Review Article

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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 material allow 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-DL-arginine-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 successfully 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.

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]. The 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
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 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.
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\textsubscript{x}PO\textsubscript{y}EO\textsubscript{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.
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 slurring 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...
Table 1: Applications of MCF silica as catalyst support in heterogeneous catalysis.

| Catalyst          | Method of preparation | Catalyst characterization | Application                                                                 | Remark                                                                                                            | Reference |
|-------------------|-----------------------|---------------------------|-----------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|-----------|
| Pd/MCFss          | Direct Synthesis      | 714 - 79 - 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%          | Hydrogenation, Suzuki and Heck coupling, hydrogenolysis.                     | Pd/MCF-imp catalyst demonstrated superior activity compared to commercially available (10 wt% Pd/C) or polymer supported Pd-Encat | 22        |
| 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 | 23        |
| Pd-NH₂-MCF        | Grafting Pd(II) in MCF silica using bipyridyl, imino pyridine, or 3-amino propyl ligands | 640 - 0.39 mmol/g<sub>cat</sub> | 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. | 24        |
| Pd-ImPy-MCF       | Grafting Pd in MCF using various silane for binding sites | 620 - 0.41 mmol/g<sub>cat</sub> | 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 | 25        |
| Pd-BiPy-MCF       | Grafting Pd in MCF using various silane for binding sites | 610 - 0.38 mmol/g<sub>cat</sub> | 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 | 26        |
| Pd-MCF-S          | 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 | 27        |
| Pd-MCF-N          | Grafting Pd in MCF using various silane for binding sites | 660 - 350 - 150 - 55%     | 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 | 28        |
| Pd-MCF-U          | Grafting Pd in MCF using 3-ureidopropyl-trimethoxysilane (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 | 29        |
| 1.0Cr-MCF         | Impregnation from Cr(NO₃)₃ · 9H₂O 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. | 30        |
Table 1: Applications of MCF silica as catalyst support in heterogeneous catalysis.

| Catalyst       | Method of preparation | Catalyst characterization | Application                  | Remark                                                                                     | Reference |
|----------------|-----------------------|---------------------------|------------------------------|--------------------------------------------------------------------------------------------|-----------|
| 2.8V-MCF       | Impregnation from NH$_4$VO$_3$ in methanol solution | SSA: 504, Dc: 181, Dw: 41, D: - | 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$_4$VO$_3$ in oxalic acid solution   | SSA: 420, Dc: 221, Dw: -  D: - | 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     | SSA: 925, Dc: 160, Dw: 60, D: 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$_4$VO$_3$ solution | SSA: 645, Dc: 230, Dw: 120, D: 0.46 VOx/nm$^2$ | 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        |
| V-MCF          | Direct synthesis     | SSA: 925, Dc: 160, Dw: 60, D: - | Liquid phase oxidation of 1,3-butadiene | W-MCF catalyst was effective as compared to WO$_3$/MCF and W-SBA-15. Very stable catalytic activity was also observed for the W-MCF catalyst | 31        |
| W-MCF(20)      | Direct synthesis     | SSA: 557, Dc: 236, Dw: 56, D: - | Liquid phase oxidation of 1,3-butadiene | W-MCF catalyst was effective as compared to WO$_3$/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$_2$O in alcoholic solution | SSA: 498, Dc: 176, Dw: 36, D: - | Liquid phase oxidation of 1,3-butadiene | W-MCF catalyst was effective as compared to WO$_3$/MCF and W-SBA-15. Very stable catalytic activity was also observed for the W-MCF catalyst | 31        |
| HPW-NH$_2$-MCF | Surface modification of MCF with APTES (aminopropyltriethoxysilane) | SSA: 170, Dc: 127, Dw: 49, D: 0.0323 mol HPW/mol APTES | O-heterocyclization 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 | SSA: 491, Dc: 170, Dw: - D: 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        |
Lilis Hermida et al. 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 CH2Cl2 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.

