

A REVIEW ON RECENT ADVANCES IN THE MODIFICATION OF POROUS SILICA NANOMATERIALS AND THEIR APPLICATIONS

Abstract

Modified porous silica nanomaterials have attracted great interest due to their potential applications in the fields of catalysis, adsorption, sensors, biological processes, chemical industries, and advanced composite materials. These enhanced physicochemical properties are due to their high surface area, modifiable pore size, adjustable framework, and well-defined host-guest chemistry. A lack of reviews that summarize the modification of porous silica nanomaterials and their diverse applications has been observed in the literature. In this article, we have summarized the recent advances in the synthesis of different transition and non-transition metal-loaded silica-based microporous, mesoporous, and micro-mesoporous composite nanomaterials. We have chosen ZSM-5, MCM-41, and MCM-48 owing to their inherent catalytic activity, which is further improved with functionalization. The synthesized nanomaterials can be used as an effective heterogeneous catalyst to improve the catalytic efficiency of various organic reactions. Water pollution is also a serious ecological hazard we face today. The major reason behind the water pollution is due to industrial waste, mining waste, sewage, pharmaceutical activities, etc. These sources contain various chemical substances, such as organic solvents, heavy metals, and textile dyes. So, these modified porous silica nanomaterials can also be used for the adsorption of heavy metal ions and for dye removal purposes. They can be also reused for several catalytic cycles without losing any catalytic activity, which confirms the true heterogeneous nature of the catalysts.

Keywords: Silica nanomaterials; catalysis; ZSM-5; MCM-41; MCM-48

Authors

Gaurisankar Phukan

Department of Chemical Sciences
Tezpur University
Tezpur, Assam, India

Priyanka Dutta

Department of Chemical Sciences
Tezpur University
Tezpur, Assam, India

Sudakhina Saikia

Department of Chemical Sciences
Tezpur University
Tezpur, Assam, India

Nand Kishor Gour

Department of Chemical Sciences
Tezpur University
Tezpur, Assam, India
nkgour1@tezu.ernet.in

Ramesh Chandra Deka

Department of Chemical Sciences
Tezpur University
Tezpur, Assam, India
ramesh@tezu.ernet.in

I. INTRODUCTION

Catalysis is defined as the phenomenon of a change in the rate of a chemical reaction in the presence of a substance called a catalyst [1]. A catalyst is defined as a substance that accelerates the rate of a chemical reaction without being practically consumed in the reaction [2]. During a chemical reaction, the bonds between the atoms in a molecule are broken and recombined to form a new molecule. The catalyst makes this process more efficient by lowering the activation energy, which is the energy barrier for a chemical reaction to occur. Biological processes in both plants and the human body are catalysed by effective catalysts found in nature. Catalytic processes are used to produce chemicals, medicines, polymers, foods, and other household items [3]. Similarly, wastewater treatment and numerous organic transformations are impossible without the aid of a catalyst.

Based on the phase of catalyst present, the catalytic reactions are classified into two types, i.e., homogeneous reactions and heterogeneous reactions. Homogeneous catalysis is defined as catalysis in which the catalyst is evenly distributed throughout the reaction medium and is present in the same phase as the reactants and products. For different kinds of organic transformations, homogeneous catalysts such as metal ions, organometallic complexes, and enzymes are utilized. Since homogeneous catalysts are molecularly scattered throughout the reaction phase, it is challenging to separate and recover the catalysts, which increases the difficulty and cost of the process [4]. Heterogeneous catalysis is defined as catalysis in which catalysts are present in different phases as the reactants and products. The main advantage of heterogeneous catalysts is that they can be easily separated from the reaction mixture and can be reused for several catalytic cycles without losing any catalytic activity. Porous silica nanomaterials are one of the very well known class of heterogeneous catalyst which have a high surface area, a large pore diameter, an adjustable pore size that can be easily modified [5].

We currently have a significant environmental issue with water pollution. Such pollution results from the excessive dumping of hazardous substances into water bodies, which reduces the water's quality and renders it harmful to people and other living things. The main causes of water contamination are due to sources like industrial waste, mining waste, sewage, agricultural, pharmaceutical activities, etc. A wide range of chemical substances, such as dyes, insecticides, organic solvents, heavy metals, dangerous industrial chemicals, and fertilizers, are included in these sources. Despite being present in small numbers, these contaminants pose serious threats to human health and all other living things [6].

