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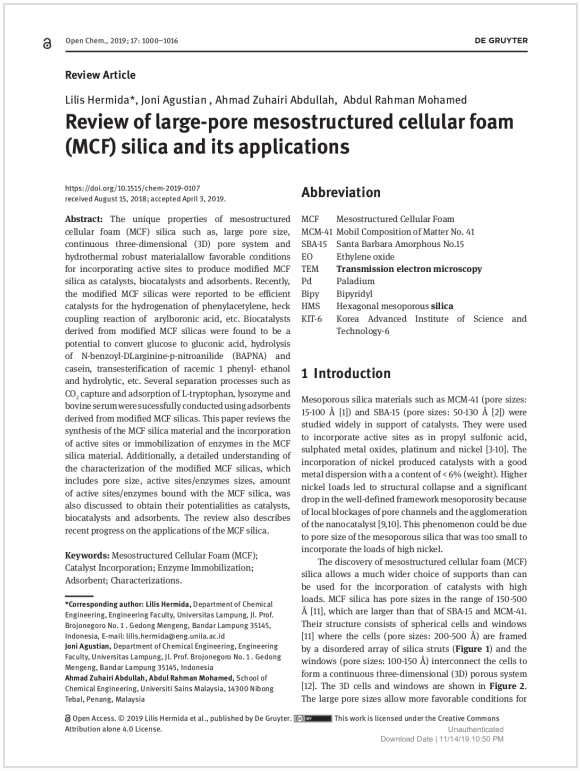

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Review Article

Lilis Hermida*, Joni Agustian , Ahmad Zuhairi Abdullah, Abdul Rahman Mohamed

Review of large-pore mesostructured cellular foam (MCF) silica and its applications

https://doi.org/10.1515/chem-2019-0107
received August 15, 2018; accepted April 3, 2019.

Abstract: The unique properties of mesostructured cellular foam (MCF) silica such as, large pore size, continuous three-dimensional (3D) pore system and hydrothermal robust materialallow favorable conditions for incorporating active sites to produce modified MCF silica as catalysts, biocatalysts and adsorbents. Recently, the modified MCF silicas were reported to be efficient catalysts for the hydrogenation of phenylacetylene, heck coupling reaction of arylboronic acid, etc. Biocatalysts derived from modified MCF silicas were found to be a potential to convert glucose to gluconic acid, hydrolysis of N-benzoyl-DLarginine-p-nitroanilide (BAPNA) and casein, transesterification of racemic 1 phenyl- ethanol and hydrolytic, etc. Several separation processes such as CO_2 capture and adsorption of L-tryptophan, lysozyme and bovine serum were sucessfully conducted using adsorbents derived from modified MCF silicas. This paper reviews the synthesis of the MCF silica material and the incorporation of active sites or immobilization of enzymes in the MCF silica material. Additionally, a detailed understanding of the characterization of the modified MCF silicas, which includes pore size, active sites/enzymes sizes, amount of active sites/enzymes bound with the MCF silica, was also discussed to obtain their potentialities as catalysts, biocatalysts and adsorbents. The review also describes recent progress on the applications of the MCF silica.

Keywords: Mesostructured Cellular Foam (MCF); Catalyst Incorporation; Enzyme Immobilization; Adsorbent; Characterizations.

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Abbreviation

MCF	Mesostructured Cellular Foam
MCM-41	Mobil Composition of Matter No. 41
SBA-15	Santa Barbara Amorphous No.15
EO	Ethylene oxide
TEM	**Transmission electron microscopy**
Pd	Paladium
Bipy	Bipyridyl
HMS	Hexagonal mesoporous **silica**
KIT-6	Korea Advanced Institute of Science and Technology-6

1 Introduction

Mesoporous silica materials such as MCM-41 (pore sizes: 15-100 Å [1]) and SBA-15 (pore sizes: 50-130 Å [2]) were studied widely in support of catalysts. They were used to incorporate active sites as in propyl sulfonic acid, sulphated metal oxides, platinum and nickel [3-10]. The incorporation of nickel produced catalysts with a good metal dispersion with a a content of < 6% (weight). Higher nickel loads led to structural collapse and a significant drop in the well-defined framework mesoporosity because of local blockages of pore channels and the agglomeration of the nanocatalyst [9,10]. This phenomenon could be due to pore size of the mesoporous silica that was too small to incorporate the loads of high nickel.

The discovery of mesostructured cellular foam (MCF) silica allows a much wider choice of supports than can be used for the incorporation of catalysts with high loads. MCF silica has pore sizes in the range of 150-500 Å [11], which are larger than that of SBA-15 and MCM-41. Their structure consists of spherical cells and windows [11] where the cells (pore sizes: 200-500 Å) are framed by a disordered array of silica struts (**Figure 1**) and the windows (pore sizes: 100-150 Å) interconnect the cells to form a continuous three-dimensional (3D) porous system [12]. The 3D cells and windows are shown in **Figure 2**. The large pore sizes allow more favorable conditions for

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Review of large-pore mesostructured cellular foam (MCF) silica and its applications