Furthermore, 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
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 N₂O [31], liquid phase oxidation of 1,3-butadiene [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 H₂ [36]. When compared with the Ni functionalized SBA-15 and Al₂O₃ 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 thiol, 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 (-NH₂) 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-41 and SBA-15 silica material [55]. A wide range of enzymes immobilized
| Enzyme carrier | Characterization of enzyme carrier | Enzymes | Binding methods of enzymes to MCF silica | Application | Remark | Reference |
|----------------|-----------------------------------|---------|----------------------------------------|-------------|--------|-----------|
|                | SSA (m²/g) Dc (Å) Dw (Å)          |         |                                        |             |        |           |
| MCF5-APTS      | 441 240 130                       | Trypsin | Bonded with various organosilanes modified MCF via glutaraldehyde (GLA) as a cross-linker | 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-linker | 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                       | Invertase | Bonded with alkyl amines functionalized MCF silica via GLA as a cross-linker | Hydrolysis of sucrose | MCF-bound Invertase had catalytic properties far superior to the corresponding SBA-15-based preparations | 54 |
| MCF-L          | 622 286 146                       | Invertase | Bonded with alkyl amines functionalized MCF silica via GLA as a cross-linker | Hydrolysis of sucrose | - 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-S          | - 178 -                           | Alkaline serine endopeptidase | Bonded with the organo-silane functionalized MCF silica via carbodimide as a cross-linker | Hydrolysis of casein | - MCF immobilized with GLA retained up to 88% of its original activity after six hydrolysis test | 56 |
| 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 | - It’s 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-NH₂        | 328 342 169                       |         |                                        |             |        |           |
| MCF-TMNCI      | 306 294 156                       |         |                                        |             |        |           |
| MCF-TBNCI      | 318 293 155                       |         |                                        |             |        |           |
| MCF-C8         | 359 331 160                       |         |                                        |             |        |           |
### Table 2: Enzyme immobilized on MCF silica and its applications.

| Enzyme carrier | Characterization of enzyme carrier | Enzymes | Binding methods of enzymes to MCF silica | Application | Remark | Reference |
|----------------|------------------------------------|---------|----------------------------------------|-------------|--------|-----------|
|                | SSA (m²/g)  | Dc (Å) | Dw (Å) |                                       |             |         |           |
| C₈-MCF         | 332        | 243    | 125   | Bonded with various long-chain alkyl groups modified MCF silica using pressure-driven method | Kinetic resolution 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 |
| C₁₆-MCF        | 252        | 225    | 106   | Bonded with the organo-silane functionalized MCF silica via glutaraldehyde as a cross-linker | Dynamic kinetic resolution of ethyl 3-amino-3-phenylpropanoate | CALA immobilized MCF silica was potential for improving the enantioselectivity and thermostability of enzymes | 61 |
| GAmP-MCF       | 407        | 267    | 130   | Bonded with the organo-silane functionalized MCF silica via glutaraldehyde as a cross-linker | Dynamic kinetic resolution of ethyl 3-amino-3-phenylpropanoate | 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 strongly pH-dependent. The highest efficiency of dye decolorization achieved at pH 5. | 62 |
| MCF            | 532        | 250    | -     | Adsorption of enzyme into MCF silica by adjusting pH of solution | Decolorization of an anthraquinone dye | | |
| AF-LMCF        | 520        | 340    | 17    | 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 materials exhibited the high catalytic activity and thermal stability. It was also reusable. | 63 |
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 trypsin 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-glycidoxypropyl-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 SBA15-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 SBA15-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], transterification 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 stable 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 CO₂ and protein. The important applications of MCF silica in separation process were summarized in Table 3.

CO₂ separation processes are becoming increasingly important due to an increased amount of CO₂ released into the atmosphere which resulted from extensive utilization of fossil fuel. High amounts of CO₂ 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 CO₂ amount [69,70]. MCF silicas which were modified using APTS and followed by
Table 3: Applications of MCF silica in separation process.

| Adsorbent     | Characterization of adsorbent | Method of preparation                                                                 | Application       | Remark                                                                                                                                                                                                 | Reference |
|---------------|-------------------------------|----------------------------------------------------------------------------------------|-------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| MCF/G4        | 151 170 84 55 %               | Modification of MCF using (aminopropyl-triethoxysilane) followed by functionalization with various amounts of melamine-type dendrimers | As a CO₂ 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 CO₂ chemisorption in melamine-type dendritic structures. | 65        |
| MCF-PEI       | 70.8 220 147 50 %             | Wet impregnation from polyethyleneimine (PEI) in methanol solution                     | As a CO₂ adsorbent| The adsorbent derived from MCF silica achieved a very high CO₂ 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(ethyleneimine) in MCF silicas prepared with various ratios of TMB and P123 | As a CO₂ 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 CO₂ capture   | At low polymer loadings, adsorbent derived from poly(allylamine) was efficient compared to that derived from linear poly(ethyleneimine). At higher polymer loading, adsorbent derived 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  | - - - 7.3 mmol N./g           |                                                                                       |                   |                                                                                                            |           |
### Table 3: Applications of MCF silica in separation process.

