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Catalytic liquid-phase oxidation in heterogeneous system as green chemistry goal—advantages and disadvantages of MCM-41 used as catalyst

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Abstract

This review article is devoted to the discoveries and/or knowledge developed in the past 10 years in the area of catalytic liquid-phase oxidation with hydrogen peroxide on mesoporous molecular sieves of MCM-41 type modified with various transition metals. The following parameters influencing activity and selectivity of the catalysts are considered: (i) nature of matrix for metal species limiting diffusion effects; (ii) isolation of metals; (iii) hydrophobicity of catalysts; (iv) nature of solvent; (v) reducibility of metal species; (vi) leaching of metal from the solid. Advantages and disadvantages of MCM-41 materials are pointed out in relation to the properties of TS-1 and TS-2 zeolites.

Keywords: T/MCM-41 (T = Ti, V, Nb, Cu, Fe, Cr); Liquid-phase oxidation; Epoxidation of olefins; Sulphoxidation; Hydroxylation

1. Introduction

Catalysis is a fundamental tool in both waste removal and pollution prevention. In environmental protection two general strategies are developed. The first one covers the “clean-up” or “end of pipe” technologies which deal with the treatment of polluted air and water. “End of pipe” has been considered a synonym for environmental protection for the past 25 years and it includes, among others, removal of nitrogen oxides, ammonia, and volatile organic compounds (VOC). The second strategy can be solved by the application of catalysts in the production processes (environmentally clean processes), called “green chemistry”. Green chemistry is the design of chemical products and processes, which reduce or eliminate the use and generation of hazardous substances [1]. The function of catalysts in the future will be no more to eliminate and destroy harmful substances in an expensive way at the end of the processes but rather to avoid the formation of such substances already in the processes [2].

The useful measures of the potential environmental impact of chemical processes are the E-factors, defined as the mass ratio of waste to desired product [3]. The highest E-factors are characteristic of fine chemicals and pharmaceuticals production. Fine chemicals are generally complex, multifunctional molecules with high boiling points and limited thermal stability. This often requires carrying out the reactions in the liquid phase and at moderate temperatures. Recently, catalytic processes have been replaced many classical routes for chemical synthesis. A wide range of these reactions covers oxidation processes [4]. Among them the liquid-phase oxidation with hydrogen peroxide (clean oxidant) plays a very important role.

Liquid-phase oxidation is performed in two ways, in homogeneous and heterogeneous systems. In heterogeneous system with clean oxidants such as H_2O_2 it is an environmentally friendly alternative to traditional oxidation employing inorganic oxidants in stoichiometric amounts in industrial organic syntheses. At present, there is a tendency to the replacement of homogeneous processes (in which recovery and recycling cause problems) by heterogeneous ones. In the latter, regeneration of the catalysts is easy but several other disadvantages appear. These disadvantages and also other features of heterogeneous mesoporous metallosilicate MCM-41 type catalysts will be considered in this paper.

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It is worthy of notice that another possibility is the application of supported liquid-phase catalysts, i.e. homogeneous catalysts working in a thin liquid film supported over a solid material which can be inert or participate to the reaction mechanism. It is discussed in the overview paper by Centi and Misono [5].

2. Catalysts and processes

MCM-41 mesoporous materials with hexagonal arrangement of pores modified via incorporation of various transition metals (e.g. Ti, V, Nb, Cu, Fe, Cr) will be discussed as potential catalysts for liquid-phase oxidation.

Three groups of oxidation processes, in which H_2O_2 is used as oxidant, will be taken into account: (i) hydroxylation of aromatics (e.g. [6–13]); (ii) epoxidation of olefins (e.g. [8–10], [12–27]); (iii) sulphoxidation of organic sulphides (e.g. [9,12,17,23,28–35]).

3. Discussion

Three oxidation mechanisms are proposed for the liquid-phase oxidation [13]. They are illustrated in Fig. 1. Homolytic pathway proceeds via free radical mechanism where in the first step metal active species participates in homolytic cleavage of O–O bond in hydrogen peroxide forming $^\bullet$OH radicals, which are intermediates in homo or heterolytic oxygen transfer process. Heterolytic pathways proceed via oxometal or peroxometal species as an active oxidant. In many cases homolytic and heterolytic pathways can afford the same products.