by Joni Agustian

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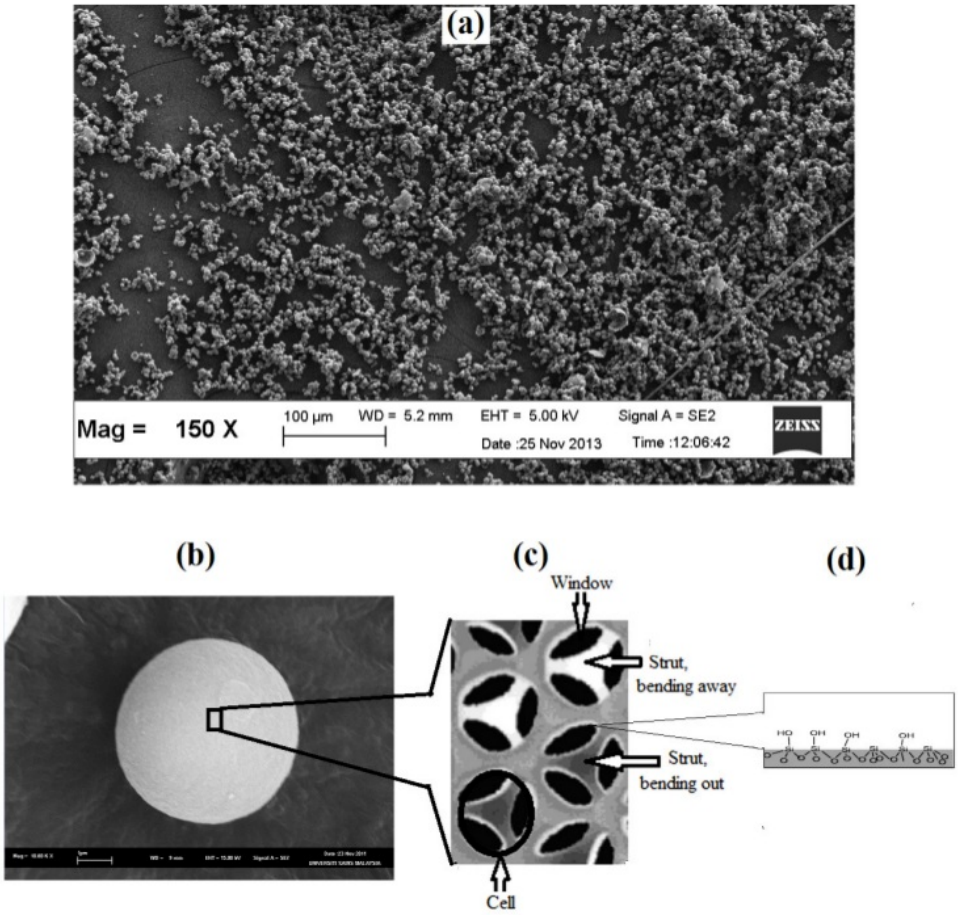

Figure 1: SEM image of (a) spherical MCF silica particles; (b) a single spherical MCF particle at higher magnification; (c) Schematic cross section of the structure exhibited by MCF silica; (d) Silanol groups (≡*Si-OH*) on wall of MCF silica.

the incorporation of active sites of catalysts or enzymes [11]. In addition, they reduce the diffusional restriction of reactants or substrates, and enable reactions involving bulky molecules to occur [11]. The MCF silica also has ultra-large pore sizes within the continuous 3D pore system [12]. Functionalization of the MCF silica is possible as well, since the silica exhibits very similar chemical properties to the MCM-41 and SBA-15[11]. In addition, MCF silica is a hydrothermal robust material [11]. The characteristics of MCF silica make applications of this silica emerging. Large pore sizes and hydrothermal properties of MCF make researches on the application of this silica important [11].

In the past few years, the scientific communities have observed significant works and rapid development of activities relating to these versatile materials. In order to understand the characteristics of the modified MCF silicas, such as pore dimensions, sizes of active sites

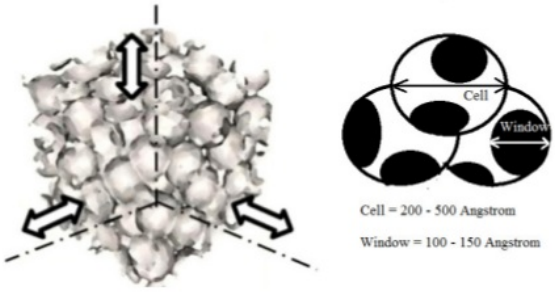

Figure 2: Three-dimensional cells and windows in MCF silica material (adapted from [28]).

or enzymes, and the number of active sites or enzymes bound with the materials, a review of the synthesis of the materials, the incorporation of the catalysts' active sites and the immobilization of enzymes need to be studied

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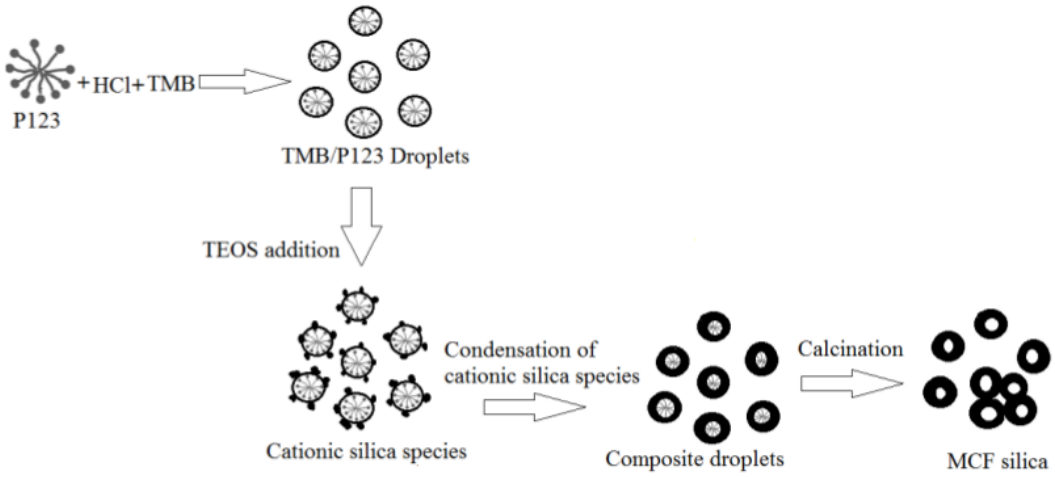

Figure 3: Formation of MCF silica particles.

and are described in this paper. This paper also presents the uses of the MCF silicas as adsorbents in the separation processes.

2 Synthesis and Formation of MCF silicas

The MCF silica is formed by adding a hydrophobic swelling agent such as 1,3,5 trimethylbenzenexylene (TMB) in a sufficiently large amount during synthesis of the SBA-15 to induce a phase transformation from highly ordered hexagonal (*P6mm*) symmetry to the MCF structure [13]. The formation of SBA-type materials is a result of the interaction of P123 (Pluronic 123) i.e. amphiphilic block copolymer (EO*x*PO*y*EO*x*) and inorganic siliceous species through hydrogen bonding [14]. The synthesis is performed under acidic conditions in which the hydrophilic head groups (EO = ethylene oxide) and positively charged silica species are assembled together by electrostatic interactions mediated by negatively charged chloride ions. By changing the size of the EO group using TMB as a hydrophobic swelling agent, the SBA-type materials differ in the pore diameter [15].

