REVIEW ON SYNTHESIS OF SELECTED MESOPOROUS PARTICLES

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ABSTRACT

The mesoporous particles include organosilicas, highly dispersed tungsten particles, mesoporous carbons, TiO_2 *and* Al_2O_3 *particles. Typical methods of synthesis include use of surfactants like CTAB and polymer like Polyethylene oxide-polypropylene oxide- Polyethylene oxide (PEO-PPO-PEO). The solution is usually maintained at basic conditions. Calcination temperature ranges between 350–850°C, forms an important step in the synthesis of Tungsten particles. Other methods include use of evaporation-induced organic-organic self-assembly or sometimes a sol-gel approach from a mixture of poly (ethylene glycol) –poly (propylene glycol)-poly (ethylene glycol) tri-block copolymer. Characterization of the mesoporous particles were carried out by* N_2*-adsorption-desorption method and analytical methods like FTIR, SEM, TEM, Wide-angle XRD, UV-Visible Diffusive Reflectance Spectroscopy etc. Certain notable applications of the particles include use of Mesoporous organosilicas as a stationary phase in HPLC for the separation of aromatic hydrocarbons and use of highly dispersed tungsten particles as a desulfurizing agent to remove sulphur from diesel. Broader scope of applications includes use of these particles as catalysts for various processes. This paper is intended to review the techniques available for the synthesis of these mesoporous materials.*

Keywords: Mesoporous, Organosilica, Polymer, Surfactant, Sol-Gel

I INTRODUCTION

Any material with pore diameter in the range of 2 to 50 nm is considered as mesoporous material. Various materials whether naturally available or synthesised are classified into several kinds by their particle size or pore size. We are interested in the pore size or pore diameter range in our work. A typical illustration of pore size measured materials include microporous materials which have pore diameters of less than 2 nm and macroporous materials which have pore diameters of greater than 50 nm and the mesoporous category thus lies in the middle. Various mesoporous materials include some kinds of silica and alumina. Certain oxides of Niobium, Tantalum, Titanium, Zirconium, Cerium and Tin are also found to be mesoporous in nature. In a mesoporous material synthesised, mesostructure obtained can be ordered or dis-ordered depending on the preparation conditions.

II SYNTHESIS OF MESOPOROUS PARTICLES

2.1. Mesoporous carbon

Ordered porous materials due to their high specific area, large pore volume and pore diameter have attracted greater technological interest with applications including adsorption. Among the porous materials, mesoporous carbon consisting of 3D porous networks are believed to be more advantageous than materials having cubic pore structure with an ordered array of pores. There are many methods to synthesise such materials. Prominent methods include **“*the one pot method*” [1]**, where a tri-block copolymer (Pluronic P123) was used as structure directing template and n-butanol was used as a co-solvent. Typical synthesis include self-assembly method where a known amount of P123 was dissolved in water and HCl and n-butanol, followed by addition of H_2SO_4, sucrose and Tetraethylorthosilicate (TEOS), which were used as sources, was added to the solution which was stirred and aged hydrothermally. As synthesised Silica/P123/n-butanol/sucrose was carbonised under N_2 atmosphere at 900^{o}C and dissolution of silica was removed by HF in water. Template-free mesoporous carbon was thus obtained.

Another popular method is the use of **“*evaporation-induced-organic self-assembly method*” [2]** where a mixture of a *x* g of P123 and (1–*x*) g of Poly (propyleneoxide)-poly (ethyleneoxide)-poly (propyleneoxide) (PPO-PEO-PPO) tri-block copolymer was dissolved in a known amount of ethanol. Low molecular weight phenolic resol precursors were prepared by melting phenol followed by addition of NaOH and addition of formalin drop wise and the mixture was stirred at 75^{o}C for 60 min. After cooling the mixture to room temperature, pH of the reaction mixture was adjusted to neutral using 2 M HCl. Final product was re-dissolved in ethanol and was added drop wise to the above ethanol solution containing the copolymer, further stirred. The solution was transferred to a dish and the ethanol evaporated at room temperature over 8h to produce a transparent membrane. The membrane was cured at 100^{o}C for 24 h in air for further thermo polymerization and the product was carbonized at 800^{o}C. The characterization was carried out using SEM (Fig. 1), TEM (Fig. 2), SAXS and N_2 adsorption-desorption method (Fig. 3). The N_2 adsorption-desorption shows a type IV hysteresis with clear desorption curve; the structure is highly ordered with narrow space distribution, as indicated by capillary condensation step in the isotherm. SEM images indicates micro-sized rope-like fiber bundle morphology. TEM images shows cubic arrays of structured carbon.

