

Heterogeneous Catalysis over Porous Materials: A Critical Review

Najirul Haque¹, Usha Mandi², Sk. Manirul Islam^{1*}, Noor Salam^{3*}

¹Department of Chemistry, University of Kalyani, Kalyani, West Bengal, India

²Department of Chemistry, Jogamaya Devi College, Kolkata, West Bengal, India

³Department of Chemistry, Surendranath College, Kolkata, West Bengal, India

*Corresponding Author's Email: noor.salam8@gmail.com, manir65@rediffmail.com

ABSTRACT

The strategy and building of porous constructions in synthesized materials that imitate structures seen natural, macro to the micro- and nanoscale ranges, has long been a vital scientific issue. Porous materials, in particular, have sparked considerable study attention due to their ability to combine the features of porous materials with polymers. To begin with, porous polymers can be engineered to have a larger surface area as well as well-constructed porosity. Second, polymeric porous materials are easily processed. They can, for example, be manufactured in moulded monolithic form or as thin films, which provides considerable benefits in many practical applications. Furthermore, unlike other forms of porous materials, such as porous organic polymers, some of them may be solved and then treated basically utilising solvent-related procedures without losing the porosity. Thirdly, the variety of polymer synthetic pathways makes it easier to design and build various porous materials capable of combining several chemical functions within the polymeric porous frameworks or at the tunable porosity over surface. This book chapter demonstrates the various applications of porous materials as heterogeneous catalyst. It also addressed current breakthroughs in their respective application areas, as well as the numerous hurdles that must be faced.

Keywords: *Heterogeneous Catalyst; Porous Materials; Catalysis*

Introduction

Physical reaction stages such as diffusion, adsorption, and desorption are as important as the chemical reaction itself in heterogeneous catalysed reactions since the starting materials must be delivered to the catalyst for the catalytic process to occur (Chongdar *et al.*, 2022). Because of the benefits of facile catalyst separation from the reaction mixture, easy catalyst regeneration after the reactions, and non-corrosive to the reactor system, heterogeneous catalysts are currently more commonly utilised in industry than homogeneous catalysts. The market share of heterogeneous catalysts is now projected to be over 90%. Heterogeneous catalysis involving liquid-solid and gas-solid phases is of special interest, in part because it allows a catalytic material to be deposited and immobilized on the surface of a solid. Surfaces represent a distinct interface between a

material's bulk structure and its external environment. Unlike atoms in the bulk, surface atoms have an asymmetric environment, with their bonds pointing inward. This arrangement exposes free bonds on the surface, making it more reactive compared to the interior of the material. Surface atoms are highly reactive and can readily engage in chemical reactions with neighboring atoms or foreign species to satisfy their bonding needs. This reactivity plays a crucial role in surface-related phenomena and interactions in various fields of science and technology (Kolasinski, 2012).

The reactivity of surface atoms is indeed vital in catalytic reactions that take place on solid surfaces. Catalysis involves the interaction of reactant molecules with the catalyst's surface, where the surface atoms facilitate the conversion of reactants into desired products. The reactivity of surface atoms is influenced by various factors such as their coordination environment, electronic structure, and accessibility of active sites. By providing an active surface with appropriate bonding characteristics, catalysts can enhance the reaction rates and selectivity, enabling more efficient and effective transformation of reactants into desired products.

Literature Review

Porous Materials in Catalysis

High BET surface area porous nanostructured materials are excellent for catalytic processes, and the main active component for catalytic system (e.g., metals, organic functional groups, etc.) in heterogeneous catalysts is most significant. As a result, researchers are currently particularly interested in designing porous nanomaterials with catalytically active centres on their surfaces. In recent times, a number of reviews by (Pérez-Ramírez *et al.*, 2008; Lopez-Orozco *et al.*, 2011) and others are reported on the synthesis and applications over porous materials. Microporous materials, such as zeolites, have caused a massive economic and environmental revolution (Li *et al.*, 2014) in the industrial production process. These microporous materials are significant in industrial-scale shape-selective catalysis. The small pore openings of microporous materials have prompted researchers to concentrate their efforts on developing materials having pores of even bigger diameters in the nanoscale realm. Through supramolecular templating routes, this leads to the discovery of ordered mesoporous silicas. Mesoporous supports, such as mesoporous oxides, phosphates, carbons, and others, play an important part in the industrial production process for fine compounds that were created subsequently. Liquid phase catalytic reactions in heterogeneous fluids over mesoporous solids result in less diffusion than other porous materials. Other mesoporous materials used in industrial catalysis include carbons, phosphates, oxides, organic-inorganic hybrid periodic mesoporous organosilicas (Fujita & Inagaki, 2008), and polymers. In this study, we focus on heterogeneous catalytic processes mediated by a wide spectrum of mesoporous materials, as well as their chemical production using a clean and green technique.

Application of Porous Materials

Oxidation Reactions over Mesoporous Materials

One of the most pressing issues confronting the chemical business today is the need for cleaner, safer, and more environmentally friendly alternative manufacturing processes. Processes must be efficient in terms of both economics and energy use. In general, catalytic oxidation of hydrocarbons is used in the production of fine compounds. The selective catalytic oxidation of organic molecules employing ecologically safe and inexpensive oxidants such as molecular oxygen and aqueous H₂O₂, as well as a heterogeneous, readily reusable catalyst, is a difficult aim for the fine chemical industry. By avoiding oligomerization of the active monomeric species, site isolation of discrete redox metal centres in inorganic matrices can provide oxidation catalysts with distinct activity and selectivities. Incorporating redox metal ions or complexes into the framework or cavities of these molecular sieves is one method of creating stable, solid catalysts with distinct activity. When oxidising organic compounds with large molecular sizes with a bulky oxidant such as tert-butyl hydroperoxide (TBHP), the use of mesoporous materials is strongly suggested by several researchers, (Delgado *et al.*, 2023).