Additionally, TMB plays an important role in determining the final structures of the mesoporous silicas. Research showed that the SBA-type materials were still formed at a ratio of TMB/P123 less than 0.2. At the ratio of TMB/P123 in the range of 0.2-0.3, mixed phase silicas in the form of SBA-15 and MCF were formed. The silica phase of MCF type materials was synthesized at the ratio of TMB/P123 > 0.3. The proposed evolution of mesoporous silica structures with the increase of the TMB/P123 ratio and the TEM micrographs is described by Lettow et al. [16]. It was reported that at the (TMB/P123) ratio of 0.2-0.3, walls of cylindrical pores began to buckle that formed spherical nodes along the length of the pores. Besides mono-disperse spheres characteristic of MCF material, SAXS (small-angle X-ray scattering) pattern of samples synthesized at the TMB/P123 ratio of 0.2-0.3 matched hexagonal (*P6mm*) characteristic of SBA-15 material. At the TMB/P123 ratio higher than 0.3, the SAXS pattern only related to mono-disperse spheres characteristic of MCF materials

Figure 3 shows a mechanistic pathway for the formation of MCF materials as suggested in the literature [11]. The process is as follows: firstly, the formation of oil-in water micro-emulsion consisting of P123/TMB droplets by mixing aqueous HCl, P123 and TMB. Second, tetraethylorthosilicate (TEOS) is hydrolyzed to form hydrophilic cationic silica species.Thirdly, the condensation of the cationic silica species generates a "soft" silica coating through hydrogen bonding between the cationic silica species with the P123-coated TMB droplets to form a composite phase. Next, aging the mixture at elevated temperatures is carried out for the formation of large window pores with narrow size distribution in the composite materials. The aging treatment would also lead to the agglomeration and packing of the composite materials. Finally, spherical particles of the MCF material are produced by filtering the mixture; the precipitated composite droplets that are obtained are dried and calcined.

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Hydrothermal stability of MCF silica has been thoroughly studied as explained by Li et al. [17]. A higher aging temperature in the preparation of MCF silica resulted in a larger micro-porosity in the MCF silica, while a higher calcination temperature contributed to a stability of MCFs in higher-temperature steam. MCF silica prepared at the aging temperature higher than 100°C and the calcination temperature of 550°C displays high hydrothermal stability at 600°C under 100% steam; however, at 800°C under 100% steam, the mesostructure of MCF completely collapsed. When the calcination temperature is increased to 900°C, the mesostructure was stable under the pure steam of 800°C. It can be concluded that the high aging temperature and high calcination temperature in the MCF preparation were in favor of the hydrothermal stability of MCF.

3 MCF Silica in Chemical Catalyses

The disposal of hazardous waste created by modern chemical industry is governed by strict environmental regulations and public legislation [3,4,7,8]. Restrictions on the use of conventional homogeneous catalytic processes are increasing since they create inherent problems such as costs separation, the handling of waste disposal, etc. [3,4,5]. Heterogeneous catalytic processes offering the advantages of simple separation and easy recovery, reuse, waste reduction, and the elimination of hazardous chemicals should improve the catalytic processes [3,4]. The development of eco-friendly, environmentally compatible, and recyclable heterogeneous catalysts for chemical synthesis is becoming an area of growing interest [3].

Similar to other mesoporous silica materials (MCM-41 and SBA-15), the MCF silica possesses a neutral silicate framework which can be easily modified by dispersion of active sides on the framework, thereby creating catalytically active sites. Methods that can be utilized for the incorporation of active sites in MCF silica include direct synthesis, post-synthesis grafting, impregnation and deposition-precipitation. Direct synthesis usually involves the reaction between active sources with TEOS in the presence of structure-directing agents that cause the active site to be anchored to the pore walls [18].

On the contrary, the post-synthesis grafting method was carried out by the incorporation of active sites in MCF silica via ligand or binding site [18]. A ligand is an ion or molecule that binds a central metal atom to form a complex (alternatively known as a coordination entity). Ligand or binding sites can be derived from organosilanes such as 3-aminopropyltrimethoxysilane (APTMS), 3-ureidopropyl trimethoxysilane (UPTMS) and 3-mercaptopropyl trimethoxysilane (MPTMS). Initially, the organosilanes were grafted on MCF silica through the reaction between free silanols on the surface of the MCF silica and the organosilanes. This was followed by the organosilanes binding the active sites.

The impregnation method involved slurrying the MCF in an aqueous solution of metal salt at room temperature for a certain period of time [19]. The mixture was then filtered, and the obtained solid was dried and calcined in air followed by a reduction in hydrogen. By using the impregnation method, metal particles were typically distributed over the internal surface of the MCF silica.

The deposition-precipitation method involved the immersion of MCF silica in excess solution of a highly soluble active precursor which allowed the interaction of the active precursor - MCF silica [20]. The deposition-precipitation of the active precursor MCF silica occurred by introducing a change to the solution in terms of pH, valence state of the precursor, and active precursor solution concentration. This was followed by a possible nucleation through the formation of colloidal nanoparticles in solution and its subsequent surface-adsorption via electrostatic attraction or hydrolysis of the soluble active species and the condensation with the support of hydroxyls to form surface-bound nuclei for the condensation of additional soluble species.

MCF silica was found to be promising as the catalyst support for a variety of catalytic applications such as hydrogenation, coupling, dehydrogenation, oxidation, deoxygenation, decomposition and photocatalytic hydroxylation. The applications of MCF silica as catalyst support in heterogeneous catalysis reported in the literatures are summarized in **Table 1**. It is shown that MCF silica was used as a support for the preparation of supported Pd catalysts for the hydrogenation of phenylacetylene under mild conditions [21]. The supported Pd catalysts were prepared via several different methods i.e. direct synthesis, impregnation from Pd colloid in MCF silica and impregnation from Pd(II) acetate solution. The Pd-supported MCF catalyst was prepared using the direct synthesis method which was the most effective for the reaction due to the coverage of the Pd nanoparticles by the MCF support. The highest product selectivity at a complete phenylacetylene conversion achieved 88% in the hydrogenation of phenylacetylene using the catalyst.

The Pd-supported catalyst derived from MCF silica was also studied for other reactions such as Suzuki coupling of aryl halides with aryl boronic acids, Heck coupling of aryl halides and alkenes, transfer hydrogenation of

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Table 1: Applications of MCF silica as catalyst support in heterogeneous catalysis.

