Review

Functionalized Ordered Mesoporous Silicas (MCM-41): Synthesis and Applications in Catalysis

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Abstract: Mesoporous silica sieves are among the most studied nano-objects due to their stable pore structure and easy preparation. In particular, MCM-41 have attracted increasing research attention due to their chemical versatility. This review focuses on the synthesis and regioselective functionalization of MCM-41 to prepare catalytic systems. The topics covered are: mono and di-functionalized MCM-41 as basic and acid catalysts, catalysts based on metallic complexes and heteropolyacids supported onto MCM-41, metallic nanoparticles embed onto functionalized MCM-41 and magnetic MCM-41 for catalytic purposes.

Keywords: mesoporous silica; molecular sieves; nanoparticles; MCM-41; heterogeneous catalysis

1. Introduction

In recent years, the use of molecular sieves in both research and industry has increased exponentially. In particular, in the field of catalysis, special attention has been paid to mesoporous molecular sieves (pore diameter between 2–50 nm). These materials are widely used as adsorbents, catalysts, and catalyst supports due to its high surface areas, large pore volumes, and well-defined pore structure [1,2].

In this context, mesoporous silicas are regarded as very versatile materials, given the possibility to be easily derivatized with a wide variety of functional groups such as acids, amines, metallic nanoparticles, and organometallic complexes through co-condensation and/or post-synthesis grafting methods [2].

Among all the types of MSN reported (SBA-n (Santa Barbara amorphous silica), MSU-n (Michigan State University silica), KIT-1 (Korean Institute of Technology), IBN (Institute of Bioengineering and Nanotechnology) and FDU-n (Fudan University)), the family of MCM-n can be regarded as one of the most studied. Because of their unique properties, MCM-41 have found uses in many biological applications such as drug delivery or cell imaging, cell labeling, and catalysis for catalyst adsorption and enzyme immobilization [3].

The aim of this review is to offer an overview of the most common applications of functionalized MCM-41 in catalysis with a special emphasis in the methodology used to prepare the catalytic system. In the context of the present paper, the concept of functionalized MCM-41 encompasses organic functionalized groups, covalently attached to the silica matrix or forming ionic pairs, and the inclusion of other elements such as Al, B, and Zr into the silica framework or magnetic nanoparticles. Each application will be illustrated with recent examples from the literature, in particular from the period 2015–2018.
In detail, in Section 3.1 simple systems consisting in MCM-41 sieves containing acidic and basic moieties and mixed acid/basic functionalities will be discussed. In Section 3.2, the preparation of metallic complexes anchored onto the nanoparticle will be described. Section 4 is devoted to review the application of solid supported heteropolyacids endowed with improved thermal stability. The following section highlights the application of functionalized MCM41 to prepare supported metallic nanoparticles onto the silica framework (5). Finally, magnetic MCM-41 sieves, which allow a better separation and reuse of solid catalyst by simple application of an external magnetic field.

2. General Synthesis of Mesoporous Silicas (MCM-41) and Applications in Catalysis

The preparation of MCM-41 was first reported by scientists of the Mobil Company in 1992 in the context of a project of the company to find materials with pores larger than that presented by zeolites. Hence the name of the resulting materials, MCM, which stands for Mobil Composition of Matter.

The synthetic methodology is based on the condensation of silica precursors, typically sodium silicate or tetraethylorthosilicate, in the presence of cationic surfactants under basic conditions [4]. In fact, this procedure is an adaptation of the method described by Stöber in 1968 for obtaining silica nanoparticles. In particular, the standard preparation consists of mixing a silicate precursor, usually tetraethylorthosilicate (TEOS), with a cationic surfactant, such as a cetyltrimethylammonium bromide (CTAB), at a temperature between 30 and 60 °C and pH = 11. The nanoparticles are formed by the sol-gel process catalyzed in basic medium [1,5].

In the first stage of the process, the hydrolysis of the alkoxide takes place. Then, the silanol groups polymerize by condensation, forming three-dimensional structures linked by siloxane bonds (Si-O-Si). In the following step, the presence of cylindrical micelles formed by the surfactant is critical, since they act as a template and will give rise to the formation of the pores. The cationic surfactant attracts the negative charges of the silica species, which are concentrated around the micelles forming a tubular silica structure. The nanoparticle increases in size until the negative charge, introduced by the silica species, is so high that it stops growing. It should be noted that the size, hexagonal shape and regularity of the particles depend on various variables such as temperature, rate of addition, agitation and the amount of catalyst used with respect to that of TEOS [1,5].

Finally, the surfactant should be removed from the inside of the pores. To do so, three methods have been recommended: reflux in acidified alcohol with hydrochloric acid, treatment with ammonium nitrate or by calcination. These treatments allow the rupture of the electrostatic interaction that exists between the groups of the cationic surfactant head and the anionic silicates, which facilitates the elimination of the surfactant in the mesopores and the final formation of the particles (Figure 1) [1].

![Figure 1. Preparation of MCM-41.](image-url)
A distinctive characteristic of MCM-41 is the presence of two defined surfaces: an internal one (pores) and an external one (Figure 2). The regioselective modification of the nanoparticles with functional groups makes MCM-41 highly versatile and enables them to perform specialized tasks, such as cooperative catalysis [4]. Two methodologies allow the functionalization of MCM-41: grafting and co-condensation. The so-called grafting is a post-synthetic method that allows the modification of the surface of the nanoparticle by incorporating functional groups by silanization. In this process, silanol groups (Si-OH) at the surface act as anchoring points when treated with a functionalized siloxane bearing the desired group (e.g., APTMS (3-aminopropyltrimethoxysilane)). Silanization proceeds either through free groups of (≡Si-OH) or silanol geminal groups (=Si(OH)₂). Importantly, the original structure of the mesoporous support is maintained after grafting (Figure 2). The co-condensation method is fundamentally based on the sol-gel process. The difference lies in the simultaneous addition of a functionalized siloxane with the silica precursor (TEOS). In comparison with the post-graft method in which the distribution of the functional groups tends to be heterogeneous, the co-condensation method is able to homogeneously distribute organic groups on the inner surface of the pores. Another advantage of the co-condensation method over the grafting method is that the morphology of the molecular sieve can be more easily controlled. In any case, each of the two functionalization methods has certain advantages. Direct functionalization of the surface in a single step of synthesis is easily achieved by grafting. However, if it is desired to obtain a homogenous and uniform surface, the co-condensation method is probably more practical.

![Figure 2](image-url). Regioselective di-functionalization of MCM-41.

3. Superficially Functionalized MCM-41

3.1. MCM-41 for Basic and Acid Catalyst

As stated before, the surface of MCM-41 can be relatively easily derivatized, allowing the introduction onto the silica of a wide variety of functional group such amines, thiols or carboxylic acids. The introduction of such functionalities opens the door to the design of tailored catalysts to perform specific tasks [6]. Arguably, in catalysis the most common functional groups introduced onto MCM-41 are amines and sulfonic acids.

3.1.1. Amino Functionalization: NH₂-MCM-41

In 2013, Mirza-Aghayan et al. [7] reported the use of NH₂-MCM-41 for the synthesis of 4H-chromene and 4H-benzo[b]pyrans as basic catalyst (Figure 3). The interest of these heterocycles lies on their pharmacological activity, mainly as anticoagulant and anticancer drugs. The NH₂-MCM-41 were prepared using the grafting methodology. Briefly, MCM-41 were refluxed in toluene in the presence of 3-aminopropyltriethoxysilane (APTES). The three-components reaction (aldehyde, malononitrile and a 5,5-dimethyl-1,3-cyclohexanedione or 1-naphthol) afforded the 2-amino-tetrahydro-4H-chromene derivatives with good to excellent yields (ca 69–90%) using only 10 mol.% of the catalyst, whereas 2-amino-4H-benzo[h]chromene derivatives required a 20 mol.% (69–93%).
Figure 3. Synthesis of 4H-chromene and 4H-benzo[b]pyrans.

The following year, Nale et al. [8] reported on the synthesis of quinazoline-2,4(1H,3H)-dione derivatives from 2-aminobenzonitriles and carbon dioxide under high pressures conditions (3.5 MPa) in aqueous medium using amine functionalized MCM-41 as catalyst. The authors claim that the synthetic methodology can be applied for the synthesis of several biologically active derivatives such as prazosin, bunazosin and doxazosin. According to the report, after completion of the reaction, NH$_2$-MCM-41 could be reused for five consecutive recycles without any significant loss in its catalytic activity (Figure 4).

Figure 4. Synthesis of quinazoline-2,4(1H,3H)-dione derivatives.

The same group [9] investigated the application of NH$_2$-MCM-41 catalysts for the reaction of carbon dioxide and aziridines yielding 5-aryl-2-oxazolidinones. Oxazolidinones are very versatile heterocycles used in organic synthesis as chiral auxiliaries. Furthermore, some derivatives are key intermediates compounds in the preparation of drugs such as linezolid (Zyvox), posizolid and torezolid. The catalyst was prepared following the co-condensation method by reaction of TEOS with 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (AEPTMS) (Figure 5).

5-aryl-2-oxazolidinones were prepared in good yields (65–99%) and excellent regioselectivity under mild and solvent free conditions in the presence of a 14.6 wt.% of amine functionalized MCM-41.
The authors claim that the developed catalyst can be easily separated by filtration. Then, after a washing process with water and a posterior drying, the nanocatalysts could be reused for successive reactions up to five consecutive recycles at least, without apparent loss of activity. A tentative mechanism of the reaction is depicted in Figure 6.

![Proposed plausible catalytic reaction pathway. Reproduced with permission from [9]. Copyright 2014 Elsevier B.V.](image)

Treatment of calcined MCM-41 (Figure 7) with 3-trimethoxysilylpropylethylenediamine, allowed Choudary et al. [10] the preparation of diamino functionalised MCM-41 sieves. The resulting molecular sieves were studied as catalyst for the aldol and Knoevenagel condensation reactions under very mild conditions. The Knoevenagel condensation renders the product with excellent yield, between 75 and 100%. Whereas the aldol condensation gave lower yields, ranging between 68 and 100%.

![Preparation of diamino-functionalised mesoporous material by anchoring 3-trimethoxysilylpropylethylenediamine moiety on calcine MCM-41. Reproduced with permission from [10]. Copyright 1999 Elsevier B.V.](image)

Another example of NH$_2$-MSN-41 for the catalysis of the Knoevenagel condensation was reported in 2015 by Zhao et al. [11]. The reaction was conducted in water and under microwave irradiation. The results showed comparable catalytic efficiencies than those obtained with the homogeneous propylamine base-catalyst (99%). Obviously, the advantage of the heterogeneous system is that it can be easily reused, in this case up to eight times. The same year, the group of Rößner et al. [12] prepared MCM-41 functionalized with quaternary amino groups by grafting pristine MCM-41 with N-(trimethoxysilyl)propyl-N,N,N-trimethylammonium chloride (TMTMAC) in toluene at reflux. The catalytic features of the system were studied using the Knoevenagel condensation of benzaldehyde...
and malononitrile as model reaction. The authors highlighted the importance of the homogeneity of the distribution of the quaternary amino group to obtain good catalytic activities.

Aminated MCM-41 are interesting catalysts from an industrial perspective given the stability and intrinsic reusability of these particles. Recently, Trisunaryanti et al. [13] reported the use of NH2-MCM-41 in the transesterification of vegetable oils to prepare biodiesel fuel from waste cooking oil. In the same work, the reaction conditions were optimized. It was concluded that applying a 4 wt.% catalyst/waste cook at a methanol/waste cook mole ratio of 15 produced a 49.98% of the desired product.

3.1.2. Acid-Derivatized MCM-41

The need for green processes have stimulated the application of solid supported acids, which minimize production of acidic waste and toxic effluents from mineral acid. In this regard, the silanol groups present on the surface of MCM-41 provide a convenient anchoring point for the inorganic sulfonic acid functionality (-SO3H), which is arguably the most studied acid group [14] (Figure 8).

Figure 8. Preparation of SO3H-MCM-41.

Sulfonic acid functionalized MCM-41 are used as catalyst for the synthesis of a wide variety of products. A survey of applications of such catalyst have been reviewed elsewhere [14]. Recent examples are the synthesis of benzal-1,1-diaceate [15], a solvent-free synthesis of 2H-indazolo [2,1-b]phthalazine-1,6,11-trione derivatives [16]; multicomponent synthesis of 1H-pyrazolo[3,4-b]pyridines and spiro-pyrazolo-[3,4-b]pyridines [17]. Another important field of application of sulfonic functionalized MCM-41 is the development of “green processes”, for instance, in the production of biodiesel [18,19]. In this regard a recent work, [20] reported a “green synthesis” of 2-amino-6-(hydroxymethyl)-8-oxo-4-aryl-4,8-dihydropyrano[3,2-b]pyridines (Figure 9).

Figure 9. SO3H-MCM-41-catalyzed synthesis of 2-amino-dihydropyrano[3,2-b]pyrane derivatives. Reproduced with permission from [20]. Copyright 2015 Springer.

Apart from the treatment of chlorosulfonic acid, SO3H-MCM-41 can be easily synthesized by anchoring 3-((3-(trimethoxysilyl)propyl)thio)propane-1-sulfonic acid onto MCM-41-type by means of the grafting methodology. The performance of these acidic sieves as catalyst was evaluated using the multi-component synthesis of 1H-pyrazolo[3,4-b]pyridines and spiro-pyrazolo-[3,4-b]pyridines. Typical yields of these syntheses ranged from 84 to 96%. The resulting catalyst could be recycled and reused with negligible loss in activity over seven cycles (Figure 10) [17].
was influenced by the pore architecture (Figure 11) [18]. The optimal conditions were found to be: 5.06 wt.% catalyst loading, 120 min, 153 °C, and 0.266 of MPMDS molar composition. Using such conditions, the corresponding fatty acid methyl ester was prepared in 95.5% yield. The performance of the catalyst was benchmarked against H2SO4 and proven to be more effective. Additionally, the catalyst could be reused up to four cycles under the optimum reaction conditions without significant loss of product yield (Figure 12).

A similar catalyst was introduced by Samart et al. [19] in 2016 for the production of biodiesel from Hevea brasiliensis oil. The authors investigated the effect on the reaction of four parameters to optimize the process: catalyst loading, reaction time, temperature and MPMDS molar composition. The optimal conditions were found to be: 5.06 wt.% catalyst loading, 120 min, 153 °C, and 0.266 of MPMDS molar composition. Using such conditions, the corresponding fatty acid methyl ester was prepared in 95.5% yield. The performance of the catalyst was benchmarked against H2SO4 and proven to be more effective. Additionally, the catalyst could be reused up to four cycles under the optimum reaction conditions without significant loss of product yield (Figure 12).
In 2014 Vrbková et al. [22] studied the aldol condensation of 4-isopropylbenzaldehyde (iPB) and propanal (PA) to yield foryclamaneldehyde (2-methyl-3-(4-isopropylphenyl)prop)-2-enal, FCA) under acidic and basic conditions using functionalized MCM-41 as catalysts. The condensation products were obtained in excellent yields (87–96%). The catalyst was prepared by nucleophilic substitution of chloro-functionalized MCM-41 with the aminoacid (Figure 13). This methodology was applied for the synthesis of 3-(2-furylmethylene)-2,4-pentanedione in 92% yield.