The most harmful metals in wastewater are lead, mercury, cadmium, copper, nickel, zinc, chromium, arsenic etc. These heavy metals are released in substantial quantities into the environment. The primary pathway by which these metals enter the environment is through waste from different industrial processes such as mining, the manufacturing of fertilizer, domestic waste, the burning of fossil fuels, and automobile exhausts [7]. Heavy metal ions have the ability to accumulate in food chains and persist in the natural ecosystem for longer periods of time. Lead poisoning impacts the central nervous system, gastrointestinal issues, and stomach pain. Hg (II) is regarded as being extremely toxic due to its ability to harm the liver, disrupt the nervous system, and affect the kidneys. Prolonged exposure to Cr (VI)

damages the kidneys and liver and produces lung irritation, lung cancer, nausea, and skin irritation [8].

At present, dyes are one of the biggest contributors to water contamination. Our ecology is harmed when industrial waste containing dye is discharged into waterways. Dyes have aromatic structures that can combine to form stable complexes, increasing their biodegradation resistance. When garbage containing dye is dumped into waterways, light cannot penetrate, which negatively affects the biological processes taking place in the aqueous medium and slows the growth of aquatic species. The dye wastewater can also be harmful to human health by causing cancer, allergies, skin rashes, etc. Therefore, it is essential to treat wastewater that contains dyes before releasing it into the environment in order to minimize environmental and health issues [9].

Porous materials are solid materials with pores or cavities within themselves. The spaces between connected atoms structured in an organized manner are known as pores in any substance [10]. The porosity of a material can be defined as the ratio of the total volume of pores and voids to the volume occupied by the material. The characteristics of a porous material vary depending on the high surface area, selective, modifiable pore size, adjustable framework, and well-defined host-guest chemistry [11]. Porous materials are widely used in various fields, such as adsorption, advanced composite materials, heterogeneous catalysis, and biological processes. Porous materials are divided mainly into three types: microporous, mesoporous, and macroporous materials [12, 13, 14] which is shown in Figure 1.

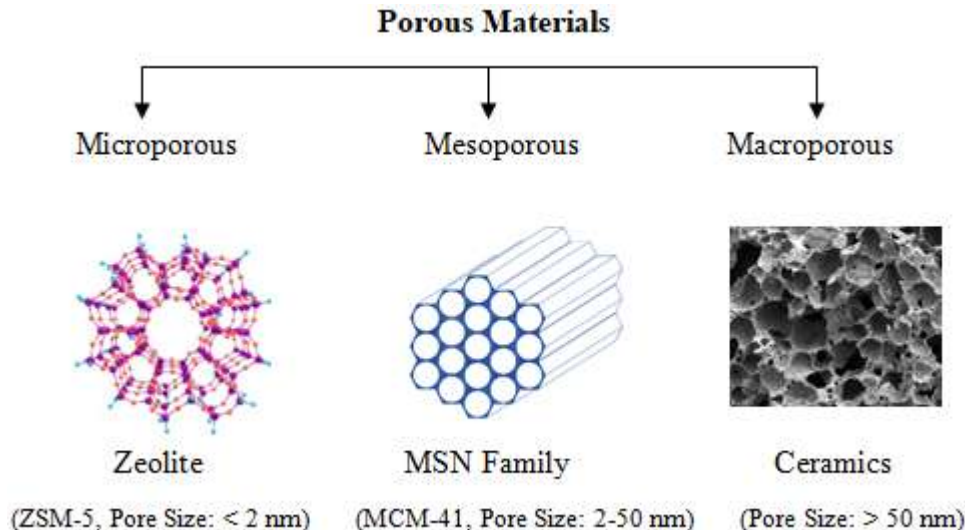


Figure 1: Classification of Porous Materials on the basis of pore size.

II. ZEOLITE AND ITS APPLICATIONS

Zeolites are crystalline aluminosilicates with a three-dimensional structure made of SiO_4 and AlO_4 tetrahedra as their main building blocks which are extensively studied and are currently relevant inorganic materials. The tetrahedra are joined by sharing an oxygen atom. Each AlO_4 tetrahedron in the zeolite framework structure carries a net negative charge, which is counterbalanced by an exchangeable extra-framework cation like Na, K, or Ca. Zeolites are

represented by the empirical formula $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M stands for the exchangeable cation having valency n for balancing the framework charge. Zeolites or molecular sieves are classified on the basis of either pore opening size or chemical composition (Si/Al ratio). Due to its inherent structural properties, this particular entity exhibits a diverse array of applications across multiple industrial domains. Zeolites can be modified with various transition and non-transition metals for advanced catalysis and wastewater treatment purposes. In addition to employing advanced experimental techniques, the utilization of computational approach has been deemed essential in advancing the field of zeolite-based technologies and in the endeavour to achieve a molecular-based design of zeolite-based materials tailored for specific applications. Catalysis is one of the domains where zeolites have abundant influence. Examples of zeolite includes mordenite, analcime, chabazite, zeolite A, ZSM-5 etc [15].