Heterolytic peroxometal pathways are favoured when the metal in its highest oxidation state is both a Lewis acid and a weak oxidant, e.g. early transition metal ions with d^0 configurations such as Mo(VI), W(VI), Ti(IV), Nb(V). Catalysis is due to the Lewis acid character of the metal ion, and metal oxidation state does not change during the catalytic cycle. Strong (one-electron) oxidants, e.g. later and/or first row transition elements such as Cr(VI), Mn(III), Co(III), and Fe(III) favour oxometal pathways and/or homolytic decomposition of hydrogen peroxide. Vanadium(V) is both a strong Lewis acid and a relatively strong (one-electron) oxidant and hence, exhibits all three types of activity. Similar behaviour seems to present niobium(V).

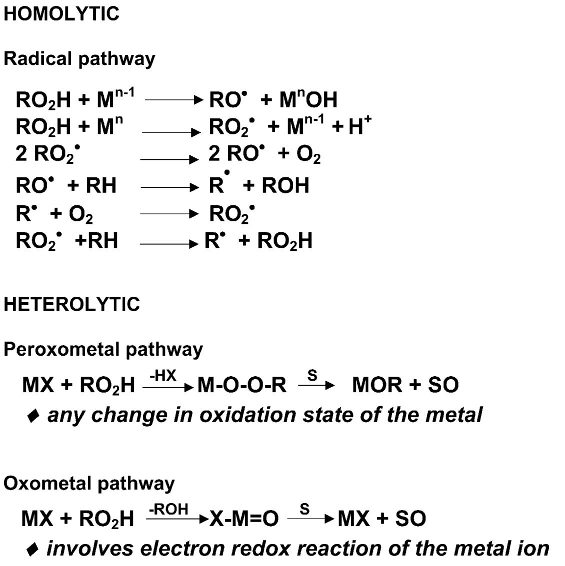

Fig. 1. Mechanisms for the liquid-phase oxidation [13].

The structure of the matrix and the surrounding of metal influence to some extent the type of pathway. Therefore, for various catalysts different pathways for the same processes can occur. Typical examples of reactions involving peroxometal pathways are olefins epoxidation, sulphoxidation, and oxidation of nitrogen compounds [13]. However, Nb/MCM-41 materials catalyse cyclohexene epoxidation via radical mechanism [22] not via peroxometal species.

3.1. *Choice of matrix for metal—effect of diffusion*

TS-1—MFI zeolite containing titanium [6]—remains the most widely studied material since, owing to the hydrophobic nature of its active sites, it can be used effectively with aqueous H_2O_2. However, its application is limited to transformations of molecules small enough to enter the relatively small pores (0.53 nm × 0.55 nm) in MFI zeolites. For example, cyclohexene is not epoxided by this system. The transformation of molecules with kinetic diameters higher than 0.6 nm, especially important for the preparation of fine chemicals, requires redox molecular sieves with higher pore diameters. Even Ti-beta containing larger pores (but still in microporous range) is not sufficient to eliminate the diffusion effects.

Since the discovery of mesoporous silicates in 1992 [36], designated as MCM-41, many works have been devoted to the synthesis of metallosilicates (T/MCM-41) containing various transition metals and their application in liquid-phase oxidations.

Mesoporous molecular sieves of M41S family (MCM-41, MCM-48) have been modified by transition metals via post synthesised grafting or tethering, or via inclusion of metal during the synthesis (isomorphous substitution). The nature of metal active species depends on metal location (extra framework or framework positions). Location of metal and sizes of metal clusters determine the diffusion effect.

Diffusion limitations and steric constraints due to reactants or transition-state intermediates are the important factors influencing the oxidation activity in the liquid phase. Phenyl sulphide was found to be unreactive towards H_2O_2 oxidation in the case of titanium silicalites with zeolite structures [28]. Non-reactivity is mainly due to its large size, which causes diffusion restrictions inside the pore channels of TS-1 or Ti-beta. Adam et al. [17] studied sulphoxidation (with H_2O_2) of thianthrene 5-oxide (SSO) on TS-1, Ti-beta, and Ti-containing MCM-41. TS-1 was inactive due to diffusion limitation and/or shape selectivity effect caused by the transition state size. The authors stated that even if SSO were to enter the TS-1 zeolite, it would occupy the available space and it should be unlikely for transition-state for oxygen transfer to be formed. The diffusion limitation generally does not occur when mesoporous metallosilicates of MCM-41 type are applied. However, it depends to some extent on the procedure of the preparation. It has been shown in [22] that the presence of extra framework metal (niobium) species in the impregnated Nb/MCM-41 strongly inhibits the activity in cyclohexene oxidation, especially in the initial stage of the reaction. This behaviour is only partially caused by the diffusion limitation, as will be pointed out below (discussion of the role of metal isolation). T/MCM-41 prepared via inclusion of metal to the skeleton of mesoporous MCM-41 does not limit the diffusion of reagents.