Various inorganic solid supports, such as silica, carbon, clay, zeolite, metal oxide polymers, and mesoporous materials, are utilized in catalytic processes. These supports offer advantages due to their high surface area, porous structure, tunable properties, thermal and chemical stability, and compatibility with different catalysts. Immobilizing or anchoring catalysts onto these solid supports enhances catalytic performance, enables catalyst recyclability, and provides control over reaction conditions (Corma, Garcia & Llabrés i Xamena, 2010). Through the process of heterogenization, it is possible to generate supported materials consisting of transition metals and Schiff base ligands in complex form. This approach allows for the immobilization of the catalytic species on solid supports, providing enhanced stability, recyclability, and control over the catalytic system. Supported polymers have become increasingly popular in catalytic oxidation due to their advantageous characteristics such as inertness, non-toxicity, non-volatility, and recyclability. These properties make them highly desirable for catalytic applications, allowing for efficient and environmentally friendly oxidation processes. Mesoporous materials have emerged as ideal catalyst supports among various inorganic supports due to their unique features. These materials possess a three-dimensional open pore network structure, high surface area, and porosity, allowing for efficient deposition of dynamic components. The uniform interconnected pores create an effective environment for interactions between the catalysts and reactants, enhancing catalytic performance. Furthermore, mesoporous materials exhibit high reusability and heat stability, making them highly suitable for catalytic applications (Kumar, *et al.*, 2014). Heterogeneous catalysts facilitate oxidation reactions by attracting oxygen from oxidants, such as TBHP (tert-Butyl hydroperoxide) and HP (Hydrogen peroxide) (Biradar & Asefa, 2012). TBHP has been utilised as an oxidant in a variety of oxidation processes throughout the last decade, including alkyl benzene and benzyl alcohol

oxidation. We have discussed heterogeneous catalysts, their production techniques on diverse substrates, and applications in specific oxidation processes in this chapter.

Oxidation of Hydrocarbons

Homogeneous transition metal complexes such as Mn, Cr, V and also Ti, have been impregnated into a various of inorganic silica frameworks, and these catalysts have been widely explored for the various hydrocarbons oxidation via liquid phase transformation such as alkenes, cycloalkenes, alkanes, as well as arenes. But, epoxidation of olefin compounds is particularly significant in organic conversion because epoxy compounds are used to make a variety of highly value-added fine chemicals such as unsaturated resins, polyurethanes, as well as glycols. The synthesis and separation of epoxides from alkene sources is similarly problematic, because subsequent oxidation to other yields often reduces the desired one (Nandi *et al.*, 2011). As demonstrated in Figure 1, Cu- and Ni-incorporated mesoporous organosilica shows also an effective oxidising catalyst for the different olefins partial oxidation such as cyclohexene, norbornene, styrene, and stilbene under moderate circumstances (Nandi *et al.*, 2011). The reaction proceeds by forming a metal a hydroperoxo active intermediate that, upon contact by the olefinic double bond, produces the matching high yield of epoxide.

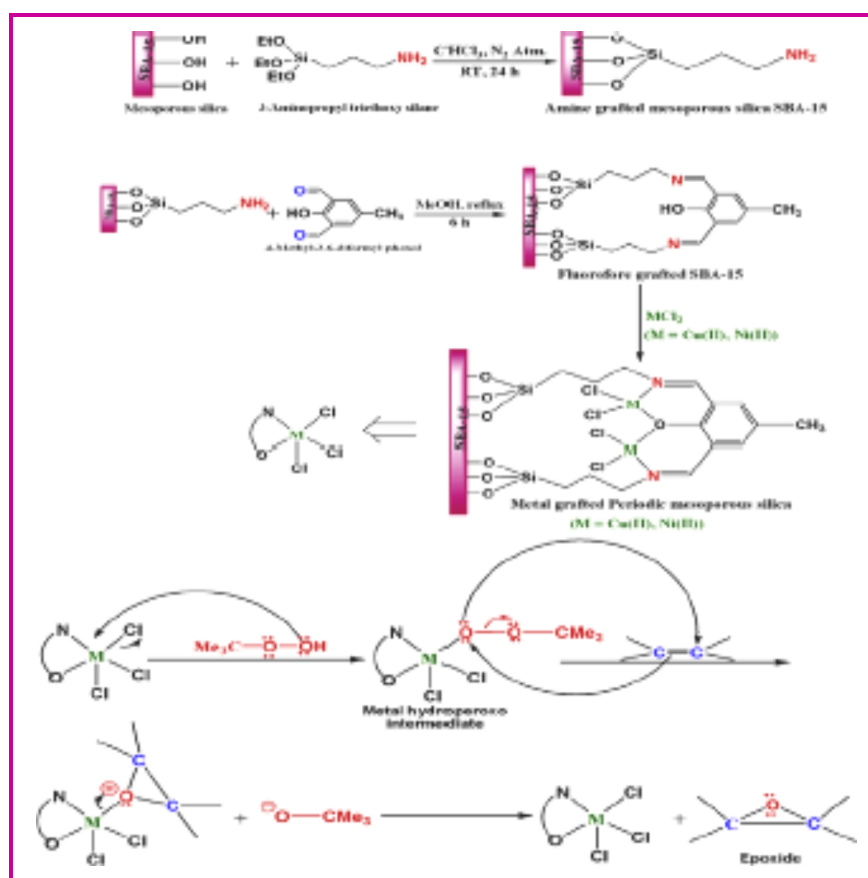


Figure 1: Different olefins Epoxidation Catalyzed by Cu- and Ni-grafted Porous Organosilica (Nandi *et al.*, 2011)

Singh and colleagues (2009) provided a description of Cr-based silica, which has demonstrated effective catalytic properties in the oxidation of aromatic compounds like ethylbenzene and typical alkanes for example cyclohexane. When ethylbenzene is oxidized, the main product obtained is acetophenone, accompanied by a certain amount of benzaldehyde. On the other hand, the cyclohexane oxidized and give the yields as cyclohexanol, cyclohexanone, and a small quantity of benzoic acid (Singh *et al.*, 2009 and Zhang *et al.*, 2023). When hydrocarbons, specifically methane, undergo high-temperature oxidation in a fixed-bed down-flow reactor utilizing a Mo-SBA-15 material and molecular O₂ gas as an environmentally friendly oxidant, a noteworthy quantity of formaldehyde is generated (Lou *et al.*, 2008).

In contrast, the partial oxidation of various unsaturated alkenes and alkynes in the liquid phase has commonly utilized hydrogen peroxide as a mild and non-toxic oxidant. An example of this is the work conducted by Vasylyev and Neumann (2004) who successfully developed a newly mesoporous material composed of a zinc-based polyoxometalate. This innovative material demonstrated efficient catalytic activity in the epoxidation reactions of allylic alcohols, employing hydrogen peroxide (H₂O₂) as the oxidant. Different metal-based polyoxometalate supported hexagonal mesoporous silicas (Cu, Co, Ni) show great promise in the propylene oxidation to acetone under molecular oxygen (Liu *et al.*, 2005). Table 1 provides a detailed summary of the many types of products produced by hydrocarbon oxidation.