1. Role of Zeolite in Advanced Catalysis : In the most recent study, Popova et al. [16] reported the synthesis of Ni/Ru-modified ZSM-5 zeolite to study CO₂ hydrogenation to produce renewable methane. The catalyst was prepared by the wet impregnation method. The characterization of the synthesized materials was performed by X-ray powder diffraction (XRD), N₂ physisorption, temperature-programmed reduction (TPR-TGA), TEM, and XPS spectroscopic analysis. From this study, it has been found that nickel and/or ruthenium oxide species were finely scattered inside the pores and external surface of the zeolite. According to XPS data, due to the increased dispersion of nickel, which is facilitated by the presence of ruthenium, the surface of bimetallic systems is richer in nickel than monometallic ones. The facilitated reducibility of nickel oxide particles in the presence of noble metals was validated by a TPR analysis. Among the tested catalysts, the composition 10Ni5RuZSM-5 exhibits the best activity and selectivity for the production of methane, attaining equilibrium conversion and 100% selectivity at 400°C. The bimetallic 10Ni5RuZSM-5 catalyst was shown to have high stability and good reusability. In the other study performed by Gautum et al. [17] in which they reported the synthesis of a cerium-modified ZSM-5 catalyst for the esterification of glycerol with acetic acid to synthesize monoacetin (MA) and diacetin (DA). Different temperatures, catalyst weights, and reactant mole ratios were used during the reaction process. Maximum glycerol conversion of 98.32% was achieved at 120°C with an acetic acid to glycerol ratio of 9:1 (molar ratio) and an 8 wt% catalyst, resulting in a combination of MA and DA. The catalyst's ability to regenerate was also examined, and up to four cycles, there was no remarkable loss in glycerol conversion. The reaction, according to kinetic analysis, follows pseudo-first-order kinetics. From the investigation, it was concluded that Ce5ZSM-5 zeolite was the appropriate catalyst.

A computational investigation was performed by Kongpatpanich et al. [18] and provided a stepwise reaction mechanism for glycerol dehydration to acrolein and acetol over HZSM-5 using the density functional theory (DFT) method. They have used embedded cluster method to show the effect of zeolite frameworks on the reaction mechanism. Gaussian software [19] was utilized to explore the reaction mechanism using DFT method. In accordance with the findings observed in experimental studies, it is determined that the proposed reaction mechanism exhibits an endothermic characteristic. Au-exchanged ZSM-5 zeolites has been studied by Maihim et al. [20] using DFT to study the dehydrogenation of ethanol along with the effect of surface oxygen. They have used M06-2X functional in conjunction with the 6-31G(d,p)/SDD basis sets to conduct all

necessary computations. The findings suggest that the existence of surface oxygen on the Au-site facilitates both the dissociation of the O-H bond in ethanol and the transformation of ethoxide into acetaldehyde. Theoretical studies provide a comprehensive depiction of the adsorption properties and reaction mechanism at the molecular level. Metal incorporated zeolites show significant catalytic activities. Li et al. [21] showed the catalytic activity and selectivity of Zr-modified H-SAPO-34 (a micro pore zeolite) and H-ZSM-5 zeolites for the conversion of methane to ethylene and propylenes. Vienna Ab Initio Simulation Package (VASP) [22] has been employed for all the DFT calculations using the exchange correlation functional PBE (Perdew-Burke-Ernzerhof) including dispersion correction. To define the electron-ion-interactions in metal modified zeolites projected augmented plane (PAW) method has been used. The introduction of Zr metal doping has been found to decrease the acidity of zeolite, thereby influencing the selectivity of methanol towards a particular product. The catalyst with weaker acid strength shows more selectivity towards ethylene. However, the modification has a different effect of catalytic activity of H-SAPO-34 and H-ZSM-5. This study provides a full reflection of a greater grasp of the framework's structure/acid strengths and how it influences the activity and selectivity.

