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A moment comes, which comes but rarely in life, when with utmost pleasure and satisfaction I am going to submit the thesis entitled ***"Synthesis, Characterization and Potential Applications of Organosilicon Based and Related Mesoporous Molecular Sieves"*** *contains solely my research activities performed in the Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata- 700032, India.*

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Preface

Mesoporous materials having high surface area with tunable pore size distribution in nano scale dimensions have attracted widespread interest in recent times. These special properties make mesoporous materials focus of great research interests in catalysis, adsorption, sensing, separation, drug delivery and controlled release of bioactive pharmaceuticals. During the past two decades a prevalent interest and incredible resonance as a fundamental and technological challenge to chemists, physicists and engineers has been gained by organic-inorganic hybrid materials and macromolecular building blocks of nanoscale dimensions. Hybrid mesoporous materials are unique and molecular control of their intrinsic topological and chemical characteristics can be explained through self-assembly and nanochemistry techniques. Post synthesis and in-situ synthesis both the techniques have been adopted to develop the organic-inorganic hybrid mesoporous materials. Furfural imine functionalized mesoporous silica has been synthesized by using CTAB as structure directing agent by applying in-situ grafting technique. This furfural imine functionalized mesoporous SBA-15 has been also developed by employing post-grafting approach. Then these two different mesoporous materials have been subjected to react with $Cu(OAc)_2$ to deliver Cu-grafted mesoporous organosilica. After Cu grafting different crystalline phases have been generated for the two different mesoporous silica materials. Also In another case $-NH_2$ functionalized mesoporous organoslica has been developed by applying in-situ grafting technique. Surface of mesoporous SBA-15 has been functionalized by reaction with 3-aminopropyltriethoxy silane. Then $-CO_2H$ functionalized mesoporous SBA-15 has been synthesized by applying Schiff-base condensation reaction. Fe_3O_4 nanoparticle has been grafted into the mesopore channel of cysteine functionalized mesoporous SBA-15 material. Thiol-ene click chemistry has been adopted to prepare cysteine functionalized mesoporous SBA-15 material.

The chapter one presents a brief introduction of the nanoporous materials along with a systematical classification of the types and scope of nanoporous materials, description of micro, meso and macroporous materials and different types of synthesis route of porous materials and their molecular level interaction. The properties and measurement methods will be briefly described in major applications in various fields. The multifunctional properties of nanoporous materials have been intensively studied and applied in the different field such as catalysis, gas storage, ion exchange, optoelectronics, solar cell and sensing materials.

The chapter two presents the characterization techniques and measurement tools. In this chapter, Powder X–ray Diffraction, N_2 adsorption–desorption, High Resolution

Transmission Electron Microscopy, Field Emission Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, Ultra Violet Visible Diffuse Reflectance Spectroscopy, Thermogravimetric–Differential Thermal Analysis, Electron paramagnetic resonance spectroscopy (EPR), Solid state ^{29}Si, ^{13}C CPMAS NMR and ^{1}H and ^{13}C NMR analysis technique are described in details.

In the chapter three a new functionalized mesoporous organosilica has been designed *via* Schiff-base condensation of furfural and 3-aminopropyltriethoxy-silane (APTES) followed by its hydrothermal co-condensation with tetraethylorthosilicate (TEOS) in the presence of a cationic surfactant CTAB. Subsequent reaction of this mesoporous organosilica with $Cu(OAc)_2$ in absolute ethanol leads to the formation of a new Cu(II)-grafted mesoporous organosilica catalyst **C**. Powder XRD, HR TEM, FE SEM, N_2 sorption and FT IR spectroscopic tools are used to characterize the materials. This Cu-anchored mesoporous material acts as an efficient, reusable catalyst in the aryl-sulfur coupling reaction between aryl iodide and thiophenol for the synthesis of value added diarylsulfides.

In the chapter four post-synthesis modification of SBA-15 has been carried out to design highly ordered acid functionalized hybrid mesoporous organosilica, AFS-1. $-NH_2$ functionalized mesoporous SBA-15 was grafted *via* reaction of 3-aminopropyl triethoxy silane followed by Schiff-base condensation of 4-formyl benzoic acid in MeOH. Powder XRD, HR TEM, N_2 sorption and CP MAS NMR spectroscopic tools are used to characterize the material AFS-1. This material has been used as an efficient heterogeneous organocatalyst for the syntheses of xanthenes under mild conditions in the absence of any other metal co-catalyst.

In the chapter five we have prepared amino-functionalized mesoporous silica through co-condensation of 3-aminopropyltriethoxy-silane (APTES) along with tetraethylorthosilicate (TEOS) in presence of a cationic surfactant CTAB hydrothermally. Small angle powder

XRD, HR TEM, FE SEM, N_2 sorption and FT IR spectroscopic tools are used to characterize the 2D-hexagonal mesostructure and to identify the presence of surface -NH_2 groups in amino-functionalized mesoporous silica material. Our experimental results reveal that amino-functionalized mesoporous silica is an efficient base catalyst for the Knoevenagel condensation of different aromatic aldehydes with malononitrile to α, β-unsaturated dicyanides under very mild reaction condition and in the presence of ethanol solvent. The isolated α, β- unsaturated dicyanides obtained through the condensation reaction further react very efficiently with cyclopentadiene to form a series of Diels-Alder cycloaddition products in excellent yields in the absence of any catalyst.

In the chapter six a magnetic nanoparticle conjugated mesoporous nanocatalyst (Fe_3O_4@mesoporous SBA-15) with a high surface area has been synthesized by chemical conjugation of magnetite (Fe_3O_4) nanoparticles with functionalized mesoporous SBA-15. Functionalized mesoporous SBA-15 containing surface carboxyl and amino groups was synthesized *via* the thiol–ene click reaction of cysteine hydrochloride and vinyl functionalized SBA-15. The catalytic activity of the robust, safe and magnetically recoverable Fe_3O_4@mesoporous SBA-15 nanocatalyst was evaluated in the Biginelli reaction under mild conditions for the synthesis of a diverse range of 3,4-dihydropyrimidin-2(1H)-ones.

In the chapter seven Surface functionalization of SBA-15 followed by its reaction with $Cu(OAc)_2$ has been carried out to develop a new Cu-grafted functionalized mesoporous material, which catalyzes one-pot three component coupling of different aryl halides with thiourea and benzyl bromide in aqueous medium to produce aryl thioethers in very good yields (80–88%).

The Chapter eight presents the summary and conclusions that has been drawn out of the research work has been carried out.