Table 1: Various Oxidation Yields Generated by Various Hydrocarbon Compounds

Oxidant reagent	Hydrocarbons	Various Oxidation yields		References
		Examples of Reactants	Possible Products Formed	
Hydrogen peroxide (H ₂ O ₂), aerial oxygen, TBHP, air, ozone, etc.	Saturated (alkanes)	Methane, butane, isobutane	Formaldehyde, maleic anhydride, methacrolein	Lou <i>et al.</i> , 2008
	Unsaturated (alkenes, allyl and alkynes)	Propylene	Acetone, propylene oxide, allyl alcohol	Liu <i>et al.</i> , 2005
		Acetylene	Ethanol, glyoxal	Alzueta <i>et al.</i> , 2008
		Allyl alcohol	Glycidol, glycerine	Vasylyev, & Neumann 2004
	Cycloalkanes and Cycloalkenes	Cyclohexane	Cyclohexanol, cyclohexanone, adipic acid	Singh <i>et al.</i> , 2009

		Cyclohexene, cyclooctene	Cyclohexene oxide, cyclohexene-1-one, cyclohexene-1-ol, adipic acid, cyclooctene oxide, etc.	Nandi <i>et al.</i> , 2011
	Aromatic hydrocarbons or arenes	Toluene, ethylbenzene, styrene, etc.	Acetophenone, benzaldehyde, benzoic acid, styrene oxide	Zhang <i>et al.</i> , 2023

Oxidation of Alcohols

Mesoporous organic-inorganic hybrid solids incorporating transition metals have demonstrated their effectiveness in selectively oxidizing primary and secondary alcohols. The resulting aldehydes and ketones from the oxidation process hold significant value as intermediate compounds in various domains such as organic synthesis, pharmaceuticals, agricultural chemicals, and more. Traditional approaches utilizing stoichiometric quantities of transition metals like chromium (Cr), ruthenium (Ru), manganese (Mn), and others often generate substantial volumes of hazardous waste, rendering them environmentally unfriendly and non-reusable (Verma *et al.*, 2011).

As a result, there is a strong demand for metal-based heterogeneous supports to promote environmentally friendly and sustainable advancements in the selectivity of alcoholic oxidation. This process utilizes non-polluting and harmless oxidants such as molecular oxygen and hydrogen peroxide (H₂O₂). Verma *et al.* (2011) have made noteworthy progress in this field, reporting high yields of ketones from secondary alcohols, diols, and α -hydroxy ketones under mild conditions. They achieved this by utilizing a silica-supported oxovanadium Schiff base complex, which proved to be an effective and recyclable catalyst for the desired oxidation reactions (Verma *et al.*, 2011).

In their research, these scientists employed tert-butyl hydroperoxide (TBHP) for the oxidation process, which can generate toxic by-products. However, they also explored an alternative approach by utilizing molecular oxygen over a cobalt Schiff base complex grafted on SBA-15 through a 'click reaction.' This novel catalyst demonstrated exceptional catalytic activity in converting secondary alcohols into ketones, even at relatively lower temperatures. This advancement holds promise for a greener and more sustainable oxidation process. In a recent development, the conversion of primary alcohols to aldehydes has been successfully achieved using a catalyst known as Au@PMO (gold nanoparticles supported on periodic mesoporous organosilica) at room temperature. Remarkably, this transformation occurs by utilizing molecular oxygen (O₂) as the oxidant. This advancement represents a significant breakthrough in the field, offering a mild and efficient method for the selective oxidation of primary alcohols without the need for high temperatures or toxic reagents. The PMO material has been demonstrated to be an excellent support for gold nanoparticles (Au), as shown in Figure 2. It exhibits high reusability with minimal metal leaching, making it an environmentally friendly option for the

selective oxidation of C_6H_5OH to C_6H_5CHO under liquid-phase conditions. This finding highlights the potential of PMO as a stable and efficient catalyst for various oxidation reactions, providing a sustainable and eco-friendly alternative to chemical transformations (Karimi & Esfahani, 2012).

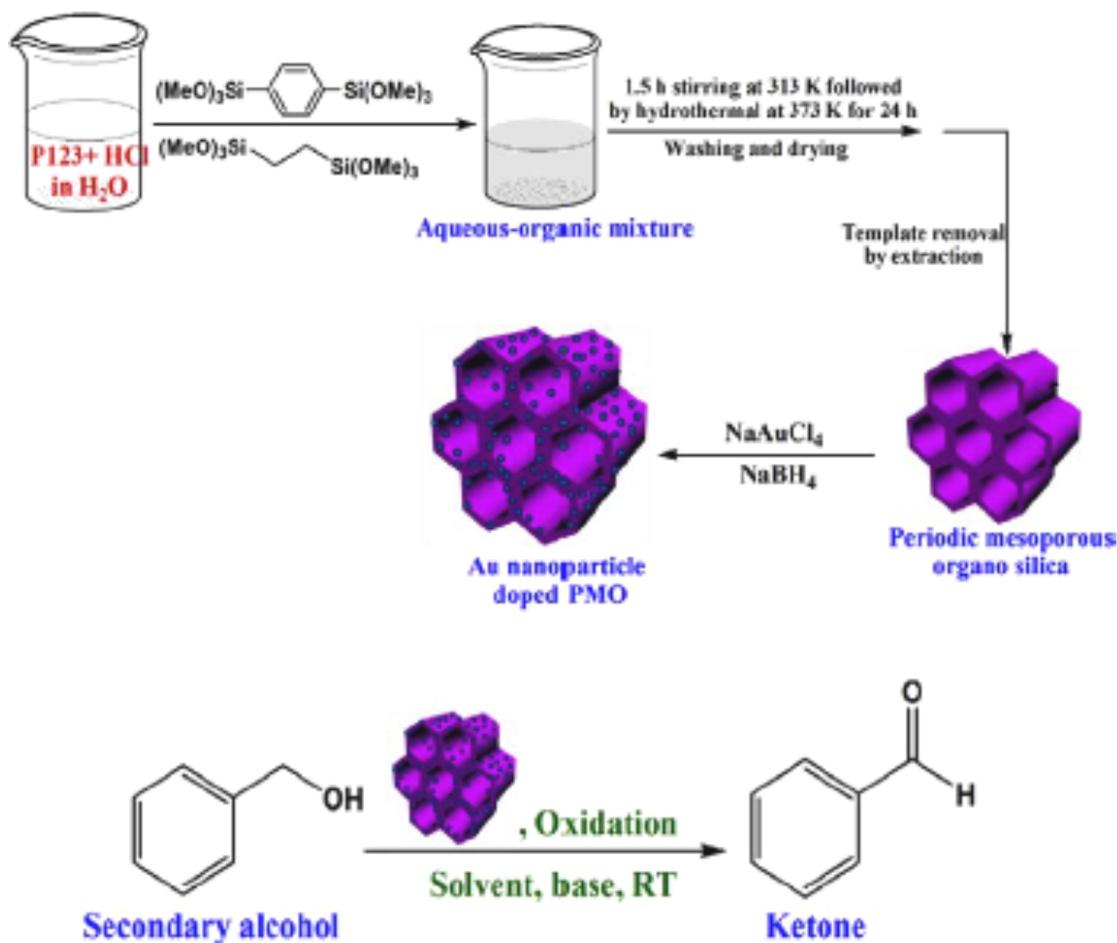


Figure 2: Schematic Illustration for The Oxidation of Alcohol Catalyzed by The Au-Supported PMO Material (Karimi & Esfahani, 2012)