- 2. Use of Zeolite in Wastewater Treatment:** Faridah et al. [23] reported the synthesis of zeolite ZSM-5-impregnated TiO_2 for photocatalytic degradation of Cr(VI). In this study, the length of UV exposure was completely randomized. The results showed that the Cr (VI) content decreased with different UV irradiation times (15, 30, 45, 60, and 75 minutes, respectively) by 17.01, 17.99, 18.99, 28.73, and 36.0%. During a 75-minute UV exposure, the Cr (VI) ion level decreased by 39.42% of its original amount. Finally, they have concluded that the longer irradiation time by ultraviolet (UV) caused a higher percentage of Cr (VI) by using a ZSM-5 impregnated TiO_2 catalyst. Lakshmipathy et al. [24] reported the synthesis of a ZSM-5/AC composite for the removal of Pb^{2+} ions from water. This study investigated the ZSM-5/AC composite's potential in a fixed-bed column as an adsorbent for the removal of Pb^{2+} ions from an aqueous solution. It was found that for the maximum removal efficiency of ZSM-5/AC for the removal of Pb^{2+} ions, a low flow rate, a higher bed height, and a lower initial inlet concentration are necessary. The process of Pb^{2+} ion adsorption involved the exchange of Pb^{2+} ions with Na^+ ions from zeolite ZMS-5 and adsorption into the pores onto activated carbon. With the aid of linear regression models like the Adams-Bohart, Thomas, and Yoon-Nelson models, breakthrough curves were predicted. Studies on desorption and regeneration indicated that ZSM-5/AC may be utilized repeatedly for a number of cycles. The results concluded that ZSM-5/AC is a highly effective composite material for removing Pb^{2+} ions from water.

Vaez et al. [25] reported the synthesis of Ag nanoparticles modified by ZSM-5/ZnO nanocomposite for the photocatalytic degradation of methyl orange dye. The characterization of the synthesized nanocomposites was done with the help of FESEM, EDX, FTIR, XRD, UV-vis, and TGA analyses. The band gap studies showed that the addition of silver nanoparticles to the ZSM-5/ZnO modification improved the photocatalytic activity of the resultant nanocomposite. The maximum value of dye degradation was about 90% when the photocatalyst was exposed to UV light for two hours at an initial concentration of 5 ppm, pH = 11, and 0.07g. It has also been found that there are no significant changes in the photocatalytic activity of the composite up to 4

consecutive cycles, which signifies the high durability of the photocatalyst under UV irradiation. Badvi et al. [26] reported the synthesis of ZSM-5/TiO₂ nano photocatalysts for the photocatalytic degradation of methylene blue dye. The sol-gel method was used to disperse TiO₂ onto the surface of the ZSM-5 zeolite. The prepared nano catalysts were characterized by using spectroscopic analysis. The results of the photocatalytic activity demonstrated that nickel nanoparticle addition improved dye degradation efficiency. The synthesized photocatalyst with 0.5% nickel nanoparticles and a 600 °C calcination temperature has a 99.80% UV photocatalytic degradation efficiency.

III. MSNs AND ITS APPLICATIONS

Mesoporous silica nanoparticles (MSNs) are made of silica (SiO₂), which has a porous, honeycomb-like structure. Ordered MSNs, termed Mobil Crystalline Materials (MCM), were first synthesized by Mobil's researchers in 1992. Examples of mesoporous silica nanoparticles include MCM-41, MCM-48, etc. MSNs can be modified with various transition and non-transition metals for waste water treatment, as supports for drug delivery systems, and as catalysts for a variety of chemical processes. Mesoporous silica nanoparticles are synthesized by the hydrothermal method by reacting tetraethyl orthosilicate with a structure-directing agent or template in a temperature range of 353–423 K for a definite period of time [27, 28]. Two important mesoporous materials are given in Table 1 along with their characteristics.

Table 1: Two Important Mesoporous Materials Along With Their Characteristics.

Mesoporous Material	Structure	Pore System	Space Group
MCM-41	Hexagonal	2-Dimensional	p6m
MCM-48	Cubic	3-Dimensional	Ia3d

