Review

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Joseph Lantos , Narendra Kumar * , Basudeb Saha *

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Article

Production of Fine Chemicals Using Microporous and Mesoporous Heterogeneous Catalysts

Joseph Lantos [1], Narendra Kumar [2,*] and Basudeb Saha [1,*]

[1] School of Engineering, Lancaster University, Lancaster, LA1 4YW, United Kingdom
[2] Laboratory of Industrial Chemistry and Reaction Engineering, Faculty of Science and Engineering, Johan Gadolin Process Chemistry Center, Åbo Akademi University, Turku, Finland
* Correspondence: Narendra.Kumar@abo.fi; b.saha@lancaster.ac.uk

Abstract: Fine chemicals are produced in small annual volume batch processes (often <10,000 tonnes per year), with a high associated price (usually > $10/kg). As a result of their usage in the production of speciality chemicals, in areas including agrochemicals, fragrances and pharmaceuticals, their necessity will remain high for the foreseeable future. This review article assesses current methods used to produce fine chemicals with heterogeneous catalysts, including both well-established methods as well as newer experimental methods. A wide range of methods utilising microporous and mesoporous catalysts has been explored, including their preparation and modification before use in industry. Their potential drawbacks, as well as benefits, have been analysed, with their feasibility compared to newer, recently emerging catalysts. The field of heterogeneous catalysis for fine chemical production is a dynamic and ever-changing area of research. This deeper insight into catalytic behaviour and material properties will produce more efficient, selective, and sustainable processes in the fine chemical industry. The findings from this article will provide an excellent foundation for further exploration and a critical review in this field of fine chemical production using micro- and mesoporous heterogeneous catalysts.

Keywords: fine chemicals; speciality chemicals; heterogeneous catalysis; microporous and mesoporous catalysts; metal organic frameworks (MOFs); zeolites; ion exchange; agrochemicals; fragrances; pharmaceuticals

1. Introduction

Fine chemicals are described as pure and complex substances, with their main cause for production to be used in further processing to manufacture speciality, high value chemicals. They are produced in small annual volume batch processes (often <10,000 tonnes per year) [1], with a high associated price (usually >$10/kg)[1]. As a result of their usage in the production of speciality chemicals, in areas including agrochemicals, fragrances and pharmaceuticals, their necessity will remain high for the foreseeable future. As a result, the way in which fine chemicals are being produced is of the upmost importance. At this moment in time, little literature exists on the production of fine chemicals with the use of micro and mesoporous catalysts. Particularly in recent years, focus has shifted away from reviewing existing catalytic methods, especially in the fine chemical industry.

The production of industrially significant complex molecules, such as fine and speciality chemicals, heavily relies on a range of organic synthetic techniques which employ several reagents and catalysts. As a result of this, significant advancements in the field of catalysis during the past two decades have been instrumental in improving precise and selective control of various reaction paths and products [2,3]. However, the main issue with soluble (typically precious metal) catalysts is often contamination of the reaction products, aside from their expense and toxicity. Additionally, these reaction promotors frequently experience moderate selectivity (towards the activation of the desired functional group), deactivation/degradation (reducing the number of turnovers or productivity), and

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complex product purification (from the high-added-value organic compounds) [4]. This emphasises the requirement for sophisticated catalysts to be used in various stages of organic synthesis that have the right design, reactivity, and long-term stability.

In an ideal scenario, heterogeneous catalysis provides a clearer means of recovering the reaction product (from the solid catalyst) in a liquid medium. This product can then be recovered using filtration or centrifugation, thereby reducing the likelihood of contaminating the intended synthetic product [5,6]. Furthermore, under more accommodating reaction conditions and longer reaction times, such a reactive solid could be used. It would work with a continuous flow of reactants to separate the product without requiring the reactor to be evacuated, and it would provide easy scale-up, step-economy, high yields, safety, and reproducibility [7,8]. Ordered porous solids are the most desirable among the various solids used as heterogeneous catalysts (such as polymers, crystalline metal oxides, amorphous carbon, etc.) in terms of the fundamental comprehension and control of the chemical transformation in pores (which have the same size, shape, and functionality throughout the crystal). This points towards a clear need to review existing catalytic porous solids as well as experimentally promising materials in development.

The purpose of this literature review is to assess current methods used to produce fine chemicals with heterogeneous catalysts, including both well-established methods as well as newer experimental methods. A wide range of methods with the utilisation of both microporous and mesoporous catalysts will be explored, including their preparation and modification prior to use in industry. Their potential drawbacks, as well as benefits, will be analysed, with their feasibility compared to newer, recently emerging catalysts. The findings of this literature review will form a basis for a critical review of the same topic, providing a platform to further critique this field in greater detail.

The motivation for conducting this critical review on both microporous and mesoporous heterogeneous catalysts in the fine chemical industry is primarily driven by the lack of recent, comprehensive literature encapsulating this rapidly advancing field. As it stands, there is a significant amount of emerging literature surrounding individual catalysts and their applications, however to the best of our knowledge, there are little to no concise and updated overall reviews. This paper aims to address this void by providing an updated and detailed examination of current advancements, methodologies, and applications of heterogeneous catalyst structures in the fine chemical industry.

2. Relevant Sections

2.1. What are fine Chemicals?

Fine chemicals are both complex and single pure chemical substances produced in relatively low annual volumes globally. These volumes are approximately <1000 MT per year, with a high price associated with them, (>10$ per Kg) [1].