3.2. *Isolation of metal species*

Isolation of metal species is another important factor, which should be considered in the discussed processes. For instance, in niobium containing catalysts, Nb dimers or oligomers cause too fast a decomposition of hydrogen peroxide. They can also lead to the decomposition of alcohol [37], which often is applied as the reaction medium. Interaction with alcohol causes the blockage of active species. The isolation of Nb species is easily reached in mesoporous than microporous materials and easily obtained when isomorphous substitution is applied during the synthesis than the post synthesis modification via impregnation or ion exchange are used.

3.3. *Hydrophobicity of the catalysts*

The importance of hydrophobicity of heterogeneous catalysts for selective epoxidation has been emphasised by Sheldon and Dakka [18]. Hydrophobicity of the catalyst surface favours the adsorption of the non-polar reactants in competition with the polar products, and then increases both activity and selectivity. TS-1 exhibits the highest hydrophobicity among titanium catalysts, but it is not active in the epoxidation of cyclohexene [19] due to the diffusion effect. Ti-beta containing aluminium is less hydrophobic (more hydrophilic). Ti/MCM-41 (without aluminium) is more hydrophilic than Ti-beta. The epoxide competes more favourably for adsorption on the hydroxylated surfaces of Ti-silicates. In this respect, the presence of silanol groups as well as =Ti–OH groups allows adsorption of the epoxide and results in the ring opening of the epoxide and the formation of diols. The diols tend to adsorb strongly on the Ti sites and lead to partial deactivation of the catalyst [16].

Corma et al. [16] proposed two strategies to improve the catalytic activity of Ti/MCM-41 in the epoxidation of olefins. The first involves the increase of the hydrophobicity of the material via silylation of the catalyst surface, and the second is based on the removal of water from the reaction media. The second strategy requires the application of *tert*-butylhydroperoxide (TBHP) instead of hydrogen peroxide as oxidant. The authors stated that in order to obtain a highly active and selective catalyst for epoxidation it is necessary to silylate Ti/MCM-41 above 40% or preferably close to 100%. Silylation of Ti/MCM-41 as well as application of TBHP as oxidant in the sulphoxidation of thianthrene 5-oxide (SSO) significantly increases both the activity and sulphoxide selectivity—Table 1 [17]. This indicates the importance of the catalyst hydrophobicity also in the sulphoxidation processes.

Table 1
Oxidation of thianthrene 5-oxide (SSO) to the sulfoxides at 293 K by titanium catalysts [17]

Catalyst	Oxidant	Conversion (%)	Selectivity to sulphoxides (%) ($\sum$SOSO)*
Ti-beta (Al free)	35% H_2O_2	14	84
Ti/MCM-41	35% H_2O_2	27	94
Ti/MCM-41 (sil)	35% H_2O_2	43	83
Ti-beta (Al free)	80% tBuOOH	3	81
Ti/MCM-41	80% tBuOOH	22	81
Ti/MCM-41 (sil)	80% tBuOOH	51	80

*Sum of *cis*- and *trans*-5,10-dioxides.

Instead of silylation of Ti/MCM-41 samples one can look for mesoporous materials containing other active metal species involving a different reaction pathway. Nb/MCM-41 seems to be very useful catalyst for both processes, epoxidation of olefins [22] and sulphoxidation of sulphides [30–32]. Very high selectivity to epoxide (99%) and 58% conversion of cyclohexene was reached on Nb/MCM-41 when acetonitrile was used as solvent and hydrogen peroxide as oxidant [22]. It is worth of note that the catalyst was dehydroxylated prior to the inclusion to solvent and reactant. Dehydroxylation causes the formation of Lewis acid centres (skeletal Nb^+) and NbO^- species [30,38]. One should emphasise that radical mechanism for the epoxidation process has been presupposed on the basis of the blockage of radical species with NO adsorption [22]. Cyclohexene conversion drastically decreases in the atmosphere of NO, which is chemisorbed on NbO^- species.

Recently, Baiker and coworkers [27] indicated that the preparation of Ti-containing catalysts via flame synthesis increases significantly the hydrophobicity of the final material making it more effective in the epoxidation process.

Hydrophobic/hydrophilic properties of Nb/MCM-41 are not sufficient for the application of this material in the reactions carried out in water medium, like the hydroxylation of phenol. In the sulphoxidation of sulphides on Nb/MCM-41 the peroxometal pathway is involved, in which Lewis acid centres (Nb^+) and weak oxidative one (NbO^-) play an important role.

Fig. 2. Formation of solvated titanium peroxo species [26].