The Reaction of Hydrogenation

The process of hydrogenation, developed by scientist P. Sabatier in 1897, is a chemical reduction method widely utilized in various industrial sectors such as the food, pharmaceutical, agricultural, and petrochemical industries. His method has been universally developed to reduce or saturate organic compounds (Song, *et. al.*, 2022). In this reaction, the typical procedure involves the addition of a pair of hydrogen atoms to unsaturated substrates that contain a double or triple bond. This results in the formation of saturated hydrocarbons or their derivatives. In some cases, hydrogenation can also be applied to saturated compounds, leading to ring-opening reactions (Kuhn *et.al.*, 2008). Due to the challenges associated with handling hydrogen gas, substitute hydrogen sources like

hydrazine and alcohols can be utilized as hydrogen donors in a process known as transfer hydrogenation. This technique is particularly valuable in organic synthesis for the asymmetric reduction of polar unsaturated substrates, including aldehydes, ketones, and imines. By using transfer hydrogenation, the selective and controlled reduction of these compounds can be achieved, offering a versatile approach to the synthesis of complex organic molecules (Paul, Pal & Bhaumik, 2010).

The non-catalytic reaction-way for reduction reactions typically demanded extremely high temperatures and pressures, making it impractical for most applications. In contrast, catalyst-mediated procedures, whether homogeneous or heterogeneous, are more enviable and cost-effective. All of them facilitate reduction reactions at lower temperatures and pressures, enhancing reaction efficiency and selectivity. Additionally, catalysts can be recycled and reused, making them economically viable for large-scale industrial processes. Overall, catalyst-mediated reduction processes offer significant advantages over non-catalytic approaches in terms of feasibility, cost, and environmental impact (Kuhn *et al.*, 2008). Indeed, catalysts play a crucial role in enabling enantioselective hydrogenation, which leads to the production of optically active products from prochiral compounds. In this context, two widely recognized homogeneous catalysts are Rh-based Wilkinson's catalyst and Ir-based Crabtree's catalyst. These catalysts have gained popularity for their ability to promote enantioselective hydrogenation reactions, allowing for the controlled synthesis of chiral compounds with specific optical properties. The development and utilization of such catalysts have significantly advanced the field of asymmetric synthesis, opening up new avenues for the production of pharmaceuticals, fine chemicals, and other important organic compounds. For industrial purposes, numerous heterogeneous catalysts have been developed specifically for asymmetric hydrogenation reactions. These catalysts enable the selective reduction of prochiral compounds to produce optically active products. The key strategy involves modifying the metal support of the catalyst with a chiral center, which imparts chirality to the catalyst and allows for enantioselective hydrogenation. By utilizing heterogeneous catalysts with chiral modifications, it becomes feasible to perform large-scale asymmetric hydrogenation reactions, offering a more practical and cost-effective approach for the industrial production of chiral compounds. Precious heavy metals such as palladium (Pd), platinum (Pt), and rhodium (Rh) are widely recognized as highly active catalysts for hydrogenation reactions. These metals exhibit excellent catalytic properties due to their ability to readily adsorb and activate hydrogen molecules. They are commonly used in various hydrogenation processes, ranging from the pharmaceutical industry to petrochemical applications.

Additionally, non-precious metals like nickel (Raney nickel) also serve as active catalysts for hydrogenation reactions. Raney nickel, a porous form of nickel, has exceptional hydrogenation activity and is often employed in industrial-scale hydrogenation processes due to its cost-effectiveness. Hydrogenation products of different substrates are given in Table 2.

Table 2: Hydrogenation Products of Different Substrates

Hydrogenating Agents	Substrates	Possible Products Formed	References
Gaseous H ₂ , hydrogen donor (cyclohexadiene, 2-propanol, hydrazine, etc.)	Alkene, R ₂ C=CR' ₂ Alkyne, RC≡CR' Aldehyde, RCHO Ketone, R ₂ C=O Ester, RCO ₂ R' Imine, RR'C=NR'' Amide, RC(O)NR' ₂ Nitrile, RCN Nitro, RNO ₂	Alkane, R ₂ CH-CHR' ₂ Alkene, cis-RHC=CHR' Primary alcohol, RCH ₂ OH Secondary alcohol, R ₂ CH-OH Two alcohols, RCH ₂ OH + R'OH Secondary amine, RR'CHNHR Tertiary amine, RCH ₂ NR' ₂ Primary amine, RCH ₂ NH ₂ Amine, RNH ₂	W. Huang, <i>et. al.</i> , 2008 J.N. Kuhn, <i>et. al.</i> , 2008 Tang <i>et al.</i> , 2010 S, Parambadath <i>et al.</i> 2009, H. Song, <i>et. al.</i> , 2022

In the catalytic hydrogenation of aromatic nitro compounds, mesoporous oxides or mixed oxides supported with nanoparticles of gold (Au), nickel (Ni), platinum (Pt), and palladium (Pd) thioether have been found to be effective catalysts. These catalysts demonstrate the capability to promote the selective synthesis of aniline from nitrobenzene, employing hydrazine hydrate as the hydrogenating agent. Importantly, these hydrogenation reactions can be carried out under mild conditions.

To enhance the catalytic performance, mesoporous oxides such as TiO₂, Al₂O₃, SiO₂, and ZrO₂ are used as supports for the nanoparticles. The synthesis of these catalysts involves a surfactant-assisted route, which enables the creation of mesoporous structures with confined thioether nanoparticles of PtPd, AuPd, or AuPt. This synthesis method enhances the dispersion and stability of the nanoparticles, leading to improved catalytic activity and selectivity in the hydrogenation of nitrobenzene to aniline.

In contrast to the previous approach, it has been found that the conversion of nitrobenzene and its derivatives to anilines can be achieved using mesostructured nickel-aluminium mixed oxides as catalysts in the presence of 2-propanol as the solvent (Paul, Pal & Bhaumik, 2010). In this system, the catalyst itself is sufficient for the reduction process, and no additional hydrogenating agent is required.