- 1. MSNs in Advanced Catalysis:** Li et al. [29] reported the synthesis of an Mn/MCM-41 catalyst for the NH₃-SCR reaction. The synthesis was performed using the hydrothermal method, and Al was used to modify MCM-41. A series of MnO_x/xAl-MCM-41 was prepared by impregnating Mn(NO₃)₂ onto xAl-MCM-41. The characterization of the synthesized materials was performed by using spectroscopic techniques. The increase in Bronsted acid sites caused by the doping of Al modifies NO_x's adsorption status on the synthesized catalyst surface, leading to various NO_x and NH₃ reaction pathways. From this investigation, they have observed that Al doping can dramatically alter MnO_x/MCM-41's capacity to remove NO_x, achieving over 90% NO_x removal efficiency at temperatures between 200 and 400 °C and around 90% N₂ selectivity between 120 and 400 °C. Wroblewska et al. [30] reported the synthesis of Ti-MCM-41 to study the influence of titanium content on the α-Pinene Isomerization Process. By using the sol-gel process, titanium-containing mesoporous silica catalysts with various Ti concentrations were prepared and characterization of the synthesized materials by spectroscopic techniques such as XRD, UV-Vis, N₂ adsorption/desorption, FT-IR, SEM, and XRF analysis. From the results it has been found that material with the molar ratio Si:Ti equal to 10:1, which contain 12.09 wt% Ti, was found to be the most active catalyst. The most suitable conditions for the α-pinene isomerization process was found to be of temperature 160 °C, a reaction time of 7 hours, and a catalyst composition of 7.5% relative to α-

pinene. From this reaction process, many useful intermediates such as camphene, α -terpinene, limonene, p-cymene, γ -terpinene, terpinolene, and α -phellandrene are produced.

Numerous research is carried out employing mesoporous silica materials as catalysts for diverse organic reactions in addition to the microporous materials. However, compared to the experimental studies, theoretical studies are limited. Chatterjee et al. [31] has performed a combined experimental and theoretical studies on the Pd supported Al-MCM-41 for the hydrogenation of phenol in supercritical CO₂ to form industrially important cyclohexanone. To carry out all the DFT calculations, they have used the DMol³ [32] code of Accelrys Inc with BLYP functional and DNP basis set. COSMO (conductor like screening model) solvation method has been utilised as a way to examine the impact of the solvent. The investigation of the reaction mechanism through DFT validates the influence of solvent on the heightened catalytic activity, as anticipated by the experimental study. Li et al. [33] have also performed a combined experimental and theoretical study on the sulphonic acid group functionalised MCM-41. They have studied the influence of water molecule in the self-condensation of cyclopentanone. The proposed reaction mechanism with Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) model has been investigated with DFT method using VASP [5] software with projector augmented plane wave method. The formation of H-bond between cyclopentanone and sulphonic acid group which is essential for the polarization of C=O bond is well illustrated by the theoretical calculation. Also, Ab initio molecular dynamics (AIMD) [34] simulation have been used to study the interaction between the H₂O molecules and sulphonic acid groups. From the kinetics study it has been confirmed that the reaction follows a 2nd order kinetics with C-C coupling as the rate determining step. Oxidation of glycerol has been studied by Yan et al. [35] using PtRu/MCM-41 nano catalyst in a base free medium. The theoretical calculation has been carried out using DMol³ program package with PBE functional and effective core potential (ECP) for Pt and Ru. Linear/quadratic synchronous transit (LST/QST) [36] method to find the transition state involved in the reaction mechanism. The DFT calculation provided additional evidence supporting the potential of PtRu bimetallic catalysts in facilitating the direct dissociation of molecular oxygen and water into hydroxyl groups. In a recent combined experimental and theoretical study performed by Snigdha K et al. [37] have used MCM-41 supported perchloric acid catalyst system for the synthesis of heterocyclic alkenes. The reported green synthesis method is carried out under solvent free system. DFT studies have been carried out to validate the experimental findings using M06 functional and 6-311G(d,p) basis set. The absence of negative vibrational frequencies in optimised geometries confirms the true minimum structures. Natural bond orbital (NBO) [38] analysis have also been performed to study the orbital contribution and HOMO-LUMO interactions and how it influences the reaction pathway. They have also evaluated the frontier molecular orbitals at the same level of theory. The computational results were found to be in strong concurrence with the experimental findings.

Akpotu et al. [39] reported the synthesis of citric acid (MCM-48) for the novel synthesis of quinoline derivatives. The synthesis was carried out using a reaction of malononitrile, ammonium acetate, 5,5-dimethylcyclohexane-1,3-dione, and aromatic aldehydes at room temperature using EtOH as the green solvent. The characterization of the synthesized materials was performed using P-XRD, SEM, TEM, TGA, FTIR, and