More recently, in 2017 Appaturi et al. [21] prepared DL-Alanine functionalized MCM-41 catalyst for the Knoevenagel reaction. The condensation products were obtained in excellent yields (87–96%). The catalyst was prepared by post-grafting of pristine MCM-41 with 3-mercaptopropyl)triethoxysilane (3-cyanopropyl)trichlorosilane and N-[3-(trimethoxysilyl)propyl)]ethylene-diamine. The synthetic procedure is outlined in Figure 14.
The best results, in terms of conversion and selectivity, were obtained using SO$_3$H-MCM-41. Interestingly, the SO$_3$H-MCM-41 catalyst only yielded 4-isopropylbenzoic acid. While the basic catalyst shown almost no activity. The authors suggest that the good performance of SO$_3$H-MCM-41 was due to the synergic effect of acid –SO$_3$H groups and acid –OH groups of MCM-41 (cf. 3.1.3). The optimization study of the reaction concluded that the optimal reaction conditions were found to be 50 wt.% of SO$_3$H-MCM-41, 100 °C and toluene as solvent. These conditions lead to a 69% conversion of 4-isopropylbenzaldehyde after 24 h and 65% selectivity to the final product.

3.1.3. Difunctionalized MCM-41

Biological reactions are commonly mediated by synergistic catalytic processes. The extraordinary efficiency and selectivity of these transformations are greatly dependant on the positions and relative distances of the active sites. In order to mimic these natural systems and to achieve such level of complexity, a rigid support is needed to arrange the proper functional groups with a specific geometry. In this context and due to the chemical versatility and particular geometry, MCM-41 emerge as an ideal building block for the design of bifunctional catalysts for tandem reactions.

A first example was presented in 2007 by Asefa et al. [23] who reported the application of amino-functionalized MCM-41 for the Henry synthesis (nitroaldol). These researchers observed differences in the conversion of the Henry reaction depending on the relative amount of amino groups and silanols and their spatial distribution. Surprisingly, MCM-41 functionalized with a lower number of amino groups displayed a superior catalytic activity. This result was rationalized in terms of increase of cooperative sites, since amino groups and silanols are found spatially spaced (Figure 15). Such catalysts were prepared either by reacting excess amounts of APTMS in ethanol or by postgrafting smaller amounts of the aminoorganosilane in toluene for a short reaction time.

![Figure 15](image-url)

**Figure 15.** Reaction mechanism to explain the enhanced efficiency of AP-E1 (a) in the Henry reaction relative to AP-T1 and AP-T2 (b). The presence of a significant number of spatially isolated silanol groups in AP-E1 leads to activation of the carbonyl group of benzaldehyde for nucleophilic attack. Reproduced with permission from [23]. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGAA, Weinheim.

In 2016 the Henry reaction catalyzed with MCM-41 was revisited. Collier et al. [24] studied the aldol and nitroaldol reaction mechanisms using a Hammett analysis to determine the effects on the catalytic activity of electron-donating and electron-withdrawing groups on para-substituted...
benzaldehydes. Furthermore, the cooperative effect of the silanol groups was assessed by reacting these groups with hexamethyldisilazane (HMDS). As a result of such capping, both reactions required more elevated temperatures to achieve measurable conversion and reduced the observed TOF values in comparison to catalysts with free silanols groups (Figure 16).

![Figure 16. Proposed mechanism for the aldol condensation of acetone and para-substituted benzaldehydes on amino-silica cooperative catalyst. Reproduced with permission from [24]. Copyright 2015 American Chemical Society.](image1)

Mukhopadhyay et al. [25] designed a functionalized MCM-41 for the preparation of substituted 2-arylbenzothiazoles by reaction of o-aminothiophenol disulfides and aldehydes through the cleavage of the S-S bond (Figure 17). The catalyst was prepared in two synthetic steps. First, MCM-41 and 3-chloropropyltrimethoxysilane (CTMS) were refluxed for 24 h in acetonitrile. Then, the resulting chloro functionalized MCM-41 were treated with 2-(piperazin-1-yl)pyrimidine) to afford the catalyst. The mechanism of the reaction and role of the catalyst were carefully studied. According to the authors, the acidic character of MCM-41 assists in the formation of an imine between the aniline and benzaldehyde and the cleavage of the disulphide bond. The 2-(piperazin-1-yl)pyrimidine moiety would be responsible for the last dehydration step, which affords the aromatic thiazole ring. The reaction for the synthesis of the heterocycles was conducted in water under a steady flow of oxygen. Typical yields of the benzothiazoles were in the range of 85 up to 98%.

![Figure 17. MCM-PP (3) catalyzed synthesis of benzothiazoles. Reproduced with permission from [25]. Copyright 2015 American Chemical Society.](image2)

The aforementioned reports base the cooperativity in the catalytic activity on the coexistence of a silanol with an additional group (amine, SO$_3$H). In 2011, Huang et al. [26] reported the preparation
of bifunctional MCM-41 decorated with site-separated amino and sulfonic groups. More specifically, the sulfonic moieties were introduced by co-condensation of TEOS and STMOS, while the amino groups were grafted selectively onto the external surface of the nanoparticle. This regioselectivity was achieved by reacting APTMOS and the MCM-41 with the template (CTAB) still inside the cavities, therefore the grafting only affected the external surface of the silica matrix. The detailed synthetic route is depicted in Figure 18. This bifunctional catalyst was applied for the one-pot, two-steps reaction of acetals to render \( \alpha, \beta \)-unsaturated nitro compounds.

![Figure 18. Syntheses of bifunctional mesoporous silica nanoparticles having sulfonic acid groups on the internal surface and organic amine groups on the external surface. Reproduced with permission from [26]. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.](image)

A different approach to prepare bifunctional catalyst was proposed the following year by Studer et al. [27]. Instead of taking advantage of the mesoporous structure, this novel methodology relies on the functionalization of the MCM-41 by means of orthogonal click reactions namely thiol–ene reaction, Cu-catalyzed 1,3-dipolar alkyne/azide cycloaddition, and a radical nitroxide exchange reaction. The synthetic pathway is straightforward and consists of the co-condensation of two orthogonally functionalized tetraethoxysilanes. As an example, in Figure 19 the functionalization of MCM-41 with sulfonic and amino groups is outlined. In short, TEOS 1, azide-terminated triethoxysilane 2 and 7-octenyltrimethoxysilane 6 were mixed under basic conditions to give azido-alkene bifunctionalized MCM-41 (10). In turn, azides reacted with terminal alkynes (4) in the presence of \( \text{Cu(SO}_4\text{)}_2 \) furnishing triazoles, which allowed the introduction of a sulfonic acid moiety. Moreover, olefins underwent addition of sulphides in the presence of \( 2,2'\text{-Azobis(2-methylpropionitrile)} \) (AIBN). This reaction led the introduction of amines by treatment of the MCM-41 11 with 8 and AIBN.
In 2013, the same group prepared and tested bifunctional mesoporous silica sieves bearing a Pd-complex and basic sites in order to introduce a cooperative active catalyst in the allylation of ethyl acetoacetate (Tsuji-Trost reaction) [28]. Functionalization of the MCM-41 was effected by post-modification using click chemistry with orthogonal siloxane as has been described before. The structure of some of the systems prepared are shown in Figure 20. The selectivity of mono versus double alkylation was achieved by control of reaction temperature (RT, 30, or 70 °C) and the nature of the catalyst. With systems 17 and 18 the reaction proceeded smoothly and the monoallylated product was obtained almost in quantitative yield. Whilst catalyst 19 provided a 1:2 mixture of mono-(33%) and bisallylated product (66%).
Tsai et al. [29] prepared bifunctional MSN-41 catalysts intended for esterification reactions, containing a Brønsted acid site of diarylammonium triflate (DAT) and a pentafluorophenyl propyl (PFP) group (Figure 21). The high reactivity displayed by this system was attributed to the formation of a surface-bound hydrophobic layer of PFP molecules, which facilitates the extrusion of one of the reaction products (water) from the mesopores by suppressing water adsorption onto the surface, thereby shifting the reaction equilibrium to completion.

3.2. Metallic Complexes

The preparation of MCM-41 decorated with metallic complexes for catalysis has been a very active field of study in recent years. Two strategies are available to build these catalysts: grafting of properly functionalized complexes to the MCM-41 and multi-step functionalization of pristine catalysts.
MCM-41. The later methodology often entails the introduction of the amino functionality. Thus, complexes can be tethered to the MCM-41 by amine or imine linkages.

In 2014, Jabbari et al. [30], reported the encapsulation of salen copper(II) complexes. The catalyst was prepared by condensation of 5-bromo salicylaldehyde with NH$_2$-MCM-41 and the subsequent treatment of these sieves with Cu(NO$_3$)$_3$. This nanocatalyst was applied for the oxidation of sulphides into sulfoxides using urea hydrogen peroxide (UPH) as oxidant. The oxidation reaction was carried out in ethanol at room temperature. The selectivity of the transformation was excellent and typical isolated yield of the products was in the range of 91 to 98% (Figure 22).

![Figure 22. Synthesis steps of Cu-salen-MCM-41. Reproduced with permission from [30]. Copyright 2014 Springer.](image1)

Ghadermazi and Ghorbani-Choghamarani et al. [31] reported the preparation of Cu(II) immobilized on Serine@MCM-41. The catalytic system was prepared by refluxing MCM-41 with serine in distilled water for 48 h. Subsequently, this Serine@MCM-41 support was treated with Cu(NO$_3$)$_3$ at reflux in ethanol to afford Serine Cu(II)@MCM-41 (Figure 23). The resulting nanomaterials were studied as a green and efficient catalytic system for the synthesis of four types of compounds: polyhydroquinolins, 2,3-dihydroquinazolin-4(1H)-ones, sulphides, and sulfoxide derivatives. Noteworthy, the researchers studied carefully the copper leaching. Using ICP-OEIS, it was concluded that the amount of copper in the fresh catalyst and the used catalyst after 11 times recycling was 0.51 and 0.45 mmol g$^{-1}$, respectively, what is considered an excellent performance for such kind of catalysts.

![Figure 23. Synthesis of MCM-41@Serine@Cu(II). Reproduced with permission from [31]. Copyright 2018 Springer.](image2)
Hajipour et al. [32] prepared Cu(II) Et-S@MCM-41 (Catalyst A, Figure 24) in two synthetic steps: treatment of NH2-MCM-41 with two equivalents of 2-chloroethyl phenyl sulfide in acetonitrile at reflux and, then, complexation with Cu (II) by exposure of the functionalized MCM-41 to Cu(OAc)2·2H2O in ethanol. The catalyst was tested for the preparation of aryl benzyl sulphides using a one-pot thioetherification reaction of aryl halides with benzyl bromide and thiourea in water in the presence of K2CO3 at 100 °C under aerobic conditions. As anticipated, the reaction of aryl chlorides presented lower yields in comparison with aryl bromides, but yields were significantly increased at longer reaction times. When electron-poor aryl bromides and chlorides were used, benzyl aryl sulphides products were obtained in higher yields compared to electron-rich aryl bromides and chlorides.

![Image of the synthesis process of Cu(II)-Et-S@mcm-41 in the three separate steps.](image)

**Figure 24.** Synthesis process of Cu(II)-Et-S@mcm-41 in the three separate steps. Reproduced with permission from [32]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In 2016, Cai et al. [33] reported the immobilization of 1,10-phenanthroline-copper (I) complex. This catalytic system was designed for the cross-coupling reaction of aryl iodides with aliphatic alcohols. The reaction of iodobenzenes with aliphatic and benzylic alcohols in the presence of 2 equivalents of Cs2CO3 as base provided the corresponding ethers in yields up to 94%. The authors examined the stability of the catalyst by using ICP analysis. The results confirmed that after eight consecutive runs, only 1.3% of copper had been lost from the support. This analysis is in agreement with an additional experiment carried out to confirm that the reaction is actually catalyzed by the heterogeneous catalyst. Briefly, after conversion of 50%, the catalyst was removed and the solution was allowed to react. After the removal of the catalyst, no further conversion was detected. The use of recyclable copper catalyst along with mild and environment-friendly reaction conditions make this methodology a powerful complement to the traditional C-O coupling reactions. The preparation of the catalyst is delineated in Figure 25.

![Image of the preparation of MCM-41-1, 10-phen-CuI.](image)

**Figure 25.** Preparation of MCM-41-1, 10-phen-CuI. Reproduced with permission from [33]. Copyright 2016 Royal Society of Chemistry.
Liu et al. [34] immobilized the complex shown in Figure 26 by electrostatic interaction. The authors reported that the catalyst was capable to effect an efficient conversion of methane into methanol without over-oxidation under ambient conditions. The efficacy of the system to mediate the catalytic conversion of these light alkanes in natural gas into liquid oxidized products was also assessed. The catalyst was prepared by ion exchange via electrostatic attraction with MCM-41 modified by grafting with anionic 3-(trihydroxysilyl)-propylmethyl-phosphonate (TP).

MCM-41-supported N_2O-type Schiff base complexes were prepared by condensation of 4-methyl-2,6-diformylphenol (DFP) with APTMS modified molecular sieves. Subsequent treatment with the appropriate Cu(II) and Ni(II) salts afforded active nanocatalysts useful for esterification, Diels-Alder cycloaddition and aldol condensation. The results were moderate to excellent regardless the metal of the complexes. Typical yields ranged from 70 up to 86%. Furthermore, the complexes were thermally stable at the reaction conditions and no leaching of the complexes was observed [35] (Figure 27).

A different approach to prepare immobilized Schiff base complexes was presented by Rangappan et al. [36] in 2016. This group designed a synthetic pathway based on the preparation of a siloxane bearing a preformed Cu(II) complex. Subsequently, this compound was anchored onto the MCM-41 by grafting (Figure 28). The as-synthesized Cu-Schiff base MCM-41 catalyst was tested for Ullmann-type coupling reaction of the aryl halides with aryl halides, phenols, amines and N-heterocyclic amines. The yields of the coupling were excellent using DMSO as solvent. As expected, iodo-aromatics provided the best yields, ranging from 85 to 90%. The catalyst was recovered and could be reused by simple filtration.
Palladium chemistry plays a pivotal role in modern organic synthesis. Palladium-based catalysts are employed in a significant number of modern synthetic transformations such as Tsuji-Trost allylation, hydrogenations, Stille, Heck, Suzuki, and Sonogashira cross-coupling reactions [37]. However, the use of homogenous Pd(0) complexes usually require a purification step for the catalyst removal. Therefore, the immobilization of palladium can simplify the synthetic procedures. In this sense, encapsulation in MCM-41 turns out to be advantageous [38,39].