Catalyst	Method of preparation	Catalyst characterization				Application	Remark	Reference
		SSA (m^2/g)	Dc (Å)	Dw (Å)	D			
Pd/MCFss	Direct Synthesis	714	-	79	-	Hydrogenation of phenylacetylene under mild condition	Among these catalysts, Pd/MCFss retained the relatively the highest product selectivity (88%) after complete conversion of phenylacetylene as coverage of Pd nanoparticles by the MCF support.	21
Pd/MCF-imp	Impregnation of Pd colloid	586	-	57	25.5%			
Pd/MCF-col	Impregnation from Pd(II) acetate solution	727	-	76	11.2%			
Pd/Urea-MCF	Grafting of Pd in MCF silica using urea ligand	-	-	-	5%	Hydrogenation, Suzuki and Heck coupling, hydrogenolysis.	Pd/Urea-MCF catalyst demonstrated superior activity compared to commercially available (10 wt% Pd/C) or polymer supported Pd-Encat	22
Pd-NH_2-MCF	Grafting Pd(II) in MCF silica using bipyridyl, imino pyridine, or 3-amino propyl ligands	640	-	-	0.39 mmol/g_{cat}	Heck coupling reaction of aryl boronic acid at 80°C	Bipyridine-based catalyst was the most efficient. The catalysts can be used for multiple catalytic cycles without activity loss.	23
Pd-ImPy-MCF		620	-	-	0.41 mmol/g_{cat}			
Pd-BiPy-MCF		610	-	-	0.38 mmol/g_{cat}			
Pd-MCF-U	Grafting Pd in MCF using various silane for binding sites	670	350	150	59.1 %	Decarboxylation of stearic acid at 300°C in a batch reactor	Urea based precatalyst (Pd-MCF-U) was the most efficient due to evenly-distributed, small palladium nanoparticles	24
Pd-MCF-S		650	370	170	-			
Pd-MCF-N		660	350	150	55 %			
Pd-MCF-U	Grafting Pd in MCF using 3-ureidopropyl-trimethoxy-silane (UPTMS) for binding sites	670	350	150	1.1 %	Decarboxylation of stearic acid at 300°C in a batch reactor	After one use, carbonaceous deposition in the spent catalyst was found to be residual reactants, solvent and product. Extractions with solvents decreased the organic content by 90% After reduction at 300oC, the regenerated catalyst showed a 19-fold increase in decarboxylation activity compared to the original spent catalyst	25
1.0Cr-MCF	Impregnation from $Cr(NO_3)_3 . 9H_2O$ in methanol solution	553	177	73	-	Dehydrogenation of propane	Chromium-supported MCF exhibited much higher activity than chromium-supported SBA-15 or MCM-41 as chromium species were well dispersed on the surface of MCF silica and ultra large pore diameters of the catalyst.	26

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Continued **Table 1**: Applications of MCF silica as catalyst support in heterogeneous catalysis.

Catalyst	Method of preparation	Catalyst characterization				Application	Remark	Reference
		SSA (m^2/g)	Dc (Å)	Dw (Å)	D			
2.8V-MCF	Impregnation from NH_4VO_3 in methanol solution	504	181	41	-	Dehydrogenation of propane	The superior performance of the 2.8V-MCF catalysts compared to V-SBA-15, and conventional V–SiO2 was attributed to the well-defined 3D mesoporous systems and the much larger pore providing more favorable conditions for internal mass transfer.	27
6%V/MCF	Impregnation from NH_4VO_3 in oxalic acid solution	420	221	-	-	Dehydrogenation of ethylbenzene	6%V/MCF catalysts exhibited far higher activity than 6%V/MCM-41 attributed to the higher reducibility and better diffusion of reactants and products.	29
V-MCF	Direct synthesis	925	160	60	0.33 VOx/nm^2	Dichloromethane decomposition	V-MCF was higher activity than V-MCF-i due to better vanadium dispersion in the catalyst.	30
V-MCF-i	Impregnation from NH_4VO_3 solution	645	230	120	0.46 VOx/nm^2			
V-MCF	Direct synthesis	925	160	60	-	Dichloromethane decomposition & Propane dehydrogenation	V-MCF was also more efficient than V-SBA-15 attributed to higher molecules diffusion and residence time inside the channels of V-MCF	28
W-MCF(20)	Direct synthesis	557	236	56	-	Liquid phase oxidation of 1,3-butanediol	W-MCF catalyst was effective as compared to WO3/MCF and W-SBA-15. Very stable catalytic activity was also observed for the W-MCF catalyst	31
WO_3/MCF(20)	Impregnation from $NaWO_4.2H_2O$ in alcoholic solution	498	176	36	-			
HPW-NH_2-MCF	Surface modification of MCF with APTES (aminopropyl-triethoxysilane)	170	127	49	0.0323 mol HPW/mol APTES	O-hetero cyclization of cycloocta-1.5-diene	The HPW-NH_2-MCF was more efficient compared to HPW-NH_2-SBA-15 and HPW-NH_2-MCM-41 The catalyst could be used for more than six times without any significant loss of activity due to the strong interaction between the NH_2 groups in the silane moieties and HPW molecules.	32
TiO_2@MCF/CH_3	Co-condensation method was followed by surface organo-grafting and post UV-irradiation	491	170	-	23.3%	Photocatalytic hydroxylation of benzene	TiO_2@MCF/CH_3 has a high selective activity due to modification of the hydrophobicity of the mesoporous siliceous cage environment,	34

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Continued **Table 1**: Applications of MCF silica as catalyst support in heterogeneous catalysis.

Catalyst	Method of preparation	Catalyst characterization				Application	Remark	Reference
		SSA (m^2/g)	Dc (Å)	Dw (Å)	D			
10%WO_3-MCF	Direct synthesis Impregnation from ammonium tungstate solution	640	235	51	54.5 mol/mol[a]	O-heterocyclization of cyclooctа-1.5-diene	10 % WO3–MCF catalyst was more active as it has small sizes of tungsten-oxide particles and stronger interaction between active tungstenoxide species and the MCF material. 10 % WO3–MCF catalyst showed far better stability	33
10%WO_3/MCF		621	223	45	41.5 mol/mol[a]			
Ni-MCF	Impregnation from $Ni(NO_3)_2.6H_2O$ in ethanol solution	734	170	-	5 %	Pyrolytic decomposition of cellulose to produce H_2	Ni-MCF was the more effective catalyst compared to Ni functionalized SBA-15 and Al_2O_3 catalysts	35

[a]: Si/W mol ratio ; Dw: window size ; Dc: Cell size ; SSA: Specific surface area ; D: Dispersion of active site

ketones, hydrogenation of olefins, reductive amination of aldehydes, hydrogenolysis of epoxides and diols [22]. The Pd-supported catalyst (Pd/Urea-MCF) was prepared by grafting the Pd in MCF silica using urea ligand. The solution of trimethoxypropyl urea in toluene was introduced into the MCF silica to form Urea-MCF. Then, the Pd was grafted into Urea-MCF using a solution of palladium acetate in CH_2Cl_2 to generate the Pd/Urea-MCF catalyst. The Pd/Urea-MCF catalyst demonstrated superior activity compared to the commercially available 10 wt% Pd/C or polymer supported Pd-Encat® due to the stabilization of the Pd on MCF silica and the large mesopores of the catalyst that facilitated reactions involving bulky substrates.