BET analysis. This method avoids the use of harsh chemicals and solvents while simultaneously offering notable improvements in reaction rates. This method has several key benefits, including an environmentally friendly catalyst, high efficiency, simpler catalyst recyclability, catalyst stability, etc. Ahmad et al. [40] reported the synthesis of Co-MCM-48 and CoMn-MCM-48 for the catalytic oxidation of toluene. The characterization of the synthesized materials was performed by using spectroscopic analysis. Hydrogen peroxide was used to oxidize toluene in order to examine the catalytic activity of Co-MCM-48 and CoMn-MCM-48. From the obtained results, it has been found that for the Co-MCM-48 catalyst, only benzaldehyde was produced, while for the CoMn-MCM-48 catalyst, a mixture of benzaldehyde and benzyl alcohol was produced. These outcomes demonstrated the great stability and activity of both catalysts for the oxidation of toluene. Ghaderi et al. [41] reported the synthesis of Zr-MCM-48, Zr-MCM-48-Mordenite, Al-MCM-48, Al-MCM-48-Mordenite, and platinum-loaded MCM-48-Mordenite catalysts to study the isomerization reaction of n-heptane. The characterization of the synthesized materials was performed by using spectroscopic analysis. From the obtained results, it has been found that the Pt/Mordenite catalyst showed higher hydrogenation and cracking activity, and the hybrid catalysts showed better isomerization selectivity. At a temperature of 200°C, the Pt/Al-MCM-48-Mordenite catalyst demonstrated the best catalytic performance, with the highest isomer selectivity of 81.9% and a satisfactory n-heptane conversion of 78.8%.

- 2. MSNs in Wastewater Treatment:** Wu et al. [42] reported the synthesis of thiol-functionalized MCM-41 as an adsorbent for the removal of Cu (II), Pb (II), Ag (I), and Cr (III) ions. The mesoporous silicas were synthesized with the help of the evaporation-induced self-assembly method. The synthesized materials were characterized with the help of FTIR, SEM, XRD, TEM, N₂ adsorption-desorption, and elemental analysis. From this experiment, it has been found that the optimal pH range for functionalized MCM-41 to remove heavy metal ions from aqueous solutions is between 5 and 6. The adsorption capacities of the thiol-functionalized MCM-41 catalyst for Cu²⁺, Pb²⁺, Ag⁺, and Cr³⁺ ions are in the order: Ag⁺ > Cu²⁺ > Pb²⁺ > Cr³⁺. The adsorbent could be regenerated without affecting its characteristics by the acid treatment process, and the removal rate was also high. Benhamou et al. [43] reported the synthesis of amine-functionalized Si-MCM-41 and Si-MCM-58 for the removal of heavy metal ions. The synthesized materials were used for the adsorption of Cd²⁺, Co²⁺, Cu²⁺, and Pb²⁺ ions from aqueous solutions. The characterization of the synthesized materials was performed with the help of spectroscopic analysis. The pores of MCM-41 and MCM-48 were expanded with two different amines, i.e., N-N dimethyldodecylamine (DMDDA) or dodecylamine (DDA). The mesoporous materials MCM-41 and MCM-48 whose pores were expanded with DMDDA have more affinity to remove the Cd²⁺, Co²⁺, Cu²⁺, and Pb²⁺ ions compared with those expanded with DDA.

Shao et al. [44] reported the synthesis of Mn/MCM-41 for the adsorption of methyl blue from aqueous solutions. The synthesized materials were characterized with the help of TEM, BET, FTIR, and XRD analysis. By changing various factors such as Mn% in Mn/MCM-41, contact time, initial methyl blue concentration, temperature, and pH, the adsorption of methyl blue by Mn/MCM-41 from aqueous solutions was studied. The Mn species of Mn/MCM-41, having a positive charge, provides a strong attraction to the methyl blue ions, which are negative in charge. From the results of this experiment,

they have found that Mn/MCM-41 was able to achieve a high methyl blue adsorption capacity of 45.38 mg g⁻¹ at 120 min, which is 8.6 times greater than the parent MCM-41. The reaction pathway followed pseudo-second-order kinetics, and the adsorption process is endothermic and spontaneous in nature. Prathipati et al. [45] reported the synthesis of Mn, and Al incorporated MCM-41 for the removal of rhodamine B and Congo red dyes. For the synthesis of this mesoporous material's co-precipitation method was applied. The characterization of the synthesized materials was performed with the help of spectroscopic analysis. The photocatalytic ability based on visible light irradiation was examined for Mn-MCM-41 and Al-MCM-41 in terms of their ability to remove the dyes. From the results obtained, it has been found that Mn-MCM-41 has more Rhodamine B and Congo Red Dyes removal ability than the Al-MCM-41 mesoporous material. The kinetic profile study revealed that the dye elimination rate complied with the Langmuir-Hinshelwood (L-H) kinetic model. Salama et al. [46] reported the synthesis of TiO₂ loaded on MCM-41 for the removal of methylene blue dye. The characterization of the synthesized materials was performed with the help of spectroscopic analysis. From the results, it has been observed that TiO₂-loaded MCM-41, where the TiO₂ content is 25%, showed higher catalytic activity towards the removal of methylene blue dye from aqueous solutions.