| Adsorbent | Characterization of adsorbent | Method of preparation | Application | Remark | Reference |
|-----------|-------------------------------|-----------------------|-------------|--------|-----------|
| MCF-1     | SSA 647, Dc 392, Dw 76 | MCF materials synthesized at various acid concentrations and aging times | Adsorption of biomolecule (L-tryptophan, lysozyme, 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     | SSA 637, Dc 404, Dw 87 | MCF materials synthesized at various acid concentrations and aging times | Adsorption of biomolecule (L-tryptophan, lysozyme, bovine serum albumin) | Protein adsorption onto MCF silica showed minimal size exclusion until the window size of the silica was barely larger than the largest protein dimension | |
| MCF-3     | SSA 711, Dc 335, Dw 167 | MCF materials synthesized at various acid concentrations and aging times | Adsorption of biomolecule (L-tryptophan, lysozyme, bovine serum albumin) | Protein adsorption onto MCF silica showed minimal size exclusion until the window size of the silica was barely larger than the largest protein dimension | |
| MCF-4     | SSA 561, Dc 354, Dw 197 | MCF materials synthesized at various acid concentrations and aging times | Adsorption of biomolecule (L-tryptophan, lysozyme, bovine serum albumin) | Protein adsorption onto MCF silica showed minimal size exclusion until the window size of the silica was barely larger than the largest protein dimension | |
| MCF-5     | SSA 637, Dc 279, Dw 156 | MCF materials synthesized at various acid concentrations and aging times | Adsorption of biomolecule (L-tryptophan, lysozyme, bovine serum albumin) | Protein adsorption onto MCF silica showed minimal size exclusion until the window size of the silica was barely larger than the largest protein dimension | |
| MCF-6     | SSA 532, Dc 388, Dw 232 | MCF materials synthesized at various acid concentrations and aging times | Adsorption of biomolecule (L-tryptophan, lysozyme, bovine serum albumin) | Protein adsorption onto MCF silica showed minimal size exclusion until the window size of the silica was barely larger than the largest protein dimension | |
| MCF(2.0)-AF | SSA 714, Dc 274, Dw 173 | MCF materials synthesized at various ratios of TMB and P123, without or with the addition of ammonium fluoride | Adsorption of bovine serum albumin (BSA) | BSA molecules were strongly immobilised in the cells of the MCF material. Among other, MCF(2.0)-AF synthesized with the addition of ammonium fluoride at TMB and P123 ratio of 2:1 showed the most effective adsorbent due to its high pore volume | 71 |
| MCF(0.35)-AF | SSA 707, Dc 246, Dw 139 | MCF materials synthesized at various ratios of TMB and P123, without or with the addition of ammonium fluoride | Adsorption of bovine serum albumin (BSA) | BSA molecules were strongly immobilised in the cells of the MCF material. Among other, MCF(2.0)-AF synthesized with the addition of ammonium fluoride at TMB and P123 ratio of 2:1 showed the most effective adsorbent due to its high pore volume | |
| MCF(2.0)  | SSA 832, Dc 285, Dw 113 | MCF materials synthesized at various ratios of TMB and P123, without or with the addition of ammonium fluoride | Adsorption of bovine serum albumin (BSA) | BSA molecules were strongly immobilised in the cells of the MCF material. Among other, MCF(2.0)-AF synthesized with the addition of ammonium fluoride at TMB and P123 ratio of 2:1 showed the most effective adsorbent due to its high pore volume | |
| MCF-AP-1  | SSA 403, Dc 315, Dw 199, D 0.22 mmol/g | Post synthetic modification of MCF using various organosilanes | Adsorption of bovine serum albumin (BSA) | Adsorbent containing aminopropyl groups (MCF-AP-1) has the highest adsorption capacity due to strong interactions established between the BSA molecules and the protonated amine groups on the surface. However, the higher content of this functionality does not lead to further improvement. | 72 |
| MCF-CM-1  | SSA 528, Dc 315, Dw 199, D 0.26 mmol/g | Post synthetic modification of MCF using various organosilanes | Adsorption of bovine serum albumin (BSA) | Adsorbent containing aminopropyl groups (MCF-AP-1) has the highest adsorption capacity due to strong interactions established between the BSA molecules and the protonated amine groups on the surface. However, the higher content of this functionality does not lead to further improvement. | |
| MCF-MP-1  | SSA 529, Dc 315, Dw 199, D 0.86 mmol/g | Post synthetic modification of MCF using various organosilanes | Adsorption of bovine serum albumin (BSA) | Adsorbent containing aminopropyl groups (MCF-AP-1) has the highest adsorption capacity due to strong interactions established between the BSA molecules and the protonated amine groups on the surface. However, the higher content of this functionality does not lead to further improvement. | |
| MCF-OC-1  | SSA 472, Dc 315, Dw 199, D 0.56 mmol/g | Post synthetic modification of MCF using various organosilanes | Adsorption of bovine serum albumin (BSA) | Adsorbent containing aminopropyl groups (MCF-AP-1) has the highest adsorption capacity due to strong interactions established between the BSA molecules and the protonated amine groups on the surface. However, the higher content of this functionality does not lead to further improvement. | |
functionalization with various amounts of melamine-type dendrimers, were studied for the adsorption of CO\textsubscript{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\textsubscript{2} chemisorption in melamine-type dendritic structures. The CO\textsubscript{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\textsubscript{2} adsorption [71].