Chemicals that fall under the branch of “fine chemicals” can be found in a range of sectors, including the pharmaceutical sector, agrochemical and life sciences sector [1]. As stated by [9], fine chemicals are usually produced in batch processes as opposed to bulk chemicals and commodities which are produced in continuous processes. This is one of the reasons behind the smaller and more tightly controlled volume of these fine chemicals being produced, increasing the value and thus market price of these fine chemicals. As well as this, fine chemicals are often required for very specific and complex processes. The fine chemical industry sits between the other 2 main sectors of chemicals: commodities and speciality chemicals, with each being the supplier and customer of fine chemicals respectively. As a result, fine chemicals possess both uses in high-value production as well as providing added value to cheaper chemical commodities. In 2021, fine and speciality chemicals represented approximately 17% of the worldwide chemical exports, with an associated value of 379 billion Euros [10]. This is because often, there are further processing stages to fine chemicals after their production, which leads to the final product being even greater in value. As stated by [11], fine chemicals are often produced to very exact specifications, for what they are, as opposed to what they

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can do, as in the example of speciality chemicals. This is due to fine chemicals being required for further processing down the line in the production of other higher-value products like those speciality chemicals mentioned above.

According to [11], fine chemicals can be split into 3 major categories, “biocides, active pharmaceutical ingredients and speciality chemicals”. These statements are supported by [12] where fine chemicals are referred to similarly as described above, as single pure substances based on exacting specifications for further processing. A further explanation for their high value and small production volumes would be the strict regulations fine chemicals often have to be produced too since the majority end up facing human use or consumption.

Areas that fine chemicals are often used in once being further developed into speciality chemicals include “adhesives, agrochemicals, biocides, catalysts, dyestuffs and pigments, enzymes, electronic chemicals, flavours and fragrances, food and feed additives, pharmaceuticals and speciality polymers.”

2.2. The use of heterogeneous catalysts in the production of fine chemicals

2.2.1. Why are catalysts used?

Catalysis in any form is essential for chemical reactions. Even in a few situations where reaction speed is already sufficient, reaction economy, yield and selectivity can be improved by the utilisation of a catalyst. An ideal catalyst is one with both a high turnover frequency (TOF) as well as an infinite amount of product produced (TON) under room temperature and atmospheric pressure. Alongside this, it should ideally feature no catalyst deactivation or poisoning.

2.3. Catalyst selection

The catalysts used in the production of fine chemicals vary drastically, being heavily dependent on the reaction and the chemicals being produced. Further to this, the choice of which catalyst to use, however, is reliant on a range of other factors. Several catalysts could be suitable for a reaction, however, others may be more optimal in terms of cost, yield, time taken for the reaction, selectivity, ability to resist catalyst poisoning or a form of deactivation, as well as minimal product damage or contamination. These factors are essential for catalyst choice in terms of its economy and lifespan consideration, as explained by [13]. Further to this, it is suggested to consider catalysts from a practical standpoint as well. It states how a catalyst in an optimal process should be “wide in scope, easy to perform and insensitive to oxygen and water”. It can be drawn from this that choosing the optimal catalyst is not as easy as the first choice. Furthering this, the impacts catalyst choice can have on a reaction illustrate the importance of selecting the right one from both an environmental and economic perspective.

Catalysts can be separated into two distinct categories, heterogeneous and homogenous. Heterogenous catalysis concerns a reaction whereby the catalyst in use is in a different phase than the reactants. Often, this occurs when the catalyst is in a solid form, with the reactants being a liquid or gas. Conversely, homogenous catalysts are in the same phase as the reactants in question. Heterogenous catalysis is often favoured and used more often in the production of fine chemicals, mostly due to its ease of recovery in comparison to most homogenous catalysts.

When referring to the porosity of a catalyst, this is usually applied to heterogeneous catalysts as opposed to homogenous catalysts. This is due to fluids being not able to possess pores, whereas solids can. Since heterogeneous catalysis usually concerns a solid catalyst, it is evident why it is applicable here. In terms of porous catalytic structures, there are 3 major categories: Microporous, mesoporous and macroporous. Microporous catalysts feature much smaller pores than found on mesoporous catalysts, with micropores considered to be 2nm or smaller in diameter, whereas mesoporous materials are generally categorised as pores with diameters between 2-50nm, as evidenced in [14]. Often these porous materials are constructed from tetrahedral units, whereby they are commonly used in environmental remediation as well as in treatment, purification, and separation.

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2.4. Mesoporous materials and their uses as catalysts in the production of fine chemicals

2.4.1. Background

Mesoporous materials are a commonly used porous structure in the field of fine chemical development. They are primarily constructed from a silica-based matrix and feature ordered, homogenous pores with a diameter range between 2-50nm [14], [15]. As a result of their extensive surface area and pore volume, accessibility to active sites within the structure is relatively uncomplicated. Furthering this, any entering reactive species can undergo significantly more rapid diffusion into the structure [16].

One major advantage of mesoporous materials would be both their chemical and physical properties, which feature exceptionally high surface areas, large pore volumes, and notably the ability they possess to have adaptive pore sizes and shapes [17]. Having this property allows for the synthesis of catalysts that can be developed and tailored to specific reactions, improving both overall efficiency and selectivity. As well as this, their porous structure can demonstrate nanoscale effects within their internal mesochannels, which can significantly influence catalytic activity [17].

