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Title

SYNTHESIS OF MCM-41 VIA DIFFERENT ROUTES

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Abstract:

This review focuses the different routes for MCM-41 synthesis such as nano-sized mesoporous silicas with metal oxide incorporation, from Glycerol and Ethylenediamine**,** from different dioxosilicon sources, synthesis of pure siliceous MCM-41 with different pore diameter, synthesis highly ordered MCM-41 with mixed surfactants, and synthesis from rice husk ash. The emerging characteristic of synthesized MCM-41 by these different routes was also discussed such as surface morphology, surface area, pore diameter and crystal sizes of MCM-41 in this review.

Keywords: Synthesis, MCM-41, Different routes.

INTRODUCTION:

Zeolite-based molecular sieves have a restricted pore diameter and the known mesoporous materials such as silica gel, activated carbon and pillard clay have irregularly spaced pore with broad pore size distribution. There has been increasing demand for crystalline mesoporous molecular sieves with pores of uniform diameter. The synthesis of the mesoporous molecular sieve MCM-41 with one-dimensional channels 16-100 Å in diameter which generates the potential for the applications of these materials in catalysis, separation, and sorption for very bulky molecules [1, 2].

In 1992, Mobil's researchers synthesized Mobil Composition of Matter (MCM) which is the initial name given for a series of mesoporous materials. MCM-41 (Mobil Composition of Matter No. 41) and MCM-48 (Mobil Composition of Matter No. 48) are two of the most popular mesoporous molecular sieves that are enthusiastically studied by researchers. The most remarkable fact about the MCM-41 and MCM-48 is that, although composed of amorphous silica wall, they possess long range ordered framework with uniform mesopores. These materials possess large surface area about more than 1000 m^2g^{-1}. Furthermore, the pore diameter of these materials can be adequately controlled within mesoporous range between 1.5 to 20 nm by adjusting the synthesis conditions and/or by utilizing different chain lengths surfactants in their preparation [1-6]. MCM-41 has a hexagonal arrangement of pores and is synthesized with positively charged surfactants as templates [2,7,8]. Chao and his co-workers noticed that Al-incorporated mesoporous silica nano-particles show higher catalytic activity toward the cumene-cracking reaction than the typical mesoporous aluminosilicate [9]. Most important potential applications of MCM-41 are the separation of proteins, the selective adsorption of large molecules from effluents and the processing of tar sand and high distillates of crude oils to valuable low-boiling products [10-19]. According to Niankai Li et. al, MCM-41s incorporated with high contents of different kinds of heteroatom such as Fe-MCM-41and V-MCM-41, which can be used in direct oxidation of phenol and in the direct oxidation of benzene respectively under room temperature [20]. MCM-41 may be act as a good adsorbent for the removal of basic dyes (Rhodamine B (RB), Crystal Violet (CV), and Methylene Green (MG)) and acid dyes (Acid Red 1 (AR1) and Erioglaucine (EG)) from water solution only if the dyes adsorption did not introduce a serious disorder on the pore structure of MCM-41 (such as RB adsorption) [21]. MCM-41 has been investigated in many applications as heterogeneous catalysis, catalyst support, adsorbent [22-24]. Mesoporous silicates have been investigated broadly in recent years for use in sensor systems applications such as supports for chemical sensing probes, pre-concentrators, molecular filters, and hard templates for the preparation of other sensing related materials [25]. A few application of mesoporous material is found for Friedel-Crafts acylation reaction [26-31]. Si-MCM-41 is rapidly increased in catalytic activity after impregnation of $GaCl_3$ or $InCl_3$ for benzene benzoylation reaction under solvent-less condition. Catalytic activity of $InCl_3$ supported on mesoporous Si-MCM-41 shows high activity in the acylation of various bulky aromatic compounds e.g. naphthalene and substituted naphthalenes in the presence of 1,2-dichloroethane solvent by acyl chlorides [32]. Mesoporous molecular sieves synthesized in non-aqueous system are used to prepare thin films, fibers, spheres or monoliths through solvent (e.g. ethanol) evaporation and growth of fiber and thin films at interface which are highly ordered potential mesochannels and distinctive benefits in electronic devices [33-35]. A nano-hybrid of Au nanoparticles and mesoporous silica could be an interesting catalyst system for versatile applications, especially for molecules too large to fit in the pore of traditional zeolites [36].