It was reported that adsorbent derived from modified MCF silica achieved a very high CO\textsubscript{2} uptake compared with adsorbents from modified MCM-41, SBA-15, HMS and KIT-6. CO\textsubscript{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-mercaptopropyltriethoxysilane (MPTS), octyltriethoxysilane (OTS), and 3-aminopropyltriethoxysilane (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\textsubscript{3}, HPW, TiO\textsubscript{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\textsubscript{2}, 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.

### Acknowledgement:
The Research University grant (No. 814181) from Universiti Sains Malaysia and Science Fund grant (No. 6013381) from the Ministry of Science, Technology and Innovation (MOSTI) to support this research are gratefully acknowledged. Lilis Hermida also thanks the Directorate General of Higher Education (DIKTI) Ministry of National Education of Indonesia for PhD scholarship. We declare no conflict of interest.

### Conflict of interest:
Authors declare no conflict of interest.
References

[1] Beck J.S., Vartuli J.C., Roth W.J., Leonowicz M.E., Kresge C.T., Schmitt K.D., Chu C.T.W., Olson D.H., Shepphard E.W, McCullen S.B., Higgins J.B., Schlenker J., A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates, J. Am. Oil Chem. Soc., 1992, 114,10834-10843.

[2] Kruk M., and Jaroniec, M., Determination of Mesopore Size Distributions from Argon Adsorption Data at 77 K., J. Phys. Chem. B., 2002, 106,4732-4739.

[3] Hermida L., Abdullah A.Z.,Mohamed A.R., Synthesis of monoglyceride through glycerol esterification with lauric acid over propyl sulfonic acid post-synthesis functionalized SBA-15 mesoporous catalyst, Chem. Eng. J., 2011, 174(2-3), 668-676.

[4] Hermida L., Abdullah A.Z.,Mohamed A.R., Post synthetically functionalized SBA-15 with organosulfonic acid and sulfated zirconia for esterification of glycerol to Monoglyceride, J. Appl. Sci., 2010, 10(24), 3199-3206.

[5] Hermida L., Abdullah A.Z.,Mohamed A.R., Effect of Functionalization Conditions of Sulfonic Acid Grafted SBA-15 on Catalytic Activity in the Esterification of Glycerol to Monoglyceride: a Factorial Design Approach, J. Porous Mat., 2012, 19, 835-846.

[6] Degirmenci V., Yilmaz A., Uner D., Selective methane bromination over sulfated zirconia in SBA-15 catalysts, Cat. Today, 2009, 142, 30-33.

[7] Huang T., Tu W., Modification of functionalized mesoporous silica on the formation and the catalytic performance of platinum nanocatalysts, Appl. Surf. Sci., 2009, 255(17), 7672-7678.

[8] Chen I., Zhou J., Wang R., Zhang J., Preparation, characterization, and performance of HMS-supported Ni catalysts for hydrodechlorination of chlorobenzene, Ind. Eng. Chem. Res., 2009, 48, 3802-3811.

