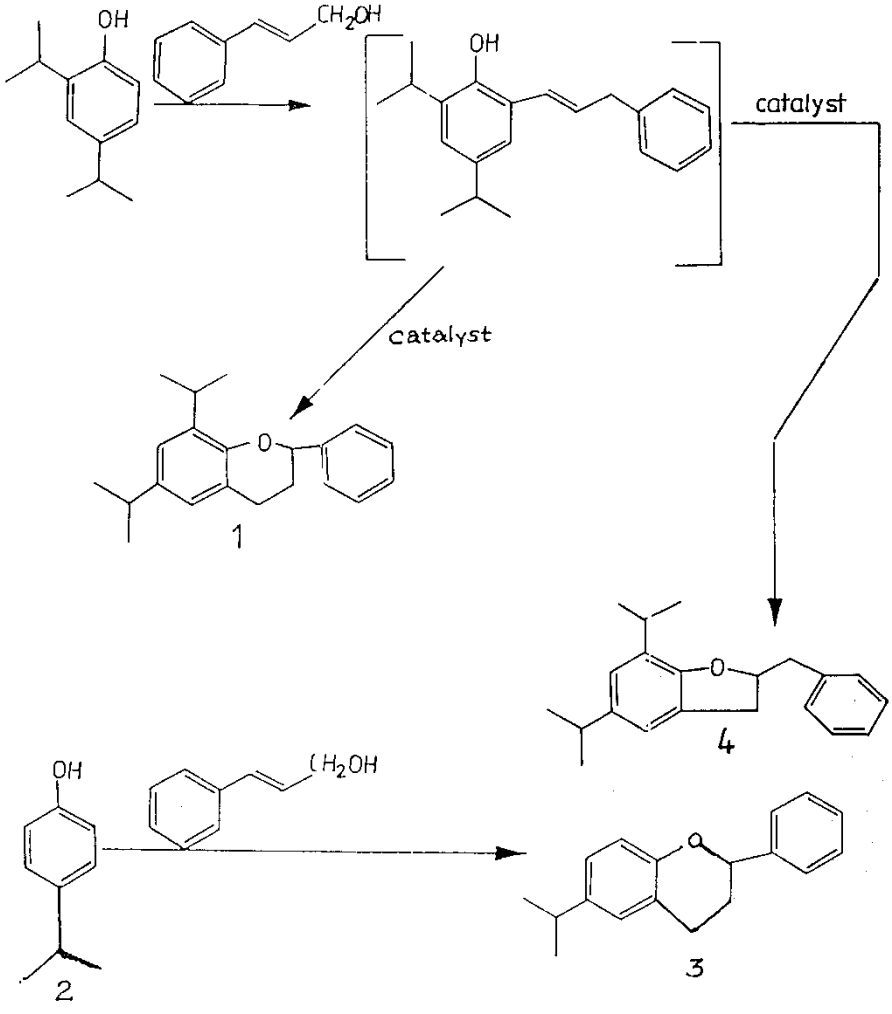
The conversion values for 2,4-di-ter-butylphenol to flavan using Th-MCM-41 and U-MCM-41 are low compared to AL-MCM-41. This result can be rationalized by the larger acidic properties of Al-MCM-41 as compared to the actinide MCM materials.

Also, they produce only two products, **1** and **4**, with no formation of compounds **2** or **3** as obtained for Al-MCM-41. Although U-MCM-41 is more acidic and active than Th-MCM-41 for the alkylation reaction, the Th-MCM-41 is more selective, allowing a better discrimination between the selectivities of compounds **1** and **4**. The previous reaction shows the catalytic potentiality of mesoporous molecular sieves towards Friedel–Craft alkylation involving bulky reactants and products.

The shape-selective effect in the catalytic alkylation of 4-ter-butyl phenol by styrene was studied by Wang et al. (67). The products obtained are 2-(1-phenyl ethyl)-4-ter-butyl phenol **1** and 2,6-bis-(1-phenylethyl)-4-ter-butyl phenol **2** over tungstophosphoric acid dispersed mesoporous silicas with varying pore diameters of 18, 30, and 100 Å. The catalyst with 30 Å pore diameter shows a better selectivity for **1** at 90% conversion of the reactant. The poor selectivity for **2** is due to the higher kinetic diameter of the molecule, which is nearly 20 Å. Therefore, a good selectivity in monoalkylated product can be obtained by adjusting the pore diameter of the catalysts.

G. Alkylation of Cresol

Alkylation of m-cresol is an industrially important reaction, which produces the precursors for a number of commercially important antioxidants and light protection agents. Vapor phase regioselective ter-butylation of m-cresol over mesoporous Al-MCM-41 molecular sieves was thoroughly



Scheme 9: Reaction of 2,4-di-ter-butylphenol with cinnamic alcohol (65).

investigated by Murugesan and coworkers (68) to produce ring-alkylated product (2-ter-butyl-5-methylphenol) with 100% selectivity in the temperature range 523–673 K at a feed ratio 1:2 (m-cresol:ter-butanol).

Comparing the ter-butylation of two substrates, i.e., phenol (64) and substituted phenol, i.e., m-cresol (68), over Al-MCM-41 in the vapor phase,

- m-cresol gave 100% selective formation of 2-ter-butyl 5-methyl phenol.
- while phenol gave p-ter butyl phenol (BP) (84.2%), o-ter-BP (8.1%), m-ter-BP (6.4%), and di-ter-BP (1.3%) respectively under the same reaction conditions.

Table 6: Alkylation of 2,4-di-ter-butylphenol (DTBP) with cinnamyl alcohol (66).

Catalyst	Conversion of DTPB (%)	Flavan yield (%)	Selectivity (%)	
			1	4
Al-MCM-41	47.2	33.9	71.8	—
U-MCM-41	15.5	8.9	34.1	65.9
Th-MCM-41	7.1	5.0	70.5	29.5

Cinnamyl alcohol = 0.134 g, 2,4-di-ter-BP = 0.206 g, solvent(isooctane) = 50 mL, T = 363K, t = 24 h.

The reason can be as follows:

During the reaction, the two ortho positions with respect to phenolic –OH group in m-cresol are not equally susceptible to electrophilic attack by ter-butyl cation, as the adjacent methyl group sterically hinders one of them. Similarly, the fourth position is also not sterically free for electrophilic substitution. So, the position ultimately left over for alkylation is only the sixth and, hence, only one product is obtained without bialkylation.

- Hence, unlike in the case of phenol, m-cresol can be regioselectively alkylated.

H. Alkylation of Naphthol

A novel catalytic result is observed for SO_4^{2-}/Al-MCM-41 molecular sieves, catalyzed methylation of B-naphthol (69a). Sulfuric acid modification of Al-MCM-41 enhances both catalyst acidity and catalytic activity, which gives a yield of β-naphthyl methyl ether (64.3 mol%) a value higher than that obtained from H_2SO_4 (55.4 mol%). The nonframework Al existing in the intra-channel space is supposed to increase the catalytic activity due to the increase of Lewis acidity.

Unlike in the case of phenol, naphthol gave only O-alkylated product, i.e., 100% β-naphthyl methyl ether on methylation. This can be explained on the basis of difference in mode of adsorption of the two substrates on the catalyst. Phenol is believed to be adsorbed through oxygen, while naphthol is through Π-bond.

I. Alkylation of Disaccharides

Alkyl glycosides are well-known mild nonionic surfactants that are widely used in detergent formulations and also as wetting agents and emulsifiers, both in food and nonfood uses. In addition, alkyl glucosides are known that exhibits liquid crystalline properties and they are readily biodegradable.

- Selective alkylation of disaccharides is normally difficult, because they are generally subjected to alcoholysis under strong acid catalysts, and as a result, alkylated monosaccharides are formed.

De Doede et al. (69b), described a process for the preparation of alkyl glycosides by reacting an alcohol with a saccharide or lower alkyl glycoside in the presence of an MCM-41 catalyst. Mono- and disaccharides, as well as their corresponding lower alkyl derivatives, are alkylated in good yield and selectivity, the observation was entirely unexpected.

J. Summary

Mesoporous molecular sieves permit the alkylation of bulk molecules for which microporosity of zeolite imposes limitations to the reaction. It is important to control both porosity and acidity to get the desired product.

However, it is still a challenge to develop a satisfactory solid alkylation catalyst that makes the chemical transformation economically feasible and environmentally friendly, which has a high yield of alkylate, selectivity to the desired product, a long life cycle, regenerateability, and greatly reduced environmental and safety risks.

III. HYDROGENATION OVER MESOPOROUS MATERIALS

Hydrogenation is a versatile reaction, widely used in organic synthesis (70, 71), and often performed by supported noble metal catalysts. The supports may be as different as carbon (70–72), silica (73), alumina (74), and polymers (75) in order to obtain higher selectivity and activity. Many traditional catalysts using microporous supports fail to achieve optimum performance because the transport of large molecules through narrow pores limits the overall rate. At the other extreme, macroporous systems are limited by low surface area, resulting in low site density. Catalysts with a mesoporous structure can achieve an optimum compromise of high site density and good transport characteristics.

These catalysts offer greater scope for the grafting of organometallic moieties on to the inner surface of the pores. This opens ready routes for the heterogenization of homogeneous catalysts, thus capitalizing on the advantages of both heterogeneous and homogeneous catalysts. Also they opened up many new strategies for shape-selective enantioselective and regioselective conversions (76).

In this section, we consider the role of mesoporous catalysts as supports in the hydrogenation of various substrates. The available literature data are given in Table 7.

Table 7: Typical data on the hydrogenation of various substrates over mesoporous catalysts.

Sl. No.	Substrate	Catalyst	Reference
(A) Aromatic compounds			
1	Benzene	Ni/Nb-MCM-41	(81)
2	Naphthalene	Noble metals containing MCM-41	(83)
3	Naphthalene	Ni-MCM-41	(82)
4	Naphthalene and Phenanthrene	Al-MCM-41	(50)
5	Tetralin	Zr/MCM-41	(84)
6	Nitro and carbonyl compounds	Co-HMA	(86)
(B) Aliphatic compounds			
1	Olefines and acetylenes	Pd/MCM-41	(87)
2	Acetonitrile	Ni supported on Zr-doped mesoporous silica	(92)
3	1,5,9-Cyclododecatriene	Ru_6Sn anchored MCM-41	(112)
(C) CO hydrogenation			
1	CO hydrogenation	Ru promoted Co/MCM-41	(104)
2	CO hydrogenation	SCMM	(105)
3	CO hydrogenation	MCM-41	(102)
(D) Enantioselective hydrogenations			
1	Cinnamic acid derivative	Organometallic compounds incorporated HMS	(109)
2	″	″	(110)
3	E-K-Phenyl cinnamic acid	MCM-41 confined organometallic compounds	(76)
(E) Others			
1	Crotonaldehyde	Tin-Oxygen lined MCM-41	(113)
2	Prostaglandin	Ru-MCM-41	(114)
3	Stearonitrile	Ru on SO_4^{2-} mesoporous Zirconia	(93)

A. Hydrogenation of Aromatic Substrates

1. Benzene

The high activity of Ni containing catalysts in the hydrogenation of aromatics is well established (77–79). Among the various parameters determining the catalytic activity in the hydrogenation process, the role of the nature of the catalyst support is important. It was concluded (80) that the specific activity of reduced Ni for benzene hydrogenation decreases with the increasing acidity of the support in the order $SiO_2 > Al_2O_3 >$ silica-alumina $>$ Y-zeolites.

Ziolek et al. (81a) studied the effect of supported Ni catalysts on three different mesoporous matrices like MCM-41, Al-MCM-41, and Nb-MCM-41

in the hydrogenation of benzene to yield cyclohexane. The results showed that the incorporation of Al or Nb into the siliceous MCM-41 framework increases the strength of Ni(metal)-support interaction (MSI), which was the highest for Ni/Nb-MCM-41. The highest dispersion of Ni was also observed for the same catalyst. The kinetic study indicates that the activation energy in the benzene hydrogenation (36.5 $KJmol^{-1}$) carried out on Ni/MCM-41 is lower than that described in the literature for Ni loaded on various supports like SiO_2, Al_2O_3, and MgO.

- The low activation energy reported in the work by Ziolek et al. (81a) confirms that mesoporous molecular sieves are good supports for Ni in the hydrogenation of benzene.

Recently, Peng Tian et al. (81b), demonstrated the use of mesoporous materials (MCM-41 and Al-MCM-41), as suitable supports for the preparation of well-dispersed supported Ru catalysts. The activities of these catalysts in hydrogenation of benzene were compared to those of Ru/HY and Ru/SiO_2 (Table 7a).

The catalytic properties were tested in benzene hydrogenation, and the intrinsic activities of all the catalysts (either supported on mesoporous materials or on zeolites) were found to be identical. It was concluded from this result that the dispersion of the Ru metallic phase was similar for all these catalysts.

2. *Naphthalene*

Aromatic saturation of oil fractions is a key process in the refining industry due to increasing demand for cleanest distillates with superior performances (70).

Vaccari et al. (82) compared the activity of Ni-containing MCM-41 catalyst with that of commercial Ni-SiO_2/Al_2O_3 catalyst in the vapor phase hydrogenation of naphthalene. The main products observed were: the fully hydrogenated products, (cis + trans) decalin, the partially hydrogenated product, tetralin, and the hydrogenolysis products, HMW (high molecular weight ring opening products). In comparison to commercial catalysts,

Table 7a. Hydrogenation of benzene (81a).

Catalyst	$V \times 10^6$ (mol g^{-1} s^{-1})	Dispersion (%)
Ru/HY	3.2	56
Ru/MCM-41	4.4	62
RU/Al-MCM-41	3.5	46
Ru/SiO_2	3.1	58

Ni-MCM-41 showed better activity both in hydrogenation and in hydrogenolysis reactions. It was also observed that the optimum temperature range of use for Ni-containing mesoporous catalysts is below 573 K, and beyond this temperature, the Ni particles tend to aggregate and, thus, cause a decrease in catalytic activity.

The behavior of different catalysts containing 1 wt.% of noble-metal ions (Rh^{3+}, Ru^{3+}, Pd^{2+}, Pt^{2+}, and Ir^{3+}) inside a mesoporous MCM-41 framework in the hydrogenation of naphthalene was investigated (83). Only the Rh- and Pd-containing catalysts were active in the tests performed at atmospheric pressure. The order of reactivity of the various metal ions was: Pt > Rh > Pd > Ru > Ir. Pt showed the best catalytic activity, with good yield values in fully hydrogenated and HMW ring-opening products, while Rh exhibited a similar ring-opening activity together with a significantly lower hydrogenation activity, mainly forming the partially hydrogenated tetralin. Finally, Pd had a very poor activity, giving rise almost exclusively to tetralin. The authors, Albertzzi et al. (83) failed to give any satisfactory explanation on the order of reactivity of the various supported noble metal catalysts. Also it is still unclear to what extent the acid sites are responsible in the formation of different types of products in the hydrogenation of naphthalene. The observation is not further supported by relevant literature.

It is clear that the mesoporous zeolite catalysts are capable of converting bulky aromatic hydrocarbons. The activity of the mesoporous zeolites can be significantly different, depending on the synthesis conditions, especially with respect to the source of aluminium.

Hydrogenation of naphthalene and phenanthrene was carried out by Reddy and Song (50) over Pt supported Al-MCM-41. The catalyst was found to be active and gave 100% conversion in the hydrogenation of naphthalene. However, the type of Al-MCM-41 support was found to have profound effect in the selectivity of the products as given in the table below.