Furthemore, the Pd(II) which was supported on the MCF silica surface-tethered bipyridyl, iminopyridine, or 3-aminopropyl ligands was used for oxidative Heck couplings of arylboronic acids and olefins, carried out under air to facilitate reoxidation of palladium without the need for an added co-oxidant [23]. It was observed that Pd(II), supported on MCF silica surface-tethered bipyridine ligands (MCF-BiPy-Pd), was the most efficient catalyst due to the most strongly chelating bipyridyl ligands. Additionally, the bipyridyl functionality in the catalyst facilitated the oxidation of Pd(0) to Pd(II) in the presence of molecular oxygen or air. MCF-BiPy-Pd catalyst could be used for multiple catalytic cycles without activity loss.

To ensure thorough metal distribution, the authors provided binding sites for loading palladium precursor salt into MCF silica by employing silane surface functionalization for the purpose of synthesizing the Pd-supported catalysts [24]. The catalysts were used for the decarboxylation of stearic acid in the presence of dodecane as a solvent to produce a diesel-like hydrocarbon of n-heptadecane. Three different silanes were used for binding sites i.e. 3-amino-propyltrimethoxysilane (APTMS), 3-ureidopropyl-trimethoxysilane (UPTMS) and 3-mercaptopropyl trimethoxysilane (MPTMS). It was determined that the Pd supported MCF catalyst (Pd-MCF-U) synthesized using UPTMS for the binding sites, was the most efficient for the decarboxylation due to the evenly-distributed, small palladium nanoparticles on the MCF silica.

Furthermore, the deactivation of the Pd-MCF-U catalyst during the decarboxylation was observed, and the nature of the cause of the deactivation was clarified [25]. It was reported that after one use, the carbonaceous deposition in the spent catalyst was found to be residual reactants, solvent and product. The carbonaceous deposition was reduced by 90% via extractions with

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tetrahydrofuran. After extraction, the spent catalyst was re-reduced 300°C for 2 hours. The regenerated catalyst showed a 19-fold increase in decarboxylation activity compared to the original spent catalyst.

Applications of MCF silica as a catalyst support for the incorporation of various active sites such as chromium, vanadium oxide, vanadium, tungsten trioxide, tungsten, and titanium oxide have also been successfully carried out. The catalysts were used for the dehydrogenation of propane [26-28], the dehydrogenation of ethylbenzene [29], dichloromethane decomposition [28,30], the epoxidation of propene with N_2O [31], liquid phase oxidation of 1,3-butanediol [32], O-heterocyclization of cycloocta-1.5-diene [33,34] and photocatalytic hydroxylation of benzene [35]. Meanwhile, nickel supporting MCF silica has been studied for the pyrolytic decomposition of cellulose to produce H_2 [36]. When compared with the Ni functionalized SBA-15 and Al_2O_3 catalyst, nickel functionalized MCF silica was the most effective catalyst for the pyrolytic decomposition of cellulose. Nickel supporting MCF has also been studied for the decarboxylation and decarbonylation of fatty acids to produce diesel-like hydrocarbons [37]. In conclusion, the effectiveness of catalysts derived from MCF silica for these reactions was mostly due to well-defined 3D mesopore systems and the much larger pore in the catalyst, strong interaction between active species and the MCF material, as well as small sizes and even distribution of active sites of MCF silica.

4 MCF Silica in Enzymatic Reactions

Although enzymatic bioprocesses have the major advantages of high selectivity and yield compared to chemical synthesis routes, the high cost of enzymes is the main problem for them to be industrially feasible [38]. Additionally, free enzymes usually have low stability towards heat, organic solvents, acids or bases and are difficult to be recovered and reused [38]. To reduce enzyme costs, the improvement of stability of enzymes is highly desirable [39,40]. Enzyme immobilization is used to improve the stability under storage as well as operational conditions with respect to the denaturation of temperature, organic solvents or autolysis [41,42]. The advantages of enzyme immobilization enable the development of continuous processes, broadening the applicable pH range [43] and avoiding products contamination by enzymes [42].

Binding enzymes in porous inorganic supports is one of the techniques to immobilize enzymes [44]. The common methods for the immobilization of enzymes on porous inorganic supports include covalent binding, electrostatic interaction, adsorption and cross-linking [45]. The covalent binding method involves surface modification of porous inorganic supports using functional groups before enzymes are immobilized. A functional group provides reactive sites for enzymes to be immobilized and offers tunable surface properties that enable the control of the position and density of the immobilized enzyme [46-50]. The functional groups usually used are thiols, carboxylic acids, alkyl chlorides, and amines and vinyl.

Electrostatic interaction of enzymes is immobilization via ionic interaction. The electrostatic interaction between an enzyme and porous inorganic support is provided by ionizing the porous inorganic supports before immobilizing the enzymes. For example, mesoporous silica support that has been functionalized with carboxylic group (-COOH) has negative charges at pH 7.5. Under the same condition, the functionalization of mesoporous silica support with amine groups ($-NH_2$) gives off a positive charge. Since enzymes usually possess a positive charge, the electrostatic interactions occur between enzymes and carboxylic groups functionalized mesoporous silica [51]. Electrostatic interaction between the enzyme and support was found to be strong enough to minimize leaching.

Adsorption is the simplest enzymes immobilization method since treatment of porous inorganic supports before the immobilization process is not required [52,53]. The immobilization primarily depends on weak van der Waals interaction. It can be noted that the enzymatic activity and stability upon immobilization via physical adsorption can be improved by enhancing interaction between substrate and immobilized enzyme or increasing spin states of the adsorbed enzyme [39,54,55].