[9] Liu D., Lau R., Borgna A., Yang Y., Carbon dioxide reforming of methane to synthesis gas over Ni-MCM-41 catalysts, App. Cat. A: General, 2009, 358(2), 110-118.

[10] Liu D., Quek X.Y., Waha H.H.A., Zeng G., Li Y., Yang Y., Carbon dioxide reforming of methane over nickel-grafted SBA-15 and MCM-41 catalysts, Cat. Today, 2009, 148(3-4), 243-250.

[11] Schmidt-Winkel P., Lukens W.W., Yang P., Margolese D.L., Lettow J.S., Ying J.Y., Stucky G.D., Microemulsion Templating of Siliceous Mesostructured Cellular Foams with Well-Defined Ultralarge Mesopores, Chem. Mat., 2000, 12, 686-696.

[12] Schmidt-Winkel P., Lukens Jr. W.W., Zhao D., Yang P., Chmelka B.F., Stucky G.D., Mesoporous silicon foams with uniformly sized cells and windows, Am. Chem. Soc., 1999, 21(1), 254-255.

[13] Schmidt-Winkel P., Glinka C.J., Stucky G.D., Microemulsion templates for mesoporous silica, Langmuir, 2000, 16, 356-361.

[14] Zhao D., Huo Q., Feng J., Chmelka B.F., Stucky G.D., Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures, J. Am. Chem. Soc., 1998, 120, 6024-6036.

[15] Zhao D., Feng J., Huo Q., Melosh N., Fredrickson G.H., Chmelka B.F., Stucky G.D., Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores, Science, 1998, 279, 548-552.

[16] Lettow J.S., Han Y.H., Schmide-Winkel P., Yang P., Zhao D., Stucky G.D., Ying J.Y., Hexagonal to Mesocellular Foam Phase Transition in Polymer-Templated Mesoporous Silicas, Langmuir, 2000, 16, 8291-8295.

[17] Li Q., Wu Z., Feng D., Tu B., Zhao D., Hydrothermal Stability of Mesostructured Cellular Silica Foams, Journal of Phys. Chem. C, 2010, 114, 5012-5019.

[18] Garcia N., Benito E., Guzman J., Tiemblo P., Morales V., Garcia R.A., Functionalization of SBA-15 by an acid-catalyzed approach: A surface characterization study, Micropor. Mesop. Mat., 2007, 106, 129-139.

[19] Gates B.C., Supported Metal Clusters: Synthesis, Structure, and Catalysis, Chemical Reviews, 1995, 95, 511-522.

[20] Louis C., in: J. Regalbuto (Ed), Catalyst Preparation Science and Engineering, Taylor and Francis Inc., New York, 2007, 319-340.

[21] Na-Chiangmai C., Tiengchad N., Kittisakmontree P., Melasamwandunrong O., Powell J., Panpranot J., Characteristics and catalytic properties of mesocellular foam silica supported Pd nano particles in the liquid-phase selective hydrogenation of phenylacetylene, Catal.Lett., 2011, 141(8), 1149-1155.

[22] Erathodyiil N., Ooi S., Seayad A.M., Han Y., Lee S.S., Ying J.Y., Palladium Nanoclusters Supported on Propylurea-Modified Siliceous Mesocellular Foam for Coupling and Hydrogenation Reaction, Chem. A European Journal, 2008, 14, 3118-3125.

[23] Ping E.W., Venkatasubbaiah K., Fuller T.F., Jones C.W., Oxidative Heck Coupling Using Pd(II) Supported on Organosilane-Functionalized Silica Mesocellular Foam, Top Catal., 2010, 53, 1048-1054.

[24] Ping E.W., Wallace R., Pierson J., Fuller T.F., Jones C.W., Highly dispersed palladium nanoparticles on ultra-porous silica mesocellular foam for the catalytic decarbonylation of stearic acid, Micropor. Mesop. Mat., 2010, 132, 174-180.

[25] Ping E.W., Pierson J., Wallace R., Miller J.T., Fuller T.F., Jones C.W., On the nature of the deactivation of supported palladium nanoparticle catalysts in the decarbonylation of fatty acids, Appl. Cat. A: General, 2011, 396, 85-90.