3.4. Role of solvent

Usually protic solvents take part in the elementary steps of the liquid-phase oxidation. Clerici and Ingallina [26] reported that the formation of solvated titanium peroxo species (Fig. 2) explains the behaviour of titanosilicate oxidation catalysts. They documented that activity for 1-pentene epoxidation over TS-1 decreases with solvent in the order $CH_3OH > C_2H_5OH > t$-BuOH and have postulated that such a strong solvent effect can only be explained by the direct involvement of the solvent in an elementary reaction step. They suggested that in the presence of ROOH and a coordinating solvent the reaction occurs with the formation of an active titanium hydroperoxo complex coordinated within a five membered ring to the solvent. The participation of solvent was also postulated in the mechanism of the sulphoxidation of organic sulphides [29]. The first step is a solvation of Ti-containing zeolites and the formed complex reacts further with RSR via a coordination between oxygen and sulphur.

Although many authors agree that titanium peroxo species formed with the participation of solvent is the active species in the epoxidation processes, no titanium hydroperoxo compounds have been prepared so far. Therefore, no direct evidence for its presence has been recorded. It is noteworthy that TS-1 is active for alkene epoxidation in the absence of solvent (although with reduced activity) and titanium peroxo species is therefore not necessary for this mode of the reaction.

The nature of solvent can also influence the selectivity of the reaction by the modification of the catalyst surface. Epoxidation of cyclohexene on Nb/MCM-41 in various solvents shows the following orders: conversion—MeOH $>$ acetone $>$ acetonitrile $>$ t-BuOH; epoxide selectivity—acetonitrile $>$ acetone $\gg$ MeOH $\approx$ t-BuOH; diol selectivity—MeOH $>$ t-BuOH $>$ acetone. It is clear that protic solvents increases acidity of the catalyst surface and by the same token epoxide ring opening becomes easier increasing diol selectivity.

Arends et al. [39] considered that the molecular sieve acts as the second solvent, extracting the substrate molecule from the bulk solvent. The exact behaviour of the molecular sieve is thus dependent on the size and hydrophobicity of the pores. Hydrophilic materials such as Ti/MCM-41 will selective absorb polar molecules.

$$\mathbf{H_2O_2 + Cu^{2+}\text{-}MCM\text{-}41 \rightarrow HO_2^{\bullet} + H^{+} + Cu^{+}\text{-}MCM\text{-}41}$$

$$\mathbf{H_2O_2 + Cu^{+}\text{-}MCM\text{-}41 \rightarrow HO^{\bullet} + OH^{-} + Cu^{2+}\text{-}MCM\text{-}41}$$

$$\mathbf{Phenol + HO^{\bullet} \rightarrow Catechol}$$

$$\mathbf{Phenol + HO^{\bullet} \rightarrow Hydroquinone\ (+\ HO^{\bullet})\ Benzoquinone + H_2O}$$

Fig. 3. Radical mechanism of hydroxylation of phenol on Cu/MCM-41 [11].

3.5. Reducibility of metal species

In the peroxo metal pathway the metal species does not change its oxidation state. Therefore, its reducibility does not play an important role. It is significant parameter in the oxometal pathways and in the radical mechanisms. Norena-Franco et al. [11] used Cu/MCM-41 catalysts for selective oxidation of phenol in aqueous and acetonitrile media. They have proposed the radical mechanism (Fig. 3) in which in the first stage Cu/MCM-41 interacts with hydrogen peroxide and yields $HO^{\bullet}$ and $HO_2^{\bullet}$ species via a redox mechanism. Hydroquinone and catechol are subsequently obtained in parallel processes, involving the attack of $HO^{\bullet}$ radicals to the aromatic ring. Benzoquinone can be formed by the consecutive oxidation of hydroquinone. The authors have found the dependence of the selectivity on the nature of copper salt used for the encapsulation. The materials prepared from copper acetate give rise to the formation of para product—hydroquinone, whereas, those obtained from Cu(II) nitrate are selective to ortho substituted catechol. It is possible that this feature is caused by the diffusion effect more pronounced for bulky acetate salt.

One of the important features affecting the reducibility of metal located in the skeleton is T–O–Si angle. V–O–Si bond angle in V/MCM-41 mesoporous molecular sieves has been considered in relation to the redox activity of the samples in the liquid-phase oxidation of cyclohexene [40]. The bond strength is closely related to the electron density of the active metal sites. The latter is "tuned" by the pore size through variation of V–O–Si bond angles. The higher T–O–Si bonds angle is, the higher pore size in MCM-41 materials can be registered. The electron density depending on the T–O–Si angle affects the effective redox potential on metal sites. The maximum activity was achieved for the metal for which reactants presumably had an intermediate strength of adsorption. Therefore, the authors [41] observed the volcano curve for the dependence of the activity on the pore size of V/MCM-41 mesoporous sieves. T–O–Si angle is easily regulated in MCM-41 materials via changing of mesopore sizes than in zeolites.