Tsai et al. [40,41] studied a highly-efficient and recyclable MCM-41 anchored palladium bipyridyl complex-catalyzed (Figure 29). The MCM-41 were prepared by grafting of the palladium bipyridyl complex onto pristine MCM-41. This catalyst was applied for the Sonogashira coupling of heteroaryl halides and acyl chlorides with terminal alkynes. Yields were high in both cases, ranging from 58 to 96%. According to the authors, satisfactory results can be achieved with catalyst loadings as low as 0.002 mol.% Pd.

![Figure 28](image1.png)

**Figure 28.** Synthesis of Cu-Schiff base MCM-41 complex. Reproduced with permission from [36]. Copyright 2016 Springer.

![Figure 29](image2.png)

**Figure 29.** MCM-41 anchored to palladium bipyridyl complex-catalyzed. Reproduced with permission from [41]. Copyright 2009 Elsevier B.V.
Dibenzo-18-crown-6 functionalized MCM-41 were prepared by Yousefi et al. [42] by reacting aminopropyl-grafted MCM-41 with 4′,4′′-diformyl-dibenzo-18-crown-6. The catalyst was very efficient for nucleophilic ring opening of oxirans in water with cyanide and azide. The reaction was carried out in water, and a variety of azidohydrins and cyanohydrins was obtained with yields between 75 and 93%. It is worth to mention that the nucleophilicity of the anion could be tuned by using the proper cation. Thus, the use of potassium salts reduced the time of reaction up to 40%. This result was rationalized in terms of better complexation of the K⁺ by the crown-ether due to the size of the cavity. Remarkably, no evidence for diols formation as reaction by-product was observed (Figure 30).

![Figure 30](image-url). Operation of catalyst in presence of nucleophile salt. Reproduced with permission from. [42] Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Nikoorazm et al. [43] anchored a palladium S-benzylisothiourea complex on functionalized MCM-41 as an efficient and reusable catalyst. This MCM-41 catalyst was used for the synthesis of 5-substituted 1H-tetrazoles. This synthesis is predicated on the [2 + 3] cycloaddition reaction of various organic nitriles with sodium azide in poly(ethylene glycol) as green solvent as a palladium complex (Figure 31).

![Figure 31](image-url). Synthesis of palladium anchored on functionalized MCM-41. steps. Reproduced with permission from [43]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fadhli-Fraile et al. [44] also used Ti/MCM-41, titanium grafted on the silica surface through the formation of Si-O-Ti bonds, for use in the epoxidation of styrene with tert-butyl hydroperoxide (THP). The catalyst was synthesized by pre-treatment of the surface of the scaffold with Ti(Oi-Pr)₄ as titanium precursor. Then, diethyl l-tartrate or diisopropyl l-tartrate (0.4 mmol) was added to the MCM-41. The resulting suspension was refluxed in toluene for 12 h to yield the desired catalyst (Figure 32).
According to the authors, Ti/MCM-41 is an active catalyst for the epoxidation of styrene with THP. However, its efficiency was not optimal, probably due to the subsequent epoxide rearrangement to phenyl acetaldehyde.

![Figure 32. Possible surface Ti species. Reproduced with permission from [44]. Copyright 2016 Elsevier B.V.](image)

Zhou and He et al. [45] anchored RhCl(CO)(PPh$_3$)$_2$ to diphenylphosphinopropyl modified (–PrPPh$_2$) MCM-41 with the aim to prepare a catalyst for the hydroformylation 1-octene. The catalytic sieves were prepared by grafting of MCM-41 with CPTMS. In the following step, diphenylphosphine was introduced by nucleophilic substitution. Finally, the as-synthetized material was exposed to PhCl(CO)(PPh$_3$)$_2$ to yield the heterogeneous catalyst. The system exhibited moderate conversions (about 84%) with loading of 1.5 wt.% in Rh. The synthetic pathway for the preparation of the functionalized particles is delineated in Figure 33.

![Figure 33. Preparation of M–PrPPh2Rh catalyst. Reproduced with permission from [45]. Copyright 2008 Springer.](image)
Havasi et al. [46] used a nickel complex anchored onto MCM-41 for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones, which are an important class of fused heterocycles with a range of pharmacological and biological activities, as antibacterial, antitumor, analgesic, antibiotic and antidepressant agents. These heterocycles were synthetized by cyclocondensation of 2-aminobenzamide with aromatic aldehydes under mild reaction condition in polyethylene glycol molecular weight 400 (PEG-400) as solvent (90–98% yield). The catalyst was prepared in two synthetic steps. First, chloro-substituted MCM-41 was obtained by grafting using CPTMS. Then, the particles were treated with dithizone in dimethylformamide at 110 °C for 30 h. Finally, the later material was refluxed in ethanol in the presence of Ni(NO₃)₂.

Wang et al. [47] synthesized Zr-Schiff base/MCM-41 using the methodology delineated in Figure 34. This catalyst was applied for the conversion of fructose into 5-hydroxymethylfurfural (HMF). The Zr/MCM-41 shown a superior activity than pure MCM-41 because of the Lewis acidity of the metal. The authors studied the effects of reaction variables such as reaction time and temperature using DMSO as solvent. The best result was obtained at 140 °C, after 4 h of reaction. The optimized yield was 92%. In addition, other sugars were also used as substrates for the synthesis of HMF. Unfortunately, the results were not as satisfactory as the observed ones for fructose.

Figure 34. Zr(IV)-salen-MCM-41 synthesis to catalyze fructose. Reproduced with permission from [47]. Copyright 2018 Elsevier B.V.

Molibdenum and Tungsten complexes [MX₂(CO)₃(L)₂] (M = Mo, W; X = I, Br; L = 2-amino-1,3,4-thiadiazole) were immobilized in MCM-41 and their catalytic activity was assessed. As delineated in Figure 35, 2-amino-1,3,4-thiadiazole was attached onto the MCM-41 by refluxing the chlorinated MCM-41 with the ligand in benzene. The required starting material was prepared by grafting of pristine MCM-41 with 3-chloropropyltriethoxysilane. Afterwards, the required complexes were prepared by exposure of the functionalized MCM-41 to the corresponding metallic salt in presence of a base. The supported complexes were tested as catalysts for the epoxidation of several olefins in the presence of tert-butyl hydroperoxide (TBHP). The conversions and TOF significantly depend on the complex and the substrate. However, the authors conclude that, in general, the immobilization of the catalysts improved their performance [48].
Mikoorazm et al. [49] prepared Co(II), Fe(III), Ni (II) and Zn(II) Schiff base complexes anchored on the internal surface of MCM-41 pores. The synthesis of these catalysts required aminopropyl functionalized MCM-41 as starting material. These mesoporous molecular sieves were reacted with 3,4-dihydroxybenzaldehyde under ethanol reflux. Subsequently, the resulting material was treated with the corresponding metallic salt to furnish the aforementioned catalysts. These catalysts exhibited good selectivity and catalytic activity in the oxidation of sulfides to sulfoxides and oxidative coupling of thiols to their corresponding disulfides using urea hydrogen peroxide (UHP) as oxidant at room temperature. The authors highlighted the absence of over-oxidation of sulfides and thiols to sulfoxides and sulfones, respectively [50] (Figure 36). A similar system was prepared by Rangappan et al. [51] by condensation of 3-aminopropyltrimethoxysilane with o-hydroxyacetophenone and exposure to Cu(CH$_3$COO)$_2$·H$_2$O to form a complex, which mimics the “CuN$_2$O$_2$” coordination site that resembles the galactose oxidase enzyme.

\[ \text{Schiff base on MCM-41 intended for the enantioselective oxidative dimerization of 2-naphtol to R/S BINOL (1,1’-Bi-2-naphthol) in the presence of oxygen. The catalyst was obtained by reaction of the Mn(III) complex with pyridine functionalized MCM-41 as depicted in Figure 37. In turn, the pyridine moiety was introduced by imine formation between an amino functionalized MCM-41 and 4-pyridinecarboxaldehyde. In the presence of a substoichiometric amount of the nanocatalyst, as low as 20 mg, binapthols were obtained in nearly quantitative yields with high enantioselectivity of up to 91% ee. These results are comparable with those found for the homogeneous catalyst.} \]

**Figure 35.** Synthesis of Materials MCM-Pr, MCM-L, and MCM-C1 to MCM-C5. Reproduced with permission from [48]. Copyright 2015 American Chemical Society.

**Figure 36.** Preparation of ordered MCM-41 mesoporous silica containing Cobalt, Niqel, Iron, and Zinc Schiff base complex.

In 2015, the group of Bania et al. [52] reported the preparation of immobilized Mn(III)-chiral Schiff base on MCM-41 intended for the enantioselective oxidative dimerization of 2-naphtol to R/S BINOL (1,1’-Bi-2-naphthol) in the presence of oxygen. The catalyst was obtained by reaction of the Mn(III) complex with pyridine functionalized MCM-41 as depicted in Figure 37. In turn, the pyridine moiety was introduced by imine formation between an amino functionalized MCM-41 and 4-pyridinecarboxaldehyde. In the presence of a substoichiometric amount of the nanocatalyst, as low as 20 mg, binaphthols were obtained in nearly quantitative yields with high enantioselectivity of up to 91% ee. These results are comparable with those found for the homogeneous catalyst.
Porphyrrins are among the most studied ligands in catalysis for the stabilization of high-valence cations. In 2015, Kong et al. [53] communicated the preparation of [5,10,15,20-tetrakis-(pentafluorophenyl)porphyrin] manganese immobilized on amino-functionalized MCM-41 (Figure 38). The porphyrin was axially coordinated to the catalyst by means of complexation of the amino group. The catalyst was applied for the hydroxylation of naphthalene in the presence of m-chloroperbenzoic acid as the co-oxidant. The system showed an average conversion of up to 31% and good selectivity 1-naphtol/2-naftol. According to the authors, this low conversion, in comparison with the homogeneous catalyst, can be explained by the axial coordination between manganese cation and the amino group. The catalyst could be reused several times (>5) without any apparent loss of activity.

Quijada et al. [54] used MCM-41 impregnated with a zirconium catalyst (Me₂Si(Ind)₂ZrCl₂) for the preparation of nanocomposites through the in situ polymerization of propylene. Three different methodologies for impregnation of the zirconocene were evaluated (Figure 39). Two of the methodologies pre-treat the MCM-41 support with co-catalyst methylaluminoxane (MAO) but differ in drying temperature and catalyst concentration. The third methodology consists of the

**Figure 37.** Synthesis of MCM-41 supported Mn-Schiff base complexes. Reproduced with permission from [52]. Copyright 2015 Royal Society of Chemistry.

**Figure 38.** Synthesis of the Mn(TF₅ PP)-MCM-41 catalyst. Reproduced with permission from [53]. Copyright 2015 Elsevier B.V.

**Figure 39.** Synthesis of MCM-41 supported Mn-Schiff base complexes. Reproduced with permission from [53]. Copyright 2015 Elsevier B.V.
pre-activation of the catalyst with MAO, followed by impregnation onto the MCM-41. The later procedure achieved about 50% higher activities compared to the other pre-activated metallocene/MAO catalysts. The smaller impregnation time and the significantly lower Zr loads are other advantages of this protocol.

Figure 39. Methodologies of impregnation for Me₂Si(Ind)₂ZrCl₂/NMCM-41. Reproduced with permission from [54]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.3. MCM-41 Functionalized with Metallic Complexes for Enzyme Entrapment

Mesoporous silica materials have been shown to be efficient supports for immobilization of enzymes. These heterogeneous catalysts have been explored extensively in organic catalysis because they can provide important advantages over the free enzyme, such as improved enzyme recovery and reutilization, easy continuous operation, higher stability of the immobilized enzyme in terms of temperature and pH. [55,56]. All of these materials exhibit very similar chemical properties, but hexagonally ordered pore size of MCM-41 are smaller (20–40 Å) than other mesoporous silica materials, such as SBA-15 (60–150 Å) and MCF (200–420 Å), restricting the enzyme loading on the pore system [57,58].

However, enzymes such as cytochrome c, lysozyme, lipase, and albumin have been successfully immobilized onto the surface of functionalized ordered mesoporous materials MCM-41. A pioneering study was reported by Diaz and Balkus in 1996 [59]. In this regard, a simple strategy for the conjugation of MCM-41 with enzymes is based on the formation of metallic chelates between the two moieties.

Faramarzi-Khoobi et al. [60] took advantage of this strategy for the immobilization of a lipase. To do so, polyethylenimine (PEI) coated MCM-41 was prepared by treatment of MCM-41 with [3-(2,3-epoxypropoxy)propyl] (EPO) in toluene at 80 °C. The, the resulting solid was exposed to different solutions of divalent metal ions (Co²⁺, Cu²⁺, and Pd²⁺). Finally, the surface of the molecular sieve was coated with the lipase through the formation of a chelate. The ions facilitate the adsorption thanks to the interaction of the thiol group of cysteine (Cys), indole group of tryptophan (Trp), and imidazole ring of histidine (His) present on lipase surface. The catalytic activity of the immobilized lipase was studied in the esterification reaction of ethanol with valeric acid. The resulting ester, ethyl valerate (green apple flavor), was obtained in good yield (60%).
4. MCM-41 as Support for Immobilization Heteropolyacids

The use of heteropolyacids (HPAs) or their more often used equivalent polyoxometalates (POMs) in acid catalyzed reactions has attracted increasing attention in the last years especially for their application in processes requiring high acidic conditions [61]. Chemically, HPAs possess both redox potential and Brønsted acidity, structural flexibility and can stabilize cationic organic intermediates. Moreover, these reagents are used in several industrial processes since they are relatively stable, strongly acidic and many of the environmental pollution and corrosion problems of the traditional technologies are avoided.

Arguably, the most important and common HPAs for catalysis are of Keggin structure, which comprise heteropolyanions of the formula \( \text{[XM}_{12}\text{O}_{40}]^{n-} \), where \( X \) is the heteroatom (P, Si, etc.) and \( M \) the addendum atom (Mo, W, V etc.), because of the higher thermal stability and easier preparation compared to others species [62]. However, the use of HPAs has encountered some difficulties, which have reduced their application in some organic transformations. The main drawbacks of this class of catalysts include high solubility in polar solvents, weak thermal stability, low specific surface area and difficulty of recovery [63,64].

To circumvent these issues, the immobilization of heteropolyacids on inorganic supports has been suggested. In this regard, MCM-41 are especially promising because they can improve their catalytic activity thanks to their high specific surface area and pore volume [65]. Furthermore, the regular pore structure and tuneable pore size enables rapid diffusion of reactants and products through the pores to minimize consecutive reactions. Usually, tungsten HPAs, in particular 12-tungstophosphoric acid (\( \text{H}_3\text{PW}_{12}\text{O}_{40}, \text{HPW, TPA} \)), are the catalysts of choice considering their stronger Brønsted acidity, lower oxidation potential and higher thermal stability [66–71].