[26] Liu Y.M., Feng W.L., Li T.C., He H.Y., Dai W.L., Huang W., Cao Y., Fan K.N., Structure and catalytic properties of vanadium oxide supported on mesocellular silica foams (MCF) for the oxidative dehydrogenation of propane to propylene, J. Catal., 2006, 239, 125-136.

[27] Liu Y.M., Feng W.L., Wang L.C., Cao Y., Dai W.L., He H.Y., Fan K.N., Chromium supported on mesocellular silica foam (MCF) for oxidative dehydrogenation of propane, Catal. Lett., 2006, 106(3-4), 145-152.

[28] Piumetti M., Bonelli B., Massiani P., Dzwigaj S., Rossetti I., Casale S., Armandi M., Thomas C., Garrone E., Effect of vanadium dispersion and of support properties on the catalytic activity of V-containing silica, Cat. Today, 2012, 179, 140-148.

[29] Chonguang L., Changxi M., Yingying N., Yinghong Y., Songyuan G., Weimin Y., Weiming H., Zi G., Ethylbenzene Dehydrogenation in the Presence of CO2 over MCF-Supported Vanadium Oxide Catalysts, Chinese J. Cat., 2010, 31, 993-998.

[30] Piumetti M., Bonelli B., Massiani P., Millot Y., Dzwigaj S., Gaberova L., Armandi M., Garrone E., Novel vanadium-containing mesocellular foams (V-MCF) obtained by direct synthesis, Micropor. Mesop. Mat., 2011, 142, 45-54.

[31] Held A., Kowalska-Kus J., Nowinska K., Gora-Marek K., MCF Material as an Attractive Support for Vanadium Oxide Applied
as a catalyst for propene epoxidation with N,O, Catal. Lett., 2018, 148(7), 2058-2068.

[32] Su Y., Liu Y.M., Wang L.C., Chen M., Cao Y., Dai W.L., He H.Y., Fan K.N. Tungsten-containing MCF silica as active and recyclable catalysts for liquid-phase oxidation of 1, 3-butanediol to 4-hydroxy-2-butanone, Appl. Cat. A: General, 2006, 315, 91-100.

[33] Gao R., Zhu W., Dai W.L., Fan K., Highly active and green amino propyl-immobilized phosphotungstic acid on mesocellular silica foam for the O-heterolysis of cycloocta-1,5-diene with aqueous H₂O₂, Green Chem., 2011, 13, 702-708.

[34] Gao R., Dai W.L., Yang X., Li H., Fan K., Highly efficient tungsten trioxide containing mesocellular silica foam catalyst in the O-heterolysis of cycloocta-1,5-diene with aqueous H₂O₂, Appl. Cat. A: General, 2007, 332, 138-145.

[35] Zhang G., Yi J., Shi H., Lee J., Choi W., Photocatalytic hydroxylation of benzene to phenol over titanium oxide entrapped into hydrophobically modified siliceous foam, Appl. Cat. B: Environmental, 2011, 102, 132-139.

[36] Widyaningrum R.N., Church T.L., Zhao M., Harris A.T., Mesocellular-foam-silica-supported Au catalyst: Effect of pore size on H₂ production from cellulose pyrolysis, Int. J. Hydrogen Energy, 2012, 37, 9590-9601.

[37] Hermida L., Amani H., Abdullah A.Z., Mohamed A.R., Deoxygenation of Palm Oil to Produce Diesel-like Hydrocarbons over Nickel Incorporated Cellular Foam Catalyst: A Kinetic Study, J Adv Chem Eng., 2016, 6(1), 1-8.

[38] Popat A., Hartono S.B., Stahr F., Liu, J., Qiao S.Z., (Max) Lu G.Q., Lee J., Choi W., Photocatalytic O-heterocyclization of cycloocta-1,5-diene with aqueous H₂O₂, J. Am. Chem. Soc., 2010, 132, 649-656.

[39] Chong A.S.M., Zhao X.S., Functionalized nanoporous silicas for the immobilization of penicillin acylase, Appl. Surf. Sci., 2004, 237, 398-404.

[40] Kim J, Grate J.W., Wang P., Nanostructures for Enzyme Stabilization, Chem. Eng. Sci., 2006, 61, 1017-1026.

[41] Marner W.D., Shahk A.S., Muller S.J., Keasling J.D., Morphology of artificial silica matrices formed via autoactivation of a silaffin/protein polymer chimera, Biomacromolecules, 2008, 9(1), 1-5.