General methods using, various chemicals, Different types surfactants, silica.

Sodium Hydroxide is mixed with distilled water. Add aluminum source at 80^0C under stirring and get clear solution for more than 30 min. Cool this solution at 0^0C in ice bath. Add

Tetraethylammonium Hydroxide in mixture drop by drop with continually stirring up to 1 h. Prepare silica source solution with distilled water and mix with previous aluminum solution. Add surfactant into mixture solution. The final prepared solutions keeps in autoclave bomb and keep at crystallization temperature for some time. After this time, collect material from bomb and wash distilled water until pH will come to 7.0. Dry the finalized product at 110 ^{0}C for 24 h.

A synthetic method of mesoporous system with composition flexibility and designed catalytic properties is much desired [9]. The development of such materials is of great importance in many areas of modern science and technology [37-40]. These materials are best appreciated in systems where molecular recognition is needed, e.g., shape-selective catalysis, selective adsorption and separation processes, chemical sensors, and nanotechnology [41]. MCM-41 is generated by removal of the encapsulated organic templates through calcination or extraction [42]. Quanchang Li et. al. discussed that the general method for preparing supported base metal oxides is impregnation, where a porous support is repeatedly dipped into a solution containing a desired catalytic agent. It is often desirable to apply the agent uniformly in a predetermined quantity to a preset depth of penetration, but penetration of the liquid solution into the porous support is hindered by air trapped in the pores. In addition, when calcination is employed, the exiting gas will remove the liquid at the exit of the pores, resulting in formation of some catalytic particles on the external surface of the porous material [43]. As a result, several groups [44-46] have reported many small particles that were formed on the external surface of porous materials if conventional impregnation was used to prepare catalysts with metal oxides supported on the surface of a mesoporous material. Generally, various techniques like pressurizing, vacuum treatment, or acoustic activation have been proposed to remove gas trapped in the pores. By virtue of its large internal surface area and favorable uniformity but easily controlled size of the pore, it has attracted considerable interest in material science and other relevant areas [47-51]. Since tunable mesopore structure is one of the distinctive features associated with this material, several parameters such as period of aging of the synthesis gel, dioxosilicon source, type and concentration of surfactant, synthesis method, calcination, pH, etc., whose cause and effect relationship on the properties of MCM-41 materials have been intensively explored [11, 52-63]. Although, several synthesis routes were developed using different dioxosilicon precursors such as TEOS, ethyl silicate, fumed silica, water glass, silica sol, etc., [52,53,54, 55,56]. No systematic review was reported via different methodology on the pathway of structural development and properties such as textural/structural, thermal stability and morphology of synthesis of MCM-41. In this paper, different methods of MCM-41 synthesis are reported herewith.

Different methods for synthesis of MCM-41

Nano-sized MCM-41 with metal incorporation

The synthetic procedure for nano-sized mesoporous silicas with metal oxide incorporation is shown below:

A clear aqueous solution of hydrolyzed inorganic precursor mixtures tetraethyl orthosilicate (TEOS) and metal alkoxides/salts with cetyltrimethylammonium bromide (CTMABr) surfactant is prepared at low pH. After that CTMABr, TEOS, and metal alkoxides is added into a highly acidic solution of HNO_3/HCl (pH~ 0.0) and stirred for a period of 6–12 min at room temperature. In the second step, a fast co-condensation reaction is achieved in ammonia aqueous solution. The acidic solution containing surfactant and hydrolyzed inorganic species was poured quickly into a 300 ml 0.125 M ammonia solution and a colloid suspension gel solution was obtained immediately; and final pH value was located in the range of 8.0–9.0 by a proper control on the ratio of acid/ammonia. The chemical composition of the gel solution in molar ratio is 1.0 CTMABr:4.5TEOS:(0.0–1.8) metal alkyloxides or salts: 24.0acid:158.0NH_4OH:11076.0H_2O. The products are obtained by filtration, washing and drying at 100 °C and then calcined in air at 560 °C to remove the organic templates [9].