The mesostructure of the catalyst is obtained through the use of lauric acid as a structure-directing agent, which helps in the formation of the desired nickel-aluminium mixed oxide with a mesoporous architecture. This mesoporous structure enhances the accessibility of the reactants to the active sites of the catalyst, thereby promoting the reduction of nitrobenzene and its derivatives to anilines.

An established catalyst with optical activity for the hydrogenation of α -(acetylamino)-cinnamic acid and its methyl ester is a mesoporous silica organic-inorganic hybrid matrix incorporating an anchored Rh complex.

A fascinating one-step hydrogenation/esterification reaction, that plays a vital role in the upgrading of bio-oil obtained from fast pyrolysis of biomass, has been effectively conducted using acetaldehyde and acetic acid on a mesoporous organosilica catalyst modified with metallic Pt. (Tang *et al.*, 2010). In contrast, a true heterogeneous catalyst has been demonstrated for the hydrogenation of nitrobenzene to aminobenzene at a temperature of 323 K under a 20 cm³/min H₂ flow. This catalyst consists of bimetal Pd-Ni nanoparticles deposited on Ti-doped hexagonal mesoporous silica, and its deposition is achieved using a simple photo-assisted deposition method (Schranck, Tlili & Beller, 2013). Conversely, a novel material for the asymmetric hydrogenation of ketones at room temperature, utilizing low to moderate H₂ pressure (<10-40 atm), is an organometallic Ir complex supported on SBA-15 with a chiral ligand. This catalyst has demonstrated good yield and enantioselectivity, reaching near about 93% enantiomeric excess (Liu *et al.*, 2010). Parambadath *et al.*, 2010 conducted an investigation on the enantioselective transfer hydrogenation of prochiral ketones using an immobilized Ru(II)-Chiral (1R,2S)-(p)-cis-1-amino-2-indanol catalyst supported on SBA-15. This catalytic system demonstrated excellent performance under mild reaction conditions, with 2-propanol acting as the hydrogen donor. Currently, this type of asymmetric transfer hydrogenation is recognized as an efficient method for synthesizing chiral molecules. It offers advantages such as low yields of side products, high productive yields, and a high enantiomeric purity. Huang *et al.*, (2008) reported the synthesis of Rh and Pt nanoparticles with a size of approximately 1 nm, which were incorporated within a fourth-generation polyaminoamide (PAMAM) dendrimer. These nanoparticles were subsequently loaded onto an SBA-15 support. The catalysts prepared in this manner were found to be effective for the hydrogenation reactions of pyrrole and ethylene. Specifically, pyrrole was converted to ethane, while ethylene was transformed into n-butylamine (Huang *et al.*, 2008). Figure 3 illustrates the schematic representation of the catalyst preparation process and the subsequent hydrogenation reaction carried out using the catalyst. Additionally, mesoporous polymers have been identified as effective supports for catalytic hydrogenation reactions (Salam *et al.*, 2014) In a recent development, a ruthenium embedded over porous cross-linked polymer functionalized with a chiral ligand has demonstrated exceptional performance in terms of both high enantioselective conversion and remarkable reusability. This catalyst has been successfully applied to the asymmetric hydrogenation of a β -keto ester, conducted in methanol at a temperature of 323 K.

The majority of hydrogenation reactions follow a straightforward mechanistic pathway that involves several key steps. Initially, the hydrogen gas and the substrate bind to the surface of a solid catalyst. Subsequently, the hydrogen molecules dissociate into atomic hydrogen species. These atomic hydrogen species then add one by one to the substrate, resulting in

the stepwise addition of hydrogen atoms. Finally, the hydrogenated product desorbs from the surface of catalyst, completing the hydrogenation process.

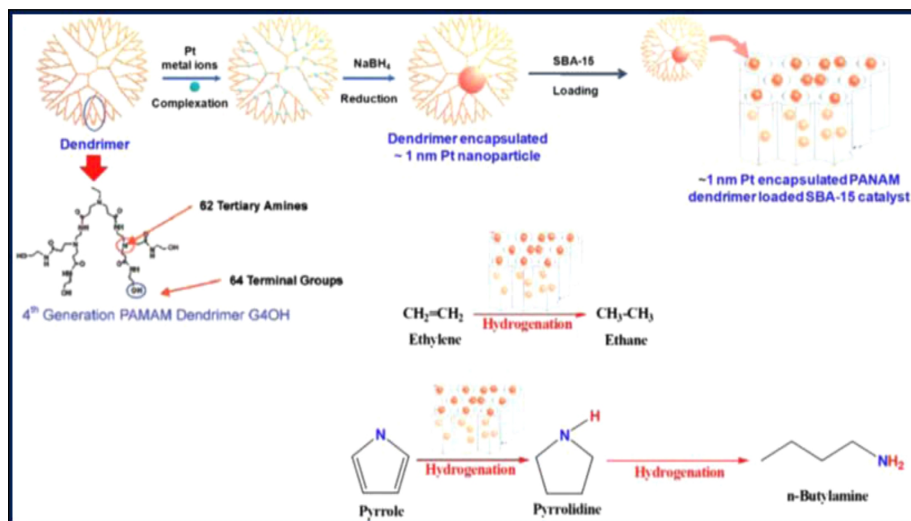


Figure 3: The Hydrogenation Reactions of Ethylene and Pyrrole Catalyzed by PANAM Dendrimer-Grafted Pt Nanoparticles Embedded Over SBA-15 Can Be Represented Schematically (Huang et al., 2008)

N-alkylation reactions

The formation of carbon-nitrogen bonds is a crucial and highly significant process in organic chemistry. It holds great importance in the development and composition of both chemical and biological systems. The N-alkylation of amines holds basic significance in organic synthesis due to the significant role of the resulting higher amines as versatile synthetic intermediates. These higher amines find extensive applications in the production of pharmaceuticals, agrochemicals, fine chemicals, dyes, surfactants, and functionalized materials. Some researchers conducted pioneering research in which alcohols were employed as direct alkylating agents for the N-alkylation of amines, utilizing transition metal catalysts. This represented the first instance of alcohol substitution by N-nucleophiles. Subsequently, significant efforts have been dedicated to the N-alkylation of amines and related reactions, focusing on the activation of alcohols through strategies such as borrowing hydrogen (BH) and hydrogen autotransfer (HA). These approaches have been extensively explored in the literature with the aim of achieving efficient and selective N-alkylation reactions. A variety of catalytic systems have been reported for N-alkylation reactions using alcohols as the alkylating agents (Pera-Titus *et al.*, 2014). The borrowing hydrogen (or hydrogen auto transfer) process involves the alcohol substitution in the presence of an amine or the N-alkylation of an amine with an alcohol, as shown in Figure 4. Mesoporous aluminosilicate nanoparticles have been found to possess unique catalytic properties for the solvent-free N-alkylation of aniline with benzyl alcohol. Under mild reaction conditions, this catalytic system enables the selective production of N-Benzylidenaniline with 100% selectivity (Sreenivasulu, Viswanadham & Saxena, 2014).