[42] Ispas, C., Sokolov, I., Andreescu, S., Enzyme-functionalized mesoporous silica for bioanalytical applications, Anal. Bioanal. Chem., 2009, 393, 543-554.

[43] Hartmann M., Ordered mesoporous materials for biodesorption and biocatalysis, Chem. Mater., 2005, 17, 4577-4593.

[44] Hartmann M., Jung D., Biocatalysis with enzymes immobilized on mesoporous hosts: the status quo and future trends, J. Mat. Chem., 2010, 20, 844-857.

[45] Zhao X.S., Bao X.Y., Guo W., Lee F.Y., Immobilizing catalysts on porous materials, Mater. Today, 2006, 9, 32-39.

[46] Zhao X.S., Lu M.G.Q., Hu X., A novel method for tailoring the pore-opening size of MCM-41 materials, Chem. Commun., 1999, 1391-1392.

[47] Zhao X.S., Lu M.G.Q., Song C., Immobilization of aluminum chloride on MCM-41 as a new catalyst system for liquid-phase isopropylation of naphthalene, J. Mol. Cat. A: Chemistry, 2003, 191, 67-74.

[48] Zhao X.S., Chong A.S.M., Lu M.G.Q., in: Lu M.G.Q., Zhao X.S. (Eds.), Nanoporous Materials – Science and Engineering, Imperial College Press, London, 2004.

[49] Thomas J.M., Johnson B.F.G., Sankar G., Midgley P.A., High-performance nanocatalysts for single-step hydrogenations, Acc. Chem. Res., 2003, 36, 20-30.

[50] Lei C.H., Shin Y.S., Liu J., Ackerman E.J., Entrapping enzyme in a functionalized nanosilica support J. Am. Chem. Soc., 2002, 124, 11242-11243.

[51] Deere J., Magnes E., Wall J.G., Hodnett B.K., Adsorption and activity of cytochrome c on mesoporous silicates, Chem. Commun., 2001, 465-465.

[52] Agustian J., Hermida L., Saccharification Kinetics at Optimised Conditions of Tapioca by Glucoamylase Immobilised on Mesosstructured Celluar Foam Silica, Eur. Chem. Tech. J., 2018, 20(4), 311-318.

[53] Zlateski V., Keller T.C., Pérez-Ramírez J., Grass N.R., Immobilizing and de-immobilizing enzymes on mesoporous silica, RSC Adv., 2015, 5, 87706-87712.

[54] Deere J., Magnes E., Wall J.G., Hodnett B.K., Mechanical and Structural Features of Protein Adsorption into Mesoporous Silicates, J. Phys. Chem. B., 2002, 106, 7340-7347.

[55] Lu S., He J., Liu Z., Tuning interfacial non-covalent interactions through biomimetic functionalization of inorganic surface: The case of lysozyme and mesocellular silica foam hybrids Chem. Eng. J., 2009, 146, 503-514.

[56] Jarzewska A.B., Szymanska K., Bryjak J., Mrowiec-Bialon J., Mrowiec-Bialon, Covalent immobilization of trypsin on to siliceous mesostructured cellular foams to obtain effective biocatalysts, Chem. Eng. J., 2009, 146, 503-514.

[57] Szymanska K., Bryjak J., Mrowiec-Bialon J., Jarzewska A.B., Application and properties of siliceous mesostructured cellular foams as enzymes carriers to obtain efficient biocatalysts, Micropor. Mesopor. Mat., 2007, 99, 167-175.

[58] Szymanska K., Bryjak J., Jarzewska A.B., Immobilization of Invertase on Mesoporous Silicas to Obtain Hyper Active Biocatalysts, Top. Cat., 2009, 52, 1030-1036.

[59] Kannan K., Jasra R.V., Immobilization of alkaline serine endopeptidase from Bacillus licheniformis on SBA-15 and MCF by surface covalent binding, J. Mol. Cat. B: Enzymatic, 2009, 56, 34-40.

[60] Actim, EDAC: Water soluble carbodiimide, downloaded from http://www.actim.com/ content/view/25/1/lang,en/ on February 2014.

[61] Zhang Y., Zhao L., Li J., Zhang H., Zheng L., Cao S., Li C., Template enhanced activity of lipase accommodated in siliceous mesostructured foams, Biochim. Biophys. Res. Comm., 2008, 372, 650-655.