During the synthetic process, no separate phase of metal oxides was formed. Al-substituted mesoporous silica (Al-MCM-41) sample is in fine-particle form of nanometer size approximately 30–40 nm. The Al- MCM-41 nanoparticles have a high surface area of about 1000 m^2/g. Under a high-magnification observation (Figure 1), it was found that the nanotubes consisted of about

10–20 nano channels. The diameter of the Al-mesoporous silica nanotubes is less than 60 nm, and the length is around 200nm. In general, the nanotubes got shorter with the increase of the metal-oxides content. That is because the incorporation of metal oxide would weaken the interactions of surfactant–silica.

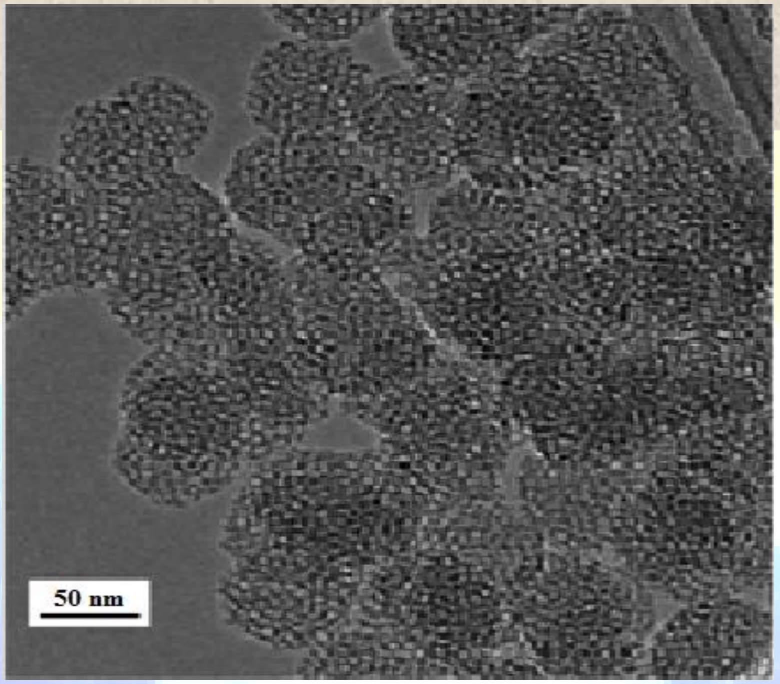

Figure. 1

The better transport of guest molecules in its nanopores is examined by looking into its catalytic application. It was observed the efficiency on catalytic reactions the catalytic materials in the cumene cracking reaction are used, which requires mesopores and strong surface acidity. Two basic concepts for creating the M-MCM-41 nanotubes or nanoparticles are: (1) A fast nucleation and growth rate leading to crystallization of small nanocrystals, and (2) Matching the condensation rate of silica and metal oxide. Based on the chemistry of silica [64], the fastest condensation rate is near neutral (pH 6.0–8.0).

MCM-41 from Glycerol and Ethylenediamine

MCM-41 can be prepared in glycerol and ethylenediamine at room temperature. The appropriate amount of cetyltrimethylammonium bromide (CTMABr), template was dissolved in solvent glycerol, glycol, water, respectively. The pH of this solution was adjusted to 12 with ethylenediamine (EDA), followed by the addition of tetraethyl orthosilicate (TEOS) with vigorous stirring for about 30 min at room temperature. The molar composition of the reaction mixture was 1TEOS:0.7 CTMABr:130Solvent(glycerol or glycol or water):13EDA. The mixture was stirred for 8 h at room temperature. Then the mixture was aged at room temperature for 24 h. The as-synthesized product was filtered and washed with deioned water to pH=7, dried at 50 °C for 24 h, then calcined at 550 °C in air for 5 h to remove the organic templates [65]. The synthesized MCM-41 by this method had larger pore diameter and narrow pore size distribution.