Cross-linking refers to the construction of three-dimensional enzyme aggregates by covalently linking the enzyme molecules to the support. The cross-linking technique is usually combined with other immobilization techniques such as adsorption, covalent binding, etc., to control the enzyme aggregate sizes, substrate accessibility to the cores of the aggregates and mechanical strength of the cross-linked enzyme. For example, an enzyme is physically adsorbed in a three-dimensional network of interconnecting cages with diameters several times higher than the enzyme size, followed by cross-linking [45].

MCF silica material is a promising candidate for porous inorganic supports for enzyme immobilization as it has an ultra-large pore size and three-dimensional interconnected pore structure that are supposed to cause less spatial restriction to enzymes than lower pore sizes and one-dimensional channels of MCM-41and SBA-15 silica material [55]. A wide range of enzymes immobilized

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Table 2: Enzyme immobilized on MCF silica and it applications.

Enzyme carrier	Characterization of enzyme carrier			Enzymes	Binding methods of enzymes to MCF silica	Application	Remark	Reference
	SSA (m^2/g)	Dc (Å)	Dw (Å)					
MCF5-APTS	441	240	130	Trypsin	Bonded with various organosilanes modified MCF via glutaraldehyde (GLA) as a cross lingker	Hydrolysis of BAPNA and casein	GLA-APTS linkage was found to be the most efficient system for covalent immobilization of trypsin	52
MCF4-AEAPTS	353	220	130	Invertase Glucoamylase	Bonded with alkyl amines functionalized MCF silica via GLA as a cross-lingker	Hydrolysis of sucrose, starch and maltose	-Glutaraldehyde amino linkage formed by AEAPTS was the most effective system for MCF-bound Invertase.	53
MCF5-APTS	441	240	130					
MCF-L	622	286	146	Invertase	Bonded with alkyl amines functionalized MCF silica via GLA as a cross-lingker	Hydrolysis of sucrose	MCF-bound Invertase had catalytic properties far superior to the corresponding SBA-15-based preparations	54
MCF- S	-	178	-	Alkaline serine en-dopeptidase	Bonded with the organo-silane functionalized MCF silica via carbodiimide as a cross-linker	Hydrolysis of casein	- MCF immobilized with enzyme was more effective than the corresponding SBA-15-based preparations. – It was reusability up to 15 cycles with 80% of the activity retained	55
MCF(46)	-	254	76	Pseudomonas cepacia lipase	-Using non-ionic template for enzyme adsorption. -GLA treatment was attempted to avoid enzyme leaching	Hydrolysis of tributyrin	- Its specific activity was higher than activity of free lipase. – immobilized enzyme treated with GLA retained up to 88% of its original activity after six hydrolysis test	57
MCF	588	-	121	Cytochrome c (CYC-Sc) and chloro peroxidase (CPO)	Adsorption of enzyme into MCF silica by adjusting pH of solution	Oxidation of styrene	Immobilization of CPO and CYC-Sc in MCF silica im-proved catalytic activity, stability of CYC-SC and CPO and increased the tolerance of enzymes toward organic solvent	60
MCF-Ph	317	310	158	*Pseudomonas cepacia* lipase and *Candida antarctica* lipase B (CALB)	Bonded with various hydrophobic/ hydrophilic MCF surface	Transesterification of racemic 1 phenyl- ethanol and Hydrolytic reaction of tributyrin and triacetin	PCL immobilized into MCFs with a hydrophobic surface exhibited much higher catalytic activity than PCL immobilized into MCFs with a hydrophilic surface.	58
MCF-NH_2	328	342	169					
MCF-TMNCl	306	294	156					
MCF-TBNCl	318	293	155					
MCF-C8	359	331	160					

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Continued **Table 2**: Enzyme immobilized on MCF silica and it applications.

Enzyme carrier	Characterization of enzyme carrier			Enzymes	Binding methods of enzymes to MCF silica	Application	Remark	Reference
	SSA (m^2/g)	Dc (Å)	Dw (Å)					
C_8-MCF	332	243	125	CALB	Bonded with various long-chain alkyl groups modified MCF silica using pressure-driven method	Kinetic resolu-tion of 1-phenyl-ethanol acylated with isopropenyl acetate	Lipase CALB immobilized on hydrophobic MCF particles by the pressure-driven method showed excellent activity. It had superior reusability and thermal stability.	59
C_{18}-MCF	252	225	106					
GAmP-MCF	407	267	130	Candida antarctica lipase A (CALA)	Bonded with the organo-silane functionalized MCF silica via glutar-aldehyde as a cross-lingker	Dynamic kinetic resolution of ethyl 3-amino-3-phenyl-propanoate	CALA immobilized MCF silica was potential for improving the enanti-oselectivity and thermostability of enzymes	61
MCF	532	250	-	Dye-decolorizing peroxidase (rDyP)	Adsorption of enzyme into MCF silica by adjusting pH of solution	Decolorization of an anthrax-quinone dye	Immobilization of rDyP in MCF was efficient compared to that in other mesoporous materials mainly because of its larger pore size and inter-pore windows Dye decolorization were stron-gly pH-dependent. The highest efficiency of dye decolorization achieved at pH 5,	62
AF-LMCF	520	340	17	Glucose oxidase (GOx)	Bonded with the organo-silane functionalized large MCF silica using various molar ratio of ATES to TEOS.	Conversion of glucose to gluconic acid	GOx immobilized on AF-MCFs mate-rials exhibited the high catalytic activity and thermal stability. It was also reusable..	63

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on MCF silica material has been reported in the literature. Studies of enzyme immobilization on MCF silica using different methods and applications are summarized in **Table 2**.

The immobilization of trysin using MCF silica as an inorganic support has been studied [56]. MCF silicas were modified with alkyl amines using various organosilanes i.e. 3-aminopropyltriethoxysilane (APTS), 2-aminoethyl-3-aminopropyl-methyldimethoxysilane (AEAPMDS), 2-aminoethyl-3-aminopropyl trimethoxysilane (AEAPTS) and 3-glicydoxypropyl-triethoxysilane (GPTS). The MCF silica modified with alkyl amines was activated with glutaraldehyde (GLA) as a cross-link and followed by the immobilization of trypsin. The activity of the MCF-based biocatalyst was examined in hydrolysis of N-benzoyl-DLarginine-p-nitroanilide (BAPNA) and casein (soluble milk protein). It was determined that MCF-based biocatalysts were more effective than silica gel- and Eupergit C-based counterparts. Moreover, they showed good storage stability at 4°C and were notably more stable than native enzyme at 50°C. These were due to the unique porous structure of the modified MCF silica. GLA- APTS linkage was found to be the most efficient system for the covalent immobilization of trypsin. The activity of the best system was higher than that of free enzymes in BAPNA and casein conversion.