2.4.2. Types of mesoporous catalysts

2.4.2.1. Organo-silica based

The use of (organo)silica-based catalysts offers a substantial reduction in the requirement of a solvent during its use in reactions, as explored during the analysis of the Asymmetric Aldol Reaction [18]. Further to this, this study determined that the silica-based catalyst structure used can be recovered and reused several times with reactivation, providing a minimal loss of activity regarding traditionally used fresh organocatalysts. It further goes on to explain that the use of silicas as a base structure for the addition of an acid or base not only proves more affordable but shows more versatility than other solid-supported materials. This has been further supported in other literature exploring the effects of using a silica-based structure during the synthesis of fine organic chemicals [19,20].

There are two methods commonly used to bind a form of organic catalyst to a silica-based structure. The first method, “post-synthetic grafting”, consists of a linear set of steps used to build up the catalyst on the silica surface [21–24]. The use of grafting as a covalent technique has been found to provide higher stability as well as reduced leaching under most mild conditions [25], both of which are ultimately desirable features during the selection of a catalyst. The second method, known as the “co-condensation method”, involves the initial synthesis of any necessary precursors. Following this, the precursors can then be incorporated into the silica support structure [26–28]. According to [25], by using precursors, various types of active sites can be installed onto the structure in specific confined places. This is further supported and evidenced by research primarily focusing on organosilica structures and their contribution to the manufacture of value-added and fine chemicals [29–31]. Benefits of this include easier modification of the catalyst, allowing its properties to be tailored to what is desired of the reaction. Such freedom to customise and alter reaction products is highly promising due to its usefulness in the fine chemicals industry. It is important to note that the development of silica-based catalyst structures can have a high associated production cost due to the often “costly surfactant structure directing agents” as stated by [25]. In many cases, high production costs pose a roadblock to more elaborate and in-depth research, resulting in discouragement of their use, particularly when more cost-efficient catalyst structures exist. It is also possible to develop a hybrid-synthetic approach, using both methods, as described by [18]. This paper determined the best catalyst for the use of a silica-based structure under solvent-free conditions with the addition of an acid, a commonly used additive during the synthesis of catalysts.

The reasoning behind utilising an acid during the synthesis of a heterogeneous catalyst is elaborate, with its main advantages including easier recovery of the catalyst in comparison to using a base, as supported by [32]. As a result of their editable pore dimensions, the use of silica structures enables catalytic reactions involving both bulky substrates and products. This widens the potential use for them across a greater range of reactions, providing an advantage over other mesoporous materials. However, in opposition to zeolites and MOFs, mesoporous silica consists of amorphous walls, which hinders their ability and thus the activity of embedded active sites.

As a result, this is leading towards further research into creating crystalline materials with ordered mesopores and inherent microporosity, with the end goal of expanding catalytic design possibilities and generating a solution or potential use for amorphous walls in porous solids.

2.4.2.1.1. Types of (organo)silica structures

- MCM-41 (M41S) [33]

Since their discovery in 1992, mesoporous molecular sieves in the M41S family have become increasingly researched across several industries. This is mostly due to their large surface area, neatly arranged pore structure, and uniform pore size [34], all of which are appealing features from a catalytic perspective. The M41S family can be classified into three categories: hexagonal MCM-41 (a commonly used catalyst in the fine chemicals industry), with its nonintersecting channels in a honeycomb pattern, cubic MCM-48, known for its intricate three-dimensional channel system, and unstable lamellar MCM-50, which tends to collapse when the template structure is removed [35,36]. MCM-41 has gained recent industrial attention in fine chemical synthesis as a result of its advantageous properties over other silica structures. These include its particularly high surface area and thermal stability as well as the fact that it inherently possesses mild acidic properties [37]. It is often used in reactions involving organic transformations, including acid/base catalysis and oxidative coupling. An example of MCM-41 being used in the production of a fine chemical would be during the manufacture of Menthol, as investigated in [38]. The paper explores the continuous one-pot synthesis of Menthol from Citronellal using MCM-41 as an alternative intermediary set of steps to the traditional synthetic route opted for in the industry, the Takasago five-step process. The benefits of using the Ru-modified MCM-41 structure over multi-step traditional methods included an easier separation of the catalyst as well as re-use of the catalyst. Further to this, the inclination towards easier catalyst and product separation would indicate lower costs as well as being regarded as more environmentally friendly, something the Takasago five-step process cannot easily deliver [39,40]. Similarly, the use of MCM-41 with a bi-functional powder catalyst in batch processes (also to produce Menthol) has been explored, with similar findings being shown. These studies have indicated the significance an active metal modification (particularly on an aluminosilicate structure) can have on a reaction, with the various side reactions being affected greatly, depending on the metal used [41,42]. In addition to this, more reaction-specific catalysts can be derived from MCM-41 to utilise specific properties it exhibits. The use of such catalysts often results in an increased cost due to the greater complexity in the catalyst production, however, the improved yield and selectivity often justify this. For example, a mesoporous Ce composite material has been derived from MCM-41 and used as a heterogeneous catalyst in the synthesis of Monoterpenoid Dioxinols. This study highlighted the advantages the MCM-41 structure can provide, with it producing the highest reaction selectivity (>90%) in comparison to other catalyst structures used in the procedure (various zeolites and metal oxides) [43]. A similar study investigating the synthesis of compounds with tetrahydropyran moiety with different heterogeneous catalysts yielded similar results with a Ce-MCM-41 structure producing both the highest yield and selectivity [44]. Another prominent modification made to MCM-41 involves the addition of Ruthenium (Ru) to the sieve structure. Research in this field has shown that the modification method used can itself influence the resulting structure and behaviour of the catalyst, as explored in [37] with differing conversion and activity rates experienced when subsequently used in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol, a fine chemical substance used in the production of perfumes. Further to this, Ru-modified MCM-41 has been used experimentally as a heterogeneous catalyst for the ring opening of Decalin, with differing preparation methods resulting in significantly varied results in terms of overall conversion, selectivity, and activity [45]