[62] Jin Q., Jia Q., Zhang Y., Yang Q., Li C., Hydrophobic Surface Induced Activation of Pseudomonas cepacia Lipase Immobilized into Mesoporous Silica, Langmuir, 2011, 27, 12016-12024.

[63] Han Y., Lee S.S., Ying J.Y., Pressure-Driven Enzyme Entrapment in Siliceous Mesocellular Foam, Chem. Mat., 2006, 18, 643-649.

[64] Águila S., Vazquez-Duhalt R., Covarrubia C., Pecchi G., Alderete J.B. Enhancing oxidation activity and stability of iso-1-cytochrome c and chloroperoxidase by immobilization in nanostructured supports, J. Mol. Cat. B: Enzymatic, 2011, 70, 81-87.
[65] Shakeri M., Engström K., Sandström A.G., Backvall J.E., Highly Enantioselective Resolution of b-Amino Esters by *Candida antarctica* Lipase A Immobilized in Mesocellular Foam: Application to Dynamic Kinetic Resolution, ChemCatChem., 2010, 2, 534-538.

[66] Shakeri M., Shoda M., Efficient decolorization of an anthraquinone dye by recombinant dye-decolorizing peroxidase (rDyP) immobilized in silica-based mesocellular foam, J. Mol. Cat. B: Enzymatic., 2010, 62, 277-281.

[67] Zhang X., Guan R.F., Wu W.D., Chan K.Y., Enzyme immobilization on amino-functionalized mesostructured cellular foam surfaces, characterization and catalytic properties, J. Mol. Cat. B: Enzymatic., 2005, 33, 43-50.

[68] Socolow R., Carbon Sequestration: State of the Science, US DoE - Office of Science (Fossil Energy), Washington DC, 1999.

[69] Sneddon G., Ganin A.Y., Yiu H.H.P., Sustainable CO2 Adsorbents Prepared by Coating Chitosan onto Mesoporous Silicas for Large-Scale Carbon Capture Technology, Energy Technol., 2015, 3, 249 – 258.

[70] Gao, F., Huang, J., Sun, H., Hu, J., Wang, M., Mi J., Wu C., CO2 capture using mesocellular siliceous foam (MCF)-supported CaO, J Energy Inst., 2019, 5, 1591-1598.

[71] Liang Z., Fadhel b., Schneider C.J., Chaffee A.L., Adsorption of CO2 on mesocellular siliceous foam iteratively functionalized with dendrimers, Adsorption, 2009, 15, 429-437.

[72] Yan X., Zhang L., Zhang Y., Qiao K., Yan Z., Komarnenic S., Komarnenic, Amine-modified mesocellular silica foams for CO2 capture, Chem. Eng. J., 2011, 168, 918-924.

[73] Subagyno D.J.N., Liang Z., Knowles G.P., Chaffee A.L., Amine modified mesocellular siliceous foam(MCF) as a sorbent for CO2 capture, Chem. Eng. Res. Des., 2011, 89(9), 1647-1657.

[74] Chaikittisilp W., Khunsupat R., Chen T.T., Jones, C.W., Mesoporous Silica Composite Materials for CO2 Capture from Simulated Flue Gas or Ambient Air, Ind. Eng. Chem. Res., 2011, 50, 14203-14210.

[75] Oosting R.S., in: Crommelin D.J.A., Sindelar R.D., Melhoorn B. (Eds.), Pharmaceutical Biotechnology: Fundamental and Applications, Springer-Verlag, New York, 2013, pp. 1-18.

[76] Kim J., Desch R.J., Thiel S.W., Guliants V.V., Pinto, N.G., Adsorption of biomolecules on mesostructured cellular foam silica: Effect of acid concentration and aging time in synthesis, Micropor. Mesopor Mat., 2012, 149, 60-68.

[77] Sezões F., Carroll M.M.L.R., Mourão P.A.M., Carroll P.J.M., Adsorption of Bovine Serum Albumin onto Mesocellular Silica Foams with Differently Sized Cells and Windows, Ads. Sci. Tech., 2010, 28(8/9), 777-788.

[78] Russo P.A., Carroll M.M.L.R., Mourão P.A.M., Carroll P.J.M., Tailoring the surface chemistry of mesocellular foams for protein adsorption, Coll. Surf. A: Physicochem. Eng. Aspects, 2011, 386, 25-35.