In general, HPAs have been introduced inside the pore structure of MCM-41 by common impregnation techniques involving passive diffusion of poly-oxometalate anions into the pores of mesoporous silica [72–74]. Unfortunately, the HPA/MCM-41 impregnated system commonly lacks of stability in polar medium because of species are not anchored strongly onto the surface. In an attempt to diminish the leaching of HPAs, functionalization of MCM-41 with an alkyl amine or other functional groups bearing positive charges on the surface for supporting heteropolyacids has been studied extensively.

In 2006, Valente et al. [75] reported the use 12-tungstophosphoric acid (HPW) supported on different MCM-41 hybrid composites for the conversion of xylose to furfural in liquid phase and they compare the catalytic performance between them and the unsupported HPW catalyst. The heteropolyacid was immobilized in medium-pore (MP) and large-pore (LP) MTS silicas by incipient wetness impregnation, giving materials with HPW loadings in the range of 15–34 wt.%. Besides, HPW was also heterogenized in aminopropyl functionalized MP and LP silicas at loadings of 15.3 and 30.6 wt.%, respectively. These catalysts exhibited higher activity than homogeneous PW, and were comparable with \( \text{H}_2\text{SO}_4 \) under similar reaction conditions, achieving a yield of 58%. The study showed that the catalytic performance of the HPW-supported catalysts depends on the interplay of several variables, such as the preparation method, type of support, HPW loading, temperature (140–160 °C) and type of solvent (toluene/water or DMSO). According to the characterization data, the authors concluded that catalytic results were at least be partly related with the presence of stronger host–guest interactions in these materials, which lead to better dispersions of the polyoxotungstate anions.

HPW anchored on amino-functionalized MCM-41 (Figure 40) was also used for the oxidesulfurization of dibenzothiophene (DBT) by Zhu et al. [76]. In an attempt to produce zero sulfur fuel and reduce the \( \text{SO}_2 \) emission, reaction conditions including HPW loading, reaction time, catalyst dosage, molar ratio of \( \text{H}_2\text{O}_2 \) to sulfur (O/S) and reaction temperature were investigated. The results showed excellent catalytic activity in the ultra-deep desulfurization of fuel oils with a conversion of DBT up to 100% when the reaction was conducted using 20% HPW–\( \text{NH}_2 \)-MCM-41 at 333 K. Noteworthy, the catalyst could be recovered by simple filtration retaining its high catalytic
activity up to five runs. The authors concluded that the good recoverability of HPW–NH$_2$–MCM-41 catalyst was attributed to HPW species are chemically immobilized on the surface of modified MCM-41.

Figure 40. Schematic procedure for the surface modification of MCM-41 silica and the subsequent immobilization of 12-tungstophosphoric acid (HPW). Reproduced with permission from [76]. Copyright 2010 Elsevier B.V.

Immobilization of phosphotungstic acid with Wells–Dawson structure (H$_6$P$_2$W$_{18}$O$_{62}$, D-HPW) on different amino siloxane functionalized MCM-41 was studied by Ding and Han et al. [77]. The amino siloxanes (3-aminopropyltrimethoxysilane (KH-540), N-(2-aminoethyl)-3 aminopropyltrimethoxysilane (KH-792) and 3-[2-(2-aminoethylamino)ethylamino]-propyl-trimethoxysilane (NQ-62)) were chosen as the grafting agents. Firstly, MCM-41 was functionalized with the amino siloxanes and, afterwards, the polyoxometalate was introduced by wet impregnation method. The catalytic activities of the three catalysts were compared with pure MCM-41 for the gas phase dehydration of glycerol to acrolein. The best catalytic performance was achieved using D-HPW/NQ-62-MCM-41. The strong interaction between amino siloxane and D-HPW generated strongly distorted heteropolyanions on the surface of the host materials. The authors suggested that this highly deformed structure probably rendered H$^+$ more active and resulted in an increase of Brønsted sites and a decrease in the amount of Lewis sites. Accordingly, glycerol conversion and acrolein selectivity was improved with the increase in the number of amine groups, D-HPW/MCM-41 < D-HPW/KH-540-MCM-41 < D-HPW/KH-792-MCM-41 < D-HPW/NQ-62-MCM-41. Modification with amino siloxane also improved the catalyst stability, decreasing the leaching ratio and the amount of coke formation. The amine groups not only interacted with the heteropolyanions slowing the leaching but also behaved as basic sites and decrease the total acidity, which was beneficial to suppress the coke formation. In order to study the recovery the D-HPW/NQ-62-MCM-41 catalyst, burn the soft coke, and avoid the decomposition of NQ-62 and D-HPW, thermogravimetric analysis was carried out. The results established that the treatment of D-HPW/NQ-62-MCM-41 catalyst at 350 °C under an oxygen flow for 3 h enables the reusability of the catalyst with a slight decrease in glycerol conversion and acrolein selectivity.

The catalytic activity of HPAs can be improved by partial substitution of redox metal ions in Keggin structure, among which the introduction of vanadium has been demonstrated to be beneficial for redox catalysis. On this subject, amino-functionalized MCM-41 has been used to strongly immobilize through hydrogen interactions a new series of vanadium-substituted phosphotungstates (Figure 41) [78]. Modification of the mesoporous materials has been accomplished using APTES as the grafting agent. Subsequently, HPW (H$_3$[PW$_{12}$O$_{40}$]) and different vanadium substituted polyoxometalates (H$_4$[PVW$_{11}$O$_{40}$], H$_5$[PV$_2$W$_{10}$O$_{40}$] and H$_6$[PV$_3$W$_9$O$_{40}$]) have been introduced inside the pores by wet impregnation. The catalytic performance of these hybrid materials has been compared...
in the selective oxidation of benzyl alcohol to benzaldehyde. The results have established that the catalytic activity to be as follows: HPW < H₃[PVW₁₁O₄₀] < H₆[PV₃W₉O₄₀] < H₅[PV₂W₁₀O₄₀], reaching 97% of conversion and 99% of selectivity in the oxidation of benzyl alcohol when H₃[PV₂W₁₀O₄₀] is employed. Using optimum reaction conditions; 30% aqueous H₂O₂ as oxidant, 0.05 g of catalyst, 5 mL of toluene as solvent, 4 mmol alcohol, H₂O₂/benzyl alcohol ratio = 5:1 at 80 °C for 8 h, the generality of the reaction has been studied. The study has verified that conversion depends on the alcohol nature: aromatic alcohols (82–100%) > cyclohexanol (~80%) > aliphatic alcohol chains (15–27%). Noteworthy, the catalyst can be recovered and reused without appreciable loss of activity. Then, it can be concluded that the hybrid system is a highly efficient recyclable catalyst for the selective oxidation of aromatic alcohols to the corresponding aldehydes.

Figure 41. Schematic representation of vanadium-substituted phosphotungstic acids immobilized on amine-functionalized mesoporous MCM-41. Reproduced with permission from [78]. Copyright 2014 Elsevier B.V.

In some applications, the presence of the support is critical in order to achieve high reaction selectivity. An example of such effect was reported by Popa et al. [79]. In 2017, these researchers carried out the preparation of novel catalysts based on molybdophosphoric acid H₃PMo₁₂O₄₀ (HPM) and molybdovanadophosphoric acid H₄PVMo₁₁O₄₀ (HPVM) Keggin-type HPAs by supporting on amino-functionalized MCM-41 and SBA-15 molecular sieves. The authors conducted thermal analysis to determine the effect of the support on heteropolyacid stability. An important mass loss above 543–553 K was observed, probably due to decomposition of amino propyl functional groups. The catalytic activity of HPA/MCM-41-NH₂ and HPA/SBA-15-NH₂ was tested for vapor-phase ethanol dehydration reaction, between 463 and 543 K of temperature range in nitrogen and air atmospheres. The results displayed an enhanced oxidation catalytic activity (formation of acetaldehyde) and a lower acid catalytic activity (formation of ethylene and diethyl ether) compared to the unsupported catalyst. At 463 K, a good selectivity was achieved albeit yields were low. However, between 483 and 503 K, acetaldehyde was obtained in high selectivity and at good values of conversion.

Ren et al. [80] reported the preparation of di-vacant Keggin based lacunary silicious polyoxometalate [γ-SiW₁₀(H₂O)₂O₃₄]¹⁻ supported on MCM-41 (physisorbed) and amino-functionalized MCM-41 (chemisorbed). Both materials were employed to investigate their activity and reusability for the oxygenation of organic sulphides using H₂O₂. To this end, MCM-41 was functionalized with APTES and then the amino moieties were protonated with nitric acid to anchor the polyoxometalate (Figure 42). The recyclability of both physisorbed and chemisorbed catalysts were tested, and the latter was clearly advantageous in maintaining full reactivity throughout recycling. The decrease in activity for the physisorbed catalyst was likely caused by the loss of catalyst back into solution. The reactivity of chemisorb catalyst was examined with several other substrates under similar conditions, revealing its utility in the removal of refractory sulfides via oxidative desulfurization. The study revealed that the selectivity to convert sulfide into the sulfoxide entirely before the appearance of sulfone was 90% using methyl phenyl sulfide and 75% using diphenylsulfide as substrates.
In addition, the inorganic–organic hybrid catalyst was recovered and reused for seven reaction runs with only slight loss of the catalytic activity.

In addition to amino-propyl grafting, other aminated modifiers have been examined. In 2015, Tayebee et al. [81] designed a novel pyridine-functionalized mesoporous MCM-41 material (TPI-MCM-41). The MCM-41 support was functionalized via co-condensation of hydroxyl groups of the support and ethoxy groups of the TPI (N-[3-(triethoxysilyl)propyl]isonicotinamide) linker (Figure 43). The heteropolyacid (H₄SiW₁₂O₄₀) was anchored to TPI-MCM-41 through electrostatic interaction in a second step. The authors fully characterized the catalysts by using various analyses such as XRD, SEM, EDX, UV-Vis, DTA-TGA, DLS, and FT-IR spectroscopy. The obtained catalyst exhibited a good dispersion of the heteropolyanions on the solid support surface and its structure was preserved after TPI immobilization. The catalytic performance of the catalyst was assessed for the one-pot synthesis of 1-amidoalkyl-2-naphthols by condensation of β-naphthol and benzaldehyde with benzamide under solvent-free conditions. The authors compared the catalytic activity of the silicotungstic Keggin-type heteropolyacid (H₄SiW₁₂O₄₀) with several heteropolyacids (H₅PMo₁₂O₄₀ (Keggin), H₃PW₁₂O₄₀ (Keggin), H₄P₂W₁₈O₆₂ (Wells–Dawson), H₆P₂Mo₁₈O₆₂ (Wells–Dawson), H₄SiW₄Mo₂O₄₀ (Si-substituted mixed metal lacunary Keggin) and H₄SiW₄Mo₃O₄₀ (Si-substituted mixed metal Keggin)). The novel system showed the best catalytic activity (95% of yield) when compared with these heteropolyacids (75–80% yield). Moreover, the catalytic performance of the catalyst was compared with some mesoporous and heteropolyacid systems reported previously in the literature (H₄P₂W₁₈O₆₂/TPI-CNT, H₅PW₁₀V₂O₄₀/TPI-SBA-15, H₅PW₁₀V₂O₄₀/Pip-SBA-15, H₆P₂W₁₈O₆₂/TPI-AlSBA-15). The results revealed the superior catalytic activity of the new TPI-MCM-41 support (94% of yield) in front of the SBA-15 systems (yields ranging between 33–55%). In addition, the inorganic–organic hybrid catalyst was recovered and reused for seven reaction runs with only slight loss of the catalytic activity.

![Figure 42. Functionalization and impregnation of MCM-41 silica. Conditions: (a) 6 M HCl reflux; (b) dried in oven at 100 °C and refluxed in toluene with attached Dean–Stark trap; (c) reflux in toluene with APTES; (d) suspend in DCM with 2 equiv. HNO₃; (e) suspend in acetonitrile solution of 1γ-SiW₁₀O₃₄(H₂O)₂⁺]. Reproduced with permission from [80]. Copyright 2014 Elsevier B.V.
The preparation of the hybrid material POM@MOF-199 was carried out by a one-pot method in the pore of MCM-41 (POM@MOF-199@MCM-41) was designed by Zhao et al. [84]. The increment of POM content in the MOF/MCM-41 structure.

PMo12W6O40@MOF-199@MCM-41 exhibited the highest desulfurization reactivity (98.5% DBT conversion) and the highest level of reusability. Additionally, a series of PMo12−xWxO40/MCM-41 ratios (20%, 40%, 60% and 80%) and different phosphomolybdenum polyoxometalates were explored. The results showed that conversion of DBT increased with the W loaded amount. Among the supported heteropolyacid catalysts, the PMo6W6O40@MOF-199@MCM-41 showed superior performance, which could be enhanced with an increment of POM content in the MOF/MCM-41 structure.

An alternative strategy to immobilize HPAs in MCM-41 is predicated on (POM)-based metal–organic framework (MOF). MOF are crystalline porous coordination polymers composed of inorganic clusters bridged by organic ligands which possess a 3D ordered porous structure [82]. POM-based MOF materials normally contain POM units and thus, generate MOF materials with open network structures [83]. POMs can be either directly part of the frameworks of MOFs or can be encapsulated within the cavities of the MOFs networks.

Following this approach, a novel catalyst containing (POM)-based metal–organic framework (MOF) in the pore of MCM-41 (POM@MOF-199@MCM-41) was designed by Zhao et al. [84]. In detail, MOF-199 is a kind of micropore MOF with Cu(II) dimers linked into paddlewheels by 1,3,5-benzenetricarboxylic acid (BTC), owning two types of cages of cuboctahedral symmetry (Figure 44). The preparation of the hybrid material POM@MOF-199 was carried out by a one-pot POM template self-construction of MOF-199 in the pore of MCM-41 via the hydrothermal method. The catalyst was synthetized mixing Cu(NO3)2·3H2O, PMo12−xWxO40 and MCM-41 in a water solution. Afterwards, (CH3)4NOH·5H2O (TMA) and BTC were added with stirring. Finally, the mixture was heated at 180 °C for 16 h in an autoclave. The hybrid POM/MOF material was exploited in the direct oxidative desulfurization of fuel oil, using dibenzothiophene (DBT) as model, in the presence of O2 as oxidant. In order to prove the synergistic effect of the hybrid system, the oxidative desulfurization rate of POM@MOF-199 and POM@MCM-41 was analyzed. As expected, POM@MOF-199@MCM-41 exhibited the highest desulfurization reactivity (98.5% DBT conversion) and the highest level of reusability. Additionally, a series of PMo12−xWxO40/MCM-41 ratios (20%, 40%, 60% and 80%) and different phosphomolybdenum polyoxometalates were explored. The results showed that conversion of DBT increased with the W loaded amount. Among the supported heteropolyacid catalysts, the PMo6W6O40@MOF-199@MCM-41 showed superior performance, which could be enhanced with an increment of POM content in the MOF/MCM-41 structure.
The incorporation of metal nanoparticles in the pores of MCM-41 produce materials with interesting catalytic capabilities [87]. The effect of the mesoporous support is twofold: the aggregation of metal nanoparticles is prevented and its dispersion is enhanced. Several methods have been reported in the literature for the preparation of MCM-41 supported metal nanoparticles, which can be categorized into two groups [88]. The first one, the so-called two-step procedure, relies on the embedding of the MNP through simple physical entrapment into the pristine MCM-41. The main disadvantage of this procedure is the possible leaching of the metal species leading to the formation of large particles because of the weak interaction between the catalyst and the silica framework [89].
The second one requires the preparation of functionalized MCM-41 with organic ligands containing one or more heteroatoms. The role of these ligands is to interact by electrostatic or non-covalent forces with the MNP avoiding migration.