MCM-41 from different dioxosilicon sources

Pure silica MCM-41 was synthesized from three different dioxosilicon sources viz. fumed silica, FS (99.8 wt.% SiO_2, surface area 360–400 m^2/g, Aldrich), spray dried precipitated silica, PS1 (99.2 wt.% SiO_2, surface area 280–320 m^2/g, V.P. Chemicals) and flash dried precipitated silica, PS2 (99.2 wt.%SiO_2, surface area 170–210 m^2/g, V.P. Chemicals). In order to investigate the influence of the type of dioxosilicon source on progressive development and quality of Si-MCM-41, all other synthesis parameters such as addition sequence, initial reaction mixture composition, synthesis temperature, ratio of charged reaction mass to autoclave volume, pH and downstream process conditions were kept constant. In typical synthesis run using fumed silica, initial gel was prepared by adding a solution prepared by dissolving 11.0 g of cetyl-trimethyl-ammonium-bromide, CTMABr, (99 wt.%, Dishman) in 50 ml of distilled water to 11.4 g of an aqueous solution of tetra-methyl-ammonium-hydroxide, TMAOH, (aq. 25 wt.% Loba Chemie) with constant stirring. To this solution, 7.5 g of FS was added slowly under stirring. Stirring was further continued for 2 h to obtain homogeneous gel. The resulting final gel thus formed has a molar composition SiO_2:0.24CTMABr:0.25TMAOH:26 H_2O. It was then transferred, sealed and heated in a sealed stainless steel (100 ml capacity) autoclave at 383 K for desired length of period. The time at which autoclave attained the 383 K temperature was taken as zeroeth hour. The product was recovered by filtration, washed thoroughly with distilled water and then dried at 373 K for 4 h. Calcination was carried out in air at 813 K for 6 h in order to drive-off the surfactant [66].

Fumed silica has yielded well ordered MCM-41 with thinner wall. Considering the magnitude of wall thickness and unit cell contraction upon calcination for each sample, it can be concluded that more contraction in unit cell results in the formation of thinner walled MCM-41. Furthermore, the morphology of MCM-41 materials was found to depend on the type of the silica source used in their preparation. When fumed silica was used as a dioxosilicon source worm/rope like morphology was observed. However, half doughnut and doughnut like morphology was observed when PS1 and PS2 were used as a dioxosilicon source [Figure2].

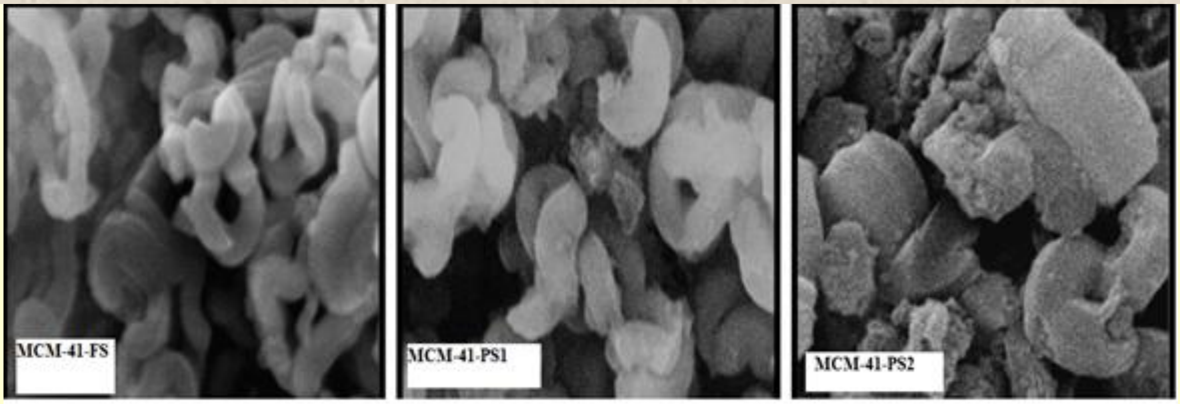

Figure 2.

Under the identical set of synthesis conditions, the reactivity trend of dioxosilicon sources observed was as: FS>PS1>PS2. In all the three systems, the unit cell parameter was found to increase with synthesis time, reaches to maximum and then decreases on further heating. MCM-41 synthesized using least expensive PS2 having less surface area has exhibited thicker pore walls but poor orderness, while MCM-41 prepared from expensive FS having high surface area has thinner pore walls and was well ordered. Thermal stability and morphology of MCM-41 materials were found to depend on the manufacturing process of dioxosilicon sources used.