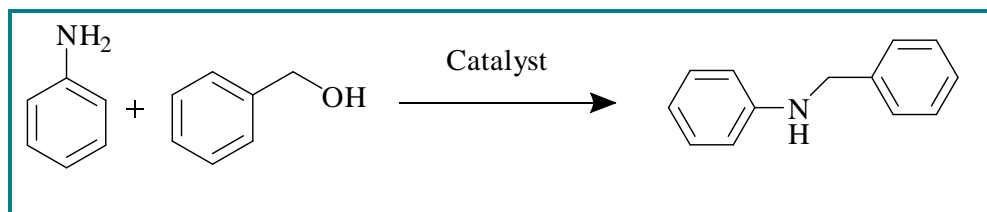


Figure 4: N-Alkylation Reaction Between Amine and Alcohol (Sreenivasulu, Viswanadham & Saxena, 2014)

A catalyst composed of a pyrimidine-substituted N-heterocyclic carbene-iridium complex supported on mesoporous silica (SBA-15) was employed for the environmentally friendly substitution reaction of primary alcohols with amines. This catalytic system facilitated the conversion of primary alcohols into secondary amine products, achieving yields ranging from 52% to 99%. (Wang *et al.*, 2013). The catalyst demonstrated remarkable recyclability, maintaining its catalytic efficiency even after being reused for more than nine cycles. Another effective catalyst employed in the substitution of alcohols with amines was a bifunctional Ir-Zr metal-organic framework (MOF) (Rasero-Almansa *et al.*, 2014). This catalyst exhibited excellent performance even in the presence of air and without the need for a base. Additionally, a cobalt nanoparticle catalyst supported on N-doped mesoporous carbon (Co/mCN-900) facilitated the reductive N-alkylation of nitroarenes with carbonyl compounds, resulting in the formation of aromatic secondary amines. Notably, this catalytic reaction proceeded under mild reaction conditions. In 2010, Luque and colleagues were the pioneers in reporting the microwave-assisted N-alkylation of amines with benzylic alcohols, utilizing nano-Fe-HMS (HMS referring to hexagonal mesoporous silica) as the catalyst. In a recent study by Paul *et al.*, 2017 a new catalyst called mesoporous silver nanoparticle-supported alumina ($\text{Ag@Al}_2\text{O}_3$) was synthesized. This innovative nanocatalyst exhibited exceptional catalytic activity in the N-alkylation of hetero (aromatic) amines and aromatic amines using alcohols as the alkylating agent. The catalytic process demonstrated green characteristics, being atom-economical and environmentally friendly. Additionally, the catalyst displayed air stability, and the active sites remained intact within the porous material without decomposition or leaching. These findings indicate that the catalyst is robust and exhibits heterogeneous behavior. (Paul *et al.*, 2017).

Acylation Reactions

The acylation of amines, alcohols, and phenols is a widely used and cost-effective method for protecting, identifying, and characterizing these functional groups in multi-step synthetic processes.

Typically, acetic anhydride and acetyl chloride are employed in the presence of acidic or basic catalysts within an organic solvent for the acylation reactions. Acetyl chloride is widely used as an acylating agent due to its availability and affordability. However, it exhibits high reactivity and instability in aqueous environments. Therefore, numerous homogeneous and heterogeneous catalysts have been documented for this organic transformation. These catalysts assist in facilitating the acylation reaction and improving its efficiency. However,

the catalysts that have been reported so far have certain limitations. These include long reaction times, harsh reaction conditions, complicated workup procedures, and in some cases, the catalysts are sensitive to moisture or expensive. These drawbacks hinder their practical application and highlight the need for alternative catalysts that can overcome these challenges. The utilization of acetic acid instead of acetic anhydride or acetyl chloride offers both economic and environmental benefits. This is because substances employed in chemical synthesis can potentially be incorporated into the desired end product or become waste by-products. As the chemical industry strives for high yield and minimal waste, there is a growing emphasis on developing processes that align with these goals. By opting for acetic acid as a reagent, it contributes to the objective of reducing waste and achieving a more sustainable and efficient production process. The concept of "atom economy" has been introduced to assess the efficiency of a reaction by considering the fate of the reactants. In the context of acylation reactions, various greener catalytic methods have been developed. These methods include the acylation of amines using organic acids, the utilization of solid-supported reagents such as polymer-bound acylating agents, arylboronic or boronic acid derivatives, and the application of microwave irradiation. A wide range of catalysts has been reported for the acylation of amines, including transition metal salts, immobilized ionic liquids on mesoporous materials, and solid acid catalyst. These advancements in catalysis contribute to the development of more sustainable and environmentally friendly acylation processes.

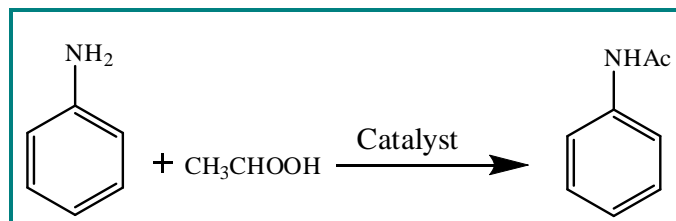


Figure 5: Acylation of Amines with Acetic Acid (Sharley & Jonathan, 2017)

Polysaccharide-derived mesoporous materials, specifically Starbon® acids, have been utilized for the efficient synthesis of various amides through acylation reactions. These reactions involve the combination of amines and acids in a 1:1 ratio. Starbon® acid, derived from renewable biomass sources, serves as a catalyst in these reactions and offers both high activity and selectivity. Moreover, the catalyst demonstrates excellent reusability, making it a sustainable and environmentally compatible option for the acylation of amines using acetic acid under microwave irradiation. The use of Starbon® acid contributes to the advancement of greener and more efficient synthetic methodologies.