A wide variety of catalytic systems using MNP supported on MCM-41 have been reported. Most of these nanomaterials have been proposed as catalysts for applications in organic synthesis. A clear example is the use of palladium nanoparticles for the catalysis of organometallic cross-coupling reactions \[88,90\]. Another metal that has lately received attention is gold, which is highly selective in hydrogenation and oxidations and plays a major role in A^3 coupling reactions, which involves multicomponent reactants \[91\]. Nickel and titanium nanoparticles have found also many applications as catalysts for hydrogenation of aromatics and epoxidations reactions \[92\]. Finally, ruthenium is employed for industrial processes such as the synthesis of paraffins, methanation of CO, or hydrogenations \[93\].

5.1. Palladium Nanoparticles Supported on MCM-41

The Suzuki reaction is one of the most versatile palladium-catalyzed cross-coupling reactions. This transformation requires as coupling partners a boronic acid and a halogenated derivative and is usually catalyzed by Pd^0 complexes.

In order to simplify the workup of the reaction, several groups have reported the encapsulation of Pd nanoparticles inside the MCM-41 channels. An example of this kind of system was reported by Yamashita et al. \[90\]. Interestingly, the authors proved that the performance of the catalyst can be enhanced if the template (CTAB) was inside the mesoporous sieves due to the basic character of the MCM-41. It was hypothesized, that more active Pd nanoparticles were generated when the template was kept within the silica framework in comparison with the removed ones. Such assumption was proven for the catalytic activity of the Suzuki reaction using Pd/MCM-41 (CTAB) and Pd/MCM-41 (non-template). The results showed a catalytic activity of 100% when the template was kept within the silica framework, whereas only a 50% of conversion was achieved when the template had been previously removed.

In 2015, Wan et al. \[88\] proposed a similar methodology. This group developed a Pd/MCM-41 catalyst by using (NH_4)_2PdCl_4 as Pd precursor. The authors postulated that surfactant micelles, which were used as a scaffold for the MCM-41 formation, helped the grafting of Pd species. As a result, highly dispersed Pd nanoparticles could be immobilized inside the channels of mesoporous SiO_2 through a one-pot reaction (Figure 45), whereas merely non-encapsulation was achieved when the CTAB was previously removed. Accordingly, these Pd nanoparticles were well protected by the channels avoiding any leakage, showing a high catalytic activity (96% of conversion for iodobenzene to biphenyl) and notable cyclability.

![Figure 45](image-url) One-pot synthesis route for Pd/MCM-41. Reproduced with permission from \[88\]. Copyright 2015 Royal Society of Chemistry.
Another relevant palladium-catalyzed reaction is the Heck coupling between olefins and organohalides. A catalyst intended for this coupling was presented in 2017 by Azarooon et al. [94]. In this catalyst, the Pd nanoparticles were immobilized by interaction with the macrocyclic ligand dibenzo-18-crown-6-ether (cf. 0), which was previously attached to the MCM-41 by means of amine groups (Figure 46). The incorporation of the nanoparticles was achieved thanks to the use of palladium acetate as a source of the metal, which was reduced to Pd0 in ethanol and stabilized within the cavity of dibenzo-18-crown-6-ether. Therefore, Pd aggregation was prevented and a high degree of metal dispersion was attained. The synthesized catalyst was successfully used for the coupling of iodobenzene and styrene. The best reaction conditions (92–98%) were found to be using water as solvent at 90 °C and in the presence of K2CO3 as base.

The presence of doping atoms within the silica framework makes a great impact in the catalytic performance of the catalyst. Bearing in mind this concept, Stepnicka et al. [95] reported the preparation of doped MCM-41, with aluminium, caesium and potassium cations as doping agents. Pd salts were incorporated within the mesoporous through a wetness method and posterior reduction of the salt with tetrabutylammonium acetate. The performance of this catalyst was assessed using the cross-coupling reaction of bromobenzene and butyl acrylate as model reaction. The authors reported that Pd@Cs+-{(Al)MCM-41 displayed a superior catalytic activity compared to related catalysts in terms of turnover number and turnover frequency [96].

Kawanami et al. [97] investigated the effect of boron as a dopant to enhance the dispersion of Pd nanoparticles. The supported catalyst was synthesized by a hydrothermal method. Briefly, CTAB, H3BO3, and a Pd salt were added sequentially to a sodium hydroxide solution. The analysis of the nanomaterial revealed that Pd particle size was dependant on the Si/B ratio, the higher the content of B the higher size of the Pd nanoparticle was. The catalytic activity of such materials was tested for the hydrogenation of nitrobenzene to aniline in supercritical CO2. The catalyst was compared with similar systems containing Al and Ga in their structure—instead of B, obtaining a faster reaction when boron was found within the silica framework [98].

By applying the same concept, Yan et al. [99] developed a series of Pd nanoparticles supported on MCM-41 for the production of biofuel γ-valerolactone (GVL) and valeric acid (VA) from biomass-derived levulinic acid (LA). The best catalytic conditions for LA hydrogenation was 5 wt.% of Pd-MCM-41, obtaining a 96.3% of GVL production at 240 °C for 10 h. In 2018, the same group [100] showed that LA can be selectively transformed into GVL and VA through Pd nanoparticles supported onto MCM-41 doped with Al (Al/MCM-41). The experiments performed with Pd/AlMCM-41 showed that the best catalytic transformation (88.5% of GVL) was achieved with 5 wt.% Pd/AlMCM-41 within...
A critical step in the preparation of the Pd nanoparticles is the reduction of Pd salts. This transformation can be achieved by many reductants, including sodium borohydride, hydrazine or a flow of H₂ (5%) [99]. Alternatively, grafted Pd nanoparticles can be produced by using hydride-functionalized MCM-41. The hydride was introduced to the silica surface through grafting procedure. Because of the strong reductive character of silicon hydride, Pd salts were immediately reduced to Pd(0) leading to the formation of small metal nanoparticles. Interestingly, conventional reducing agents produced metal aggregation, hence catalytic activity is clearly diminished. TEM and BET observations concluded that Pd nanoparticles were preferentially located in the outer part of the MCM-41, which is consistent with the presence of hydride groups. The obtained system was used as a catalyst for methane oxidation, obtaining better activity than Pd-SBA. Hydride groups in the latter catalytic system were preferably located in the inner part of the particle due to presence of large pores, hence reactants were less capable to reach the active sites [101].

5.2. Gold Nanoparticles Supported on MCM-41

Gold is a usual metal catalyst for the A³ multicomponent coupling of aldehydes with alkynes and amines, which leads to the formation of propargyl-amines. Typically, cationic gold species present the best catalytic activity. Unfortunately, these catalysts are quickly reduced to non-active Au species during the activation of alkynes/alkenes.

With the aim to overcome this drawback, Feiz and Bazgir et al. [91] prepared gold nanoparticles supported on thiol functionalized MCM-41 (MCM-SH). The introduction of such functional group was achieved by sequential treatment of MCM-41 with thionyl chloride and 2-mercaptoethanol. Finally, an Au salt was dispersed within the silica matrix and reduced to metallic Au using NaBH₄ (Figure 47). Gold nanoparticles were immobilized within the silica matrix due to the electrostatic/covalent bond between the metal and the thiol group.

![Figure 47. Schematic description for preparation of Au@HS-MCM nanocomposite. Reproduced with permission from [91]. Copyright 2015 Elsevier B.V.](image_url)

The optimal catalytic activity of these MCM-41 in the catalysis of the A³ coupling reaction was achieved using a loading of 2 mol.% Au, a temperature of at 80 °C and water as a solvent. The catalyst could be recovered and reused 5 cycles without a significant loss of activity. The proposed reaction mechanism starts with the alkyne absorption on a gold atom at the support interface, followed by its deprotonation. This intermediate reacted with an iminium cation, formed from the condensation of the aldehyde and the amine, affording the corresponding propargylamine (Figure 48).
Although it is well established that -SH groups improves the dispersion of the MNP onto the surface of the MCM-1, Yang et al. [102] demonstrated that amines display a similar effect thanks to the formation of a partial covalent bond. Au catalyst prepared using this methodology have showed highly stable and reusable capability while recycling the same sample.

Accordingly, Au nanoparticles deposited on functionalized NH$_2$-MCM-41 have been studied as catalysis of different types of reactions. In 2018, Qu et al. [103] studied the oxidation of HCHO in Au/NH$_2$-MCM-41. The authors reported that formaldehyde activation merely depended on the oxidation state of Au and its particle size. The results established that the best catalytic activity was obtained with Au nanoparticles of 2–4 nm, which were highly dispersed on the silica framework thanks to the amine groups. Moreover, amine groups partially inhibited the reduction of Au (electron-deficient) to Au$^0$. The coexistence of both species along with the optimal size of the MNP (2–4 nm) provided the highest HCHO oxidation at 55 °C, whereas non-aminated MCM-41 required 200 °C due to the presence of gold aggregations.

Yang et al. [102] compared the catalytic performance of gold nanoparticles supported on aminated MCM-41 and SBA for the aerobic oxidation of 1-phenylethanol and some para-derivatives. The best catalytic results were observed in the case of NH$_2$-MCM-41 with a 2.4 wt.% of Au and a size of 1–3 nm. Interestingly, molecular sieves with a higher gold weight ratio (10.3%) produced metal nanoparticle aggregates of about 5–15 nm. Again, the formation of these aggregates reduced the oxidation activity. The authors concluded that the degree dispersion of Au is of paramount importance for the reaction yield.

Besides, Finashina et al. [104] studied the intramolecular hydroamination of 2-(2-phenylethynyl)aniline to form 2-phenylindole. As mentioned above, the presence of amine groups within the silica matrix prevents Au agglomeration leading to small metal nanoparticles (3 nm), while Au aggregates were formed in the non-aminated MCM-41. A yield of 22% was obtained for this catalyst system, whereas a 72% was achieved by the -NH$_2$ functionalized one.

A different approach was presented in 2001 by Satry et al. [105], to obtain gold nanoparticles in amine functionalized MCM-41. The methodology relies on spontaneous reduction of chloroaurate ions within the silica matrix (Figure 49). It was hypothesised that hydroxy groups spontaneously reduce chloroaurate ions on the inner surface of the silica support. Thus, the gold nanoparticles are formed within the pores due to the interaction between the amine and the hydroxy functionality. The as-synthesized catalyst showed a good catalytic activity for the hydrogenation of a broad substrate scope. For instance, styrene was hydrogenated to ethylbenzene in a 30% of conversion and a 100% of selectivity [106].
Alternatively, bimetallic nanoparticles with Au-Pt were synthesized by simultaneous reduction of HAuCl₄ and HPtCl₆ by NaBH₄. These metals were deposited into an amino functionalized MCM-41. The catalytic activity for the hydrogenation of aromatic nitro compounds of Au-Pt/MCM-41 was found to be superior to monometallic Au nanoparticles [107] (Figure 50).

![Figure 49](image1.png)

**Figure 49.** The probable structure of the NH₂-MCM-41 material before and after immersion in HAuCl₄ solution. Reproduced with permission from [105]. Copyright 2001 Royal society of chemistry.

Interestingly, Ratnasamy et al. [108] used the same catalyst for the selective oxidation of CO in the presence of an excess amount of H₂. The authors reported that the best Au:Pt ratio was 5:95 decreasing the amount of CO to 0.3% at moderate temperatures (80 °C), whereas almost non-conversion was found for monometallic or bimetallic with higher rates of Au. Moreover, its activity was not even increased at higher temperatures (150–200 °C). It is worth noting that at such conditions, the oxidation of H₂ was enhanced, while the oxidation activity of CO decreased. This bimetallic catalyst was used for 16 h with no apparent deactivation.

On the other hand, Mou et al. [109] studied the CO oxidation using as catalyst Au and Ag. Catalyst introduction was successfully achieved through the dispersion of AuCl₄⁻ and AgNO₃ followed by a posterior reduction with a H₂ flow. Besides, amine functionalization of MCM-41 enabled to control the size of the bimetallic nanoparticles from 4–6 nm to 20 nm [110,111]. Thereby, its catalytic activity was enhanced achieving a reaction rate of 1.097 mol g⁻¹ h⁻¹ with a ratio of Au:Ag = 8:1 at 30 °C. Surprisingly, the catalyst was still active working at 79 °C after one year of storage at ambient conditions.

C. Torres et al. [112] developed a series of Au/MCM-41 catalyst modified with Ti, instead of -NH₂ or -SH groups, in order to achieve a good dispersion and stabilization of gold nanoparticles within the framework. The catalytic test for hydrogenation of nitro compounds showed that modified Au-MCM-41 with Ti gave a better conversion rate than the unmodified catalyst. The improvement of the catalytic activity was ascribed to the effect of Ti on the gold nucleation and growth as the structural characterization pointed out.
Similarly, Yamashita et al. [113] used doped silica framework with Ti (Ti/Si = 0.01) for the preparation of H2O2. Again, the presence of Ti enhances metal dispersion within the MCM-41. Besides, the photocatalytic character of such dopant allows the metal nanoparticle formation through the photo assisted deposition method (Figure 51). Palladium nanoparticles were successfully deposited onto Ti/MCM-41 and its catalytic activity was tested in the production of H2O2 from H2 and O2 and compared to the typical impregnation method obtaining a concentration of 50 and 30 mM of H2O2, respectively. Notably, bimetallic Au-Pd were also deposited within a Ti modified MCM-41 through the photocatalytic deposition method achieving a higher H2O2 formation than the Pd monometallic catalyst.

![Figure 51. The formation of charge transfer excited state with tetrahedrally coordinated Ti oxide moiety within Ti-MCM-41 by UV light irradiation and its application for the synthesis of nano-sized metal particles. Reproduced with permission from [113]. Copyright 2009 Springer.](image)

Clearly, the presence of doping atoms into the silica matrix imparts a strong effect on the performance of the catalyst. Another example was given by Pescarmona et al. [114] who studied the incorporation of gold nanoparticles within Sn modified MCM-41 through impregnation method and posterior calcination. Au catalyst and Sn-MCM-41 possess two independent important roles for the selective transformation of glycerol. The first one promotes the oxidation of glycerol to trioses, whereas the solid acid Sn-MCM-41 catalyzes the rearrangement of the intermediate trioses to methyl lactate. Au/Sn-MCM-41 showed better catalytic performance than a benchmark solid acid catalyst (zeolite). The authors postulated that the best catalytic activity for the glycerol conversion was achieved with a particle size of 3 nm.