Source	Selectivity of the products
(i) Pseudo boehmite	Large amount of intermediate product tetralin
(ii) Aluminium isopropoxide and aluminium sulphate	The conversion of tetralin to decalin was almost complete

- The conversion of tetralin to decalin was low for entry (i), due to its poor acidity, which in turn results from the poor incorporation of Al in the framework.

In the case of hydrogenation of phenanthrene, the main products were di-, tetra-, and octa-hydrophenanthrenes. The authors (50) suggested the occurrence of isomerization of sym-octa-hydrophenanthrene to sym-octa-hydroanthracene

along with hydrogenation. The catalytic reduction of aromatic rings requires higher temperatures, 373–473 K than do these for ordinary double bonds.

3. Tetralin

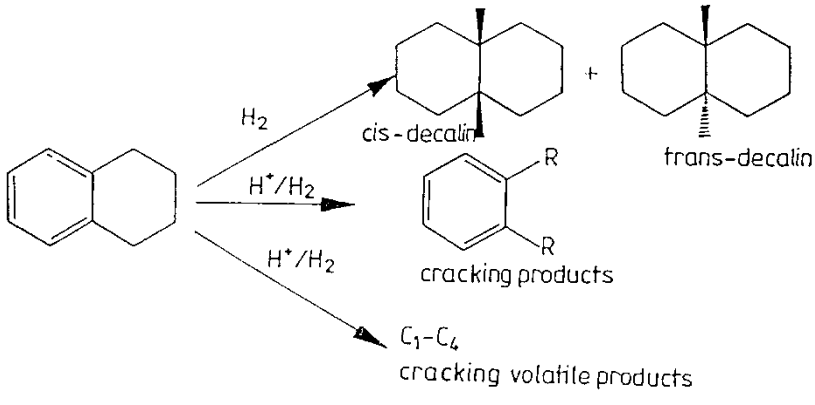
Hydrogenation of tetralin over catalysts based on Zr doped MCM-41, with different Ni loadings was investigated by Vaccari and coworkers (84). On analysis the reaction products gave more than 50 different compounds (Scheme 10), cis- and trans-decalins were the main compounds among them.

- The catalytic support was found to be appropriate for attaining a high loading of metallic Ni with a suitable degree of dispersion.

On supported noble metal catalysts, aromatics hydrogenation can be performed at relatively low temperature, i.e., far from the thermodynamic equilibrium. But the main drawback of these catalysts is that they can be easily poisoned by small amounts of organic sulfur and nitrogen compounds present in the feed.

Well-dispersed Ru catalysts supported on pure-silica MCM-41 and Al-MCM-41 samples were tested in the tetralin hydrogenation in pure H_2 and in the presence of H_2S by Peng Tian et al. (81b). The results were compared with those of Ru/HY and Ru/SiO_2.

- The mesoporous materials–supported catalysts were found to be much less active than the zeolite-supported catalysts in the hydrogenation of tetralin in the presence of H_2S. It is proposed that the lower activity of the former is either due to their milder acidity or to the localization of the Ru nanoparticles on alumina islands.



Scheme 10: Reaction network for catalytic hydrogenation of tetralin (84).

- It has also been observed that the poisoning of the metallic sites is similar on both acidic and nonacidic mesoporous materials, which indicate that either the acidity of these materials is too low to bring about sulfur resistance of the metallic phase or the Ru nanoparticles are not located in the vicinity of these acidic sites.

4. Nitro and Carbonyl Compounds

The reduction of nitro and carbonyl compounds is important in organic synthesis. It has been observed that controlling the reduction rate is quite difficult with highly active homogeneous catalysts (85).

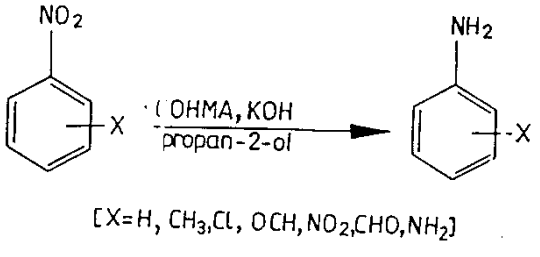
Recently Selvam et al. (86) reported an efficient and selective method for the catalytic transfer hydrogenation (CTH) of nitro and carbonyl compounds over CoHMA catalysts using KOH and propan-2-ol. (Schemes 11 and 12). The results are given in Table 8. The catalyst was found to be highly efficient in reducing a large number of substrates. However, the activity was significantly influenced by the nature/position of the substituents on the aromatic ring.

It was believed that the substrate might be adsorbed on to the acidic sites of CoHMA and propan-2-ol on the basic sites. Subsequently, hydrogen may be transferred from the alcohol to adjacent substrate molecules.

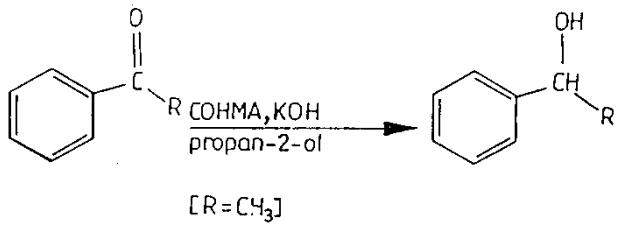
B. Hydrogenation of Olefins

The hydrogenation of alkenes is known to be a structure-insensitive reaction and the rate of the reaction is then representative of the metallic surface area exposed by the solid and accessibility of the reactant.

Choudary et al. (87) compared the catalytic activity of mesoporous Pd/Si-K10 and Pd/MCM-41 with a microporous Pd/Y zeolite for the hydrogenation of alkenes, alkynes, and semihydrogenation of alkynes. Electron micrographs showed a better dispersion of Pd on MCM-41. Also, the amount of Pd is more accessible on MCM-41 than on Si-K10 or the NaY zeolite. The higher activity



Scheme 11: Catalytic transfer hydrogenation of nitro-compounds (86).



Scheme 12: Catalytic transfer hydrogenation of carbonyl compounds (86).

displayed by Pd/MCM-41 in the reactions might be due to the broader porosity and better dispersion of Pd.

- Thus Pd/MCM-41 shows superior activity over Pd/Si-K10, Pd/Y zeolite, polymer-anchored (88) and clay-anchored catalysts (89, 90) in the hydrogenation of alkenes and alkynes under identical conditions.

The mechanism of the heterogeneous catalytic hydrogenation of double bonds is not thoroughly understood. According to the currently accepted mechanism, the olefin is adsorbed on to the surface of the metal with its less hindered side attached to the catalyst surface. The fact that addition of hydrogen is generally also from the less hindered side indicates that the hydrogen, too, is probably adsorbed on the catalyst surface before it reacts with the olefin.

1. Hydrogenation of Nitriles

Few review articles are available in open literature regarding hydrogenation of nitriles to amines (91). Transition metals including Co, Ni, Ru, Cu, Rh, Pd, and Pt are known to catalyze this reaction.

The kind of metals used has a profound influence on the product selectivity.

(a) Pd and Pt—preferentially form tertiary amines

(b) Cu and Rh—selective towards secondary amines

(c) Co, Ni and Ru—high selectivity for primary amines

Ni supported on zirconium-doped mesoporous silica catalysts, with varying nickel loadings (4–26 wt.%), was evaluated by Lopez and co-workers (92) and these catalysts were found to show very high catalytic activity in the gas phase hydrogenation of acetonitrile. The detected reaction products were ethylamine, diethylamine, triethylamine, N-ethyl-ethylimine, methane, and traces of ethane. More condensation products appeared for the catalysts with low Ni loading (i.e., more acidic catalyst).

Table 8: Hydrogenation of nitro- and carbonyl compounds (from Ref. (86)).

Entry	Substrate	Product	Reaction time (h)	Yield% 1st run	Yield% 6th run
1	Nitrobenzene	Aniline	2	91	91
2	2-Chloro nitrobenzene	2-Chloroaniline	1.5	83	83
3	3-Chloro nitrobenzene	3-Chloroaniline	1.5	88	88
4	4-Chloro nitrobenzene	4-Chloroaniline	1.5	93	93
5	4-Bromonitrobenzene	4-Bromoaniline	1.5	90	89
6	4-Fluoronitrobenzene	4-Fluoroaniline	1.5	84	84
7	2-Nitrotoluene	2-Toludine	2	67	66
8	3-Nitrotoluene	3-Toludine	2	81	81
9	4-nitrotoluene	4-Toludine	2	83	80
10	4-Nitroanisole	4-Anisidine	5	88	87
11	2-Nitroaniline	1,2-Diaminobenzene	3	92	90
12	3-Nitroaniline	1,3-Diaminobenzene	3	86	86
13	Benzaldehyde	Benzylalcohol	1.5	96	96
14	Acetophenone	1-Phenylalcohol	3	96	95
15	3-Dinitrobenzene	3-Nitroaniline	3	71	69
		1,3-Diaminobenzene		16	17
16	2,4-Dinitrochlorobenzene	4-Chloro-3-Nitroaniline	3	81	80
17	2,4-Dinitrofluorobenzene	4-Fluoro-3-Nitroaniline	3	79	80
18	2,4-Dinitrotoluene	4-Methyl-3-Nitroaniline	3	78	78
19	2-Nitrobenzaldehyde	2-Aminobenzaldehyde	4	81	80
20	3-Nitrobenzaldehyde	3-Aminobenzaldehyde	4	90	90
21	4-Chloro3-Nitrobenzaldehyde	4-Chloro-3-Aminobenzaldehyde	4	88	88
22	4-Nitroacetophenone	4-Aminoacetophenone	4	85	85
23	Benzophenone	Benzhydrol	5	90	90
24	β-Hydroxy-α-naphthaldehyde	β-Hydroxy-α-naphthyl-alcohol	5	78	78

- Further experimental work is necessary to shed more light on the mechanism operating in the gas-phase hydrogenation of acetonitrile with this family of catalysts.

Hydrogenation of large molecules such as stearonitrile (n-$C_{17}H_{35}CN$) under high H_2 pressure in the liquid phase was carried out by Huang and Sachtler (93) over Ru-supported microporous and mesoporous sulfated zirconia. Ru/mesoSZ showed higher activity in the reaction, which can be, explained by the difference in diffusion rates between microporous and mesoporous supports. Both catalysts produce predominantly primary amines and show good activity. Unlike the case of mesoporous catalyst, the reaction seems to be partially diffusion controlled for the microporous catalyst.

- These results show the superiority of the mesoporous over the microporous support, which conforms to the expectation that for large molecules, wide pores improve accessibility of sites and facilitate diffusion of reactants and products. This contradicts the observation by Volf et al. (91b), that the catalyst support has little effect on hydrogenation activity and selectivity.

C. CO Hydrogenation (Fischer–Tropsch synthesis)

Cobalt catalysts are excellent ones to obtain high yield of long chain hydrocarbons in the Fischer–Tropsch synthesis (FTS) (94–96). The activity of Co catalyst is proportional to the number of exposed Co atoms (97). A requirement for a highly active Co catalyst is, therefore, a high dispersion of Co metal. This is usually done by deposition of a Co salt on high surface support, such as silica and alumina with subsequent reduction.

The chemical nature of the support, its texture, and surface acidity have influence on Co dispersion, properties of reduction as well as the interaction between metal and support. The nonuniform pore-size distribution of supports, such as Al_2O_3, SiO_2, TiO_2, and ZrO_2 might lead to a wide distribution of hydrocarbon products.

- In several cases use of mesoporous materials as metal catalyst supports resulted in significant improvements when compared to conventional commercial catalysts due to superior dispersion of the active metals. (98–100).
- The catalytic feature of the mesoporous materials used as support is that they facilitate selective formation of long chain hydrocarbons (wax), due to the uniform mesopore characteristics.

The promotion of supported Co catalyst with noble metals; transition metal oxides, and rare earth oxides have been reviewed by Adasina (101).

The effects of different supports like MCM-41 and modified hexagonal mesoporous silica (HMS), on the activity and selectivity for FTS over supported Co catalysts was investigated by Yin et al. (102). Higher CO conversion, C_{5+} selectivity, and wax yield are reported over Co/HMS catalyst than they are over Co/MCM catalyst. This is due to the fact that HMS mesoporous support possesses shorter channel and larger textural mesoporosity than MCM-41 support (103). Also, addition of a small amount of Mn (<2 wt.%) as promoter to Co/HMS catalyst helped to increase the yield of wax, which might be ascribed to the fact that MnO partially segregates the active Co sites and prevents the formation of methane at a high reaction temperature of 523 K.

The extent of reduction of the bimetallic CoRu catalysts is usually found to be higher than it is in the corresponding monometallic Co catalysts due to H_2 spillover from the activation of H_2 on the more easily reduced Ru to cobalt oxide (97). Iglesia (94) reported that the addition of Ru to Co catalysts enhances,

1) catalytic rate,
2) C_{5+} selectivity,
3) reducibility of Co oxide, and
4) stability of Co catalysts and it decreases the carbon deposition rates during FTS (97).

A study of CO hydrogenation on MCM-41 and SiO_2 supported Ru-promoted Co catalysts was carried out by Goodwin et al. (104). The catalysts with 14 wt.% Co and 0.5 wt.% Ru showed relatively high activities and properties closer to those of commercial type catalysts.

- Thus, by providing high activity and unrestricted diffusion of FT reactants and products, bimetallic Co supported MCM-41 can be potentially used for FTS as well as other catalytic applications.
- But one should give more importance to modify the MCM-41 supports to increase its hydrothermal stability since normally these reactions take place at temperatures >473 K.

Iwasaki et al. (105) synthesized a uniform silicate crystalline mesoporous material (SCMM) and used it as support of 5 wt.% Co catalysts for FTS. The conversion of CO was higher than was that on silica gel. The pore size and surface charge characteristics in SCMM significantly affected the selectivity of hydrocarbons.

D. Enantioselective Hydrogenations

The need to develop effective catalysts for enantioselective synthesis is becoming important. The enantioselective catalyst systems developed mostly involve expensive chiral ligands and, in many cases, expensive metals such as Pd and Rh. Covalent attachment of chiral catalysts to heterogeneous solid supports such as silica and zeolites (106), layered clays (107), or polymers (108) has been shown to give highly effective enantioselective hydrogenation catalysts.

Incorporation of homogeneous organometallic catalysts like Rh-BPPM and Ru-BINAP into hexagonal mesoporous silica's (HMS) and their use for enantioselective hydrogenation of α-acetamidocinnamate, α-acetamidocinnamic acid (Scheme 13), and itaconic acid (Scheme 14), in aqueous media were described by Anderson and coworkers (109). In all the three reactions, the activity of the catalysts was in the order Rh-BPPM > Ru-BINAP. More forcing conditions were required to achieve acceptable conversions for Ru-BINAP. No loss of activity and enantioselectivity was observed for these catalysts even after recovery.

(a) Heterogeneous hydrogenation of sodium α-acetamidocinnamate in water

Catalyst	Conv (%)	Enantiomeric excess % (R)
Rh-(S,S)-BPPM	100	49
Ru-(R)-BINAP	81	48

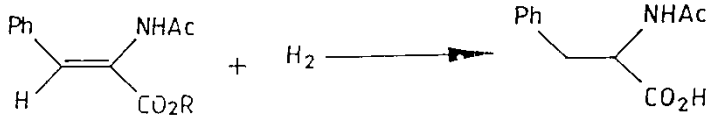
(b) Heterogeneous hydrogenation of sodium K-acetamidocinnamate in water

Catalyst	Conv (%)	Enantiomeric excess % (R)
Rh-(S,S)-BPPM	100	49

Reactions carried out in 1:1 MeOH-H_2O (v/v) at 500°C for 20 h under 0.2 Mpa H_2 pressure.