A recent study by Shyamaprasad and colleagues described the acylation reactions of alcohols, phenols, and amines using mesoporous aluminophosphate solid acids as catalysts. The remarkable catalytic activity of aluminophosphate was attributed to its high surface area, surface acidity, and mesoporous structure. Notably, the reactions were carried out under solvent-free conditions, making the method environmentally friendly and suitable for industrial applications. The absence of solvents reduces the environmental impact and

improves the overall sustainability of the process. This research contributes to the development of greener and more efficient catalytic systems for acylation reactions. The acylation of various alcohols using acetic acid as the acylating agent has been investigated in the presence of sulfonic acid functionalized periodic mesoporous organosilicas (PMOs). The study demonstrates that the catalysts with high surface hydrophilicity exhibit a high selectivity for the formation of mono-acylated products. In contrast, catalysts with relatively higher hydrophobic characteristics exhibit enhanced selectivity towards the formation of di-acylated products. This observation indicates that the surface properties of the catalysts play a crucial role in determining the selectivity of the acylation reaction. The findings provide valuable insights for the design and optimization of catalysts for selective acylation reactions (Karimi *et al.*, 2015).

Sustainable Production of Biodiesel

The utilization of lignocellulosic biomass for the production of chemicals, fuels, and energy has gained significant attention due to the increasing global energy consumption and the gradual depletion of fossil fuel resources. Lignocellulosic biomass, which includes plant materials such as agricultural residues, forestry residues, and dedicated energy crops, offers a renewable and abundant source of carbon that can be converted into valuable products. By efficiently converting lignocellulosic biomass, it is possible to reduce reliance on fossil fuels, mitigate greenhouse gas emissions, and promote a more sustainable and environmentally friendly approach to energy and chemical production. The development of technologies for the efficient conversion of lignocellulosic biomass holds great promise for achieving a more sustainable and diversified energy future. The utilization of lignocellulosic biomass and its derivatives for the production of chemicals, fuels, and energy has gained significant attention due to the increasing global energy demand and the depletion of fossil fuel resources. Various conversion methods, such as gasification, fermentation, hydrogenolysis, and chemical transformation, can be employed to extract value-added platform molecules and biofuels from lignocellulosic biomass and its derivatives. Levulinic acid (LA) and its esters have emerged as highly promising platform chemicals with diverse applications in the biofuel, solvent, polymer, and specialty chemicals industries (Figure 6). LA is typically produced through acid-catalyzed hydrolysis of lignocellulosic biomass, including cellulose, glucose, and fructose. It can be further upgraded catalytically into levulinate esters, γ -valerolactone (GVL), α -methylene- γ -valerolactone, olefins (via ring-opening and decarboxylation of GVL), 2-methyl tetrahydrofuran (via 1,4-pentanediol), 5-nonanone (via pentanoic acid), and diphenolic acid. These derivatives serve as important intermediates for the synthesis of various products such as biofuels, solvents, epoxy resins, polycarbonates, and more. Levulinate esters have proven to be valuable in applications such as plasticizers and solvents, and they have also been proposed as fuel additives. One specific example is ethyl levulinate, which can be utilized as a diesel miscible biofuel in regular diesel car engines at concentrations of up to 5 wt.%. This is possible due to its physicochemical properties, which are comparable to those of biodiesel fatty acid methyl esters (FAME). The use of ethyl levulinate as a biofuel additive offers a potential alternative

to conventional diesel fuels, contributing to the development of more sustainable and environmentally friendly transportation options.

The production of levulinate esters from cellulosic biomass not only provides a cost-effective alternative method for their synthesis but also offers the potential to decrease reliance on petroleum-derived fossil fuels. In acid-catalyzed esterification reactions, various heterogeneous acid catalysts have been identified as effective. These catalysts include acid resins, heteropolyacids, zeolites, metal oxides, and metal salts, among others. These catalysts play a crucial role in promoting the esterification reaction, facilitating the conversion of levulinic acid or its derivatives with alcohols to form the desired levulinate esters. The utilization of such heterogeneous acid catalysts enables sustainable and environmentally friendly production of levulinate esters from cellulosic biomass, contributing to the overall goal of reducing dependence on fossil fuels.

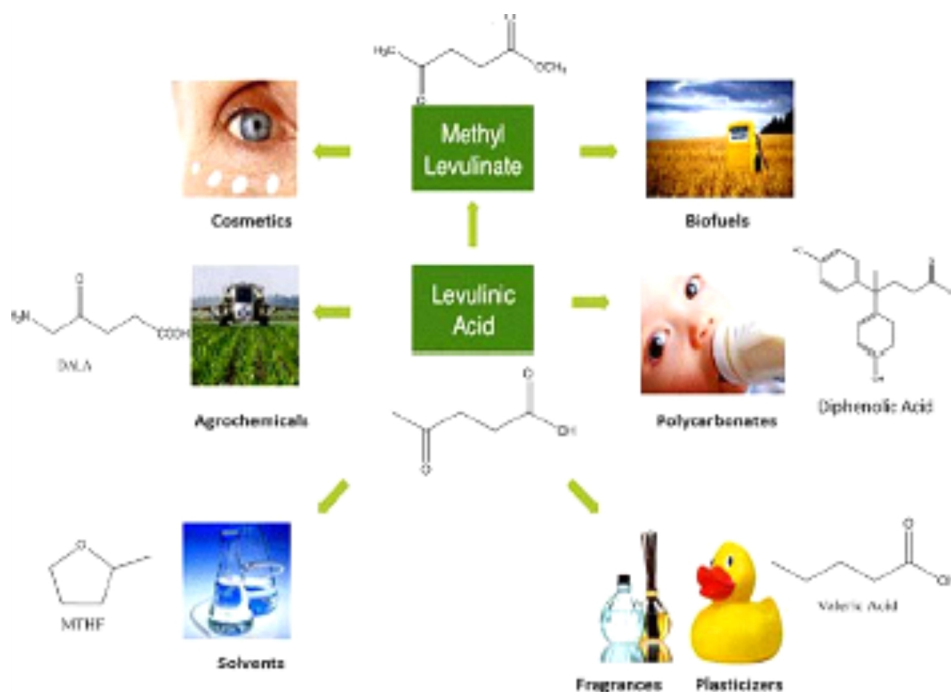


Figure 6: Levulinic Acid Derivatives and their Applications (Pileidis & Titirici 2016)

The esterification reaction by levulinic acid (LA) with alcohols, such as ethanol or 1-butanol, can occur at room temperature, but it proceeds slowly and requires acceleration either through elevated temperatures (70–100 °C) or the use of a catalyst to achieve a desirable conversion rate within a reasonable timeframe. By applying higher temperatures, the reaction kinetics are enhanced, leading to increased reaction rates and improved conversion. Alternatively, the addition of a catalyst can facilitate the esterification process by lowering the activation energy, allowing the reaction to proceed more rapidly even at lower temperatures. These strategies ensure efficient and timely conversion of LA and alcohols to the desired ester products.