5.3. Nickel Nanoparticles Supported on MCM-41

MCM-41 supported nickel catalysts have attracted wide attention for their extensive applications in industrial processes such as hydrogenation of aromatics, production of synthesis gas, methanation of CO2, and syngas methanation [92].

Immobilization of nickel nanoparticles inside of MCM-41 (Figure 52) was achieved by using H2N-MCM-41 by Zhu et al. [92]. As stated before, amino functionalization was reported to inhibit the aggregation of MNP on the mesoporous enhancing their dispersion. The resulting catalyst was applied for the methanation of synthetic gas. The stability of the system was carefully studied since the formation of [Ni(CO)4] during the catalytic process, which deactivates the catalyst. Gratifyingly, such deactivation was not observed when using amino-functionalized MCM-41 as support, because of
the low formation of the later complex. Furthermore, the presence of amine groups in the catalysts avoided metal sintering, increasing its thermal stability and hence the catalytic activity.

A different approach to avoid the aggregation and migration of metal nanoparticles to the outer part of the silica framework is predicated on the incorporation of a doping agent within the silica matrix [95].

In this regard, Williams et al. [115] employed aluminium salts in order to create acidic sites within the silica framework of the MCM-41. The resulting nanomaterial was studied for the biomass gasification of wood sawdust to produce H2. The catalyst was stable and no sintering was observed after the gasification at 800 °C. The same system was studied for the oligomerization of ethylene and compared to two typical acidic porous aluminosilicates: nanocrystalline β-zeolite and silica-doped alumina Siralox-30 by Martínez et al. [116]. The authors concluded that the production of oligomers with more than 5 carbon-chain was maximal, with a value of 12 mmol/(Kg_catalyst · s), for the case of Ni/Al-MCM-41.

In 2018, Abu-Darieh et al. [117] introduced gallium as a doping agent to develop a potential Ni/MCM-41 catalyst for methane reforming. The authors reported that Ga affected the surface area, decreasing the number of basic sites and then increasing the catalytic activity. The 2% gallium loading showed the highest methane conversion of 88%. In the same year and with the same aim, Wang et al. [118] prepared an analogous system but replacing Ga with CeO2. The introduction of CeO2 improved the stability and the reduction of nickel species inside the mesoporous support, resulting in a good stability and better catalytic activity.

Pirouzmand et al. [119] prepared Ni/MCM-41 by direct synthesis and wet impregnation methods with the aim of study the template effect in the CO2 hydration catalysis. The authors employed a calcination method to remove the template from Ni/MCM-41 and compared its catalytic activity to Ni/MCM-41 containing the template inside the pores. As a result, the template-containing catalyst displayed a higher catalytic activity, probably due to the presence of strong basic sites, which lead to a major grafting of metal nanoparticles within the silica matrix. Zheng et al. [120], studied the same effect in a catalysis for the hydrodechlorination of 1,2-dichlorethane. By contrast to the later report, these authors reported that the strong electrostatic repulsive interactions between Ni (II) and CTAB lead to aggregation of Ni nanoparticles upon calcination resulting in a low dispersion of the nickel source (Ni(NO3)2) into the mesopores of MCM-41.

5.4. Ruthenium Nanoparticles Supported on MCM-41

Supported ruthenium nanoparticles have emerged as versatile catalysts in industrial processes such as hydrogenation and oxidation reactions. Carrillo et al. [121] reported the use of an amino functionalized MCM-41 catalyst which enhance the dispersion of Ru nanoparticles inside the support by covalent interaction between the metal and the ligand. Therefore, the leaching of metal nanoparticles

![Figure 52. Schematic representation of NiO/NH2-MCM-41. Reproduced with permission from [92]. Copyright 2016 Royal Society of Chemistry.](image_url)
was precluded. The resulting materials showed high catalytic activity in a tandem oxidation-Wittig olefination of different benzyl alcohols (Figure 53).

In 2016, Roy et al. [122] developed a Ru nanoparticles supported on a CeO$_2$ doped MCM-41 for the treatment of phenol-containing wastewater. The use of metal catalysts for the removal of such pollutants represents a more environmentally friendly alternative, in contrast to the most commonly used methods such as incineration and biological treatments. The main drawbacks of these methods are the generation of noxious compounds and highly toxic effluents. On the other hand, the use of unsupported metal catalyst is not recommended because of their low reusability. For this reason, Ru nanoparticles on a silica support have been proposed to overcome this issue. Moreover, doping of the MCM-41 framework with 14 wt.% CeO$_2$ enhanced the dispersion of the metal catalyst (93%) and inhibited its aggregation. This catalytic system was employed in the wet air oxidation of phenol achieving up to 99% of conversion and could be used up to 15 days without any leaching of the catalyst.

Another example of Ru nanoparticles supported on MCM-41 was reported by Liu et al. [93]. This group synthesized a series of zirconia-modified MCM-41 supported ruthenium-lanthanum catalysts by double solvent impregnation method. The purpose of the synthesized catalyst was the hydrogenation of benzene to cyclohexene, which is a valuable intermediate for the synthesis of nylon-6 and nylon-66. The critical issue in this procedure is to avoid the over-oxidation of cyclohexene to cyclohexane. Thereby, it is relevant to promote the desorption of the previously hydrogenated cyclohexene from the catalytical system. To this end, the modification of MCM-41 with zirconia creates a thin layer of water that improves the hydrophilicity of the silicate matrix promoting the desorption of the synthesized cyclohexene. The authors have postulated that tetragonal zirconia-modified MCM-41 (Figure 54) showed higher hydrophilicity and more abundant surface hydroxyl groups than MCM-41 modified by monoclinic and amorphous zirconia. Moreover, tetragonal zirconia MCM-41 supporting ruthenium showed a better performance in the hydrogenation of benzene to cyclohexene (55.8%). It is noteworthy, that cyclohexene selectivity (82.1%) was enhanced due to the hydrophilicity introduced by tetragonal zirconia.

![Figure 53](image1.png)

**Figure 53.** Proposed mechanism for the alcohol oxidation-Wittig olefination showing alcohol oxidation and olefination as coupled processes. Reproduced with permission from [121]. Copyright 2017 Royal Society of Chemistry.

![Figure 54](image2.png)

**Figure 54.** Zirconia-modified MCM-41 supported Ru-La catalyst. Reproduced with permission from [93] Copyright 2014 Elsevier B.V.
5.5. Titanium Nanoparticles Supported on MCM-41

TiO$_2$ is a widely used photo-catalyst due to its lower cost, nontoxic nature and chemically inertness. Unfortunately, during the preparation process, the oxide can easily agglomerate what leads to a material with an unsatisfactory catalytic performance. To optimize the performance and inhibit the aggregation of the catalyst, the use of MCM-41 as support have been recommended.

In 2015, H. Entezari et al. [123] studied the encapsulation of TiO$_2$ within the silica framework for the removal of sulphur compounds of liquid hydrocarbon fuels. The authors reported that the catalytic activity of supported TiO$_2$ was higher than the unsupported ones due to long-lived photo induced charge separation, large pore size and high specific surface of MCM-41, which can adsorb some bulky species. However, TiO$_2$ exhibits low catalytic activity under visible light conditions because it has a large band gap energy of 3.2 eV corresponding to a threshold wavelength of 388 nm. In order to overcome such issue, the doping of the silica framework with non-metallic elements such as carbon, sulphur and nitrogen have become an interesting strategy for improving the visible light activity of the catalyst. Among them, the authors selected carbon as doping agent of MCM-41 to enhance visible light activity of TiO$_2$/MCM-41. Thereby, carbon modified TiO$_2$/MCM-41 catalyst was used for the oxidative desulfurization of dibenzothiophene under visible light and mild conditions within 5 h achieving a photocatalytic degradation of 95.6% for DBT with Si/Ti = 5 ratio. Moreover, the catalyst system could be reused at least two times without a significant loss of catalytic activity.

In 2017, Yamashita et al. [124], prepared TiO$_2$/MCM-41 catalyst with alkali metal cations embebed (Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) within its pores. In this regard, a previous post-modification of the MCM-41 with carboxylic acid groups was needed. Therefore, alkali cations were successfully anchored onto the silica matrix by an ion-exchange process. This catalytic system was assessed for the photocatalytic degradation of phenol in water under UV light irradiation (Figure 55). It was concluded that the strong interaction between the aromatic ring and the alkali metal cations, was responsible for the high catalytic activity observed.

![Figure 55. Schematic illustration of alkali metal cations-anchored mesoporous silica with catalytic centres. Reproduced with permission from [124]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.](image)

Pescarmona et al. [125] studied the functionalization of Ti/MCM-41 with methyl groups in order to increase the hydrophobicity of the support, which minimize the presence of water within the pores and stabilize the MNP. Besides, the diffusion of non-polar alkenes through the pores is favored. Ti/MCM-41 methyl functionalized was satisfactory synthesized by hydrothermal method and was tested for the epoxidation of cyclohexene obtaining a higher TOF in comparison with the unmodified Ti/MCM-41. On the other hand, a complete regeneration of the catalyst through simple washing was not achieved. It was reported that a gradual deposition of the product on the catalyst inhibits the conversion of cyclohexene.

6. Magnetic Core Shell Nanoparticles

As stated before, MCM-41 are endowed with ideal features as supports in catalysis because of the inherent stability of SiO$_2$ and the ordered mesoporous structure, which allow a high loading
of the catalyst [126]. However, the inefficiency of separation methods such as centrifugation and filtration, hamper the sustainability and economy of their use in bulk organic transformation catalysis. To overcome this drawback, magnetic nanoparticles (MNPs) have emerged as a powerful solution to optimize the operations of separation and reuse of solid catalysts by the simple application of an external magnetic field [127–129].

Magnetic MCM-41 consist of magnetic particles located in the core or within/onto the silica framework. The most common magnetic materials used are Fe$_3$O$_4$ (magnetite), γ-Fe$_2$O$_3$ (maghemite), α-Fe$_2$O$_3$ (hematite), MnFe$_2$O$_4$, and CoFe$_2$O$_4$ since these compounds are easy to synthesize with size-monodisperse particles and with high saturation magnetization. Among these, monometallic iron particles are arguably the most studied systems [130,131].

6.1. General Synthesis of Magnetic MCM-41

Several methods to synthesize iron-oxide-based nanomaterials have been developed [132]. These methods include micro-emulsion [133,134], thermal decomposition of iron complex in an organic solvent [135], co-precipitation from the Fe$^{2+}$/Fe$^{3+}$ mixed salt solution in an alkaline medium [136,137], hydrothermal synthesis [138,139] and the use of successive redox reactions in solvothermal conditions under microwave irradiation [140].

A typical procedure to prepare magnetic particles in the mesoporous material is based on the deposition of magnetic nanoparticles on the external surface of MCM-41 by thermolysis of Fe(NO$_3$)$_3$ [141]. Similar approaches rely on the wet impregnation and chemical vapor deposition. Arruebo et al. [142] used wet impregnation of iron precursor followed by repeated cycles of oxidation and reduction to obtain magnetic MCM-41, while Zhang et al. [143] employed chemical vapor deposition to prepare iron oxide nanoclusters in MCM-41 from volatile Fe(CO)$_5$. An alternate common approach is to graft magnetic nanoparticles on the nanoparticles. Hyeon et al. [144] deposits molybdenum oxide catalyst on the mesoporous silica shell coated on dense silica-encapsulated magnetic iron oxide nanoparticles. Other works reported single-pot synthesis of magnetic mesoporous materials by adding iron (III) ethoxide during the synthesis of mesoporous silica and chemically transform it to superparamagnetic γ-Fe$_2$O$_3$ particles [145–147]. Chen et al. [148] reported a simple synthesis method for embedding the magnetic iron oxide nanoparticles inside MCM-41. According to these authors, magnetic mesoporous molecular sieves can be prepared by adding the magnetic colloid to an ammonia solution containing CTAB as a template. The silica precursor, tetraethyl orthosilicate (TEOS) was then added and the mixture was allowed to react at room temperature under well-mixed conditions.

In attempt to improve the preparation of magnetic MCM-41, Iamamoto et al. disclosed a new method which relies on the coating of Fe$_3$O$_4$ nanoparticles with a thin silica layer before preparation of the mesostructured framework [149]. The catalyst preparation procedure is depicted in Figure 56. First, Fe$_3$O$_4$ particles were coated with SiO$_2$ resulting in the formation of the silica-Fe$_3$O$_4$ composites with a nonporous silica layer of 5 nm of thickness (denoted as Fe$_3$O$_4$@nSiO$_2$). Then, a MCM-41-type ordered mesoporous silica structure was grown on the support to yield the Fe$_3$O$_4$@nSiO$_2$@MCM-41 system. At this step, mesitylene could also be incorporated as a structure expanding agent for the production of larger pores.
After obtaining the optimum reaction conditions, the scope of the reaction was investigated affording the products in yields ranging from 25 to 80%.

Khorshidi et al. [152] studied the performance of this sulfonated catalyst for the three component reaction of indoles, aldehydes and thiols to furnish the desired 3-[(aryl)(arylthio)methyl]-1H-indoles through the two component reaction between (E)-3,5-bis(benzylidene)-4-piperidones and guanidine carbonate [151]. The efficiency of the catalysts was due to the synergetic effect of Brønsted basicity of –NH and Lewis acidity of the Fe$^{3+}$ groups. Mild reaction conditions, good to high yields, simple work-up and ease of recovery and reusability of the catalyst, make this MCM-41 system attractive and useful for the formation of these cyclic compounds.

Silica supported sulfonic acid has received considerable attention as an inexpensive, nontoxic and recyclable catalyst for numerous organic transformations [14]. Among them, magnetite MCM-41 (Fe$_{3}$O$_{4}$@MCM-41-OSO$_{3}$H) has been widely used because of its paramagnetic character and recyclable catalyst for numerous organic transformations [14]. Among them, magnetite MCM-41 has been functionalized with the amino moiety by the post-modification method from the reaction of (E)-3,5-bis(benzylidene)-4-piperidones and benzamidine hydrochloride under solvent free conditions by Shadjou and Hasanzadeh [150]. Using 0.04 g a(Fe$_{2}$O$_{3}$)-MCM-41-nPrNH$_{2}$ in solvent free conditions at temperature of 130 °C during 1:20 h the desired product was furnished in 98% yield. A new series of phenylpyrido[4,3-$d$]pyrimidin-2-amino derivatives have been synthesized in the presence of amino modified magnetic MCM-41 from the reaction of (E)-3,5-bis(benzylidene)-4-piperidones and guanidine carbonate [151]. The efficiency of the catalysts was due to the synergetic effect of Bronsted basicity of –NH$_{2}$ and Lewis acidity of the Fe$^{3+}$ groups. Mild reaction conditions, good to high yields, simple work-up and ease of recovery and reusability of the catalyst, make this MCM-41 system attractive and useful for the formation of these cyclic compounds.