In another paper from the same group, (110), the authors reported that the hydrogenation catalysts obtained by incorporating Ru or Rh species into mesoporous silicas that were modified by external surface deactivation and/or internal derivatization show no improvement over catalysts prepared using the non-modified mesoporous silicas.

Raja and Thomas (76), recently studied the selective hydrogenation of various cyclic polyenes like 1-hexene, 1-dodecene, naphthalene, 1,5-cyclooctadiene, I, 5,9-cyclodecatriene, and 2,5-norboradiene under solvent-free conditions over anchored bimetallic nanoparticle catalysts (Ru_6 and Pd clusters encapsulated in MCM-41), and they displayed high activity even at low temperature. These catalysts are found to be superior in performance to their monometallic analoges and, more importantly, yield a higher selectivity for hydrogenated products, which suggests a possible synergism between the two bimetallic nanoparticles.



Scheme 13: Enantioselective hydrogenation of sodium K-acetamidocinnamate (109).

The same group (76) reported the enantioselective hydrogenation of E-α-phenyl cinnamic acid and ethyl nicotinate using a constrained chiral catalyst, derived from 1,1′-bisdiphenylphosphinoferrocene and anchored within MCM-41, the outer wall of which were previously deactivated via treatment with Ph_2SiCl_2. The results are given in Table 9. It was found that MCM-41 anchored species catalyzed the reaction with higher enantiomeric excess than did the homogeneous catalyst and resulted in a racemic product.

- The previously available procedure (111) for producing the biologically relevant nipecotinate entailed a two-step process with the use of a chiral modifier, such as dihydrocinchonidine.

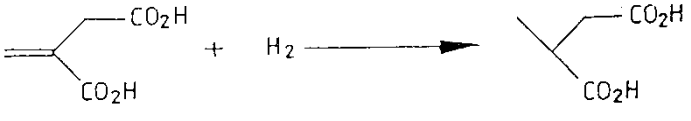
Finally, the selective hydrogenation of polyenes such as, 1,5,9-cyclododecatriene over bimetallic catalysts like Ru_6Sn-anchored MCM-41 was reported from the same group (112), which emphasizes the solvent free routes for such processes.

- These results show the considerable potential that these types of catalysts offer, and how, by careful design of an active center, a heterogeneous catalyst may be engineered. Their performance is far superior to their free, homogeneous analogue.

E. Hydrogenation of Other Molecules

1. *Reduction of Crotonaldehyde to Crotyl Alcohol*

Burch and coworkers (113) showed that tin-oxygen species modified mesoporous silicas, made by chemical reaction of $SnEt_4$ vapor with surface silanol groups (chemical vapor deposition method) of the support, displayed a substantially higher activity than bulk tin oxide in the selective reduction of



Scheme 14: Enantioselective hydrogenation of itaconic acid (109).

Table 9: Enantioselective hydrogenation of E-α-phenyl cinnamic acid and ethyl nicotinate (76).

Dppf-ferrocenyl-diamine-Pd-catalyst	Substrate	Conv. (mol%)	Pdt. Distribution		Enantiomeric excess (%)
			A	B	
Homogeneous	E-α-Phenyl cinnamic acid	23.6	83.5	16.8	—
Tethered silica	E-α-Phenyl cinnamic acid	19.8	44.1	55.3	36.1
MCM-41 confined	E-α-Phenyl cinnamic acid	62.0	100	—	90.7
Homogeneous	Ethyl nicotinate	15.9	27.3	72.5	—
Tethered silica	Ethyl nicotinate	12.6	16.9	83	2
MCM-41 confined	Ethyl nicotinate	35.5	5.2	94.5	17

For E-α-phenyl cinnamic acid, A = 1,2-diphenyl propionic acid, B = 2,2/3,3-diphenyl propionic acid. For ethyl nicotinate, A = 1,4,5,6-tetrahydronocotinate, B = ethyl nipecotinate.

crotonaldehyde to crotyl alcohol using propan-2-ol as the hydrogen transfer agent. Improved dispersion of the reactive tin-oxygen species over layers inside the MCM channels, which yield more active sites per gram of tin are responsible for the excellent catalytic activity.

2. Hydrogenation of Prostaglandin Intermediates

Ru-MCM-41 catalysts prepared by deposition of Ru from different precursors (ruthenium acetylacetonate, ruthenium chloride, and ruthenium hexamine chloride) were investigated by Parvulevscu et al. (114) in the diastereoselective hydrogenation of class F prostaglandin intermediates. The measurements indicated that Ru is homogeneously distributed on the surface of MCM-41 and that using the hexamine chloride complex allows a better penetration of Ru inside the mesoporous tubes than do the other two precursors.

- Hydrogenation of prostaglandin F intermediate on Ru-MCM-41 catalysts has been found to occur diastereoselectively even in the absence of chiral modifiers.

F. Summary

1) The high surface area of the ordered mesopores together with the presence of groups able to be functionalized have been of great use to support metal

oxides and organometallic compounds, achieving high dispersion of the active phase in the case of mesoporous solids.

2) The relative ease with which synthesis conditions can be modified to engineer pore sizes and mesoporous architectures could be used to prepare asymmetric catalysts for the stereo-selective generation of chiral products with the desired purity in the enatioselective hydrogenation of various substrates using mesoporous catalysts.

3) The stability and reactivity of these types of catalysts, however, still deserve efforts to allow industrial application of such materials.

IV. OXIDATION OVER MESOPOROUS MATERIALS

One of the foremost challenges currently facing the chemical industry is the need for alternative production technologies that are cleaner, safer, and environmentally friendly. Processes should be efficient both in terms of economy and energy consumption. Catalytic oxidation of hydrocarbons in general is employed in the manufacture of fine chemicals.

The selective catalytic oxidation of organic compounds using environmentally friendly and cheap oxidants, such as molecular oxygen and aqueous H_2O_2, and a heterogeneous, easily recyclable catalyst is a challenging goal of the fine chemical industry (115–119).

Site isolation of discrete redox metal centers in inorganic matrices can afford oxidation catalysts with unique activities and selectivities by circumventing the oligomerization of the active monomeric species. One way of designing stable, solid catalysts with unique activities is through incorporation of redox metal ions or complexes into the framework or cavities of these molecular sieves.

As already pointed out by several researchers (120–123), the use of mesoporous materials is recommended highly if one oxidizes organic compounds of large molecular sizes with a bulky oxidant such as ter-butyl hydroperoxide (TBHP).

In this part of the review, we tried to point out the pros and cons of using mesoporous materials as oxidation catalysts. The available literature data are summarized in Table 10.

A. Aromatic Hydrocarbons

Saturated hydrocarbons are among the most abundant of all naturally occurring organic molecules and they are the most difficult to oxyfunctionalize at lower temperatures in a controlled manner.

Owing to high surface area and pore volume, it is possible to obtain highly dispersed and isolated active sites in the silica framework of MCM-41 molecular sieves. Transition metals such as Ti, V, Mn, Fe, Co, Cr, and Mo were

Table 10: Oxidation of substrates over mesoporous catalysts.

Sl. No.	Substrate	Catalyst	Reference
A. Aromatic substrates			
1	Benzene	Cu-MCM-41	(155)
2	″	Cu-MCM-41	(133)
3	″	V-MCM-41	(136)
4	″	(Fe-, Co-, Ni-) MCM-41	(138)
5	Toluene	Cr-MCM-48	(140)
Phenol and substituted phenols			
6	Phenol	Cu-MCM-41	(141)
7	′	Fe-MCM-48	(142)
8	2,6-di-ter-Butylphenol	Ti-MMS	(143)
9	Trimethyl phenol	Cu-MCM-41	(156)
10	″	″	(155)
11	″	Ti-MMM	(157)
12	″	SBA-15	(159)
13	Naphthol	(Ti-, Zr-) MCM-41	(160)
14	″	(Ti-, V-) MCM-41	(204a)
15	Anthracene	Modified MCM-41	(163)
Alkylaromatics			
16	Alkylaromatics	Cr-MCM-41	(168)
17	Alkylarenes	″	(167)
18	Styrene	Cr-MCM-48	(180)
19	″	Fe-MCM-41	(181)
20	″	(Fe-, Co-, Ni-) MCM-41	(138)
21	″	Mn-MCM-41	(179)
22	Stilbene	Modified MCM-41	(163)
23	″	Mn-MCM-41	(176)
24	″	Mn-MCM-41	(179)
B. Hydrocarbons			
25	Methane	Mo-SBA-1	(215)
26	″	Vox/MCM-41	(214)
27	Propane	V-MCM-41, V-MCM-48	(221)
28	Octane	Ti-MMM-1	(216)
29	Isobutane	MCM-41	(222)
30	Cyclohexane	(Fe-, Cu-) MCM-41	(129)
31	″	Cr-MCM-41	(218)
32	″	Ti-MMM-1	(216)
Alkenes			
33	Propene	Au/Ti-MCM-48	(231)
34	″	()/HMS	(224)
35	″	Au/Ti-MCM-48	(232)
36	Olefines	Mn-salen MCM-41	(236)
37	Alkenes and alkanes	Modified Ti-MCM-41 and Ti-MCM-48	(255a)
38	Alkene + Thioether	Ti-, V-MMM	(242)
39	″	Ti-MMM	(243)
40	Trichloroethylene	Cr-MCM-48	(233)
41	Cyclohexene	Cr-MCM-41, Cr-MCM-48	(253)
42	″	Ti-MMS	(143)
43	″	Ti, V-MCM-41	(204a)

(*continued*)

Table 10: Continued.

Sl. No.	Substrate	Catalyst	Reference
44	″	Mn-Porphyrin-HMS	(252)
45	″	Cr-MCM-41	(167)
C. Alcohols			
46	Alcohol	Cu-, Zn-MCm-41	(194)
47	″	TEMPO-MCM-41	(187)
48	Methanol and ethanol	CuCl/MCM-41	(204)
49	α-Eicosanol	Ti-MCM-41	(196)
D. Oxides and Sulphides			
50	Sulphide	Ti-MCM-41	(259a)
51	″	M-MCM-41	(259b)
52	N_2O	Fe-MCM-41	(263)
E. Others			
53	D-glucose	Ti-MCM-41	(266)
54	Norbornylene	Ti-, Zr-MCM-41	(160)

introduced in MCM-41 molecular sieves by direct synthesis (124–128), impregnation (125, 127), or complexation (Fe, Cu, Mn) on organofunctionalized Si-MCM-41 (129).

Recently, serious effort has been devoted to studying the catalytic properties of these so-called redox molecular sieves in the liquid-phase oxidation of organic compounds (129, 130).

1. Benzene

Phenol is an important compound for industry and pharmaceuticals. Although the direct oxidation step of benzene to phenol is the most economical route, until now only the indirect manufacturing processes have been operated. The reason resides in the fact that the oxidation capability of phenol is higher than that of benzene and the selectivity of one-step oxidation of benzene into phenol is generally not high.

- It is not easy to get the relatively higher conversion of benzene oxidation due to the difficulty of overcoming its resonance energy.

The hydroxylation of aromatic hydrocarbons to phenols and phenol derivatives with H_2O_2 was reported to proceed readily over transition metals incorporated into microporous zeolites (131). But in most of the cases, these catalysts generated some deep oxidation side products such as p-benzoquinone and hydroquinone (132).

Tsuruya et al. (133) compared the catalytic activity of Cu-supported MCM-41 with that of Cu catalysts supported on other oxides in the oxidation of benzene to phenol. Both molecular oxygen as an oxidant and ascorbic acid as

a reductant were found to be necessary for phenol formation using the Cu-MCM-41 catalyst. Selective formation of phenol along with accumulation of H_2O_2 was observed over Cu-supported MCM-41. Similar observation of in situ generation of H_2O_2 was reported earlier for Pd-containing catalysts (134, 135) in the hydroxylation of benzene, where Pd was used for activating the H_2 molecule to produce H_2O_2.

The V-MCM-41 and V-MCM-48 showed higher catalytic activity than did microporous materials such as VS-1 and V-BEA (136) in benzene hydroxylation using 30% H_2O_2 as oxidant. Under the higher temperature and higher acidic conditions, enhancement in catalytic activity was observed. Decrease in conversion due to the decomposition of H_2O_2 was reported at 353 K. Beside high surface area and large pore size, V-MCM-41 was found to possess more surface vanadium species according to UV-Vis DRS, which seems to be responsible for the higher activity of this material. The same group reported the oxidation of benzene over a bicatalytic system with Pd-metal catalysts (137).

Parvulescu and Su (138) studied the liquid phase oxidation of benzene over Fe-MCM-41, Co-MCM-41, and Ni-MCM-41 catalysts using H_2O_2 as the oxidant. The activity and efficiency of H_2O_2 increase with metal content and depend on the reaction parameters such as temperature, molar ratio of the reactants and the solvent, and the nature of the reactor. Co-MCM-41 gave the highest conversion, and leaching of metal ions was observed in the case of Fe-MCM-41.

2. *Toluene*

Partial oxidation of aromatic substrate gives rise to a variety of products with oxidation taking place in the side chain as well as in the ring positions. Oxidation of toluene over metal-substituted mesoporous solids results in both side chain oxidation to yield aldehyde and acid as well as undergoing ring hydroxylation to give cresols depending on the nature of the oxidizing agent, i.e., either 70% TBHP or 30% H_2O_2.

Recently, heteroelements-incorporated mesoporous-aluminophosphate materials were reported to possess excellent catalytic activity (139). Vapor phase oxidation of toluene over mesoporous Cr-$AlPO_4$ with molecular oxygen as oxidant was carried out by Subrahmanyam et al. (140), and the activity was compared with that of Cr-MCM-48. On the surface of the mesoporous Cr-$AlPO_4$, both oxidation and dealkylation reactions take place simultaneously, leading to benzaldehyde and benzene as main products along with CO_2 and CO. Whereas the redox nature of Cr-MCM-48 governs the oxidation of toluene, giving aldehyde as the main product. The formation of benzene as a result of dealkylation reaction predominates on acid (Al^{3+}) sites, whereas, on redox sites ($Cr^{5+/6+}$) oxidation of toluene is taking place, leading to benzaldehyde (Table 11).

Table 11: Vapor phase oxidation of toluene over Cr-$AlPO_4$ and Cr-MCM-48 (140).