The immobilizations of invertase and glucoamylase on MCF modified with alkyl amines via GLA as a cross-link were studied as well [57]. Various organosilanes i.e. APTS, AEAPMDS, AEAPTS and GPTS were used to modify MCF with alkyl amines. Activities of the immobilized enzymes were examined for hydrolysis of sucrose, starch and maltose. It was reported that systems with large protein bonding capacities appeared not the most active. The efficiency of immobilization was controlled by the amino group content. GLA-amino linkage formed by AEAPTS with two amino groups was found to be the most effective system for MCF-bound invertase. The GLA-amino linkage formed by APTS was suitable for the immobilization of glucoamylase. It was reported that the MCF-bound invertase derived from MCF with ultra large mesopores had catalytic properties far superior to the corresponding SBA-15-based preparations in hydrolysis of sucrose [58].

MCF silica immobilized with alkaline serine endopeptidase using 1-[3-(dimethylamino)propyl]-3-ethyl carbodiimide hydrochloride (EDAC) was also conducted [59]. EDAC is used as a versatile coupling agent to form amide and thus to cross-link enzyme to surfaces [60]. Activity of the enzyme immobilized MCF was observed in hydrolysis casein. The activity was found to be more effective compared with the activity of corresponding SBA-15-based preparation. The enzyme immobilized MCF performed the highest activity at 60°C, which was higher than the free enzyme (at 55°C). The enzyme immobilized in MCF was reusable up to 15 cycles with 80% of the activity retained.

Other enzymes such as *Pseudomonas cepacia* lipase, *Candida antarctica* lipase B (CALB), cytochrome c (CYC-Sc), chloroperoxidase (CPO), *Candida antarctica* lipase A (CALA), dye-decolorizing peroxidase (rDyP) and glucose oxidase (GOx) have been successfully immobilized onto MCF silica by various binding methods as shown in Table 2. The applications of the enzyme immobilized MCF silica reported in the literature include hydrolysis of tributyrin [61], transesterification of racemic 1 phenylethanol [58], hydrolytic reaction of tributyrin and triacetin [62], kinetic resolution of 1-phenylethanol acylated with isopropenyl acetate [63], oxidation of styrene [64], dynamic kinetic resolution of ethyl 3-amino-3-phenyl-propanoate [65], decolorization of an anthraquinone dye [66], conversion of glucose to gluconic acid [67]. It can be concluded from the literatures that effective enzyme immobilized MCF silicas for the reactions were mainly attributed to a higher amount of enzymes bound with a carrier matrix derived from MCF silica, a higher accessibility of substrate to active sites located in 3D pore system with ultra-large pore size of the immobilized enzyme, and a stabile nature of bonds formed between enzymes and the carrier matrix.

5 MCF Silica in Separation Processes

In addition to the heterogeneous catalysis and enzymatic bioprocess, MCF silica was also promising for the application in the separation process. Since MCF silica has larger pore sizes and pore volume among all mesoporous materials (such as MCM-41, HMS, SBA-15) discovered during the last decade, it has been widely exploited for separation processes of CO_2 and protein. The important applications of MCF silica in separation process were summarized in **Table 3**.

CO_2 separation processes are becoming increasingly important due to an increased amount of CO_2 released into the atmosphere which resulted from extensive utilization of fossil fuel. High amounts of CO_2 in the atmosphere is a major cause for several environmental phenomena including global warming [68]. Functionalization of MCF silica with chitosan dan CaO were observed as an adsorbent to reduce the CO_2 amount [69,70]. MCF silicas which were modified using APTS and followed by

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Table 3: Applications of MCF silica in separation process.

Adsorbent	Characterization of adsorbent				Method of preparation	Application	Remark	Reference
	SSA (m^2/g)	Dc (Å)	Dw (Å)	D				
MCF/G4	151	170	84	55 %	Modification of MCF using (aminopropyl-triethoxysilane) followed by functionnalization with various amounts of melamine-type dendrimers	As a CO_2 adsorbent	The adsorbent modified with highest organic loading was very active since it had the highest content of primary amines groups which were active for CO_2 chemisorption in melamine-type dendritic structures.	65
MCF-PEI	70.8	220	147	50 %	Wet impregnation from polyethy-leneimine (PEI) in methanol solution	As a CO_2 adsorbent	The adsorbent derived from MCF silica achieved a very high CO_2 uptake compared to that derived from MCM-41, SBA-15, HMS and KIT-6. It also exhibit good stability after 8 cycles of adsorption/desorption.	66
MCF/x.1200	-	-	-	8.9 %	Impregnation of linear poly(ethyleneimine) or branched poly(ethy-leneimine) in MCF si- licas prepared with various ratios of TMB and P123	As a CO_2 adsorbent	Amine modified MCF's were better adsorbents than amine modified SBA-15 at elevated temperature in a vacuum swing adsorption process. Amine modified MCF derived from branched poly(ethyleneimine)was more effective than that derived from linear poly(ethyleneimine).	67
MCF/x.2500	-	-	-	66.5 %				
MCF/y.1200	-	-	-	71.4%				
MCF/y.2500	-	-	-	68.4%				
PAA_MCF_33	-	-	-	5.7 mmol N./g	Impregnations of various polymers with different loading in MCF	For CO_2 capture	At low polymer loadings, adsorbent de-rived from poly(allylamine) was efficient com-pared to that derived from linier poly(ethyleneimine) At higher polymer loading, adsorbent de-rived from branched poly(ethyleneimine) was the most efficient due to favorable display of the primary amines sites at the end of each chain, making these important sites highly accessible.	68
PEIBr_MCF_28	-	-	-	6.5 mmol N./g				
PEILn_MCF_32	-	-	-	7.3mmol N./g				

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Continued **Table 3**: Applications of MCF silica in separation process.