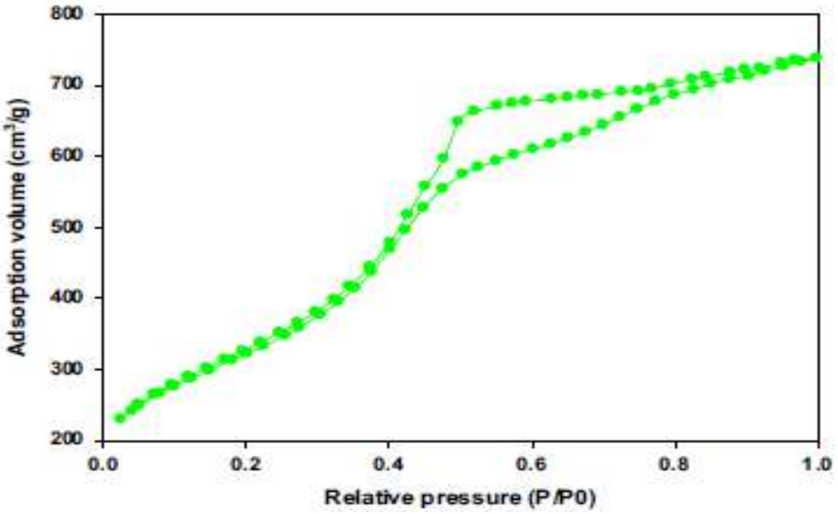

Fig. 1: N_2 adsorption-desorption isotherms of mesoporous carbons [1].

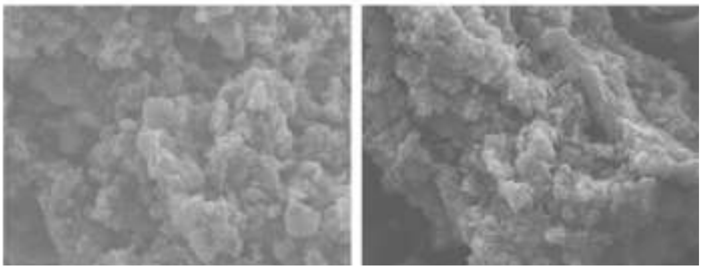

Fig. 2: SEM images for mesoporous carbon [1].

Fig. 3: TEM images for mesoporous carbon [1].

2.2. Mesoporous TiO_2

TiO_2 has been widely studied as an effective catalyst because of its confined porous structure and high surface area to volume ratio and should also in principle have high photo-catalytic activity [3-4]. Various approaches to the synthesis of mesoporous TiO_2 with special morphology have been studied.

One such method is the synthesis of well-defined spherical mesoporous TiO_2 with a specific mono-disperse size using a ***"sol-gel"*** process [5]. It is prepared using a mixture of a titanium precursor and a tri-block copolymer surfactant in aqueous solution. A known amount of the tri-block copolymer surfactant Poly (ethylene glycol) – poly (propylene glycol)-poly (ethylene glycol) was dissolved in a known amount of distilled water. After the surfactant had dissolved sufficiently, a known amount of sulphuric acid was added. Titanium (IV) isopropoxide was mixed with 2, 4-pentanedione in a separate beaker and dropped slowly into each surfactant solution with vigorous stirring. Reaction was carried out at 55^oC. Light yellow powder was obtained which was aged at 90^oC for 10 h. Resulting powders were filtered and thoroughly washed with water and alcohol and to eliminate the residual surfactant, powders were calcined at 400^oC.

Another modified approach to the above mentioned method is the synthesis of crack-free Mesoporous titania on a macroporous support without intermediate layers by ***"nano-particle modified polymeric sol-gel process"*** **[6]**. TiO_2 sol was synthesised via polymeric route where Ti $(OC_4H_9)_4$ and acetylacetone (acac) was added to the solution of L64 (pluronic di-functional block copolymer) in C_4H_9OH, HNO_3 and water was added drop wise to the solution to obtain a stable and transparent sol. The molar ratio of $Ti(OC_4H_9)_4$:L64:acac:C_4H_9OH:HNO_3:H_2O was 1:0.06:1:9:0.1:3. TiO_2 nanoparticle (Degussa P25) was added to the sol and dispersed by stirring. Tubular ZrO_2 support membranes were prepared by dip coating the fresh sol on support via a circulation process. P25 was well dispersed in the sol by ultrasonification during the coating. The coated films were dried and aged for 12 h and calcined in air at 400^oC for 4 h. Tubular anatox TiO_2 ultrafiltration membranes of mesoporous pore size were obtained. Characterization of the TiO_2 membranes carried out using N_2 adsorption-desorption method (Fig. 4) and SEM (Fig. 5, 6). N_2 adsorption-desorption for different concentrations of P25, it showed type IV isotherm, which is an indication of well-defined pore structure. SEM images of TiO_2 showed cracks on the surface, but when P25 was used the surface was void of cracks. The cross-sectional view indicates a TiO_2 layer which is 2 microns thick, above the support.