Catalyst	Conversion (%)	Product selectivity (%)		
		Benzaldehyde	Benzene	CO_2 and CO
Cr- $AlPO_4$	1.40	60.4	3.0	36.6
Cr-MCM-48	2.20	44.76	—	55.24

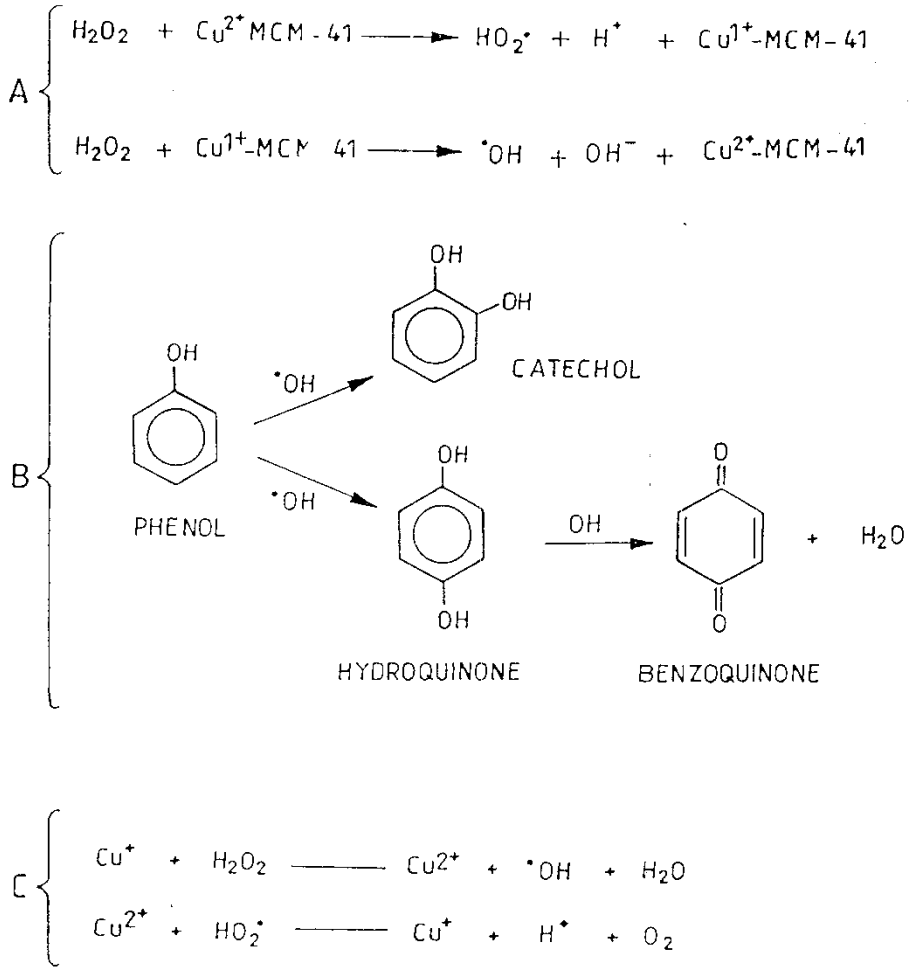
- Mesoporous Cr-$AlPO_4$ exhibits both acidic and redox properties by promoting dealkylation and oxidation in a concerted manner, whereas, under identical conditions, Cr-MCM-48 promotes only oxidation.
- The absence of coupled products indicates that the reaction is taking place in a concerted manner where the adsorption of toluene takes place parallel to the lattice.
- In the case of 30% H_2O_2 as oxidant, all heterogeneous catalysts show selectivity to side chain oxidation leading to aldehyde or acid. Homogeneous catalysts are selective to ring oxidation leading to cresols.

3. Phenol and Substituted Phenols

The strong demand in the chemical industry for phenolic compounds led to the development of improved catalyst-based technologies for partial oxidation reactions. Franco and coworkers (141) studied the oxidation reaction of phenol using H_2O_2, employing Cu-modified (Cu^{2+} acetate and nitrate salts in alcoholic solution over MCM-41) catalysts. Catechol, hydroquinone, and benzoquinone are the major products formed along with very low production of tars.

- In the case of phenol, substitution at both ortho and para positions are possible thermodynamically, while kinetic factors favor ortho substitution. It was observed that the acetate groups impose relatively larger steric constraints on ortho positions than nitrate groups. The mechanism of the reaction is given in Scheme 15.

Li et.al. (142) investigated the potentiality of Fe-MCM-48 in the hydroxylation of phenol using 30% H_2O_2 as the oxidant at 333 K. The results of the reaction of Fe-MCM-48 was found to be superior to that of TS-1 in terms of conversion and selectivity. The framework isolated Fe^{3+} species was found to be active centers in the hydroxylation of phenol.



Scheme 15: Reaction path for the hydroxylation of phenol (141).

3.1. 2,6-di-ter-Butylphenol

Ahn et al. (143) compared the catalytic activity of Ti-MMS (Ti-containing mesoporous molecular sieves with a one-dimensional channel system) prepared in the presence of fluoride ion with that of other Ti-substituted mesoporous materials in the oxidation of 2,4-di-*ter*-butylphenol with H_2O_2 as the oxidant. The Ti-MMS showed catalytic activity close to that of Ti-MCM-41 of the same metal loading, but was less active than were Ti-HMS and Ti-MCM-48. It seems that the presence of titanium in isolated tetrahedral sites is not a prerequisite for 2,6-DTBP oxidation using mesoporous molecular sieves (144).

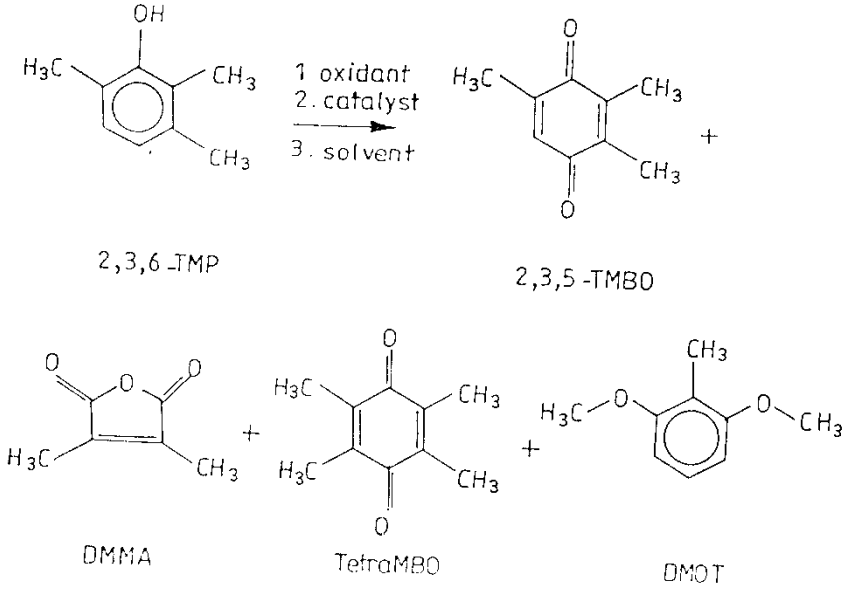
3.2. Trimethylphenol

Quinone derivatives play an important role in biosystems and are useful intermediates of fine organic chemical synthesis. Trimethylbenzoquinone (TMBQ) is a key intermediate in making vitamin E (145). In the literature, various homogeneous catalysts and oxidants were tried in the oxidation of trimethylphenol (TMP) to 2,3,5-trimethyl-1-4-benzoquinone (TMBQ) (146–154).

Cu(II) substituted molecular sieves were found to be efficient catalysts in liquid phase oxidation of aromatic compounds. Tsai et al. (155, 156) studied the oxidation of 2,3,6-TMP to 2,3,5-TMBQ when H_2O_2 was used as oxidant and CH_3CN as solvent at 333 K over Cu, Al-substituted MCM-41 samples. The optimal TMBQ selectivity was observed over MCM-41 concomitantly substituted with Cu(II) and small amounts of Al(III). The main liquid products obtained in the reaction are listed in Scheme 16.

The reaction was found to be extremely sensitive to the oxidant and solvent used (Table 12). A 98% TMP conversion and higher than 85% TMBQ selectivity were obtained in 20 min when acetonitrile or benzaldehyde was the solvent and *tert*-butylhydroperoxide was the oxidant.

- Different from Ti- or V-substituted molecular sieves, oxygen gas could also be an effective oxidant with Cu, Al-MCM-41 catalyst. But in this case, the authors found that benzaldehyde was the only effective solvent and the



Scheme 16: Reaction products in the liquid phase oxidation of trimethyl phenol over CuMCM-41, where DMMA is dimethylmaleic anhydride and DMOT is dimethoxytoluene (155).

Table 12: Effect of solvent and oxidant in TMP oxidation over 2%Cu, 2%AlMCM-41 catalyst (155).

Solvents	Oxidant	Reaction period	Conversion (%)	TMBQ yield (%)	TMBQ selectivity (%)
C_2H_5OH	H_2O_2	20 min	2.0	0	0
CH_3CHO	H_2O_2	20 min	68.0	1.3	1.9
CH_3CN	H_2O_2	20 min	63.7	46.7	73.3
CH_3CN	TBHP	20 min	97.8	83.2	85.1
CH_3CN	O_2	6 h	17.3	0	0
Ph-CHO	H_2O_2	20 min	87.0	68.7	78.9
Ph-CHO	TBHP	20 min	98.0	87.5	89.3
Ph-CHO	O_2	2 h	43.2	22.3	51.6
Ph-CHO	O_2	4 h	71.4	40.9	57.3
Ph-CHO	O_2	6 h	82.4	44.6	54.1

conversion and selectivity were lower than those obtained with other strong oxidants such as H_2O_2 and TBHP.

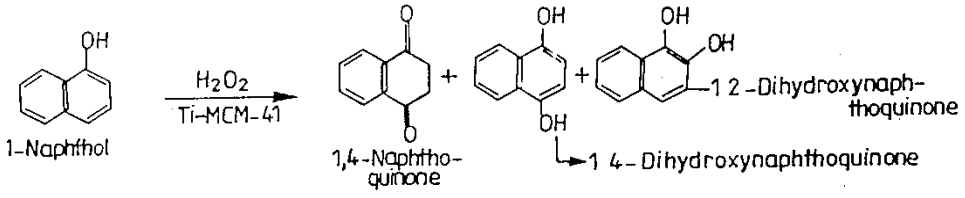
The same reaction was reported over various Ti-containing mesoporous silicate materials with aq. H_2O_2 by Kholdeeva et al. (157). For samples with similar Ti loading, both catalytic activity and TMBQ yield appeared to fall in the order TiO_2-SiO_2 aerogel > Ti-MMM > TiO_2-SiO_2 xerogel and correlate with average mesopore diameter and mesopore volume. It has been shown that the Ti, Si-catalyst-based TMP oxidation process is comparable to the $CuCl_2$-based process (158), in which molecular oxygen is employed as the oxidant.

- Despite the absence of leaching, some loss of catalytic activity was observed after recycling due to the low hydrolytic stability of the structure of these materials.

Recently, Trukhan et al. (159) compared the catalytic properties of Ti-SBA-15 with that of Ti-MMM and TS-1 in the TMP oxidation. The Ti-SBA-15 was found to be stable towards water and H_2O_2. The catalytic activity and the TMBQ yield was in the order Ti-MMM > Ti-SBA-15 > TS-1. The relatively low catalytic activity of Ti-SBA-15 was attributed to the low titanium dispersion and its poor accessibility for reactants due to the thick walls. Unlike in the case of Ti-MMM, Ti-SBA-15 did not show any loss of activity after recycling.

3.3. *1-Naphthol*

Both Ti-MCM-41 and Zr-MCM-41 were found to be active in the hydroxylation of 1-naphthol with H_2O_2 as the oxidant (160). The reaction was highly selective for 1,4-naphthaquinone (100 mol% selectivity with Ti-MCM-41 and



Scheme 17: Oxidation of 1-naphthol (160).

90–95 mol% with Zr-MCM-41). The minor products include 1,4-dihydroxynaphthalene and 1,2-dihydroxynaphthalene (Scheme 17).

Both Ti and Zr samples exhibit similar activities in the oxidation reaction, in agreement with the earlier observation made by Gontier and Tuel (161a) in the case of Ti-MS and Zr-MS catalysts. The Ti samples are easier to reduce than are Zr samples. The ESR studies on reduced samples of Ti- and Zr-MCM-41 reveal the presence of metal ions located inside the pore walls (species I′) and at the surface of the pores (species I″).

The latter are highly reactive towards aerial oxidation and form $M(O_2^-)$ species, an active intermediate invoked in the oxidation reactions involving metallosilicates (Fig. 1).

In a similar paper, Laha and Kumar (161b) discussed the hydroxylation of 1-naphthol to 1,4-naphthoquinone, using both aqueous H_2O_2 and TBHP as oxidants and acetonitrile as solvent over Ti-MCM-41 and V-MCM-41 catalysts. The catalysts showed comparable activities in the presence and absence of promoter.

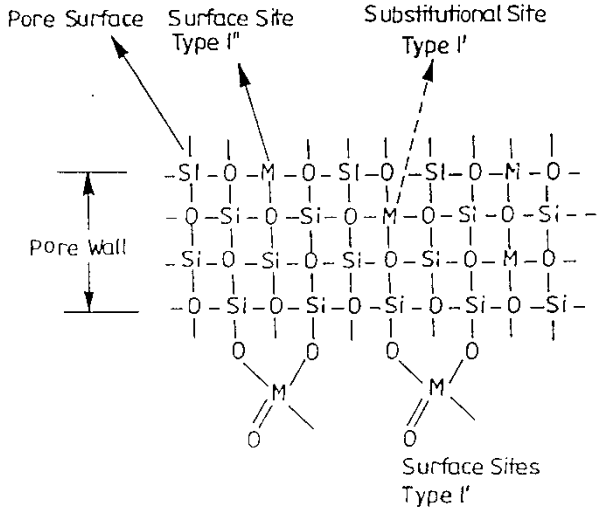


Figure 1: Locations of Ti and Zr ions in (M)-MCM-41 (160).

4. Anthracene

The oxidized product of anthracene, 9,10-anthraquinone, is widely used in the synthesis of dyes and during the large-scale synthesis of H_2O_2 (162). Conventionally this was obtained by the oxidation of anthracene using chromic acid or vapor phase oxidation with air.

The effect of transition metals (Cr, Mn, Co, Cu, Fe, V, Ni, Zn, and Ti) incorporation on MCM-41 catalyst in the liquid-phase oxidation of anthracene in benzene as solvent with *ter*-butyl hydroperoxide (*ter*-BHP) at 353 K was reported by Srinivas et al. (163) (Scheme 18). Cr-MCM-41, which was found to be the best catalyst in the reaction, gives a conversion value of 79.5% and selectivity of 97.9%. The conversion was below 10% when H_2O_2 was used as the oxidant. Higher yields were reported by using solvents having lower dielectric constants, when *ter*-BHP was used as the oxidant.

- In the case of apolar aprotic solvents of lower dielectric constants, the solute-solvent interaction is less. So, in order to reduce the role of the solvent, in the previous reaction, benzene with a low ε value was chosen.

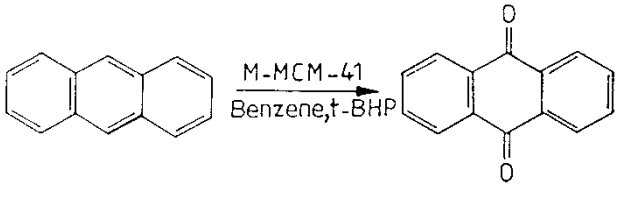
B. Oxidation of Alkylaromatics

1. Alkylarenes

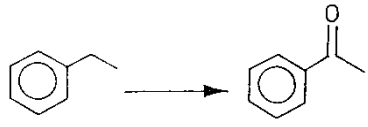
The C-H bond activation at the benzylic position by transition metal complexes under mild conditions is an important transformation in the synthetic organic chemistry. Hexavalent chromium catalysts are extensively used for the transformation of alkylaromatics to aromatic ketones and acids in homogeneous phase (164–166).

Sivasanker et al. (167) reported an efficient catalytic method for benzylic oxidation of alkylarenes to the corresponding carbonyl compounds in good yields using Cr-MCM-41 catalyst and 70% *ter*-butyl hydroperoxide (TBHP) in MeOH as oxidant (Scheme 19). The results are given in Table 13.

- It was been found that a variety of benzylic CH_3 groups are oxidized to acids in moderate yields while the corresponding benzylic CH_2 groups are smoothly oxidized to ketones in excellent yields (entries 6, 7).