Taba et al. [47] reported the synthesis of amine-functionalized MCM-48 for the adsorption of heavy metal ions from an aqueous solution. The parent MCM-48 was synthesized by the post-synthesis method using colloidal silica, cetyltrimethylammonium bromide, and Triton X-100. Modification of parent MCM-48 was performed by using 3-aminopropyl trimetoxysilane (3-APTMS) as the amine source. The synthesized mesoporous materials were characterized with the help of XRD and FTIR analysis. The amine-functionalized MCM-48 was used for the adsorption of Cu²⁺ and Mn²⁺ ions. Variables such as pH, contact time, and initial concentrations of Cu²⁺ and Mn²⁺ ions were utilized to analyse the adsorption process. From the kinetic studies, it was found that the adsorption pathways follow pseudo-second order. Both Cu²⁺ and Mn²⁺ ion adsorptions on NH₂-MCM-48 followed Langmuir and Freundlich isotherms. From the results, it has been concluded that the Mn²⁺ ion (0.80 mmol g⁻¹) has a higher adsorption capacity than the Cu²⁺ ion (0.52 mmol g⁻¹). Vatandous et al. [48] reported the synthesis of MCM-48 and amine-grafted MCM-48 for the adsorption of Cd(II) and Pb(II) ions from an aqueous solution. The synthesized mesoporous materials were characterized with the help of SEM, XRD, and N₂ adsorption-desorption analysis. From the results, it was found that for both adsorbents, Cd (II) and Pb (II) ions may be removed most effectively at pH levels of 5 and 4, respectively. According to the Langmuir model, amine-grafted MCM-48 has a greater maximum adsorption capacity than MCM-48 for both Cd (II) and Pb (II) ions, which are 82.7 mg/g and 119.24 mg/g, respectively.

Shaban et al. [49] reported the synthesis of a nickel oxide/MCM-48 composite for the degradation of Congo red dye. The synthesized materials were characterized with the help of XRD, SEM, and UV-Vis spectrum analysis. The energy of the bandgap is lowered to 2.4 eV by loading Ni₂O₃ onto MCM-48. The multilayer chemisorption process that makes up the MCM-48/Ni₂O₃ adsorption mechanism suited the Freundlich equilibrium model quite well. From the results, they have concluded that the Ni₂O₃/MCM-48 composite has a higher adsorption capacity for Congo red dye by 17.5% and 32.2% than the adsorption capacity of MCM-48 and Ni₂O₃, respectively. The chemisorption

adsorption mechanism that occurs in multilayer form across the heterogeneous surface was demonstrated by the synthesized $\text{Ni}_2\text{O}_3/\text{MCM-48}$ composite. Pan et al. [50] reported the synthesis of nanoscale zero-valent iron (NZVI) incorporated in MCM-48. The characterization of the synthesized materials was performed with the help of a scanning electron microscope (SEM), an X-ray diffractometer (XRD), an energy dispersive spectrometer (EDS), and a transmission electron microscope (TEM). According to the results of the MB degradation experiment by using the nanoscale zero-valent iron (NZVI)-MCM-48 composite, under ideal conditions, which include an initial wastewater concentration of 10 mg/L, an initial pH of 6, an addition of 0.8 g/L, and a reaction time of 60 min, the MB decolorization rate is 853 mg/g and the chemical oxygen demand (COD) removal rate is 821 mg/g.

IV. MICRO-MESOPOROUS COMPOSITE NANOMATERIALS AND THEIR APPLICATIONS

A composite material refers to a heterogeneous substance that results from the combination of two or more distinct materials possessing contrasting physical and chemical properties. The constituent elements persist as discrete entities within the final configuration. Micro/mesoporous zeolitic composites (MZCs) are a significant category of hierarchical zeolitic materials that have garnered growing interest in recent times [51]. Despite the exceptional properties exhibited by zeolites as a result of their unique structures, they remain constrained by a significant limitation stemming from this very characteristic. Due to its microporous nature, zeolite has a diffusion constraint for larger molecules, which reduces its efficiency as a catalyst. This selective mass transfer can also block the pore size of the zeolites causing the deactivation of the catalyst [52]. However, while the discovery of mesoporous materials has addressed the issue of diffusion of large molecules, it has not successfully replicated the fundamental characteristics of zeolite. Therefore, the incorporation of a supplementary mesoporous phase that is interconnected with the microporosity of zeolites results in the formation of a hierarchical porous system in MZCs. This hierarchical structure enhances molecular transport while maintaining the inherent catalytic properties of zeolites [53].