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Rostamizadeh et al. [153] reported the preparation of the maghemite ($\alpha$-$\text{Fe}_2\text{O}_3$)-MCM-41-$\text{SO}_3\text{H}$ for the synthesis of $N$-aryl-2-amino-1,6-naphthyridine derivatives. The magnetic catalyst was prepared directly through the reaction of chlorosulfonic acid with silica-coated sieves ($\alpha$-$\text{Fe}_2\text{O}_3$)-MCM-41. Because of the low stability of Fe$_3$O$_4$ nanoparticles in the presence of chlorosulfonic acid, the desired catalyst was not formed and a non-magnetic catalyst was obtained instead (Figure 57). Therefore, (Fe$_3$O$_4$)-MCM-41 was calcined at 450 °C and converted to its stable form ($\alpha$-$\text{Fe}_2\text{O}_3$)-MCM-41. The catalyst showed high efficiencies due to the synergetic effect of Brønsted acidity of $\text{-SO}_3\text{H}$ and Lewis acidity of the Fe$^{3+}$ groups.

![Figure 57. Preparation of ($\alpha$-$\text{Fe}_2\text{O}_3$)-MCM-41-$\text{SO}_3\text{H}$)](image)

Alternatively, Shariati and Golshekan et al. [154] studied the decoration of MCM-41 with sulfonic acid in two steps by the oxidation of mesoporous structure with thiol groups on the surface. The co-condensation of Fe$_3$O$_4$ and TEOS with terminal trialkoxy organosilanes incorporating the thiol group ((RO)$_3$Si(CH$_2$)$_2$SH) in the presence of structure-directing agent (CTAB) leads to the formation of Fe$_3$O$_4$@MCM-41 with thiol residues anchored covalently onto the silica network (Fe$_3$O$_4$@MCM-41-SH). The oxidation of thiol groups rendered the final sulfonic acid functionalized system (Fe$_3$O$_4$@MCM-41-$\text{SO}_3\text{H}$) (Figure 58). The applicability of the nanocomposite was assessed at room temperature for the preparation of 12-aryl-benzo[$\alpha$]-xanthenonederivatives by the one-pot three-component reaction of various arylaldehydes, $\beta$-naphthol and 1,3-cyclohexadione. The study showed the unique advantages of these molecular sieves, such as their high magnetic properties, high density of sulfonic acid functional groups of the nanocomposite surface, simple synthesis of the catalyst in solvent-free conditions and room temperature, excellent yields, shorter reaction time, activity as stereoselective catalyst and easy separation.
Cai et al. [155] reported a new magnetic mesoporous solid acid catalyst containing NiFe$_2$O$_4$ nanoparticles as the magnetic material (SO$_3$H-MCM-41@NiFe$_2$O$_4$). The system was prepared by impregnation-pyrolysis decoration method (Figure 59) and its catalytic activity was compared to SO$_3$H-MCM-41@Fe$_2$O$_3$ synthetized by one-step sol–gel route. The magnetic mesoporous systems were, afterwards, functionalized with the thiol groups by grafting and then oxidised using H$_2$O$_2$. The catalytic performance of these two catalysts was evaluated using a three-component condensation of aromatic aldehydes, 2-naphthol and benzamides to give the corresponding 1-amidoalkyl-2-naphthols. The NiFe$_2$O$_4$ system exhibits better catalytic activity (92% of yield in 4 h) than SO$_3$H-MCM-41@Fe$_2$O$_3$ nanoparticle analogue (70% of yield in 7 h).

**Figure 58.** Synthesis of Fe$_3$O$_4$@MCM-41-SO$_3$H by thiol oxidation (R:CH$_2$CH$_2$SH). Reproduced with permission from [154]. Copyright 2013 Elsevier B.V.

**Figure 59.** Synthesis of SO$_3$H-MCM-41@NiFe$_2$O$_4$ by grafting and oxidation of MCM-41@NiFe$_2$O$_4$. Reproduced with permission from [155]. Copyright 2014 Springer.
6.3. Magnetic MCM-41 to Embed Ionic Liquids

In the field of catalysis, ionic liquids (ILs) play an important role as solvents and organocatalysts [156]. Unfortunately, their high cost, difficulty in products separation and recyclability hamper their further application at industrial scale. On the other hand, ILs are highly viscous, which often limits mass transfer during catalytic reactions. To overcome these shortcomings, the immobilization of ILs onto the solid supports has become a green approach for their catalytic applications [157,158].

The use of supported Fe₃O₄@MCM-41-SO₃H in the presence of the Brønsted acidic ionic liquid 1-methylimidazolium hydrogen sulphate [HMim][HSO₄] has been evaluated [159]. Three types of MCM-41 mesoporous magnetite catalyst, Fe₃O₄@MCM-41-(CH₂)₃-SO₃H, Fe₃O₄@MCM-41-SO₃H and Fe₃O₄@MCM-41-SO₃H@[HMIm][HSO₄] were compared. The catalyst performance was studied for the preparation of spiro[benzo[5,6]chromeno[2,3-d]pyrimidin-indolines] by using a variety of structurally diverse α or β-naphthols, barbituric acid and isatin derivatives under solvent-free conditions. The reaction test showed a satisfactory catalytic performance when the reaction was carried out in the presence of Fe₃O₄@MCM-41-SO₃H@[HMIm][HSO₄], achieving high yields (90–95%) and good reaction rates (15–30 min). Furthermore, it can be easily separated from the reaction medium with a permanent magnet and directly reused without any deactivation even after five rounds of application.

Dual acidic ionic liquid (DAIL) (1-Methyl-3-(4-sulfobutyl) imidazolium hydrogen sulfate) has been also supported on magnetic MCM-41 [160]. The system has been successfully used for one-pot three-component synthesis of some new and known 2-amino-4H-chromenes in aqueous conditions (Figure 60). The catalytic activity of (α-Fe₂O₃)-MCM-41-DAIL was compared with reported catalysts and its building components, showing that the use of DAIL, (α-Fe₂O₃)-MCM-41 or MCM-41 alone as catalyst was not sufficient to run the reaction to completion. It is hypothesized that the novel catalyst was more efficient due to the Brønsted dual acidic property of the IL together with the Lewis acidity of ferric oxide and the high surface area of MCM-41. The study also evaluates the scope and generality of the reaction showing a marked efficiency for all the substrates tested.

![Figure 60. Synthesis of 2-amino-4H chromenes in the presence of (α-Fe₂O₃)-MCM-41-DAIL catalyst. Reproduced with permission from [160]. Copyright 2016 Springer.](image)

6.4. Magnetic MCM-41 Decorated with Metallic Complexes

Encapsulation of metalloporphyrins in porous compounds protects them from harsh reaction condition and also results in catalysts that mimic the features of natural enzymes (cf. 3.2). MCM-41, with its large pore size and a high amount of silanol groups on the surface of its channels, acts as an attractive candidate for encapsulate metalloporphyrins via physical adsorption or covalent linkage [161].
Zanardi et al. [150] reported the immobilization of manganese porphyrin (MnP) on Fe₃O₄@SiO₂@MCM-41 as a catalyst for hydrocarbon oxidation in the presence of iodosylbenzene (PhIO). The authors synthesized the catalyst with two different pore sizes, the Fe₃O₄@nSiO₂@MCM-41-MnP and Fe₃O₄@nSiO₂@MCM-41(E)-MnP (expanded porous structure), using mesitylene as an expanding agent for the production of larger pores. The synthetic method for the preparation of the catalyst is illustrated in Figure 56. Magnetite sieves were first coated with a thin silica layer (Fe₃O₄@nSiO₂) before the preparation of the mesostructured composites. The MCM-41 framework was functionalized with APTES to enable the covalent immobilization of Mn(III)-5,10,15,20-tetrakis(pentafluorophenyl) porphyrin onto the MCM-41 via an aromatic nucleophilic substitution reaction. The oxidation of (Z)-cyclooctene and cyclohexane was performed to assess the catalytic activity of the composites and to evaluate the accessibility of substrate and oxidant molecules to the catalytic sites. The study concluded that Fe₃O₄@nSiO₂@MCM-41(E)-MnP provided higher yields than Fe₃O₄@nSiO₂@MCM-41-MnP (93% vs. 77%, respectively). This result can be attributed to the greater textural mesoporosity volume of Fe₃O₄@nSiO₂@MCM-41(E)-MnP, which increases diffusional processes that facilitate the access to the region of the framework-confined mesoporosity. The recycling studies demonstrated that Fe₃O₄@nSiO₂@MCM-41(E)-MnP catalyst was also more stable than Fe₃O₄@nSiO₂@MCM-41-MnP. Both heterogeneous catalysts were selective for the oxidation of cyclohexane to cyclohexanol and no cyclohexanone formation was observed. The higher selectivity for the alcohol product in comparison to homogeneous MnP indicates a P450-type biomimetic behavior favored by the inorganic support.

MnP was also bonded to MCM-41 using imidazole as axial ligation (Fe₃O₄@MCM-41-Im@MnP) [162]. Fe₃O₄@MCM-41 were functionalized with 3-chloropropyltriethoxysilane and then with imidazole (Figure 61). The catalytic performance was studied in the epoxidation of different olefins varying catalyst amounts, oxygen donors and reaction media. The optimum reaction conditions were reached using 100 mg of catalyst, acetonitrile/water mixture as solvent in the presence of NaIO₄ as the oxygen source. The activity and selectivity of the heterogeneous catalyst was comparable to those of its homogeneous analogue (MnP). The reaction of different cyclic and linear alkenes was also investigated to examine the scope of the method. Using the optimized reaction conditions, the epoxide was afforded with high selectivity and good yields, ranging between 50 and 98%. Moreover, the novel catalyst was compared to a system reported earlier, which contains the manganese porphyrin complex supported on amorphous silica (Fe₃O₄@SiO₂@MnTPPCl). This study provides evidence of the matrix effect on catalyst performance, which leads to the separation of active catalytic sites and thereby increases the catalytic activity.
Rayati et al. [163] immobilize a molybdenum Schiff base complex (dioxomolybdenum(VI) complex) onto magnetite sieves by an hydrogen bonding ((α-Fe₂O₃)–MCM-41–Mo(O)₂L). The results showed an efficient and highly selective oxidation of a wide range of olefins using hydrogen peroxide and tert-butyl hydroperoxide as oxidizing agents. Complete selectivity for epoxide formation was obtained in the case of cyclooctene, 1-octene, indene, and 1-methyl cyclohexene, while the oxidation of styrene substrates led to the formation of the corresponding substituted benzaldehyde.

Nunes and Vaz et al. [164] reported a novel mesoporous nanocomposite material comprising helical chiral channels, with magnetic iron nanoparticles attached to the silica MCM-41 framework, as support for a molybdenum complex. The helical mesoporous magnetic nanocomposite (magMSh) was prepared (Figure 62) using an entropy-driven procedure with achiral cationic surfactant template (CTAB) and a co-surfactant (ammonia) in the presence of silica-coated magnetic MCM-41 that were co-condensed with TEOS. Afterwards, a bipyridine derivative was grafted to the inner silanol surface and used as ligand to coordinate a Mo(II) precursor complex [MoI₂(CO)₃(CH₃CN)₂]. The derivatized chiral nanocomposite (magMSh-bpy-Mo) was used as an efficient and reusable catalyst precursor for the asymmetric epoxidation of olefins using tert-butyl hydroperoxide as oxygen donor. The catalysis of cis-cyclooctene, R-(+)-Limonene and trans-hex-2-en-1-ol yielded the epoxide without any formation of by-products and conversions raging between 98 and 100% when toluene was used as solvent at 353 K or 383 K. The authors suggested that the good stereoselectivity arises from the confinement effect imposed by the helical rigid chiral channels. In addition, data obtained from the selective adsorption of enantiopure D- and L-phenylalanine supported the presence of channel chirality and proved the utility of this novel magnetic system for chiral recognition applications.
6.5. Magnetic MCM-41 to Incorporate Metal Nanoparticles

Homogeneous metal catalysts have been extensively studied in synthetic organic chemistry because of their high selectivity and catalytic activity. Unfortunately, such catalysts are not endowed with high reusability and their use leads metal contamination on the final products (cf. 0). In attempt to solve these shortcomings, a great number of metal-based catalytic species have been immobilized on different heterogeneous supports containing superparamagnetic materials. MCM-41 functionalized with organic moieties can be used as support of metal nanoparticles increasing their dispersion and catalytic performance.

A Pd Schiff base complex immobilized onto the surface of magnetic MCM-41 (Fe$_3$O$_4$@MCM-41@Pd(0)-P2C) has been designed as a novel reusable magnetic catalyst [165]. The catalyst was prepared by modification of Fe$_3$O$_4$@MCM-41@nPr-NH$_2$ using pyrrole-2-carbaldehyde in ethanol and heating under a N$_2$ atmosphere. The metal was introduced into the pores from a solution of Pd(OAc)$_2$ in ethanol, to finally reduce Pd(II) using NaBH$_4$. The obtained palladium system was successfully used in Suzuki–Miyaura (88–98% yield) and Heck (80–96% yield) reactions, employing polyethylene glycol (PEG) as a green solvent. The broad substrate scope, simple experimental procedure and catalyst separation, utilization of an inexpensive and readily available catalyst with excellent reusability, non-chromatographic purification of the products, simple recrystallization from diethyl ether and the use of green solvent were the merits of this novel catalyst.

The same research group also reported a Pd(0)-S-propyl-2-aminobenzothioate complex immobilized onto functionalized magnetic MCM-41 (Fe$_3$O$_4$@MCM-41@SPATB) as an efficient and recyclable nano-organometallic catalyst for Suzuki, Stille and Heck reactions [166]. For the preparation of Fe$_3$O$_4$@MCM-41@Pd-SPATB (Figure 63), Fe$_3$O$_4$@MCM-41 was functionalized with (3-mercaptopropyl)trimethoxysilane (MPTMS) and, afterwards, with S-propyl-2-aminobenzothioate, providing the denoted Fe$_3$O$_4$@MCM-41@SPATB. Finally, Pd(0) was introduced by impregnation and reduction. The protocol was carried out also in PEG-400 as green solvent achieving good to excellent yields in short reaction time for all the reactions tested.
Jiang et al. [167] reported the catalytic hydrogenation of aqueous bromate using a catalyst that contains Pd nanoparticles supported on amino functionalized magnetic MCM-41. The heterogeneous system was synthesized using two different methods, deposition-precipitation (DP) and impregnation (IMP). The catalysts were functionalized with different loading amounts of –NH$_2$ to evaluate the impact on Pd nanoparticle dispersion and the catalytic behavior. The study of the liquid phase catalytic hydrogenation of bromate established that DP catalyst exhibited a better activity than IMP as a result of improved Pd dispersion. The authors concluded that it was feasible to improve hydrogenation efficiency (100% of conversion) by applying DP catalyst prepared using 0.25 APTES:magMCM-41 ratio. Noteworthy, a decline in activity was observed with a further increase of NH$_2$ loading. The optimized catalyst could be reused five times without significant loss of activity (<6%).