Scheme 18: Oxidation of anthracene to 9,10-anthraquinone over M-MCM-41 (163).



Scheme 19: Catalytic oxidation of alkylarenes to carbonyl compounds (167).

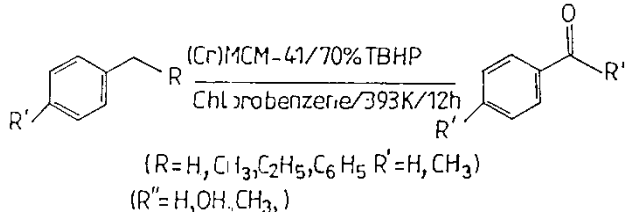
- It is also remarkable that benzene and naphthalene are selectively hydroxylated to give hydroquinone and 1-naphthol respectively, while the corresponding aliphatic analogues are oxidized to a mixture of ketones and alcohols (entries 10, 11).
- From ESR spectral evidence, it appears that the oxochromium(V) species present in the Cr-MCM-41 framework was responsible for the C-H bond activation.

In another paper, Selvam et al. (168) reported a high substrate conversion and product selectivity in the liquid phase catalytic oxidation of alkylaromatics over Cr-MCM-41 in the presence of chlorobenzene and TBHP (Scheme 20).

Unlike earlier reports, both on microporous (169) and mesoporous (170) molecular sieves, where the presence of Cr(V) is always noted, a complete oxidation of trivalent to hexavalent chromium is evidenced in this work, which is found responsible for the higher conversion and selectivity.

Table 13: Catalytic oxidation of alkylarenes with 70% TBHP catalyzed by Cr-MCM-41 (167).

Entry	Substrate	T/h	Conv. (%)	Products (% yield)
1	Toluene	20	50	Benzoic acid (45)
2	o-Xylene	18	36	o-Toluic acid (30) + Phthalic acid (5)
3	p-Xylene	20	35	o-Toluic acid (35) + Terephthalic acid (5)
4	Mesitylene	15	40	3,5-Dimethylbenzoic acid (25) + 5-Methylisophthalic acid (15)
5	2-Methyl naphthalene	20	60	2-Naphthoic acid (55)
6	Ethylbenzene	12	88	Acetophenone (85)
7	Tetralin	12	85	1-Tetralone (80)
8	Benzene	12	8	Hydroquinone (8)
9	Naphthalene	12	6	1-Naphthol (6)
10	Cyclohexane	12	25	Cyclohexanone (15) + Cyclohexanol (10)
11	n-Heptane	12	20	2-Heptanone (10) + 3-Heptanone



Scheme 20: Catalytic oxidation of alkylaromatics over (Cr)MCM-41 (168).

The authors reported the formation of a catalytically active peroxo-complex (b), by the interaction of the hexavalent Cr in the matrix (a) with TBHP (Scheme 21).

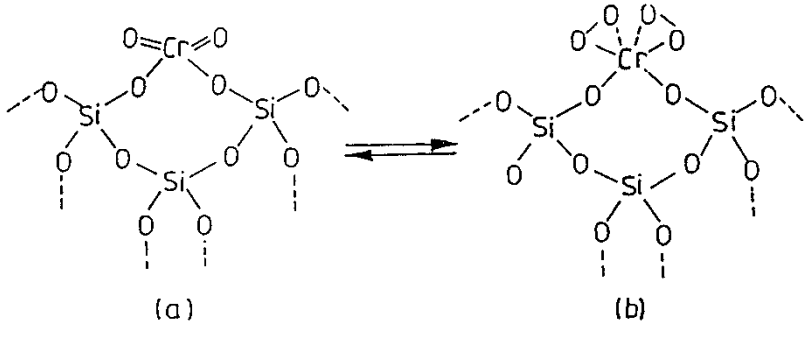
Subsequently, the substrate molecules interact with this peroxo-species to give the final product, which proceeds through two steps, i.e., hydroxylation followed by oxidation at the benzylic position.

2. *Stilbene*

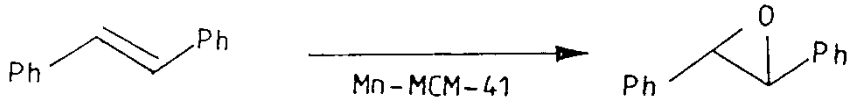
Porous materials, which contain Mn were found to be active for several oxidation reactions (171–175). Iwamoto et al. (176) reported the catalytic ability of Mn/MCM-41 for epoxidation of stilbene and its derivatives with TBHP as oxidant (Scheme 22). The catalysts showed the best performance with TBHP as oxidant at 328 K using a combination of two solvents 9 : 1 (V/V) of MeCN and DMF.

Oxidation of several diaryl-substituted olefins was also carried out over the same catalyst systems (Scheme 23). The results are given in Table 14.

It was found that all the trans- and cis-olefins gave the corresponding trans-oxides as the sole epoxide product. Also, trans isomers were more rapidly oxidized than cis isomers. In general, trans isomers could reach the active sites more easily in pores due to smaller steric hindrance than that of cis isomers. But this result is contradicted by the higher activity of the cis isomers on Mn-salen complex (177) and Ti-MCM-41 (122).



Scheme 21: Formation of catalytically active peroxo complex (168).



Scheme 22: Epoxidation of trans-stilbene on Mn-MCM-41 in MeCN (176).

- In general, two kinds of reaction mechanisms have been suggested for the metal ion catalyzed epoxidation (178). The first is a concerted addition of oxygen, which is widely reported on various ions. The second is a radical epoxidation mechanism.

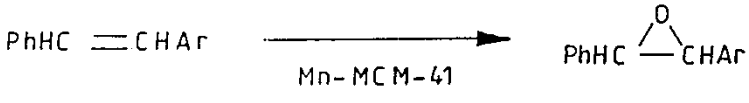
The epoxidation over Ti-MCM-41 (122), cis-stilbene oxide was the sole oxidation product in the cis-stilbene oxidation, which suggests the radical free oxidation mechanism.

On the other hand, the authors suggest that Mn-MCM-41 follows the second route. The active oxygen species on Mn reacts with stilbene to yield an intermediate radical that has a long enough lifetime to rotate around the single C-C bond and isomerize. Thus, the thermodynamically stable trans isomer could become the major product.

Recently Takehira et al. (179) supported the above mechanism in epoxidation of stilbene over Mn-MCM-41 prepared by two different methods, i.e., by (i) direct hydrothermal synthesis (DHT) and by (ii) template ion exchange method (TIE).

- Thus, irrespective of the synthetic methods, it is likely that the epoxidation reactions with TBHP over Mn-MCM-41 proceed through a radical intermediate.

The effect of transition metals (Cr, Co, Cu, Fe, V, Ni, Zn, and Ti) incorporation on MCM-41 catalyst in the liquid-phase oxidation of trans-stilbene in benzene as solvent with ter-butyl hydroperoxide (*ter*-BHP) at 353 K was reported by Srinivas et al. (163). The conversion was increased by about 8–10 fold, on substituting transition metal ions in the MCM-41 matrix. At the same time, these catalysts promote other side reactions including oxidation and C-C bond cleavage.



Scheme 23: Catalytic epoxidation of stilbene derivatives on Mn-MCM-41 (176).

Table 14: Oxidation of diaryl-substituted olefins over Mn-MCM-41 catalyst (176).

	Starting olefin		Yield of oxide (%)		Recovered olefin (%)	
Entry	**Ar**	**Config.**	***Trans***	***Cis***	***Trans***	***Cis***
1	C_6H_5	*trans*	93	0	3	0
2	4-Cl-C_6H_4	*trans*	81	0	5	0
3	4-Me-C_6H_4	*trans*	97	0	2	0
4	4-tBu-C_6H_4	*trans*	70	0	3	0
5	2-$C_{10}H_7$	*trans*	62	0	1	0
6	C_6H_5	*cis*	50	<1	7	39
7	4-Cl-C_6H_4	*cis*	46	0	9	44
8	4-Me-C_6H_4	*cis*	73	0	9	18
9	4-tBu-C_6H_4	*cis*	60	0	5	20
10	2-$C_{10}H_7$	*cis*	82	0	5	13

Reaction Conditions: 0.50 mmol *trans*-stilbene, 0.050 mmol Mn in Mn-MCM-41, 10 Cm^3MeCN + DMF (9 : 1 v/v), 7.0 mmol TBHP (70% in H_2O), 348 K, 48 h under Ar atmosphere.

3. *Styrene*

Sakthivel et al. (180) compared the catalytic activity of (Cr)MCM-41 and (Cr)MCM-48 in the liquid-phase oxidation of styrene to acetophenone with 70% TBHP as oxidant and chlorobenzene as solvent. Higher conversion due to the presence of higher Cr content in the matrix was reported in the case of (Cr)MCM-48. However product selectivity was comparatively lower in the case of (Cr)MCM-48 than (Cr)MCM-41 owing to the formation of some unidentified products.

Fe-MCM-41 synthesized by both direct hydrothermal (DHT) and template ion exchange (TIE) methods were tested in the epoxidation of styrene using 30% H_2O_2 as the oxidant (181). Apart from styrene oxide and benzaldehyde as the major products, styrene glycol and benzoic acid were also formed by the hydrolysis and oxidation of styrene oxide and benzaldehyde, respectively. It was observed that keeping a low concentration of H_2O_2 could raise the selectivity to styrene oxide and the efficiency of H_2O_2 for the reaction.

- The tetrahedrally coordinated and atomically isolated iron sites were responsible for the conversion of styrene. It was also observed that the iron located inside the framework of MCM-41 was stable towards leaching, whereas the iron in the extra framework position leached out to the liquid phase during reaction.

Parvulescu and Su (138) studied the liquid-phase oxidation of styrene to benzaldehyde over Fe-MCM-41, Co-MCM-41, and Ni-MCM-41 catalysts using

H_2O_2 as the oxidant. Among the various catalysts screened, Co-MCM-41 gave the highest conversion.

The effects of solvents and oxidants on the epoxidation of styrene were performed over Mn-MCM-41 by Takehira et.al. (179). A good selectivity to styrene oxide was observed when a mixture of DMF and MeCN were used as the solvent (Table 15).

Also, H_2O_2 and PhIO gave poor conversion and selectivity when compared to TBHP. With 30% H_2O_2 aqueous solution, the rapid decomposition of H_2O_2 occurred and no oxidation product was obtained. Also, the efficiency of TBHP for the conversion of styrene was remarkably higher over the DHT samples than TIE samples.

C. Oxidation of Alcohols

1. Benzyl alcohol

Heterogenization of homogeneous organic catalysts facilitates separation and catalyst recycle. It was shown that the control of both textural and chemical characteristics of these hybrid organic-inorganic materials is of major importance for tuning their catalytic properties (182–186).

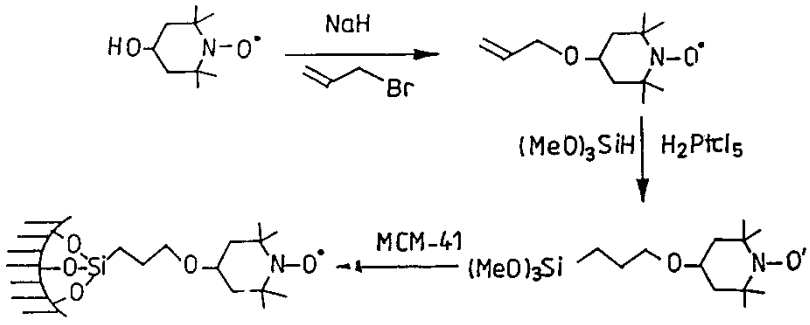
Oxidation of benzyl alcohol over TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy radical) anchored MCM-41 catalysts was reported by Brunel et al. (187) and is found to be active and reusable in the reaction.

- Unlike the case of zeolites, MCM-41 is not crystalline, but it consists of amorphous walls around the channels. The amorphous nature of the pore walls gives rise to a substantial number of silanol groups present at the pore wall offering the possibility of grafting catalytically active groups (188, 189) (Scheme 24).

Table 15: Effect of solvents and oxidants on the epoxidation of styrene (179).

Run	Solvent (mL)	Oxidant (mmol)	Styrene conversion (%)	Styrene oxide (%)	Benzal dehyde (%)	PhAcH
1	DMF (10)	TBHP(10)	3.2	62.5	37.5	0.0
2	DMF MeCN (1 + 9)	TBHP(10)	10.9	70.3	27.2	2.5
3	MeCN (10)	TBHP(10)	13.4	64.6	27.8	6.6
4	MeOH	TBHP(10)	4.8	20.0	40.0	0.0
5	DMF + MeCN (1 + 9)	H_2O_2(9.79)	0.4	0.0	100.0	0.0
6	MeCN (10)	PhIO	3.3	25.7	74.3	0.0

Catalyst: Mn-MCM-4-DHT, T = 333 K, t = 24 h.



Scheme 24: Synthesis of TEMPO-ether-MCM-41 (187).

2. *Methanol and Ethanol*

Catalysts based on Cu and Cu/Zn mixed oxides are of great importance for several industrial scale catalytic processes (190, 191). Because of the difficulty in introducing a divalent cation in the tetravalent silicon framework, only a few reports are available in the literature regarding the synthesis of Cu incorporated mesoporous materials, (127, 192, 193) and the redox properties of such systems have not been completely exploited so far as a catalyst.

Velu et al. (194) reported the selective oxidation of methanol and ethanol to formaldehyde and acetaldehyde (~90mol%) over CuMCM-41 and CuZnMCM-41 catalysts, synthesized at room temperature by the method of direct insertion of metal ions. Cu^{2+} ions were found to adopt a distorted octahedral coordination both in as-synthesized and calcined samples. The Cu^{2+} ions in the catalyst were reduced completely to metallic Cu at 503 K–533 K in the presence of H_2 gas.

- The ease of reducibility of copper in these materials has been found to be an important factor that determines the catalytic activity.

On the other hand, the reducibility of Cu^{2+} was inhibited by the copresence of Zn^{2+}. The presence of Zn^{2+} along with Cu^{2+} decreases the catalytic activity in the partial oxidation of methanol while some promotional effects were observed in the partial oxidation of ethanol.

3. *α-eicosanol*

Utilization of aliphatic primary alcohols as raw materials to produce the corresponding acids is one strategic method; it has not been realized on an industrial scale.

- Recently, the use of molecular sieve materials having active redox sites was found to be an effective and promising catalytic route for the selective oxidation of long chain primary alcohols.

The advantages of Ti-MCM-41 as an epoxidation catalyst for large molecules, which cannot diffuse in the pores of microporous materials, have been verified earlier (195). Kan et al. (196) reported the catalytic oxidation of α-eicosanol to eicosanoic acid over transition metal ions (Cr, Cu) and peroxotungsto-phospho-quaternary ammonium supported Ti-MCM-41 catalyst. It has been shown that temperature has a profound influence on the oxidation activity and the oxidation took place at 403 K and 363 K with O_2 and H_2O_2 as oxidants, respectively. The yield of eicosanoic acid was very low when using H_2O_2 as oxidant. Cr/Ti-MCM-41 showed higher activity than did Cu/Ti-MCM-41. CuO formation, covering the active sites of the catalyst, was reported in the latter case. Supporting peroxotungsto-phospho-quaternary ammonium onto Ti-MCM-41 was found to improve the activity of the catalyst.