3.6. Leaching of metal species

Rapid leaching of metal ions is a general problem associated with the use of heterogeneous metal catalysts in liquid-phase oxidation. Small amount of leached metal may have a significant effect on the observed catalytic re-

Table 2
Leaching of Nb and V to methanol containing various components

Catalyst	Components in the solution	Weight percentage of metal leached	
		Nb	V
Nb/MCM-41-32	Methanol	0.5	–
Nb/MCM-41-32	Methanol +H_2O_2	28	–
Nb/MCM-41-32	Methanol + methyl-phenyl sulphide	0.3	–
Nb/MCM-41-32	Methanol + methyl-phenyl sulphide + H_2O_2	2.8	–
Nb,V/MCM-41-32	Methanol + methyl-phenyl sulphide + H_2O_2	0.1	43
V/MCM-41-32	Methanol + methyl-phenyl sulphide + H_2O_2	–	71

The process was performed at 323 K in the presence of 0.04 g of the catalysts [43].

sults, making conclusions drawn from the physico-chemical characterisation invalid. Leaching is a result of solvolysis of the metal–oxygen bonds, through which the active species is attached to the support by polar molecules such as H_2O, ROH, or RCO_2H. It is commonly recognised that the metal–oxygen bonds in the molecular sieves are more stable than in that formed on the supports as silica or alumina. However, mostly redox molecular sieves do not present long- and even short-term stability (the exception is believed to be TS-1 [39] and Nb/MCM-41 [32]). However, even TS-1 and Nb/MCM-41 in some conditions are not stable. For example, the basic conditions used for ammoxidation of ketones with NH_3/H_2O_2 catalysed by TS-1 may also lead to leaching of titanium. It was also found that by-products formation caused the loss of Ti from TS-1 [20].

Various factors influence the metal leaching from the catalysts. There are: (i) nature of transition metal; (ii) nature of solvent; (iii) nature of oxidant; (iv) temperature; (v) the structure of matrix. They are widely discussed in [42] and are related to the mesoporous molecular sieves of MCM-41 type containing various transition metals (Ti, V, Cr, Mn, Fe, Co) applied as catalysts for oxidation of cyclohexane. Leaching was estimated on the basis of Si/M changes. The highest leaching was observed on Cr/MCM-41 when cyclohexane was used as reactant and solvent, and TBHP as an oxidant.

Among metallosilicate T/MCM-41 materials the lowest leaching of metal has been reported in the case of Nb/MCM-41 applied in sulphoxidation of organic sulphides [32] and hydroxylation of phenol on Cu/MCM-41 [11]. Recently [43] the influence of various components on niobium leaching from Nb/MCM-41 has been demonstrated (Table 2). The highest niobium leaching is caused by hydrogen peroxide. But when sulphide is first added to the solution and next H_2O_2, niobium leaching is negligible. It means that the adsorption of methyl-phenyl sulphide on the catalyst surface protects niobium from leaching or that the sulphoxidation is so fast that hydrogen peroxide is immediately used in the reaction and cannot cause niobium leaching. Vanadium is leached very easily from both V-containing materials. The level of vanadium leaching is lower when niobium is present in the mesoporous structure of the solid.

4. Summary

T/MCM-41 (T = transition metal element) exhibits several advantages for their use in liquid-phase oxidation with hydrogen peroxide. There are as follows: (i) no diffusion limitation especially if metal is located in the skeleton of MCM-41; (ii) relatively easy isomorphous substitution of metal into the framework; (iii) isolation of metal—easily reached than in zeolites; (iv) reducibility of metal species, important in oxometal and radical pathways, is easily regulated by changing of pore sizes determining T–O–Si angle.

Hydrophilicity of T/MCM-41 materials decreasing activity and selectivity in reactions using aqueous H_2O_2 as oxidant, and leaching of metal species from the solid, making the recovery of the catalyst unable, are more pronounced in MCM-41 materials than in metal containing zeolites. However, they can be avoided by several ways. One can apply TBHP instead of H_2O_2 as oxidant or use a different metal species than Ti, which changes the reaction route making the hydrophilicity of the catalyst unimportant. On the other hand silylation process can be applied increasing the hydrophobicity of T/MCM-41. Leaching of metal to the solution can be avoided or minimised by a choice of a proper metal, proper reaction medium (e.g. aprotic solvent), or appropriate sequence in the admission of components to the reactor (e.g. blockage of metal species by chemisorption of reagent).

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