- SBA-15 [46]

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The newly discovered Santa Barbara Amorphous (SBA) family has also gained popularity because of its stronger walls, making it more stable in high-temperature and high-pressure conditions, and its larger pore size in comparison to M41S. SBA-1, which possesses a cubic assembly of rounded micelles and SBA-15, with its highly organized hexagonal structure and larger pores compared to MCM-41, are the two most common variants in the SBA family. The large pores that SBA-15 possesses are particularly useful in accommodating larger molecules, opening the range of possible reactions it can be used in. The synthesis of all these mesoporous silicas generally occurs in acidic or basic environments and involves using surfactants or some type of amphiphilic triblock copolymers as structure-directing agents [34].

It is also common to produce hybrid catalytic systems by functionalizing SBA-15 with differing organic or inorganic moieties, such as ferrocene in the hydroxylation of Benzene to produce Phenol [47]. By doing so, the selectivity of the reaction can be improved, along with the catalytic activity. Further examples of this include the bi-functionalisation of SBA-15 in preparation for its use as a catalyst during the synthesis of 5-Hydroxymethylfurfural [48], a commonly used starting material for fine chemical production.

2.4.2.2. Metal-organic frameworks

Metal-organic frameworks (MOFs) are a highly studied family of porous materials, regularly used in the fine chemical industry. Often used as heterogeneous catalysts, they are a form of hybrid solid, capable of being structured in either a two- or three-dimensional way. They are effectively formed by the self-construction of cationic systems fulfilling a node role with polytopic organic ligands acting as a form of linkers. They have gained popularity recently within the catalyst industry due to their customisable structures, allowing for more control over the catalyst's properties. As stated by [49], metal-organic frameworks hold several advantages over traditional zeolites. The number of possible zeolites for catalytic use is limited, whereas the number of potential metal-organic framework structures is almost infinite. Furthering this, because of their high porosity and surface area, they can retain up to 50-150wt% of occluded solvent [49], meaning it can in some cases hold ten times as much solvent by weight than a zeolite can. Moreover, their high surface area allows for greater exposure of active sites, facilitating improved catalytic efficiency and selectivity. This characteristic is particularly beneficial in fine chemical synthesis, where precise control over the reaction conditions and product quality is essential.

In terms of their synthesis and development, MOFs can be tailored to incorporate various functional groups and metal centres, creating a platform for the design of catalysts with more specific activities and selectivities. This flexible aspect has widened the possibilities for catalytic development and provided stability in challenging catalytic processes. According to [50], newer self-assembly synthesis methods for MOFs have been studied in recent years, including hydro- or solvothermal processes in a bid to develop more effective methods. With the benefits of utilising MOFs as heterogeneous catalysts, it is evident why research efforts have been pursued in this field.

However, the practical implementation of MOFs as heterogeneous catalysts also presents challenges related to their potential structural degradation over prolonged use, leading to a decrease in catalytic activity. Furthering this, MOFs can express stability issues in particular situations, such as organic transformation under extreme conditions (acid/basic environments, high temperatures etc.), as has been explained by [50]. Moreover, the potential diffusion limitations arising from their intricate pore structures can impact mass transport and reaction kinetics, influencing overall catalytic performance. Diffusion limitation often leads to further catalyst deactivation from pore blockages and poisoning. However, this becomes less of a problem in liquid phase reactions with MOFs as a heterogeneous catalyst structure. Unlike traditional zeolites, which often experience diffusion limitations in liquid phase reactions and often excel in gas phase reactions, MOFs traditionally possess a greater available number of pores and pore sizes, increasing their validity and uses in liquid phase reactions, which are used more regularly in fine chemical production [51].

Furthering this, the advantages of MOFs (with regards to other micro/mesoporous materials) remain true for oxidation reactions, with the added factor that MOFs contain a high amount of transition metals that are considered the conventional type used for oxidation sites. This is a major point of consideration since zeolites and other mesoporous aluminosilicates are null in terms of activity for oxidation reactions.

Some studies have explored the removal of metal from MOFs, leading to the development of carbon-based metal-free catalysts. This is achieved through carbonisation at high temperatures under inert atmospheric conditions, which can lead to an increased surface area and larger pore volume. There is significant existing literature on such cases focusing on the removal of metal from MOFs to form a carbon-based structure used for a range of reactions such as Suzuki-Miyaura coupling reactions, including [52–56].

An additional field of research with high potential concerning MOFs includes the development of non-noble metal-based catalysts such as Ni and Fe. This is due to their intrinsic magnetic properties which can promote easier and more successful recycling of the catalysts as well as improving their life cycle, with predominant use in the oxidation of alcohols to esters. [57–59].