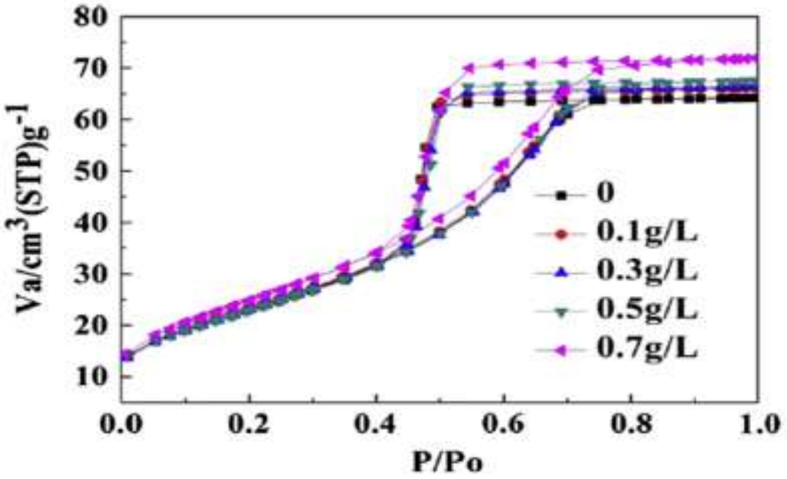

Fig. 4: N_2 adsorption-desorption isotherm for TiO_2 with different concentration of P25 at 400°C [6].

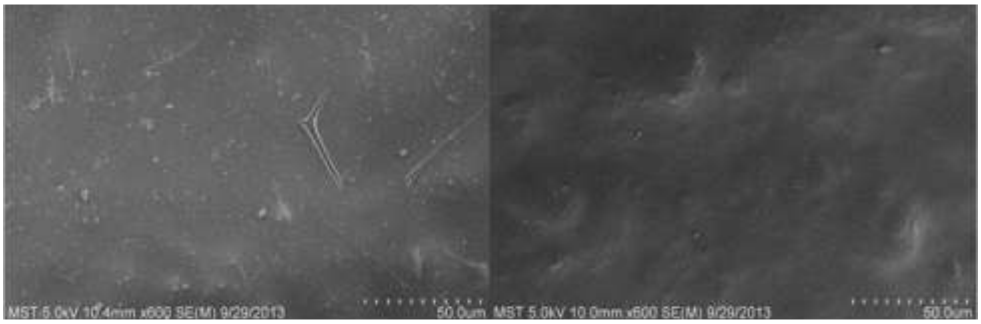

Fig. 5: SEM image of TiO_2 material without P25 and with P25 [6].

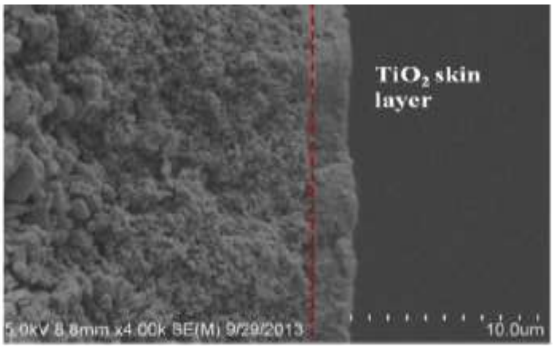

Fig. 6: SEM image of cross-section of P-TiO_2 membrane [6].

2.3. Mesoporous Alumina

These have highly uniform channels, large surface area and highly ordered arrangement of particles. The common templates used for structure directing agents are anionic, cationic and non-ionic in nature. One of the notable methods of preparation is ***"Triton-100 directed synthesis of Mesoporous γ -Alumina from coal-series Kaolin"*** [7], where meta kaolin is leached with 6 M HCl; the leachate collected as the aluminium source to which NaOH is added to transform $AlCl_3$ to $NaAlO_2$. Further, addition 6 M HCl to the above solution precipitates Boehmite, which is used the precursor. The molar ratio of Al^{3+}:TX-100:H_2O is 1:0.03-0.15:52. The solution was treated, washed with distilled water and dried. This was then calcined at 550°C to remove TX-100. Upon calcinations the hydroxyl (Al-OH) could be transformed to O-X-O (Al-O-Al bridges). The best Mesoporous structure is obtained when the molar fraction of TX-100 added is 0.12. The alumina thus formed has potential applications in adsorption and catalytic properties.