4. Oxidative carbonylation of methanol

Dimethyl carbonate (DMC) is an important chemical material in the chemical and motor fuel industries. It can be used as an intermediate to substitute for highly toxic phosgene and dimethyl sulfate in many chemical processes owing to the presence of two methyl groups and one carbonyl group in its molecule. A number of catalysts were tested for the oxidative carbonylation of methanol to DMC (197–203).

$$2CH_3OH + 1/2O_2 + CO \longrightarrow CH_3O - CO - OCH_3 + H_2O$$

The gas phase oxidative carbonylation of methanol with CO and O_2 was carried out at 403 K over CuCl/MCM-41 material by Li et al. (204) and the catalyst showed good activity and selectivity of DMC in the reaction. The Si-O^-Cu^+ was found to be the active catalytic center in the reaction. The catalyst had a 100% selectivity of DMC based on conversion of methanol: the conversion of methanol was around 5–10 wt.%.

- Zeolites, with strong acid sites strongly adsorbs methanol in its cages and catalyze the formation of by-products: dimethyl ether, methyl formate, and dimethoxymethane. But in the case of MCM-41 materials with low strength of acid sites, the by-products formation is observed only at a higher temperatures.

D. Oxidation of Hydrocarbons

1. Methane

Formaldehyde is an important base product of the chemical industry conventionally produced by catalytic oxidation or oxidative dehydrogenation of methanol. Intensive efforts were made to develop a heterogeneous catalytic

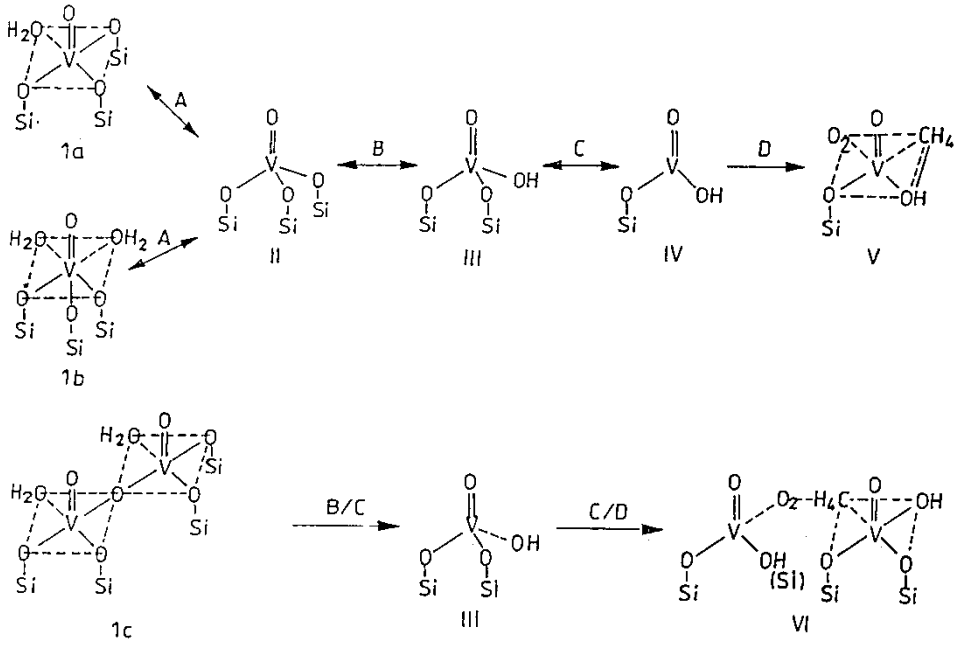
process for direct synthesis of HCHO by partial oxidation of methane (205–211). The highest space-time yield (STY) of HCHO was obtained with vanadium oxide highly dispersed on precipitated silica (212, 213).

The potential of mesoporous siliceous materials like MCM-41 and MCM-48 as supports for the highly dispersed vanadium oxide species in the oxidation of CH_4 to HCHO by air was investigated by Berndt et al. (214). The catalyst was found to be equally active as VOx/SiO_2.

The proposed mechanism of formation of active sites on the catalyst and their interaction with the reactants are given in Scheme 25.

- The high and thermally stable surface areas of MCM-41 and MCM-48 are favorable for achieving a high concentration of isolated vanadium oxide species, which are generally considered as active sites for the partial oxidation of methane.

Numerous efforts to accomplish the partial oxidation of methane at atmospheric pressure encountered the problem of low oxygenates selectivity due to further oxidation to CO and CO_2, under the severe conditions employed for methane conversion.



Scheme 25: Scheme of the formation of active sites in Vox/MCM-41 catalyst and their interaction with O_2 and CH_4 in the oxidation of CH_4 to HCHO (214).

- It is conceivable that the large pores of MCM-type materials with a three-dimensional channel system facilitate the easy discharge of the produced oxygenates to the outside of the pore, preventing the deep oxidation.

Dai et al. (215) reported that the oxidation of methane over Mo-SBA-1 materials synthesized by direct synthesis. These materials exhibit higher activity and selectivity for HCHO formation than does Mo/SBA-1, due to the high dispersion and isolation of Mo in the SBA-1 framework.

2. Octane

Oxidation of octane using H_2O_2 over a mixed phase catalyst, Ti-MMM-1 (microporous-mesoporous material), was reported by Landry et al. (216) and the activity was compared with TS-1 and Ti-MCM-41. Ti-MMM-1 showed a better conversion than the other catalysts. But the explanation given by the authors for the enhanced activity, based on the presence of formation of some microporous crystallites, is not very clear.

3. Cyclohexane

MCM-41 molecular sieves contain a large number of silanol groups at the surface of their channels, which enables its organofunctionalization by the reaction with $SiR(OCH_3)$ compounds where R is a functionalized organic group (249).

Oxidation of cyclohexane using H_2O_2 over organofunctionalized and metal complexed catalysts like $M(NC_3)$ Si-MCM-41, where M = Fe or Cu was investigated by Carvalho et al. (129). The proposed structure of the active site of $Fe(NC_3)$ Si-MCM-41 is given in Fig. 2.

The catalyst showed a good activity, which was attributed to the presence of the Fe atom, which is octahedrally coordinated with four nitrogen ligands in the same plane. However, leaching of metal ion is observed significantly, which was due to the complexation of iron by polar product molecules. In contrast, Cu (NC_3) Si-MCM-41 was found to become deactivated after the first cycle.

Saktivel and Selvam (218) reported (Cr)MCM-41 molecular sieve as an efficient catalyst for cyclohexane oxidation under moderate reaction conditions. H_2O_2 was found to be the suitable oxidant for high substrate conversion and selective formation of cyclohexanol. The mechanism of cyclohexane oxidation over (Cr)MCM-41 is given in Schemes 26 and 27.

The mechanism suggested by the authors is as follows: At first, acetic acid interacts with H_2O_2, leading to the formation of peroxyacetic acid 2a, which further reacts with chromate species 2b to produce the chromium peroxo species 2c, which then interacts with ketone to produce a chelate complex of type 2d followed by reaction with cyclohexane, which leads to the cyclohexyl radical 2e. This in turn reacts with peroxyacetic acid 2a and H_2O_2 through a

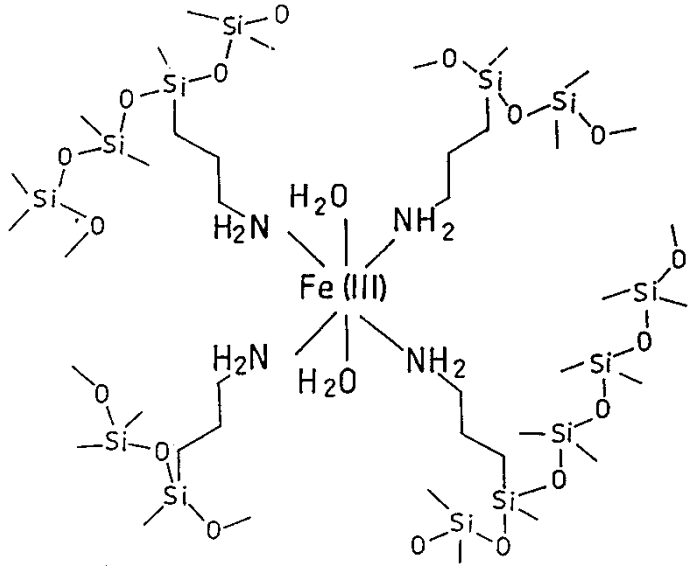


Figure 2: Proposed structure of the active site of $Fe(NC_3)$Si-MCM-41 (129).

chain transfer free radical reaction to produce the desired product cyclohexanol (see Scheme 27).

The use of a stronger oxidizing agent like TBHP results in the formation of cyclohexanone as the major product. Ti-MMM-1 was also tried in the oxidation of cyclohexane using H_2O_2 as oxidant by Landry et al. (216) and found to be more active than TS-1 and Ti-MCM-41.

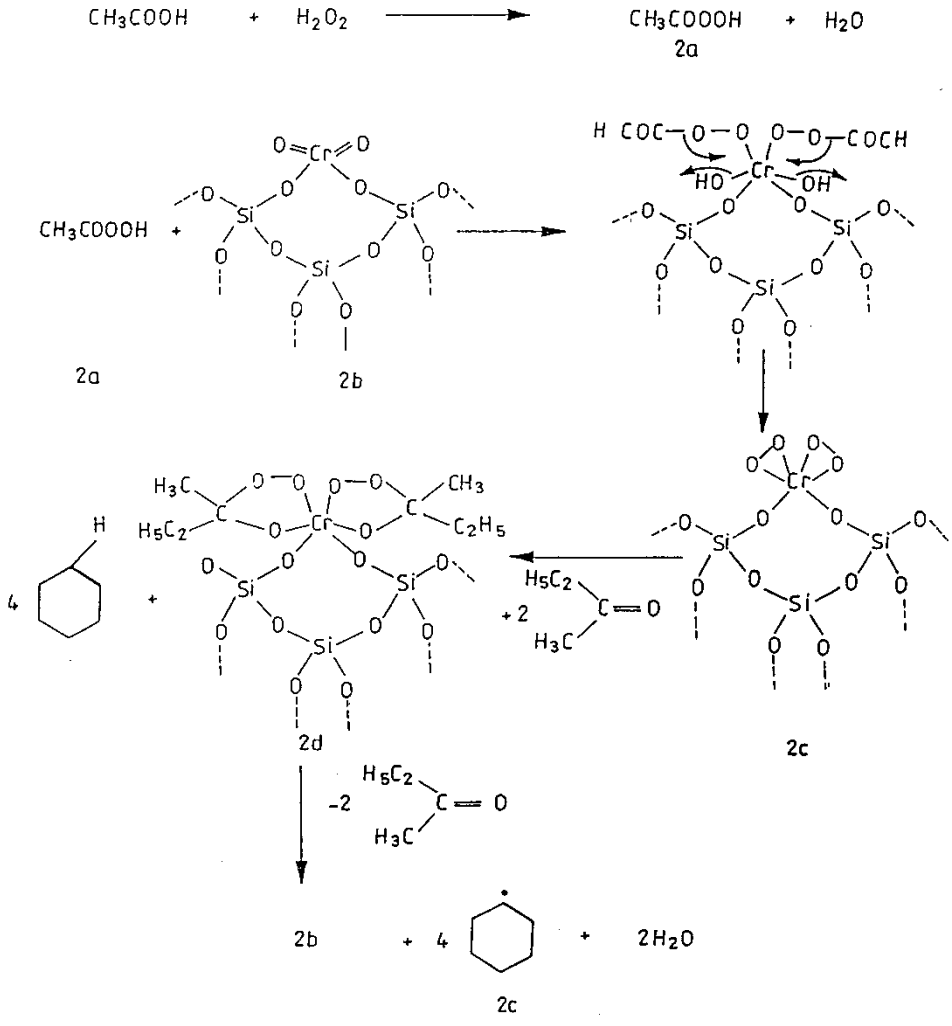
E. Oxidative Dehydrogenation Reactions

1. *Propane*

The oxidative dehydrogenation (ODH) of alkanes is a demanding process, because the olefins formed are more reactive than are the starting substrates. Hence, the knowledge of the possible reaction centers and the local environments of the metal ions in the catalyst are of great importance in designing an active and selective catalyst (251, 252).

V-containing MCM-41 and MCM-48 were used for the selective oxidation of propane in gas phase by Nieto et al. (221) and found that their catalytic behavior strongly depends on the V content and catalyst preparation procedures.

The better selectivity to propylene (68.9%) over these materials was attributed to the better dispersion of isolated V species present in the catalyst. Partially oxygenated products are also observed as a consequence of the presence of polymeric V^{5+} species.

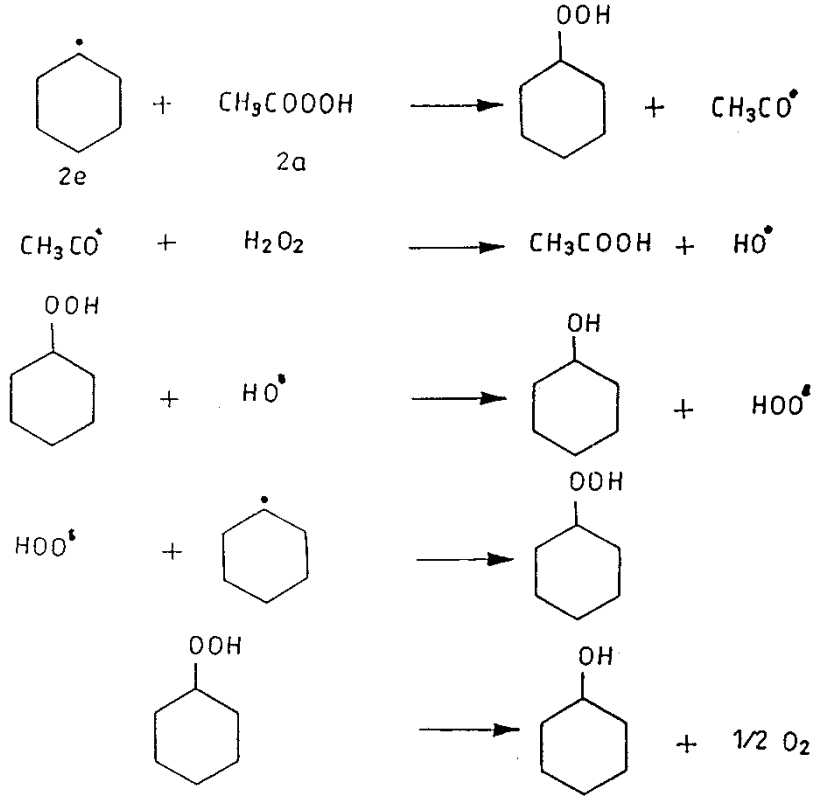


Scheme 26: Possible reaction pathway for the oxidation of cyclohexane over (Cr)MCM-41 catalyst (218).

2. *Isobutane*

Oxidative dehydrogenation of isobutene over [Si,V]-MCM-41 samples with different V content was carried out by Sulikowski et al. (222). The authors identified five different V^{5+} species, three of them belonging to the monodispersed VO_4 tetrahedra chemically bound to the wall of the [Si,V]-MCM-41.

As reported in the case of ODH of propane (221), these active centers were found to be responsible for the high activity and olefin selectivity in the isobutene transformation over [Si,V]-MCM-41.



Scheme 27: Possible reaction pathway for the oxidation of cyclohexane over (Cr)MCM-41 catalyst (218).

F. Oxidation of Alkenes

1. Propylene

Depending upon the reaction conditions and catalysts used, propylene can be converted to acrolein and acrylic acid by oxidizing the allylic C-H bonds (223, 224), to propylene oxide (PO) by oxidizing the C=C double bond (225) and to acetone by oxidizing the 2-carbon (226).