2.4.2.3. Zeolites

Zeolites are crystalline aluminosilicates that are well-known for their widespread uses as catalysts in the manufacturing of fine chemicals. Occurring naturally or being chemically synthesised, the main reasoning behind their utility is their distinct molecular-scale structure of organised, linked channels and consistent pore size. It is important to note that although zeolites are typically microporous, the recent emergence and development of mesoporous zeolites have significantly increased their utility, particularly in reactions involving big molecules. They are used in a vast range of reactions, with ion-exchanged zeolites being one of the most frequently used catalysts in history [60]. Depending on the form taken, their uses vary significantly. For example, in their proton exchange form, they fulfil a large role in the oil refining industry because of their strong acidic and shape-selective properties [61,62]. Further potential uses for zeolites include types of water purification, large biomolecule separation as well as the removal of some radioactive contaminants [63–65]. The use of zeolites for large molecule separation features across a vast range of reactions during fine chemical production, often capitalising upon the nature of their hierarchical structure. They act to increase the effective hydrogen-to-carbon ratio of chemical products through a range of intermediate dehydrogenation/hydrogenation, oligomerisation and cracking reactions. Subsequent carbon bond-forming reactions can then occur on the Zeolite structure, such as aldol condensation and Diels-Alder reactions to form larger molecules and aromatics [66–68]. An example of utilising the hierarchical nature of zeolites during processes involving large organic molecules includes such reactions as the pyrolysis of wood polymer to produce aromatics [69]. ZSM-5 is discussed as one of the more widely used zeolite catalysts in aromatics production due to its greater efficiency, with utilisation as fuel additives [70], solvents [71] or types of polymer synthesis [72]. Its microporous structure however is noted as a major limiting factor as a result of reduced diffusivity for larger molecules. This further highlights the advantage of hierarchical zeolite structures, illustrating a strong use case for mesoporosity in zeolites.

Since the orientation of individual pores is usually random and the sizes and shapes of the mesopores have no impact on the zeolite's crystal structure, the mesopore system in mesoporous zeolites can be considered a non-crystallographic pore system. Since this pore system is not atomically ordered, mesoporous zeolites are regarded as hierarchical porous materials - they possess more than two pore size distributions [73,74]. Hierarchical zeolite materials can be separated into three categories: hierarchical zeolite crystals, nanosized zeolite crystals, and supported zeolite crystals, with all types varying in pore size and structure. Hierarchical zeolite crystals have extra pores within each crystal, either mesopores (under 50 nm) or macropores (over 50 nm) and include an additional mesopore system alongside the standard micropores. Nanosized zeolite crystals are smaller, and their mesoporous system comes from their packing structure. Supported zeolite crystals are essentially dispersed in another material's pore system, leading to a mix of micro and mesopores, (depending on the support structure). In order to alter a zeolite structure into a mesoporous form, the zeolite crystals themselves must be altered, with either a top-down or bottom-up approach [75].

The top-down method, known as post-treatment, involves the use of an acid or base component to remove any Si or Al species from the template. This method, known as demetalation, is commonly done via the use of dealumination and desilication, both of which have been studied in [76–78]. Conversely, the bottom-up approach, known as direct templating, entails the direct synthesis of mesoporous zeolites in the presence of mesoscale organic porogens and organic directing agents. Various bottom-up methods exist, with one common approach being some type of solid templating. For example, templating can be completed through a range of carbon nanomaterials [79–82] to produce a variety of common zeolites such as ZSM-5, zeolite-β, zeolite-X, zeolite-A, and zeolite-Y. Carbon-based templates produced through carbonisation can also be built upon to produce types of zeolites [83], as well as the use of aerogel [84,85], polymer [86], resin [87,88] and solid biological templates [89].

Other templating approaches to producing hierarchical zeolites include delamination, the process of synthesizing layered precursors as lamellar precursors with an additionally intercalated surfactant. This surfactant can then be removed, leading to the collapse of the structure, and the formation of an accessible zeolite material that exhibits mesoporosity [90,91].

Whilst the development of zeolites possessing mesoporosity possesses advantages, the negative environmental drawbacks that their synthesis produces remain a significant issue. Significant emissions are produced during their manufacture due to the application of different multifunctional templates, their subsequent removal, or the release of acids and alkalis used in zeolite dealumination and desiccation [92]. Furthermore, even the processes currently in use to create microporous zeolites are not environmentally friendly because they all require the use of artificial chemicals containing silicon and aluminium which are derived from natural silicate or aluminosilicate minerals. These derivations occur through labour-intensive procedures that result in significant waste production and energy consumption [93].

2.4.2.3.1. Types of Zeolites

The classification of a zeolite is governed by its silica/aluminium ratio within the structure [94]. For example, a zeolite labelled as high-silica would have a large Si:Al ratio, whereas low-silica or Al-rich would indicate that the structure has a low Si:Al ratio. In terms of the ratio number itself, its classification is dependent on the type of zeolite. For BEA zeolites, low-silica refers to a ratio less than 5, whereas high-silica refers to a ratio greater than 10 [95,96]. For X and Y zeolites, high silica indicates a ratio greater than 3, while low silica would correspond to ratios between 3 and 1.5 [97–99]. For ZSM-5 zeolites, high-silica corresponds to a ratio above 20 whilst low-silica indicates a ratio below 15 [95,100,101].