Another method of producing ***"thermally stable Mesoporous alumina using bayberry tannin (BT) as the template"*** [8] and aluminium nitrate as the precursor. Aluminium nitrate solution (0.8 mol/l) and BT solution (3 wt. %) was mixed and the pH was maintained at 5.5 using Ammonia solution. The obtained suspension was heated in an autoclave at 150°C under the N_2 atmosphere. The solution filtered, washed with distilled water, dried and calcined in aerobic atmosphere to remove bayberry tannin. The calcination was carried out in the temperature range of 700°C to 900°C; even on increasing the temperature to 900°C, the product obtained was stable. It is used for shape selective catalysis (Hydrogenation reaction). The TEM images of the catalyst is shown in Fig. 7. The Pd particles are 7.2 nm and 7.5 nm respectively in the Pd-Alumina prepared and reference. Pd is well dispersed in both the structures. The prepared structure is more active than reference, due to difference in the texture.

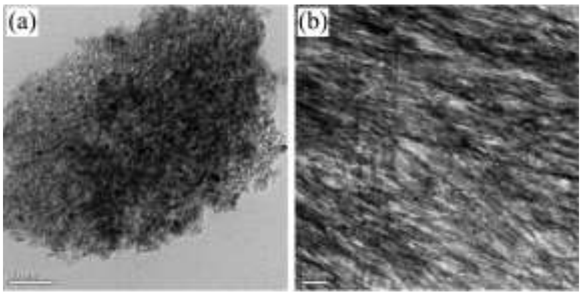

Fig. 7: TEM image of (a) Pd-Alumina (prepared) and (b) Pd-Alumina (reference) [8].

2.4. Mesoporous Silica

Mesoporous silicas are a class of inorganic materials, which possess interesting properties such as stable Mesoporous structure, large surface areas, high pore volumes, well-ordered pore structures, and narrow pore-size distributions with relatively large-pore diameters (2–50 nm). Silicas have no inherent catalytic property but can be used as supports functionalized either by framework substitution or by post-synthesis surface modification. ***"Synthesis and characterization of periodic Mesoporous organosilicaswith uniform spherical core-shell"*** [9] was carried out using stationary phase as the core. Silica core was synthesized using "Stober" method. Non-porous silica spheres were activated with 10% HCl followed by reflux. Addition of ammonia solution was done to maintain basic condition.

Stirring was carried followed by addition of CTAB, PEO-PPO-PEO, ethanol and distilled water solution to silica sol .The dispersion was filtered and newly formed particles served as starting seed particles for the next stage. Characterization for morphological study of core-shell particles was carried out using FTIR, SEM, N_2 adsorption-desorption method and the chromatographic evaluation done by HPLC. This material showed high column efficiency for fast separation of aromatic hydrocarbon. Another prominent application of Mesoporous silica is ***"Preparation of highly dispersed tungsten species within mesoporous silica by ionic liquid"*** [10]. Preparation of W-mesoporous silicas was carried out in the following manner: $T_8W_2O_{11}$ was dissolved in ethanol and followed by addition of distilled water. Tetraethylorthosilicate (TEOS) was added drop wise, the pH was adjusted between 9 and 10; solid products obtained were calcined at various temperatures (350, 450, 550, 650, 750, 850^{o}C). The product thus obtained was used as a desulfurizing agent for diesel. Fig. 8 shows the High Resolution TEM (HRTEM) image. The dark spots indicates highly dispersed W species in Silica. The pore structure is distorted and wormhole structure.

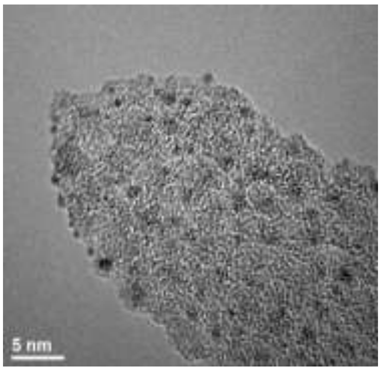

Fig. 8: HRTEM image of tungsten on Silica [10].

III CONCLUSION

Various methods of obtaining mesoporous particles in the laboratory scale have been discussed. Typical methods were the sol-gel approach and use of tri-block copolymers. In certain synthesis procedures, use of surfactants was evident. A unique method of using of obtaining Alumina mesoporous particles using bayberry tannin as template was also discussed. Characterization of the thus synthesised materials was done using analytical methods like SEM, TEM, FTIR etc. For certain materials like mesoporous silica, calcination played an important role in the formation of the ordered mesostructure.

IV ACKNOWLEDGEMENTS

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