Propylene oxide is an important building block for polyether polyols, which are used to make polyurethanes (227). Commercially, PO is manufactured by either chlorohydrin or coproduction routes (228). But both of them show low selectivity for PO.

Use of Au supported on TiO_2, TiO_2-SiO_2, (229) and titanosilicates: TS-1, TS-2, Ti-beta, and Ti-MCM-41 (230) catalysts in the vapor phase epoxidation of propylene to propylene oxide using H_2 and O_2 was reported earlier by Uphade et al. (231). Recently, Au supported on Ti-MCM-41 and Ti-MCM-48

catalysts was employed for the previously reaction by the same group (231, 232). Au/Ti-MCM-48 showed better performance than did Au/Ti-MCM-41, which was attributed to its three-dimensional pore system, which was more resistant to blockage by extraneous materials like oligomers of PO and bulkier organic compounds than was the unidimensional pore system of hexagonal Ti-MCM-41.

The proposed reaction mechanism for propene epoxidation over these catalysts is given in Fig. 3.

According to the mechanism proposed, H_2O_2 formed from H_2 and O_2 over the gold surface is first converted into a hydroperoxo-like species on the Ti^{4+}-SiO_2 surface, which reacts with propene preadsorbed on the SiO_2 surface, giving PO.

Heteropoly acid catalysts are attractive since they have both strong acidity and redox properties. The transition metal salts (Cu^{2+}, Co^{2+}, and Ni^{2+}) of 10-molybdo-2-vanadophosphoric acid $[H_5(PMo_{10}V_2O_{40})]$ supported on HMS material catalysts were used for the oxidation of propylene to acetone by molecular oxygen (224). It was reported that by supporting $CuH_3[PMo_{10}V_2O_{40}]$ on HMS, the propylene conversion was increased from 1.3% to 17.8%. The catalyst gave a selectivity of 84.2% for acetone at 423 K.

- Because the allylic protons of propylene posses high acidity, propylene is easily oxidizable to acrolein and acrylic acid by molecular oxygen. But by controlling the acidity and oxidation ability of the heteropoly compound and the nature of the counter ion, the efficient and selective oxidation of propylene to acetone is possible.

High valent d^0 transition metal complexes, such as Mo^{VI}, V^V, and Ti^{IV} are effective catalysts for the selective epoxidation of olefins by alkyl hydroperoxides (ROOH) ((239b–d)).

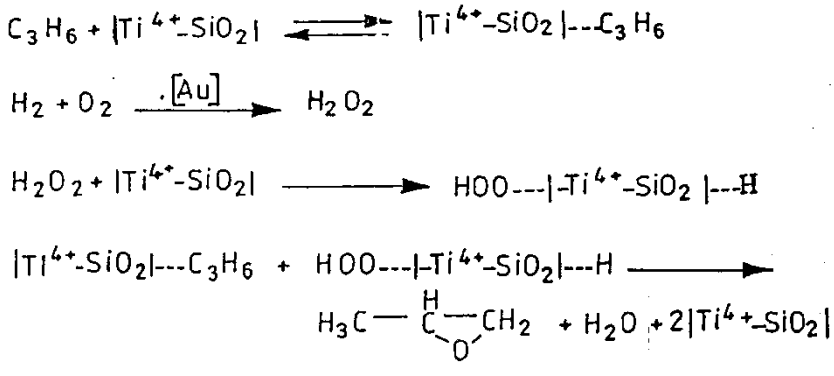


Figure 3: Proposed mechanism for epoxidation of propene over Au/Ti-MCM-41 catalyst (231).

Nunes et al. (239e) prepared heterogeneous olefin epoxidation catalysts by immobilization of dioxomolybdenum complexes in MCM-41 and MCM-48 catalysts functionalized with a bidentate 1,4-diazabutadiene ligand; and these are found to be active for the epoxidation of olefins using TBHP as the oxidant.

However, the authors confirmed that most of the observed activity is due to leached molybdenum species in solution.

- In fact, leaching is a particular problem for heterogeneous catalysts in liquid-phase oxidation catalysis owing to the strong complexing and solvolytic properties of oxidants and products (239f).

2. Trichloroethylene

Catalytic oxidative destruction of chlorinated volatile organic compounds (CVOC) is one of the important treatment strategies for environmental protection. Kawi and Te (233) reported the application of Cr/MCM-48 catalysts in the oxidative destruction of trichloroethylene and the catalyst was found to show excellent catalytic activity (100% conversion at 673 K) and catalytic stability (stable for 72 h).

3. Cyclohexene

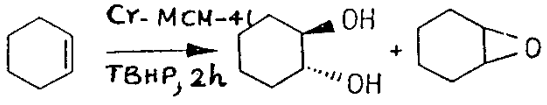
The immobilization of transition metal complexes on solid supports can provide catalysts that are easier to handle and possibly exhibit improved activities and selectivities expected to be induced by the support (234, 235).

Choudary et al. (236) reported the use of anchored Mn(II) salen complexes prepared by different methods in the epoxidation of olefins. Irrespective of the method of preparation, the catalysts were found to be active in the epoxidation of various substrates using PhIO as the oxidant.

Ti- and V-containing mesoporous mesophase materials (MMM) are reported as prospective catalysts for the H_2O_2-based oxidations (237–241). However, the problem of metal leaching was observed in most of the cases. Even though TBHP is less active than is H_2O_2, usually no leaching of Ti- and V- was observed in the oxidation of alkenes using TBHP as oxidant (237, 241).

Kholdeeva et al. (242, 243) studied the catalytic activity of C16-(Ti, Si)-MMM and C16-(V,Si)-MMM in the oxidation of alkenes with H_2O_2 and found that no leaching of Ti ions occurred even after recycling, whereas V leaching was found to be considerable. Thus the oxidation process with aqueous H_2O_2 was reported to be truly heterogeneous in nature over C16-(Ti, Si)-MMM catalyst.

Sivasanker et al. (167) reported the conversion of cyclohexene to trans 1,2-diol as the major product in a single step [Scheme 28], produced by the ring opening of the epoxide, which was the primary product over Cr-MCM-41 catalyst and 70% ter-butyl hydroperoxide (TBHP) in MeOH as oxidant.



Scheme 28: Single step catalytic conversion of cyclohexene to trans-1,2-diol (167).

Epoxidation of cyclohexene with H_2O_2 over Ti-MMM catalyst was reported by Ahn et al. (143). The major product were cyclohexene diol and its methyl ethers as reported by Chen et al. (241) for Ti-MCM-41. It was believed that the Lewis acid sites of Ti-containing mesoporous materials convert the initially formed cyclohexene oxide to diols and mono- and di-alkyl ethers via further reaction with water and methanol (244).

Metalloporphyrins are well known for their ability to catalyze selective oxidation processes with a variety of oxygen donors (245). Several methods for immobilization of porphyrin molecules on MCM-41 type materials were reported (246–251). Mn(TMPyP) (chloro[meso-tetra(4-N-methylopyridinio)-porphyrinato] manganese(III) tetrachloride (Fig. 4) supported Al-substituted mesoporous silicas of MMS type was used for the epoxidation of cyclohexene with iodosyl benzene by Potowicz et al. (252).

The materials gave only allylic oxidation products and no epoxide. It was argued that the effect is due to the narrowness of the structural pores, which prohibits the formation of the transient complex required for the formation of the epoxide. Schematic representation of the reaction pathways in

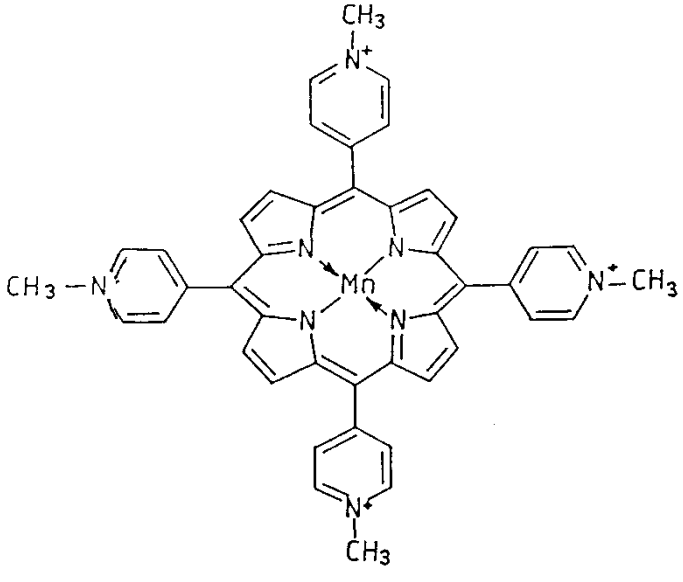
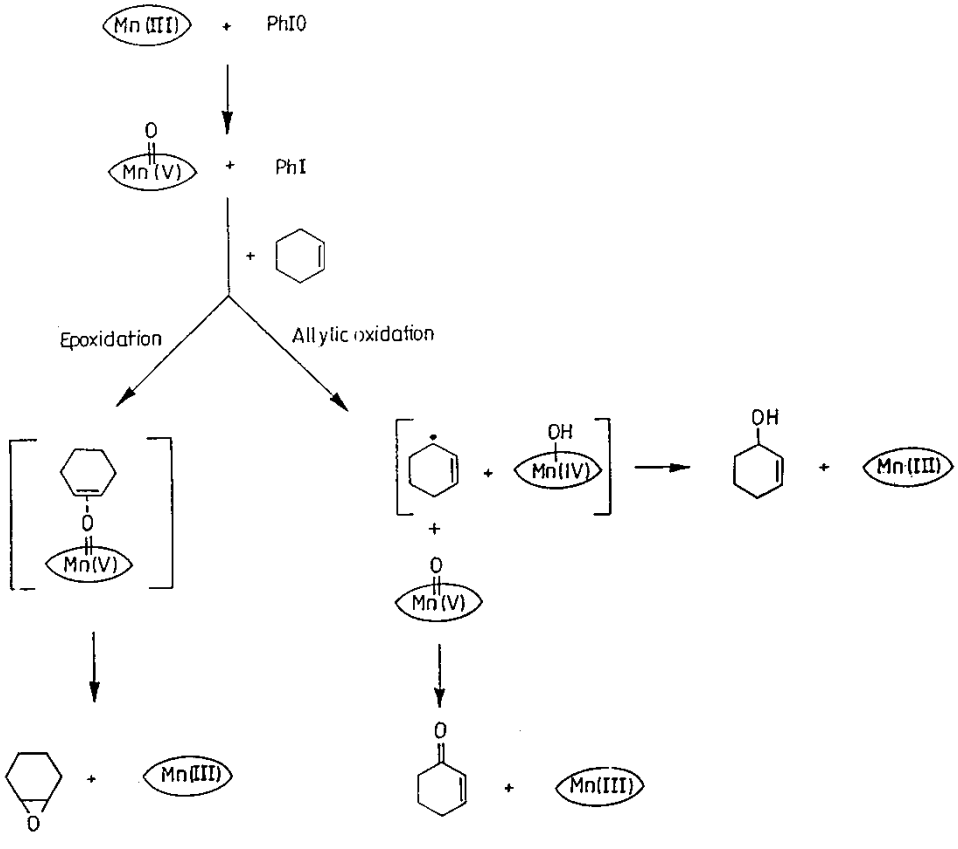


Figure 4: Structure of manganese porphyrin, Mn(TMPyP) (252).

cyclohexene oxidation with PhIO in the presence of Mn(III) porphyrin catalyst is given in Scheme 29.

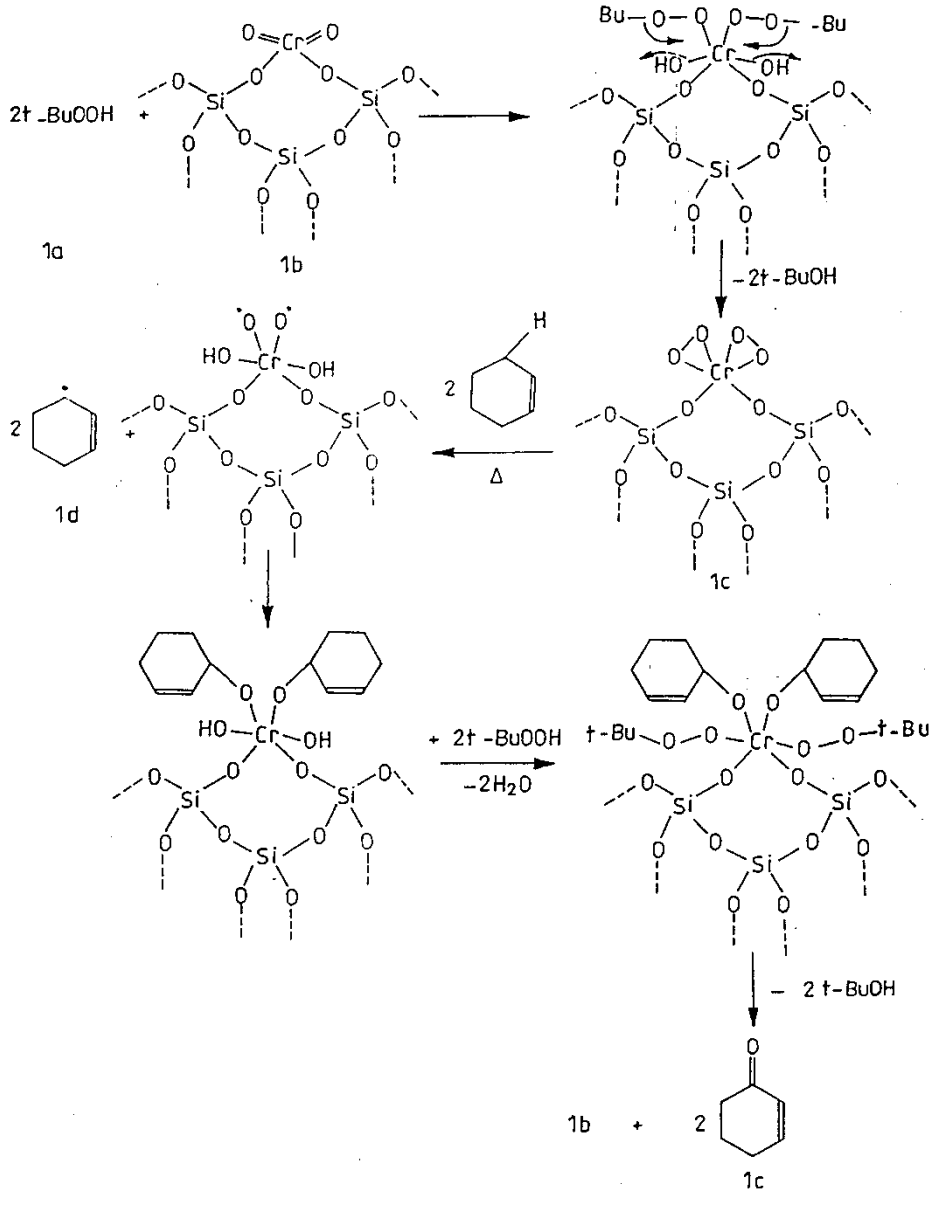
Laha and Kumar (161b) studied the promoter-induced synthesis of MCM materials and found that promoters having a high polarizing ability [(Z/r)value] were more effective in reducing the synthesis time of these materials. Comparable catalytic activities, in the presence and absence of promoters were reported in the epoxidation of cyclohexene over Al-, Ti-, and V-MCM-41 materials. Cyclohexene oxide was the major product when UHP or TBHP were used as the oxidants. In the presence of aqueous H_2O_2, the selectivity of cyclohexene oxide was low, mainly due to its isomerization and hydrolysis to produce cyclohexanediol.