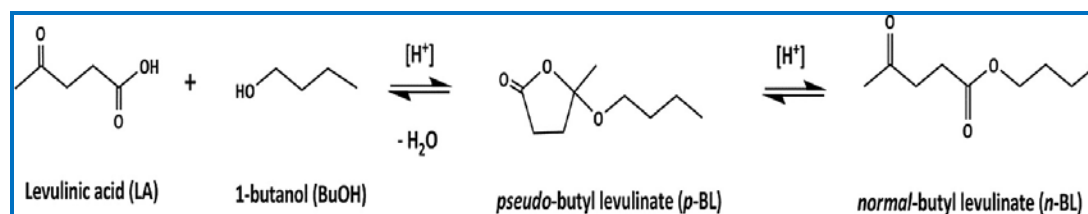


Figure 7: Levulinic acid Esterification with BuOH to *n*-butyl Levulinate (Kuwahara, Fujitani & Yamashita, 2014)

Solid acids, such as zeolites and sulfated mixed oxides, have been employed in the esterification reaction between levulinic acid and alcohols. Examples of these solid acids include sulfated zirconia (SO₄²⁻/ZrO₂), titania (SO₄²⁻/TiO₂), niobia (SO₄²⁻/Nb₂O₅), and stannia (SO₄²⁻/SnO₂). These solid acid catalysts exhibit strong acidity, which promotes the esterification reaction by facilitating the protonation of levulinic acid and alcohol molecules, leading to the formation of ester bonds. The presence of sulfated species enhances the catalytic activity of these solid acids, making them effective in promoting the esterification reaction and achieving high conversion of levulinic acid with alcohols.

The sulfated mixed oxides, which possess highly acidic sites, have emerged as the most talented materials for the esterification reaction caused by levulinic acid with alcohols. These catalysts demonstrate excellent catalytic activity, ensuring efficient conversion of levulinic acid to esters within an appropriate reaction time. The presence of robust acid sites on the sulfated mixed oxides facilitates the protonation of levulinic acid and alcohols, thereby promoting the esterification reaction and enhancing overall catalytic performance. Consequently, these sulfated mixed oxides are highly regarded as effective catalysts for the esterification process.

The activity of the sulfated mixed oxides is influenced by the quantity and strength of acid sites as well as the preparation conditions. Enhancements in catalyst activity can be achieved by optimizing the synthesis conditions, increasing the density of acid sites, and improving the dispersion of sulfate species. To this end, the introduction of mesopores in the mixed oxides using a surfactant-induced self-assembly approach represents a potential strategy. This approach allows for the controlled creation of mesopores, which can facilitate improved accessibility of reactants to the active acid sites, leading to enhanced catalytic activity. An alternative approach involves achieving a fine dispersion of the active oxide phase on a suitable neutral support with a larger surface area, such as mesoporous silica materials. By dispersing the active oxide phase evenly on the support material, the catalyst's efficiency can be improved. This strategy allows for better interaction between the active sites and the reactants, leading to enhanced catalytic performance. The high surface area and structural characteristics of mesoporous silica materials make them well-suited for supporting and stabilizing the active oxide phase, thereby promoting effective catalytic reactions. Both methods, namely the introduction of mesopores and the diffusion of the active oxide

phase on a larger surface area support, contribute to enhancing the catalytic activity of these materials in liquid-phase reactions. The resulting high surface area allows for higher dispersion of the active species and an increased density of acid sites, which are crucial for catalytic activity. Additionally, these methods facilitate improved mass transport of reactant and product molecules, leading to enhanced reaction rates. Overall, these approaches improve the accessibility of the active sites and promote efficient molecular interactions, thereby enhancing the catalytic performance of liquid-phase reactions. W. Ciptonugroho *et al.*, 2016 reported the synthesis of $\text{WO}_x/\text{mesoporous-ZrO}_2$ catalysts via evaporation induced self-assembly (Ciptonugroho *et al.*, 2016). The catalysts were evaluated for the esterification of levulinic acid with 1-butanol. Catalysts containing 20–25 wt.% WO_3 demonstrated the formation of WO_3 nanoparticles along with polytungstic species and tetragonal ZrO_2 . These catalyst materials displayed a significantly high concentration of surface acid centers, ranging from 0.10 to 0.11 mmol/g, with a predominance of Brnsted acidity. Notably, this led to a remarkable enhancement in catalytic activity for the esterification reaction, with turnover frequencies (TOFs) reaching up to 0.16 s⁻¹. Cheng *et al.*, 2016 investigated the esterification of levulinic acid with *n*-hexanol using mesoporous HSiW/MCM-41 as a catalyst (Cheng *et al.*, 2016).

Conclusion

Porous materials are required to possess two fundamental characteristics: a significant pore volume and a well-defined pore structure tailored to achieve the desired performance of the material. The pores within the material can be considered functional phases that designers and users aim to optimize for the material's performance. These pores play a crucial role in enhancing the material's properties and functionalities by providing an optimized environment for specific applications. This chapter highlights the significance of porous polymeric materials in advancing future research in chemistry. Mesoporous materials, in particular, offer unique properties that make them valuable in this field. These materials possess a high surface area, a uniform pore size distribution, abundant, well-distributed active sites, and facilitate the easy diffusion of large molecules through their channels. These characteristics make mesoporous materials highly desirable for various applications, as they provide an ideal platform for carrying out chemical reactions and promoting efficient molecular interactions. The use of functionalized porous solids as heterogeneous catalysts offers numerous advantages. These materials enable the development of interactive materials where multiple physical properties can interact at the nanoscale. Additionally, functionalized porous solids are environmentally friendly as they are non-corrosive and non-hazardous. They also facilitate easy recovery and reusability of catalysts, making them highly attractive for sustainable and efficient catalytic processes. By leveraging the unique properties of functionalized porous solids, researchers can explore new avenues in catalysis and advance green chemistry practices.

The use of transition metal-grafted mesoporous polymeric materials as catalysts has shown remarkable advancements in various organic reactions. This thesis discussion highlights the significant progress made in the development of supported reusable catalysts and their

application in different reactions. The incorporation of porous materials as catalyst supports has proven to be highly beneficial, enabling enhanced recyclability of the catalysts and achieving higher catalytic activity compared to their unsupported counterparts. This emphasizes the potential of porous material-supported catalysts to improve the efficiency and sustainability of catalytic processes. Overall, the findings presented in the thesis underscore the importance and effectiveness of transition metal-grafted mesoporous polymeric materials as highly active and reusable catalysts in organic chemistry.

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