Taking into account the soft interaction between Au and S and the resulting semi-covalent bond, magnetic MCM-41 have been functionalized with thiol groups to incorporate Au nanoparticles [168]. Firstly, magnetic sieves were embedded in MCM-41 framework and subsequently functionalized with (3-mercaptopropyl)trimethoxysilane (MPTMS) (Figure 64). Then, HAuCl$_4$ was deposited into ($\alpha$-Fe$_2$O$_3$)-MCM-41-SH and reduced to create fine Au nanoparticles bonded to thiol groups. The optimization of the reaction indicated that the best conditions were achieved using H$_2$O as solvent at 80 °C and solvent-free at 70 °C gave the best yields (98% and 100%, respectively). The hydration of a range of alkynes and aliphatic alkyne was investigated to ascertain the scope of the methodology (90–100% of yield). In order to extend the applicability of this catalyst, the authors also reported its catalytic performance in Ullmann homocoupling of aryl iodides to produce symmetrical biaryls [169]. Short reaction time, high selectivity, no observation of undesired side products and utilization of green and magnetically separable catalyst were the advantages of this procedure. This protocol produces very finely Au nanoparticles distribution on the pore surface resulting in excellent catalytic behavior.
The incorporation of metal on the magnetic catalyst can be also accomplished adding a silicon precursor that contains the metal source. In this sense, it was reported the synthesis of Fe$_2$O$_3$/MCM-41 silicoaluminate magnetic catalyst prepared employing a modified assembling method that introduces clinoptilolite as aluminium natural source [170]. The Fe$_2$O$_3$/MCM-41 catalyst was prepared coating Fe$_2$O$_3$ nanoparticles with a layer of SiO$_2$, and then synthetizing the mesoporous framework by using natural clinoptilolite. The catalyst was employed for hydrothermal liquefaction (HTL) of microalgae and deoxygenation upgrading of derived biocrude and its model compounds under the absence of hydrogen. Chlorella, palmitic acid and methyl palmitate were chosen as reactants. The magnetic Fe$_2$O$_3$/MCM-41 catalyst showed good performance; in the 320–350 °C regime and under subcritical water, palmitic acid conversion was improved by 14–29%. Methyl palmitate conversion was 56% and decarboxylation selectivity to pentadecane was improved to 62% carrying on the deoxygenation at 342 °C.

A strategy to assemble superparamagnetic iron oxide and platinum nanoparticles onto mesoporous MCM-41 silica host with a high degree of spatial precision has been reported by Santamaria and Martinez et al. [171]. The system was prepared by a size-exclusion strategy that allows a highly precise segregation of iron nanoparticles outside the MCM-41 and platinum inside the pores. The direct assembly of magnetic nanoparticles onto the outer surface of silica framework was carried out using nanoparticles with a size larger than the MCM-41 pores and grafting covalently through a peptide-like bonding onto their external surface. Magnetic functionalized MCM-41 with carboxylic groups on the surface (DMSA–Fe$_2$O$_3$) were obtained via a ligand-exchange reaction of triethylene glycol by meso-2,3-dimercaptosuccinic acid (DMSA). These carboxylic groups were suitable for the later condensation reaction with the MCM-41 amino silica groups to anchor the magnetic nanoparticles through a peptide-like link. This procedure endows a strong superparamagnetic response and overcome the drawbacks associated with the encapsulation of magnetic cores within the mesoporous silica shell (formation of irregular core/shell structures and low magnetization saturation values due to poor magnetic cores encapsulated). Furthermore, this protocol allows to preserve a regular porous structure capable to host other functional guest species.

![Figure 64. Preparation of (α-Fe$_2$O$_3$)-MCM-41-SH-Au. Reproduced with permission from [169]. Copyright 2014 Elsevier B.V.](image)
Secondly, the preformed Pt nanoparticles (1.5 nm) were “electrostatically pumped” within the channels of the magnetic amino-functionalized MCM-41 to confer a catalytic functionality (Figure 65). The Pt nanoparticles were stabilized with tetrakis(hydroxymethyl)phosphonium chloride (THPC) (THPC—Pt NPs) proving a high negative surface charge (−30 mV) and strong adhesion to the positively charged NH$_3^+$ mesoporous silica pores (27 mV). A sufficient high repulsion among NPs provided the “pumping” effect and propelled them within the channels. Hence, the penetration depth of the Pt-NPs can be explained as a result of the interplay between the particle—wall electrostatic attraction and the repulsive forces between neighbouring Pt-NPs.

The catalytic performance of this multi assembled nanoplatform has been evaluated in the selective hydrogenation of p-nitrophenol (4-NP) by NaBH$_4$ as a model reaction at room temperature. The reaction has been monitored along the time measuring the 4-NP absorption peak at 400 nm. The results proved the efficiency of the catalyst, reaching a k-value comparable to the best catalyst reported in the literature for 4-NP hydrogenation. This multifunctional hybrid catalyst performed an excellent catalytic activity and could be efficiently reused during 4 cycles with negligible catalyst loss.

![Figure 65. Pt nanoparticles pumped within the channels of the magnetic MCM-41 nanospheres. Reproduced with permission from [171]. Copyright 2017 American Chemical Society.](image)

### 6.6. Magnetic MCM-41 to Immobilize Enzymes

Enzyme immobilization onto MCM-41 supports improves thermal and pH stability and enables easier separation, recyclability and reutilization of the enzymes (cf. 3.3). Embedding MCM-41 with magnetic nanoparticles enhances fast separation by applying a magnetic field and allows bulk operation and enzyme reusability.

Jing et al. [172] immobilized porcine pancreas lipase (PPL) onto magnetic MCM-41 and compared three different attachment methods. For the support preparation, Fe$_3$O$_4$ nanoparticles were synthetized using the solvothermal method and then coated with mesoporous silica. The enzyme PPL was immobilized by covalent attachment, physical absorption and cross-linking methods (Figure 66). For the covalent bonding, the requisite support was prepared by grafting of MCM-41 with 3-chloropropyltriethoxysilane (CPS or CPTMS). The as-synthetized support can react covalently with biological macromolecules containing amino groups. The physical adsorption was carried out without MCM-41 surface modification, while for the cross-linking method, the mesoporous nanoparticle was grafted with APTES and treated with the PPL solution using glutaraldehyde as a coupling reagent.

PPL was immobilized onto the three mesoporous magnetic sieves and the as-synthesized catalysts were studied. Enzyme immobilization was determined analysing by Bradford method the PPL supernatant. Optimal concentration of the enzyme, reaction temperature and time of incubation were found to be 0.30 mg mL$^{-1}$, 30 °C, and 4 h for all these three materials. The results showed that covalent attachment exhibit the best immobilization efficiency (maximum 96%) and was not sensitive to an increase in temperature or enzyme concentration. The cross-linked PPL nanoparticle also exhibited an enhanced immobilization when compared with the PPL attached by physical absorption. Activity of
the different immobilized PPL and non-immobilized one was determined using olive oil as substrate. The activity performance, stability and reusability studies confirm the same trends. Maximum relative activity (up to 96%), high stability and reusability (83% 56 days and 86.7% ten cycles) have been achieved using the covalent bonding method when the enzymatic reaction was carried out at optimum temperature and pH (35 °C and 7.5, respectively). Based on the results obtained, chemically covalent attachment to the enzyme without a cross-linking agent instead of physical adsorption seems to be an appropriate immobilization method.

Figure 66. Schematic representation of Fe₃O₄-MCM-41 nanoparticles formation and enzyme immobilization. Reproduced with permission from [172]. Copyright 2015 Springer.

In this regard, Candida rugosa lipase was bound to Fe₃O₄@MCM-41 nanocomposite by using glutaraldehyde as a cross-linking specie [173]. To prepare the catalyst, MCM-41 was derivatized with APTES and the lipase was immobilized on the magnetic nanocomposite by cross-linking with glutaraldehyde (Figure 67). The enzymatic catalyst was used for the interesterification of lard and soybean oil mixtures in aim to modify the physicochemical properties of vegetable oils in the food industry because the formation of trans fatty acids is avoided. The immobilized lipase displayed a better catalytic activity towards the interesterification reaction and no trans fatty acids were detected in the interesterified blends. The enzymatic catalyst displayed good magnetic properties and could be facilely separated by applying an external magnetic field and reused for four times without significant loss of catalytic efficiency.
Ates et al. developed magnetic Fe₃O₄@MCM-41 functionalized with CPTMS for the immobilization of L-asparaginase (L-ASNase) [174]. To this purpose, CPTMS was used as a surface-modifying agent for covalent binding of L-ASNase on the magnetic sieves (Figure 68). The immobilization efficiency onto Fe₃O₄@MCM-41-Cl was as high as 63%. The catalytic activity, reusability, storage, pH, and thermal stabilities of the immobilized L-ASNase were investigated and compared with the free enzyme. It was found that both L-ASNase forms exhibited the highest activity at pH 8.5, however the immobilized enzyme retained over 85% activity in a broad pH range. The residual activity of soluble L-ASNase at temperatures higher than 60 °C was negligible, while immobilized one retained below 80% activity. It was evidenced that immobilized L-ASNase was more stable towards pH and temperature compared with soluble enzyme. The results in thermal stability showed that at catalytic activity was maintained after 180 min at 55 °C (69.7%) while soluble enzyme was totally inactivated. Furthermore, could be reused for 18 cycles retaining 42.2% of its original activity.

Figure 67. Synthesis of the magnetic MCM-41 immobilized Candida rugosa lipase. Reproduced with permission from [173]. Copyright 2016 Springer.

Figure 68. Schematic illustrates steps of magnetic Fe₃O₄@MCM-41-Cl nanoparticle preparation, modification, and the immobilization of L-ASNase. Reproduced with permission from [174]. Copyright 2018 Springer.
In another attempt to immobilize L-ASNase, the authors functionalized Fe₃O₄@MCM-41 magnetic sieves employing (3-glycidyloxypropyl) trimethoxysilane (GPTMS) \[175\] and 3-mercaptopropyltrimethoxysilane (MPTMS) \[176\] as the grafting agents. The generated epoxy (Figure 69) and thiol functionalities were used to covalently bind the L-ASNase. The enzyme activity at different pH and temperatures were determined measuring the concentration of ammonia produced during catalysis of L-asparagine. The two immobilized L-ASNase had greater activity compared to free enzyme, especially at high pH and temperature values. Regarding GPTMS functionalization, the highest relative activity for the native and immobilized L-ASNase was observed at pH 8.5 and 9.0, respectively. The temperature conditions analysis showed that at pH 8.6 the optimum activity was at 50 °C for soluble enzyme and 55 °C for the immobilized. The authors also studied the thermal stability at 55 °C and found that the immobilization had a great effect in denaturalization. The immobilized L-ASNase maintained more than 92% of its initial activity after incubation for 3 h while the native enzyme was deactivated due to denaturation. Moreover, immobilized L-ASNase showed higher kinetic values, storage stability and an excellent reusability, retaining 93.9% of their initial activity after 5 successive cycles and 65% after 10 cycles.

The properties of thiol-functionalized Fe₃O₄@MCM-41 magnetic sieves, including pH, temperature, kinetic values, thermal stability, reusability, and storage stability were also investigated and compared to native enzyme. The results showed that pH and temperature stability of immobilized enzyme were also significantly higher than those of free enzyme, obtaining a faster decrease on stability. For instance, the free L-ASNase still retained 73% of its initial activity, whilst the immobilized L-ASNase retained 81% after 3 h incubation. Besides, at 50 °C native enzyme lost 70% of its initial activity and immobilized enzyme still retained 94% after 3h. Noteworthy, the immobilized enzyme kept 63% of its original activity after 16 times of reuse. The study confirmed that functionalized Fe₃O₄@MCM-41 sieves have high efficiency for L-ASNase immobilization and could be reused several cycles maintaining a good performance.

![Image](image-url)

**Figure 69.** Schematic depiction of magnetic Fe₃O₄@MCM-41 sieves preparation, epoxy modification and L-ASNase immobilization. Reproduced with permission from [175]. Copyright 2018 Elsevier B.V.
7. Concluding Remarks

In this review article, the main types of functionalized MCM-41 for the immobilization of catalysts have been presented. The catalytic systems discussed include: mono and di-functionalized MCM-41 as basic and acid catalysts, catalysts based on metallic complexes supported by MCM-41, metallic nanoparticles embed onto functionalized MCM-41 and magnetic MCM-41 for catalytic purposes. Similarly to other supports, such as SBA-15, MCM-41 are cheap, synthetically versatile, and can be reused. However, an advantage over other systems is that MCM-41 have been extensively studied due to their applications in biological applications. The chemical versatility of MCM-41 relies not only on the easy preparation of the molecular sieves, but on the straightforward regioselective functionalization, both within the inner walls of the pores and the outside surface of the particle. The functionalization of the particles can be accomplished either by grafting or post-functionalization.

Both methodologies of functionalization allow the preparation amino and acid derivatized particles or even mixed functionalizations $\text{NH}_2/\text{SO}_3\text{H}$. Many important reactions can benefit of these catalysts, such as aldol condensation, Knoevenagel to name some. Furthermore, the functionalization of the MCM-41 opens the door to the preparation of more sophisticate systems incorporating metallic complexes, which catalyze palladium cross-coupling reactions (e.g., Sonogashira, Tsuji-Trost reactions), cicloadditions, and hydroformylations among others.

Functionalization not only enables the decoration of the MCM-41 with a wide variety of functional groups or complexes but improves the dispersion of metallic nanoparticles absorbed onto the surface of the MCM-41, minimizing the aggregation of the metallic fragments and avoiding their migration. The obtained hybrid catalysts exhibited excellent catalytic activity and reusability, as a result of a better embedment of the metal catalyst, in comparison with traditional physical entrapment methods. Following this strategy metal nanoparticles such as Pd, Au, Ni, Ru, and Ti nanoparticles could be efficiently deposited on MCM-41 support. Besides, the presence of basic or acid sites, by doping the support with metal cations, enhance the dispersion of the metal nanoparticle within the silica matrix.

The incorporation of a magnetic particle in the core of the MCM-41 give rise a novel family of catalytic systems characterized by a high recovery and reusability. These features make magnetic MCM-41 ideal supports for industrial applications or solid phase synthesis.

In our opinion, the present challenges in the field of MCM-41 in catalysis are twofold: the scale up of the synthesis and the design of “click” methodologies for the decoration of the molecular sieves. In order to be implemented in industrial processes, large amount of homogeneous MCM-41 must be produced to satisfy the needs of the demand. Moreover, there is still a need for straightforward methods of functionalization to provide the optimum catalyst avoiding tedious and long synthetic procedures.

To conclude, the available methodologies to prepare and characterize molecular sieves are mature enough to allow specialists in catalysis to improve the behavior of their systems by anchor them onto MCM-41. This review has shown the main results in the field that give support to this statement.

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