Allylic oxidation of cyclohexene was carried out over (Cr)MCM-41 and (Cr)MCM-48 molecular sieve catalysts by Selvam et al. (253). Higher selectivity was observed for 2-cyclohexen-1-one, which can be explained based on the reaction mechanism (Scheme 30).



Scheme 29: Schematic representation of the reaction pathways in cyclohexene oxidation with PhIO in the presence of Mn(III) porphyrin catalyst (252).

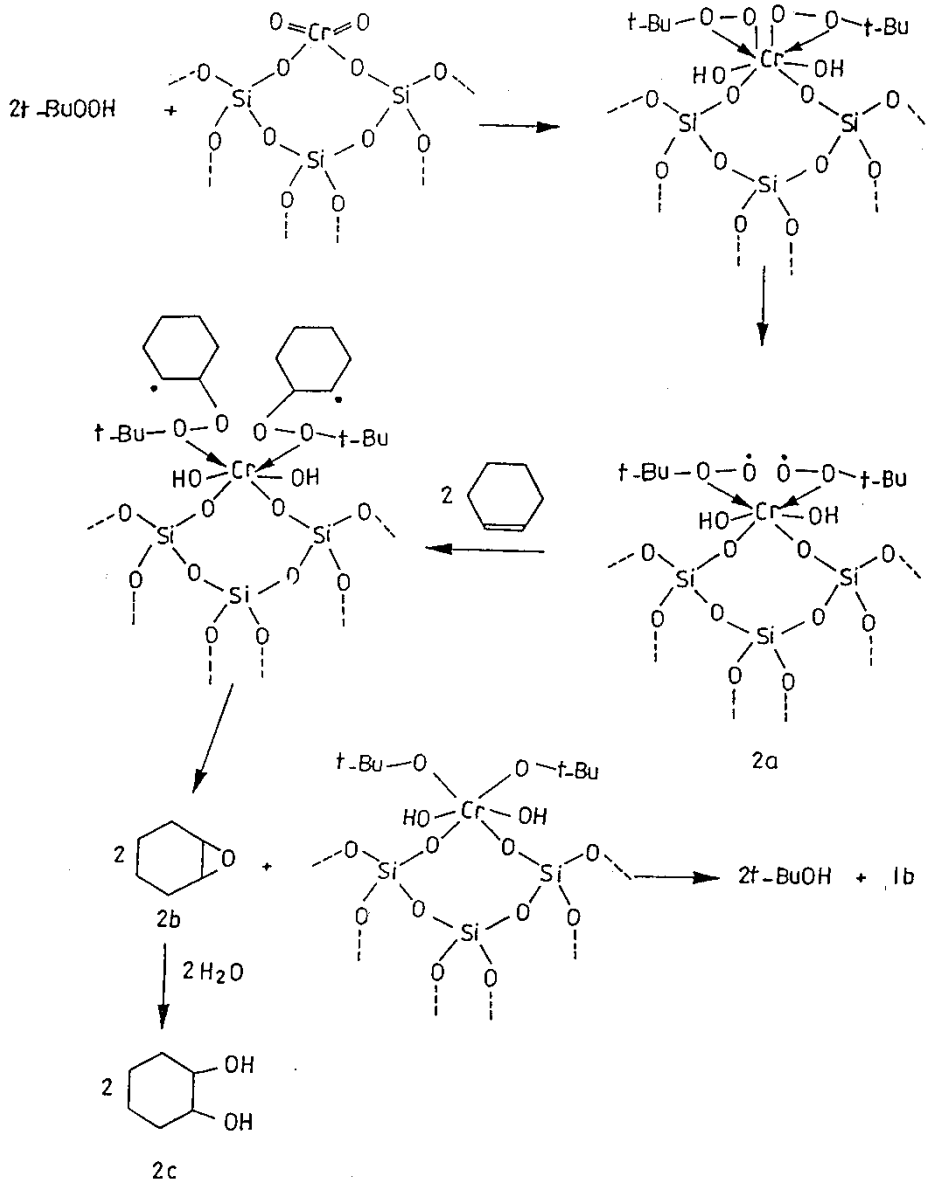
According to Scheme 30, TBHP **1a** interacts with chromate species **1b** to produce chromium peroxospecies **1c**. The latter further reacts with cyclohexene, by abstraction of hydrogen from the allylic position, leading to allylic free radical **1d**. The resulting species is then oxidized to 2-cyclohexen-1-one **1e**; i.e., via the formation of cyclohexyl chromate ester.



Scheme 30: Possible reaction pathways for the allylic oxidation of cyclohexene over (Cr)MCM-48 (253).

Another mechanism, suggested to explain the formation of cyclohexene oxide at a lower oxidant:substrate ratio (1 : 1), is given in Scheme 31.

According to the second mechanism, TBHP **1a** interacts with chromate species **1b**, leading to tertiary butyl peroxy radical **2a**. The interaction of **2a**



Scheme 31: Possible reaction pathways for the allylic oxidation of cyclohexene over (Cr)MCM-48 (253).

with the double bond of cyclohexene results in the formation of epoxide **2b**, which was further oxidized into diols (1,2-cyclohexandiol, **2c**).

- The second pathway is in good agreement with earlier observations under homogeneous reaction conditions (254).

Bhaumik and Tatsumi (255a) observed remarkable enhancement in activity by trimethylsilylation of Ti-MCM-41 and Ti-MCM-48 in the oxidation of cyclohexene, hexane, and pent-2-en-1-ol using H_2O_2 as the oxidant.

4. Cyclooctene

Currently, heterogeneous epoxidation is a very active topic in the field of catalysis due to the significant industrial interest (255b, c).

Postsynthetic grafting is the most popular way to anchor organic groups in a specific manner to the surface of a mesoporous material, which finally results in hybrid organic inorganic materials (255d–k).

Mingjun Jia et al. (255l), reported a hybrid heterogeneous catalyst system, which is synthesized by covalently anchoring oxodiperoxo molybdenum chelate complexes onto the surface of a mesoporous Si-MCM-41 material. This material is highly active and truly heterogeneous for the liquid-phase epoxidation of cyclooctene with t BuOOH as the oxygen source.

In a recent work by the same authors (255m), two different mesoporous materials, Si-MCM-41 and Al-MCM-41, were used to anchor catalytically active oxodiperoxo molybdenum sites via the silylated ligand (3-triethoxysilyl propyl)[3-(2-pyridyl)-1-pyrazolyl]acetamide.

The modified Mo-containing MCM-41 materials were tested as catalysts for the epoxidation of cyclooctene with t BuOOH as the oxygen source at a reaction temperature of 334 K. The samples showed good activities and high selectivities (nearly 100%) to cyclooctene epoxide.

- Modified aluminosilicate MCM-41 materials show better activity than do the corresponding siliceous materials, which might be due to the higher Lewis acidity of Al-MCM-41 caused by the incorporation of the aluminum into the mesoporous material.

The excellent stability of these catalysts can be attributed to the covalent grafting between the organic ligand system and the inorganic mesoporous material, to the mild reaction conditions during the generation of the grafted system, and to the strong binding between the $MoO\text{-}(O_2)_2$ unit and the chelating ligand.

- They have also found that the catalytic properties (activity and recyclability) of the supported materials can be improved by further silylation

with Me_3SiCl to remove residual Si-OH groups from the mesoporous surface.

However, there are some major drawbacks related to the post-synthesis grafting procedure:

- The distribution of the organic group is generally not uniform all over one channel (255i–k) and the loading with larger and sterically demanding organic functionalities is often low, mainly constrained by diffusion limitations.

An alternative way to overcome these problems would be to prepare *hybrid* mesoporous materials by a template-directed synthesis, which is usually based on the co-condensation of organosilane precursors with other silica reagents (e.g., tetraalkoxysilanes) in a templating environment.

Even though many reports were available in this field, it still is a challenge to obtain hybrid mesoporous materials containing a specific organic functional group in a one-step synthesis.

The main difficulty related to this is:

- to control the preparation conditions in a way that a hybrid material with uniform distributions of organic functional groups and a highly ordered channel system is obtained.
- Additionally, the organic precursor has to be stable throughout the hydrothermal synthesis of the material and has to survive the surfactant removal process.

In a recent report, Mingjun Jia et al. (255n), synthesized a new organic-inorganic hybrid mesoporous MCM-41-type material by co-condensation of tetraethyl orthosilicate (TEOS), and chelate ligand (3-trimethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl] acetamide in the presence of the CTAB template and coordinating it with the catalytically active $MoO(O_2)_2$ moieties, which results in the formation of highly active heterogenized catalysts for the liquid-phase epoxidation of cyclooctene with tBuOOH with excellent stability against leaching.

G. Oxidation of Sulfides, SO_2, and N_2O

1. Enantioselective oxidation of sulfide to sulfoxide

Three kinds of efforts have been devoted to realization of asymmetric reactions on heterogeneous catalysis:

1) Supporting of active homogeneous catalysts on porous supports (256).
2) Use of asymmetric surface of the solid. This is achieved on quartz (257).
3) Preparation of active sites for the asymmetric reaction on an achiral heterogeneous catalyst (258).

One of the reasons for the failure in the asymmetric reaction on solid catalysts is the low uniformity of the active sites. Hence, by keeping two parameters, i.e., use of a solid material with a uniform surface and the uniform introduction of catalytically active sites onto the surface, one may succeed in developing a solid catalyst giving high enantioselectivity.

Asymmetric oxidation of aryl methyl sulfide over transition metal ions substituted MCM-41 was studied by Iwamoto et al. (259) with H_2O_2 in the presence of optically active tartaric acid as chiral modifier (Fig. 5). The catalysts were prepared by the template ion exchange method (TIE).

High chemical and optical yields of methylphenylsulfoxides were reported over Ti-MCM-41. The same catalyst, Ti-MCM-41 prepared by a hydrothermal synthesis route (DHT) was found to be active by Corma et al. (239a) for oxidation of sulfide in the absence of any chiral modifier although the products were racemic.

2. Sulfur dioxide

The oxidation of SO_2 is the basic step in the production of H_2SO_4. Conventionally, V_2O_5 catalysts were employed for this purpose. Schuth et al. (260) reported the catalytic efficiency of Fe-MCM-41 (prepared by different methods) in the oxidation of sulfur dioxide. The activity was compared with vanadium-based commercial catalyst and an iron-on-silica catalyst. The Fe-MCM-41 catalysts prepared by incipient wetness technique were found to be stable up to 1023 K and showed higher activity than the other materials.

Use of nitrous oxide as an oxidant with transition metal containing porous catalysts such as Fe-MCM-41 and Fe-ZSM-5 was previously reported by

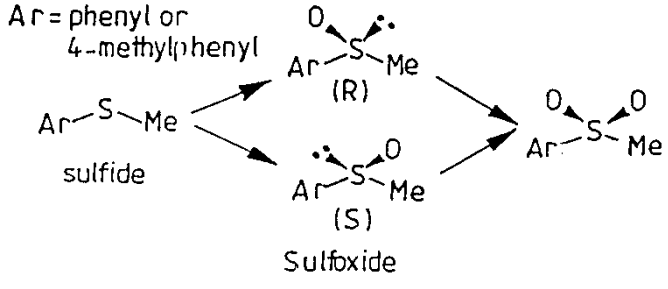


Figure 5: Asymmetric oxidation of arylmethyl sulphide (259).

several authors (261, 262). Stockenhuber et al. (263) recently reported an interesting observation that Fe-MCM-41 materials convert nitrous oxide into adsorbed nitric oxide at room temperature.

H. Other Molecules

1. *D-Glucose*

The renewable character of carbohydrates as well as their biodegradability played an important role in applying them as chemical feedstock during the last decade. Titania is known to be an effective catalyst for the cleavage of diols when H_2O_2 is used as an oxidant (264, 265).

Oxidation of D-glucose with H_2O_2 over different Ti-containing zeolites (Ti-Y, Ti-L, Ti-mordenite, and TS-1) and mesoporous molecular sieves (Ti-MCM-41) was reported by Velarde et al. (266). The performance of the various catalysts is given in Table 16. The main reaction observed in all cases (different Ti-containing zeolites and mesoporous molecular sieves) was the oxidation of the aldehyde carbon. Beside the formation of gluconic acid, the oxidation of the primary hydroxyl group and also a further oxidation to lower acids, such as tartaric, glyceric; and glycolic acids were detected, which indicates that oxidative destruction of D-glucose occurs stepwise.

In contrast to the results previously obtained (264, 267), by the oxidative cleavage of *trans*-1,2-cyclo-hexanediol, neither the conversion nor the selectivity of the oxidation of D-glucose seems to be determined by the pore size or the Ti species of the catalysts used.

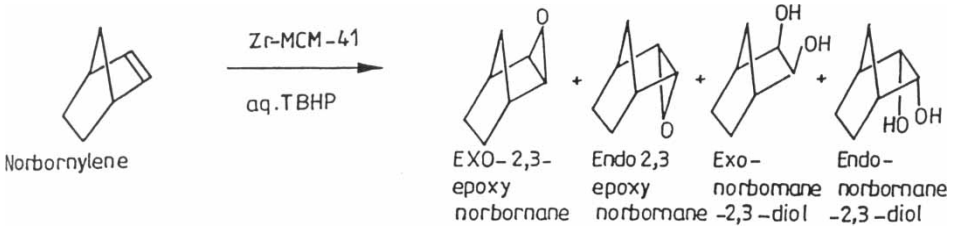
2. *Norbornylene*

Both Ti-MCM-41 and Zr-MCM-41 were found to be active in the hydroxylation of norbornylene with H_2O_2 as the oxidant (157). The reaction yielded exo- and endo-epoxides (Scheme 32), which opened up further during the reaction to give the corresponding diols.

The reaction is found to be more selective for exo- than it is for the endo-epoxide. Ti-MCM-41 gave slightly higher conversion than did Zr-MCM-41.

Table 16: Oxidation of D-glucose using Ti-containing catalysts (266).

Catalyst	SiO_2/Al_2O_3	Si/Ti	Conversion (%)	Gluconic acid (%)	Glycolic acid (%)
TS-1	—	46.0	27.3	11.9	0.0
Ti-DM	>350	23.1	23.1	11.8	5.9
Ti-L	5.5	12.8	19.9	12.7	4.3
Ti-Y	16	4.6	23.2	27.9	8.4
Ti-MCM-41	—	51.6	25.4	21.5	10.5



Scheme 32: Oxidation of norbornylene (160).

I. Summary

Transition metal-incorporated mesoporous materials have proved to be potential catalysts in the oxidation of various substrates. The reactions were found to be extremely sensitive to the oxidant and solvents used.

Despite the fact that H_2O_2 is more expensive than is molecular oxygen, it can be the oxidant of choice for fine chemicals because of its simplicity of operation (117).

The leaching of active components is a common problem in liquid-phase oxidation reactions employing heteroelements incorporated in mesoporous catalysts. The problems of titanium leaching and catalyst deactivation in the presence of aqueous H_2O_2 still considerably restrict the possibility of practical applications of these materials (118, 119, 268–270).

V. CONCLUDING REMARKS

The M41S type materials appeared to be promising acid and redox catalysts and were also successfully applied as supports for active sites. One of the major obstacles to be overcome for further progress is the limited thermal and hydrothermal stability of the system. Inspite of the intensive effort, an easy method for improving the hydrothermal stability of these materials has not yet been developed. More research work is expected to expand into this area.

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