Miao et al. [54] reported the synthesis of Ni/ZSM-5@MCM-41 micro-mesoporous composite nanomaterial for the CO_2 methanation reaction. First, using kaolinite tailings as the starting point for a two-step hydrothermal process, ZSM-5@MCM-41 with a core-shell structure was prepared. Later, ZSM-5@MCM-41 was coated with the Ni catalyst using constant volume impregnation with ultrasonic assistance. Additionally, Ni/ZSM-5 and Ni/MCM-41 catalysts were also synthesized. The characterization of the synthesized micro-mesoporous composite was performed with the help of X-ray diffraction (XRD), N_2 adsorption-desorption, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD) and reduction (TPR), and thermal gravimetric analysis (TGA) analysis. From the results of this experiment, they have concluded that the synthesized Ni/ZSM-5@MCM-41 micro-mesoporous composite catalyst demonstrated good CO_2 hydrogenation performance with CH_4 selectivity and CO_2 conversion upto 80% and 97% at 400 °C. The composite catalyst's performance nearly did not degrade during the stability test, which lasted 80 hours. Jermy et al. [55] reported the synthesis of ZSM-5/MCM-41 composite as a fluid catalytic cracking (FCC) catalyst for increasing the propylene yield from the catalytic cracking of vacuum gas oil (VGO). The synthesized

materials MCM-41, ZSM-5, and ZSM-5/MCM-41 composites were characterized with the help of spectroscopic analysis. When compared to the parent ZSM-5 and MCM-41, the characterization results demonstrated that the ZSM-5/MCM-41 composites comprised secondary building units with varied textural qualities. In comparison to 8.6 wt% over the traditional ZSM-5 additive at a similar gasoline yield penalty, the maximum propylene yield of 12.2 wt% was obtained over the ZSM-5/MCM-41 composite addition. Given the relatively high-octane value of the gasoline fraction, the ZSM-5/MCM-41 composite has a great advantage as a fluid catalytic cracking (FCC) additive.

He et al. [56] reported the synthesis of a Pd/ZSM-5/MCM-48 composite catalyst for the benzene oxidation reaction. The synthesized catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption and desorption, and thermogravimetric analysis (TGA) analysis. The results of the catalytic activity showed that Pd-loaded ZSM-5/MCM-48 composite catalysts have much higher catalytic activity than that of the Pd/ZSM-5 and Pd/MCM-48 catalysts. All the synthesized catalysts are stable and active in the complete oxidation of benzene. According to this study, new composite materials have the potential to operate as catalysts that facilitate the removal of volatile organic compounds (VOCs). These innovative Pd-loaded composite catalysts are promising materials for removing volatile organic compounds (VOCs) in general and may also find use in separation and adsorption. Di et al. [57] reported the synthesis of a ZSM-5/MCM-48 aluminosilicate composite catalyst for the conversion of methanol to gasoline. The composite material was synthesized using a two-step crystallization process. The characterization of the synthesized composite materials was performed with the help of spectroscopic analysis. From the characterization results, it was found that during the conversion of methanol to gasoline, the ZSM-5/MCM-48 composite catalyst has high stability, activity, and a low production of aromatic hydrocarbons.

V. CONCLUSION

Porous silica materials have been identified as an important class of catalytic materials. Their catalytic activity also differs depending on the pore diameters that they have. This chapter focuses on the investigation of the modified microporous silicate ZSM5, as well as the mesoporous materials MCM-41 and MCM-48, along with their composite. These materials have been chosen due to their potential applications in various catalytic domains, specifically wastewater treatment and organic reactions, with particular emphasis on the dominant presence of zeolite as the active site in the composite material. Recent experimental and theoretical investigations have demonstrated that the introduction of modifications or fictionalizations in the aforementioned species results in an augmentation of their catalytic activity for the targeted transformations. Also, composite formation leads to more efficient catalysts compared to their individual counterparts. However, the research conducted on composites of ZSM-5/MCM-41 and ZSM-5/MCM-48 and their respective fictionalizations is quite limited, with a lack of theoretical studies addressing this topic. Furthermore, it is noteworthy that there is a lack of theoretical studies pertaining to the alterations of porous silica nanomaterials. Thus, there is much potential for advancement in the domains of theory and experimentation with regard to the modification of porous silica nanoparticles.

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