- BEA (Zeolites- β)
- FAU
- Zeolite-y
- ZSM-5
- Zeolites-A
- Zeolites-X

2.4.2.4. ZIFs

Zeolitic imidazolate frameworks (ZIFs), a popular porous hybrid structure developed in recent years, have become a focus in the heterogeneous catalytic industry for several reasons. Possessing a crystalline structure with the ability to express hierarchical porosity, they are a subclass of MOFs, combining some of the most desirable properties of both MOFs and Zeolites. They differ in structure from traditional MOFs since they are composed primarily of Zi (ii), Co (ii) and imidazolate linkers, as opposed to the wide range of metals and organic linkers MOFs can be composed of. When compared to traditional MOFs, ZIFs typically exhibit much greater stability in terms of thermal, hydrothermal, and chemical properties [102,103]. This includes their ability to be boiled in various organic and alkaline solutions without the loss of crystallinity or a reduction in porosity [104]. In addition, the tetrahedral crystalline structure of a ZIF is like that of a zeolite, with the aluminium and/or silicon being replaced by either zinc or cobalt (transition metals). This mixed structure they possess is one of the main advantages they hold over zeolites – they can be exposed to a greater range of surface modifications. As well as this, their tunable pores (due to their metal ions) and their high porosity make them extremely suitable as a catalyst support structure for a range of reactions [105]. The main routes for the manufacture of ZIFs, are either through solvent-based synthesis or solvent-free synthesis [105]. The most commonly used solvents include water, methanol, or ethanol. It is not uncommon however to employ other solvents such as dimethylformamide or diethyl formamide, with the solvent chosen being dependent on the specific process. From here, the chemical route taken can vary, with a wide range of methods being available, subject to the solvent chosen. Older methods include solvothermal synthesis, whereby organic solvents are used in the formation of a ZIF. As discussed above, preliminary solvents used in experimental work include various alcohols as explored in [104]. More recent works include the incorporation of bases to deprotonate specific linkers and provide a higher yield and greater rate of reaction. Such cases in the literature include pyridine [106] and triethylamine [107]. Findings from both papers provided a strong argument for the use of a basic solvent in conjunction with ZIF structures, with its main benefit being highlighted as the reusability of the ZIF structure (due to its retention of catalytic activity). Both studies did note the impact the reaction solvent can have on its catalytic performance, however, indicating some drawbacks in terms of the reactions they are suitable for use in. Whilst solvothermal synthesis can offer a wider range of choices regarding the type of ZIF developed and greater flexibility in terms of the solubility of the precursors, the associated drawbacks of organic solvents often reduce industrial popularity. The negative environmental impacts, in addition to the high costs and some cases toxicity to humans is driving research in ZIF development towards cleaner alternatives. Research shows that the use of aqueous mediums (hydrothermal synthesis) can produce higher yields than organic solvents in reduced timeframes, but require additional linkers, such as in the case of the development of ZIF-8 nanocrystals [108], or even nano-sized ZIF-67 crystals [109]. Further, more recent research in this field has been conducted in a bid to develop this greener method, with various modifications to the process. These include the use of surfactants to regulate the size of the crystals in a ZIF structure. Successful examples include the research conducted whereby the diameter of the crystals produced could be controlled [110], or whereby the impact the surfactant used has on the hierarchical structure of the ZIF was explored [111]. Newer solvent-based methods of ZIF production include microwave synthesis and ionothermal synthesis. The former involves the use microwave-assisted heating technology and has been shown to drastically shorten the synthesis time, as well as produce a higher yield whilst reducing the number of ligands present without the use of deprotonating agents, [111,112]. The latter, ionothermal synthesis, involves the use of ionic liquids (as solvents) in an open system. There has been minimal research in this field thus far, despite the possibilities it has been shown to possess. These include using the ionic solvent as a template to prevent competitive interaction, the wide range of novel structures that could be developed with further experimental work (as explored Martins et Al in [113]) and its possibilities to be incorporated with other synthesis methods, such as microwave synthesis [114].

A small number of promising novel solvent-free synthesis routes exist. Despite their lower cost and being significantly more eco-friendly, very little has been done in this area of research. Some studies include the synthesis of ZIFs using a dry-gel conversion, with the synthesised ZIF structures showing promising results. These include excellent reactivity and catalytic activity as well as strong reusability [104,115].

The uses of ZIFs as catalysts in the fine chemical industry are garnering traction, with catalysis roles in various scientific sectors, including pharmaceuticals [116,117], organic chemical production (hydrocarbon separation) [118], aromatics and biomass conversion [119]. Notably, all this research conducted on ZIF structures as catalysts are remarkably novel, with their use appearing earlier in other fields, such as gas and energy storage [120–122] as well as drug delivery [123,124]. Whilst minimal, the positive findings from this early research are indicative of the potential uses of ZIFs as catalyst structures, and it can be anticipated that further investigation into their catalytic benefits will prove popular and essential as the fine chemical industry continues to evolve and seek cleaner and more efficient production methods.

2.4.2.5. Carbon-based

Mesoporous carbon-based heterogeneous catalytic structures possess highly desirable physical and chemical features, particularly regarding the synthesis of products in the fine chemical industry. Notable properties include a high surface area (contributing to higher catalytic activity), significant pore volume, good thermostability due to their composition of carbon atoms linked in a framework, enhanced mass transfer and relatively uncomplicated diffusion [125]. Due to their excellent conductive abilities, carbon-based catalysts are often used in electrochemical-based reactions [126,127]. The processes for the synthesis of carbon-based catalysts have changed over time due to the development of novel processes with greater simplicity and fewer environmental drawbacks. Typically, carbon-based structures are microporous, so methods to introduce mesoporosity have been created. Initially, mesopores in carbon structures were created in the spaces between carbon particles, such as in carbon aerogels, or by enlarging micropores via oxidation during the activation process, such as in activated carbons [128]. These methods, however, resulted in difficulties such as the struggle to regulate the structures shape or a loss in carbon yield.

There are three major categories of methods for the synthesis of carbon-based structures:

- Activation methods.
- Catalytic activation methods (using metal ions).
- Template methods.