Adsorbent	Characterization of adsorbent				Method of preparation	Application	Remark	Reference
	SSA (m^2/g)	Dc (Å)	Dw (Å)	D				
MCF- 1	647	392	76	-	MCF materials synthesized at various acid concentrations and aging times	Adsorption of biomole-cule (L-tryp-tophan, lyso-zyme , bovine serum albumin)	MCF materials synthesized using 3.5 M HCl with an aging time of 20 h (MCF-3) was best adsorbent for adsorption of biomolecule because of its large and narrowly distributed window pores. Protein adsorption onto MCF silica showed minimal size exclusion until the window size of the silica was barely larger than the largest protein dimension	70
MCF-2	637	404	87	-				
MCF-3	711	335	167	-				
MCF-4	561	354	197	-				
MCF-5	637	279	156	-				
MCF-6	532	388	232	-				
MCF(2.0)-AF	714	274	173	-	MCF materials syn-thesized at various ratios of TMB and P123, without or with the addition of ammonium fluoride	Adsorption of bovine se-rum albumin (BSA)	BSA molecules were strongly immobilised in the cells of the MCF material. Among other, MCF(2.0)-AF synthesized with addition of ammonium fluoride at TMB and P123 ratio of 2 showed the most effective adsorbent due to its high pore volume	71
MCF(0.35)-AF	707	246	139	-				
MCF(2.0)	832	285	113	-				
MCF-AP-1	403	315	199	1.22 mmol/g	Post synthetic modifi-cation of MCF using various orga-nosilane	Adsorption of bovine serum albumin (BSA)	Adsorbent containing aminopropyl groups (MCF-AP-1) has the highest adsorption ca-pacity due to strong interactions established between the BSA molecules and the protonated amine groups on the surface. However the higher content of this functio- nality does not lead to further improvement.	72
MCF-CM-1	528	315	199	1.26 mmol/g				
MCF-MP-1	529	315	199	0.86 mmol/g				
MCF-OC-1	472	315	199	0.56 mmol/g				

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functionalization with various amounts of melamine-type dendrimers, were studied for the adsorption of CO_2 [71]. It was found that the MCF modified with the highest organic loading of APTS was very active since it had the highest content of primary amines groups, which were active for CO_2 chemisorption in melamine-type dendritic structures. The CO_2 adsorption capacity of adsorbents derived from functionalized MCF silicas were higher than that of unfunctionalized MCF silica. MCF modified with amine using polyethyleneimine (PEI) in methanol solution was also observed for CO_2 adsorption [72]. It was reported that adsorbent derived from modified MCF silica achieved a very high CO_2 uptake compared with adsorbents from modified MCM-41, SBA-15, HMS and KIT-6. CO_2 adsorption using amine modified MCF with different pore sizes [73] and poly(allylamine)-MCF silica [74] were also reported.

The development of methods for protein separation is important for the growth of modern biotechnology and bioscience, as bioseparation represents a major manufacturing cost (~ 50-80%) for many products such as therapeutic proteins [75]. Adsorption of various proteins i.e. L-tryptophan, lysozyme and bovine serum albumin onto MCF silica with different structures were studied [76]. The MCF silicas were prepared at various HCl concentrations (1.6 – 5.4 M) and aging times (20-72 h). It was found that optimal synthesis conditions to produce large and narrowly distributed window pores were 3.5 M HCl with an aging time of 20 h. Adsorption capacity of L-tryptophan on MCF silica was several times higher than that of lysozyme and bovine serum albumin on MCF silica.

MCF materials synthesized at various ratios of 1,3,5-trimethylbenzene (TMB) to Pluronic123 (P123) without or with the addition of ammonium fluoride were used for the adsorption of bovine serum albumin [77]. The bovine serum albumin molecules were strongly immobilized in the cells of the MCF material. MCF silica synthesized with the addition of ammonium fluoride at a ratio of TMB to P123 of 2, showed the most effective adsorbent due to its high pore volume. Modifying the surface of MCF silica for the adsorption of bovine serum albumin molecules was also studied [78]. MCF silica materials were modified with various organosilanes i.e. chloromethyltriethoxysilane (CMTS), 3-mercaptopropyltriethoxy silane (MPTS), octyltriethoxysilane (OTS), and 3-aminopropyltri ethoxysilane (APTS) using post synthesis method. MCF silica containing aminopropyl groups was found to have the highest adsorption capacity due to strong interactions between the bovine serum albumin molecules and the protonated amine groups on the surface. However, the higher content of this functionality did not lead to further improvement.

6 Conclusion and Future Direction

As the incorporation of high amounts of active sites (>6 wt%) or immobilization of enzymes in mesoporous silicas pore sizes (MCM-41, HMS, SBA-15 etc.) led to the damage of structure and framework mesoporosity, the MCF silica allowed the choice of supports and more favorable conditions for these uses since it had larger pore sizes (150-500 Å) and hydrothermal robustness. To obtain potentialities of the catalysts, enzymes and adsorbents derived from MCF silica, a detailed understanding of the characterization of the synthesized materials (pore size of synthesized materials, sizes of active sites/enzymes, amount of active sites/enzymes bound with MCF silica, etc.) needed to be constructed as presented in this review. The effectiveness of the catalysts or adsorbents derived from MCF silica were mostly due to well-defined 3D mesopore systems, large pore sizes and strong interactions between active species and the MCF material as well as small sizes, high amounts and evenly-distributed active sites of MCF silica. Moreover, effective immobilized enzymes of MCF silica were mainly attributed to a high amount of enzymes bound with this material, high accessibility of substrate to the active sites located in ultra-large pore sizes of MCF and a stable nature of formed bonds between enzymes and MCF silica.

The incorporations of metals, metal oxides and acid catalysts such as Pd, V, W, WO_3, HPW, TiO_2 and Ni in MCF silica proved suitable as catalysts for various heterogeneous reactions. Enzymes such as Trypsin, Invertase, Glucoamylase immobilized in MCF silica exhibited their effectiveness for various enzymatic processes. In the future, the incorporation of other active sites such as ZrO, Sn, Al, Fe in MCF silica and/or immobilization of other enzymes in MCF silica will need to be investigated to expand the application of MCF silica materials. Furthermore, the regeneration and reusability of catalysts derived from this material also needs to be studied in more detail to obtain the more effective catalyst or bio catalyst.

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Conflict of interest: Authors declare no conflict of interest.

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