Pure siliceous MCM-41 with different pore diameter

By adjusting the composition of reaction mixtures and controlling the crystallization variables without addition of auxilliary organics, the pore of MCM-41 was synthesized with different pore diameter. Pure siliceous MCM-41 with different pore diameters were hydrothermally synthesized with the following molar composition: SiO_2:xCTMABr:0.14M_2O:26.2H_2O, where x was varied between 0.06 and 0.15; M represents cations, such as tetramethylammonium (TMA^+), tetraethylammonium (TEA^+), or Na^+ that were added as hydroxides. In a typical synthesis, an aqueous solution of tetramethylammonium silicate obtained from the reaction between silica (Aerosil 200, Degussa) and tetramethylammonium hydroxide solution (25% TMAOH, 10% SiO_2), was added to an aqueous solution containing 9.86 wt % cetyltrimethylammonium bromide (CTMABr). Then, amorphous silica was added under continuous stirring. The homogeneous gel (pH = 13.8) was sealed in Teflon-lined stainless steel autoclaves and heated at 150 °C under static conditions. The time of crystallization was varied from 1 to 10 days. The resulting solid products were recovered by filtration and then washed and dried at 60 °C for 24 h. The occluded organic was removed by heating the samples at 540 °C under a continuous flow of N_2 for 2 h, before a flow of air was passed at 540 °C for 6 h [67].

Indeed, by working at a CTA^+/SiO_2 ratio between 0.09 and 0.15, highly crystalline MCM-41 type materials are produced with a pore size in the highest range of those stated in the original Mobil patent [3], but avoiding the use of any swelling organic compound into the synthesis gel. On the other hand, the values of pore diameter reported here are 20-30 Å larger than those published previously by Khusalani et. al. and Cheng et. al. [68,69]. CTA^+/SiO_2 ratios below 0.09 speed the swelling rate, but poorly crystalline MCM-41 materials are produced. Finally, by increasing $CTMA/SiO_2$ ratio to 0.20 results in the formation of mesoporous material with distribution a bimodal pore distributions with two major channel opening centered at 44 and 48 Å. To obtain a swollen, uniformed, and well-crystallized mesoporous material, the optimum range of CTMA $/SiO_2$ ratios is found to be between 0.09 and 0.15. Another important factor that influences the swelling process is crystallization temperature. A strong increase in the swelling rate is observed by increasing the temperature of crystallization to 175 °C. At this temperature, a crystallization time as short as 14 h produces a MCM-41 type solid with a unit cell of 70 Å which is larger than that obtained at 135 °C after 50 days of heating. Moreover, when the synthesis is carried out under dynamic conditions, that is, when the autoclaves were rotated at 60 rpm, a benefit in the swelling process is observed being the swelling completed after 1 week at 135 °C instead of the 1 month necessary under static conditions. The swelling process is also observed by replacing TMA^+ in the gel by TEA^+ or even by inorganic cations such as Na^+. Na^+ seems to give less stable mesoporous materials and with a lower swelling rate than those obtained in the presence of tetraalkylammonium cations (TAA^+). Elemental and chemical analyses confirm that the TMA+, TEA+, or Na+ cations are incorporated in the mesoporous products during the synthesis, although Na+ is included into the final solid in a lower molar fraction than the others.It is notable that the swelling of mesoporous materials is always accompanied by a gradual increase in the content of TAA^+ cations but a with slight decrease of the $CTMA^+$ content. Thus, the larger the pore, the higher the content of cations in the products is.

Highly ordered MCM-41 with mixed surfactants:

Highly ordered form of MCM-41 can be prepared with various pore diameters if micelle packing is suitably controlled with mixed surfactants of n-alkyltrimethylammonium bromide (ATMABr) and n-alkyltriethylammonium bromide (ATEABr) according to the length of the C_{12}–C_{22} alkyl groups. The synthesis of ATEABr was carried out by the reaction of 1-bromoalkane with triethylamine in acetonitrile solution under reflux [70] ATMABr surfactants were synthesised similarly using 1-bromoalkane and trimethylamine in a pressure vessel in order to prevent loss of trimethylamine. Synthesized surfactants were purified twice via dissolution in chloroform and subsequent re-crystallization by the addition of ethyl acetate. R. Ryoo et. al. and J. M. Kim et. al. discussed the synthesis of MCM-41 silica in a similar way, except for the use of ATEABr–ATMABr mixtures [71,72]. The silica source is taken as aqueous solution of sodium silicate with Na/Si = 0.5 (2.4 mass% Na_2O, 9.2 mass% SiO_2, 88.4 mass% H_2O). It is then added drop wise to an aqueous solution of an ATEABr–ATMABr mixture at a given temperature while the solution is stirred vigorously. After continuously stirring for 1 h, the resultant gel mixture is heated for 24 h at 373 K. The mixture after heating is cooled to the same temperature as before the initial mixing, and the pH of the mixture is adjusted to 10 with acetic acid. The mixture after the pH adjustment is heated again for 48 h at 373 K. pH adjustments and subsequent heating is repeated once more before the precipitated MCM-41 product is finally filtered off. The product is washed with EtOH–HCl–H_2O(84.1:1.0:14.9 mol/mol) and calcined in air at 823 K [59].

The synthesis of C_{16}–C_{20}MCM-41 by the addition of ATEABr showed a significant improvement of the structural order up to an optimum ATEABr/ATMABr ratio, after which the structural order was progressively lost. Highly ordered C_{22}MCM-41 can also be obtained using ATMABr as the single surfactant and sodium silicate as the silica source if the pH of the starting mixture is carefully adjusted to 8 before heating, as reported by Namba et al. [8]. A lamellar or disordered mesophase is obtained if the pH is not adjusted at all, or adjusted after heating. The effect of the pH adjustment is evidence for the mesophase-formtion mechanism that takes place co-operatively by the silica source and surfactants [73]. The reversibility of the formation of the silica–surfactant mesostructure is another important factor that affects MCM-41 synthesis. The formation of the hexagonal mesophase at pH 8 is not easily reversed and consequently the synthesis becomes very sensitive to the timing and temperature for the pH adjustment during the silicate polymerisation. On the other hand, the synthesis using C_{22}ATEABr can be performed more easily at sufficiently high pH where the formation of the hexagonal mesostructure is reversible.

The surface curvature of micelles can also be controlled using other mixed surfactant systems such as cationic–neutral and cationic–anionic [74]. In addition, the mixed surfactant idea may be used to adjust the surfactant's head group size proportionally to the increase in the diameter of the micelle, when organic additives are used to increase the pore diameter.

MCM-41 from rice husk ash

Silica from rice husk ash was generated by the process of fluidized bed gasification a biomass fired power plant. Rice husk ash was boiled in 1 M HCl at 80 °C for 1 h. After acid pretreatment, the ash was rinsed with distilled water, dried in an oven at 110 ° C overnight and then calcined in a muffle furnace at 650 °C for 4 h. Then, the extracted silica from rice husk was utilized as a siliceous raw material for MCM-41 preparation. Hexadecyltrimethylammonium bromide (CTMABr) and extracted silica from rice husk ash was used as reactant for MCM-41 synthesis. The process of synthesis, called sol-gel method, was carried out with the molar composition of $4SiO_2$:$1Na_2O$:1CTMABr:$200H_2O$. The mixture was adjusted the pH value to 10 and stirred constantly for 48 h at room temperature. Afterward, the suspended solid was filtered and rinsed with ethanol solution. The filtered solid was calcined at 550 °C for 5 h.

The Scanning Micrographs of rice husk ash (RHA)-MCM-41 and commercial sodium silicate (SDS)-MCM-41 is given in Fig. 3 (a) and (b), respectively. These images exhibited the agglomerated particles with the uniform size in a range of 0.3-0.5 μm, smaller than that of the extracted silica (50 μm) about 100 order of magnitude. This is because the well-organized assembly of silicate ions reacted with the cationic template in adequate crystallization.