Activation methods are regarded to be the most widely used techniques [125], with two subcategories: chemical methods and physical methods. In physical methods, materials are heated to between 400–900 °C in an oxygen-free environment (using gases like nitrogen or helium) to create a carbon-rich "char." This char is then exposed to higher temperatures (800–1000 °C) and oxidising agents (such as steam or carbon dioxide) to develop a mesoporous structure [129,130]. Chemical activation, on the other hand, streamlines this process by integrating the heating and exposure to oxidising chemicals into a single phase. Usually, chemical activation entails impregnating a carbon source with specific compounds and heating it to 400–700 °C [131] to cause it to thermally breakdown. Zinc chloride ($ZnCl_2$), aluminium chloride ($AlCl_3$), magnesium chloride ($MgCl_2$), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3), phosphoric acid (H_3PO_4), and sodium hydroxide (NaOH) are common chemicals utilised in this procedure [131–133]. The choice of chemical is very important because it has a big impact on the activation process's mechanism and necessary temperature.

Chemical activation offers several advantages over physical activation, including lower energy consumption and activation temperatures, higher carbon yields, and faster processing times. However, in some cases, physical activation is preferred due to its relatively smaller impact on the environment, its readily available activating agents, and its simple technology [134–136]. In some cases, combining both types of activation methods produces better activation and so is employed regularly.

Catalytic activation utilising metal ions can also be employed to create mesoporous carbon-based catalysts. By acting as catalysts to activate carbon precursors, metal ions such as iron (Fe), nickel (Ni), and cobalt (Co) can speed up the activation process. They can help provide stability and control the development of the mesopores. These metal ions are particularly efficient at accelerating the char activation process, which leads to a greater volume of mesopores [137]. In some cases, where any water-based solutions are used, the metal ions can leach out of the structure, reducing its lifespan and in turn activity.

The third method, templating, has two distinct sub-categories; hard and soft templating. Hard templating uses pre-made inorganic or organic templates such as colloidal silica or mesoporous silica. These templates are filled with carbon precursors and then carbonised. The template is then removed using an acid or base by chemical etching, leaving behind the carbon-base structure [128].

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The soft-templating method uses self-assembling molecules such as metal-organic frameworks and surfactants as templates. These materials are then bonded (often through hydrogen bonding) with carbon precursors. A calcination process is then used at temperatures up to 900°C [138,139] to remove the templates, leaving behind the mesoporous structure [140]. One reason behind the development of mesoporous molecular sieves over zeolites is their ability to process heavy oil fractions, something other mesoporous structures can't deliver [141–143]. Further to this, mesoporous carbon structures can exhibit high selectivity and research has proved their ability to increase the reaction rate, as evidenced by literature investigating the dehydrogenation of ethanol to acetaldehyde [144]. Their excellent selectivity was determined to be significantly greater than that produced using SBA-15 as a catalyst support. These findings are owed to the inert nature of the carbon structure, inhibiting any additional secondary or side reactions. Such findings prove particularly beneficial in the fine chemical industry, where high selectivity of desired products is paramount to increase the efficiency of valuable and expensive processes. Further to this, the natural hydrophobic properties of the carbon structure provide an enrichment potential for organic compounds, deepening its uses as a highly selective catalyst support for organic reactions. An additional study utilising mesoporous carbon structures incorporated with the catalyst (as opposed to supporting it as traditional research investigates) highlighted their reusability in the production of γ-valerolactone [145]. Further to this, the study illustrates their stability in an acidic aqueous medium. It is this high stability that proves the development of mesoporous carbon structures incorporating catalysts directly carries excellent potential, drawing further attention to carbon-based structures and the further benefits that can be evoked through additional research.

2.5. Microporous materials and their uses as catalysts in the production of fine chemicals

2.5.1. Background

Microporous materials contain crystalline structures with interconnected cages or channels. Their classification as microporous is determined by their smaller pore diameter of less than 2nm [14].

The two main types of microporous structures used in industry are crystalline zeolites (aluminosilicates) and activated carbons [146]. Both types of structures can be modified to be mesoporous, along with other less common microporous structures such as metal-organic frameworks (MOFs). Further types of microporous structures such as metal oxides and aluminophosphate will be reviewed below. Typically, microporous materials are synthesised under solvothermal conditions, with the individual parameters being altered depending on the reaction. The most altered parameters when developing microporous structures include the starting compound, any solvent used, the temperature, pressure and any additional charge-compensating ions [147].

2.5.2. Types of microporous catalysts

2.5.2.1. Zeolites

Microporous zeolites offer similar advantages to mesoporous/hierarchal zeolites, however with less methodology and steps in terms of their development. As described previously, zeolites can occur naturally or can be synthetically developed.

Worldwide, both academic and industrial facilities have conducted extensive research on differing types of microporous zeolites. Reasoning behind this includes their desirable abilities and properties, such as consistent channel systems, tunable Brønsted and Lewis acidic sites, coke resistance, ion-exchange, and thermal stability features. The procedure for developing synthetic zeolites varies slightly from the method mentioned above to produce mesoporous zeolites. Since zeolites are generally microporous beforehand, with further processing required to make them mesoporous, there are usually fewer steps involved.

There are a range of different methods available for the synthesis of zeolites, with the most common ones listed below, taken from [148].

- Hydrothermal synthesis
- Solvothermal synthesis
- Ionothermal synthesis
- F^- synthesis
- Microwave-assisted hydrothermal synthesis
- Micro-emulsion based hydrothermal synthesis
- Dry-gel conversion synthesis
- Combinational synthesis.