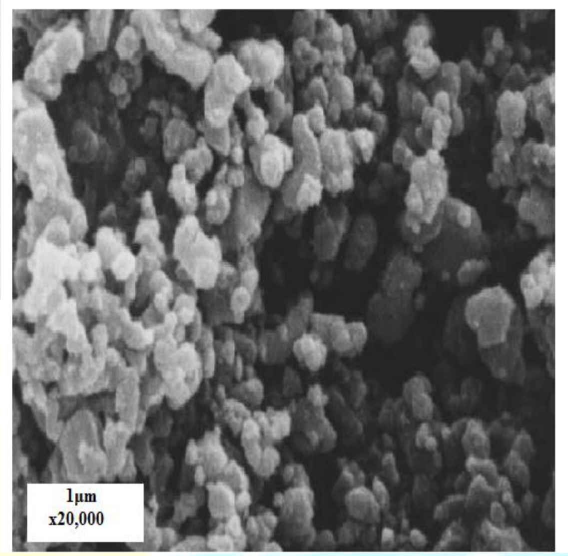

Fig 3(a) SEM images of RHA_MCM-41

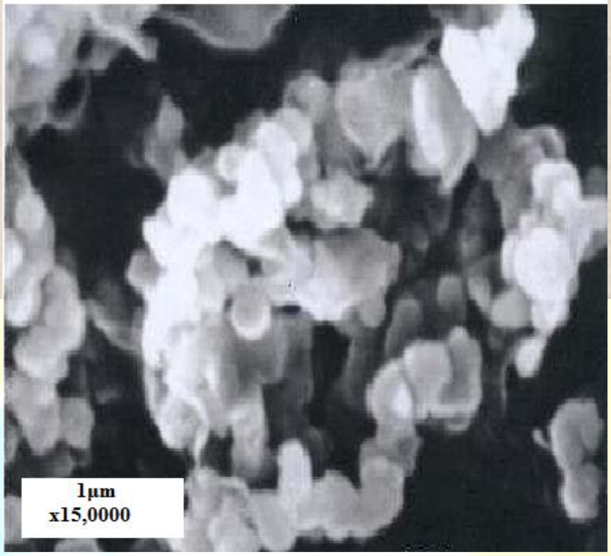

Fig 3 (b) SEM images of SDS_MCM-41

RHA_MCM-41 possessed the surface area 730 m^2/g whereas SDS_MCM-41 gave the surface area 960 m^2/g. Both synthesized MCM-41 has average pore diameter was centered around 2.2 nm. The pore volume of RHA_MCM-41 and SDS_MCM-41 was 0.87 and 0.70 ml/g, respectively. According to the porosity data, the pore diameter of the MCM-41 particles is not affected by the source of silica but it is significantly controlled by the length of carbon chains in the molecules of organic template. Even though, the crystallinity characteristics and the porosity properties of MCM-41 synthesized from rice husk ash were similar to those of MCM-41 synthesized from commercial silica.

Conclusion and Remarks

The mesoporous molecular sieve MCM-41 with one-dimensional channels 16-100 Å in diameter which engenders the potential for the applications of these materials in catalysis, separation, and sorption for very bulky molecules. As per reaction condition, catalyst MCM-41 requires in different shapes, in different pore diameter, larger surface area etc. Therefore, it is necessity that MCM-41 should be synthesized via different routes. In this review paper, it was discussed in detail with different methods. Al-substituted mesoporous silica (Al-MCM-41) is in fine-particle form of nanometer size approximately 30–40 nm with high surface area of about 1000 m^2/g. Synthesized MCM-41 in glycerol and ethylenediamine solvent had larger pore diameter and narrow pore size distribution. During synthesis of MCM-41 with different dioxosilicon sources, morphology of MCM-41 was observed that worm/rope, half doughnut and doughnut for fumed silica, spray dried precipitated silica (PS1) and flash dried precipitated silica (PS2), respectively. At a CTA^+/SiO_2 ratio between 0.09 and 0.15, highly crystalline MCM-41 type materials are produced with a pore size in the highest range with pore diameter 20-30 Å. Highly ordered MCM-41 with mixed surfactants was synthesized with effect of various pH and ratio of mixed surfactants. Crystallinity characteristics and the porosity properties of MCM-41 synthesized from rice husk ash were similar to those of MCM-41 synthesized from commercial silica. But, MCM-41 synthesized from rice husk ash possessed the surface area 730 m^2/g, whereas MCM-41 synthesized from commercial silica gave the surface area 960 m^2/g. This listing of possible various synthesis methods will be helpful. It gives an idea about the access various properties of MCM-41.

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