Despite the desired properties microporous zeolites possess, there is a current drive for extensive research around modifying and developing them further. The reasoning behind this is to enhance their uses and resolve their inability to catalyse reactions with larger particles. One potential route for doing so would be the modification to a hierarchal zeolite, as written above in the mesoporous zeolite section. There are a number of alternative routes, however. In the editorial section prepared for microporous zeolites and their applications [149], Kumar discusses the approach of embedding microporous zeolites in amorphous silica, referring to a study conducted on selective catalysts for the Methanol to Olefin process [150]. The cause for this methodology lies in the potential of being able to customise and specifically tailor available acid sites in the catalyst structure. The paper revealed the higher catalytic activity the synthesised zeolite possessed, as well as a much higher selectivity ratio. These findings support explanations in wider literature proposing that the strength, availability and type of acid sites available in a catalyst can alter the propylene selectivity and rate of formation of intermediary products. The impact modifications on a zeolite structure can have on a reaction is analysed in [151], with its influence and impacts explored. The paper explains how preparation, precursors or pre-treatment can impact and alter the physico-chemical and catalytic properties of a material. It also elects to take an environmentally friendly approach during the preparation of the catalyst, by electing to leave out any aqueous or organic solvents using a solid-state ion exchange method. One notable finding from the paper regarding zeolite performance, however, concerned the deactivation of the zeolite structures with extended reaction times, being caused by carbonaceous deposits resulting in pore blockages in the zeolite. These findings suggest that an avenue for future research such incorporate exploration into the reduction or prevention of deactivation to extend the lifespan of zeolite structures and reap their full selectivity benefits. Similarly, Kumar has assessed the impact the chosen preparation method has on the catalytic behaviour of modified zeolite extrudates, [152]. The study revealed that the different ways of platinum deposition onto the structure impact the metal-to-acid site ratio, subsequently altering the acidity and strength of the catalyst structure. It also concluded that the choice of synthesis method impacts the overall conversion, with zeolite extrudates prepared via in-situ synthesis producing the highest conversion. Alternatively, zeolite catalysts can be prepared via the use of various impregnation methods. In [153], H-Y5.1 Zeolite catalyst prepared via wetness impregnation was used across a range of reactions in the production of hexadecane with isoeugenol, with the ratio between Fe and Ni in the catalyst being varied. Findings from the study showed a reduction in specific surface area and a decrease in pore volume due to a blockage in the larger pores in the material. The study also showed a change in the acid sites dependent on the catalyst structure used, with Fe leading to a decrease in strong acid sites and an increase in medium Brønsted sites whilst the Ni increased the weak and medium Lewis sites. These papers illustrate the effect the preparation method and support design have on a reaction and highlight the drawbacks of zeolites in terms of pore blockage tendencies. A clear link between the acidity and ending selectivity of a reaction can be seen, indicating the importance of correct catalyst preparation. This is especially important in the fine chemical industry, where the economy of reactions and selectivity to desired products can dictate the financial outcome and viability of a particular product.

2.5.2.2. Activated carbons

Carbon based structures, as well as being mesoporous, can possess micropores. Whilst their ability to adsorb large organic materials is reduced in comparison to mesoporous carbon-based structures, they feature an enlarged specific surface area. This aids their ability in the adsorption of volatile molecules, as well as hydrogen storage and CO_2 capture [154,155].

One common approach to developing activated carbon-based catalysts involves the use of developing biomass as a precursor [156–158]. Once the carbon has been obtained, it can be activated using pyrolysis in an inert atmosphere, just as mesoporous carbon is activated. It is then developed through physical or chemical activation to improve its porosity [159]. Several studies have found that the use of biomass as a precursor provides a high oxygen content, leading to greater porosity and surface area [160].

The surface reactions on carbon can be complex due to the interaction of numerous oxygen groups. These can be divided into two main groups, the basic and acidic oxygen groups [161,162]. The surface activity and catalytic behaviour of the structure is usually dependent on these surface groups, with studies conducted into the impact these groups have [163,164].

Like mesoporous carbon-based catalysts, they are often modified or “doped” with additional materials to alter the available specific surface area and increase micropore development, for example through nitrogen doping [165–168]. There are countless other examples of such experimental work, for example, the modification of carbon nanospheres with phosphorus [169], the synthesis of a dual-modified phosphomolybdic acid/silver carbon composite [170], the production of jet fuel through the hydrodeoxygenation of isoeugenol over a carbon-supported platinum catalyst [171] and many more [172,173]. One common drawback that occurs when a microporous carbon structure is utilised would be the frequency of pore blockage. This is a common occurrence in microporous structures due to their smaller pore size, resulting in a subsequent loss in activity and catalytic deactivation. Whilst microporous carbon structures possess several advantages over their mesoporous counterparts, it is clear that pore blockage tendencies are much higher, illustrating a major hindrance to their wider use. A study conducted on the kinetics and deactivation of catalysts in the hydrogenation of β-sitosterol to β-sitostanol utilising both micro and mesoporous carbon supports [174] re-iterated catalyst deactivation as a prominent issue when using carbon-based catalyst structures, suggesting the utilisation of a greater amount of catalyst to combat this problem. The reasoning behind this is to counter the catalysts' adsorbent properties, so activity can remain higher for prolonged periods. Further to this, the differing conversions obtained between the micro and mesoporous carbon were analysed, whereby it was found that the mesoporous carbon structure provided higher overall conversions than its counterpart. In addition, deactivation occurred at a slower rate for the mesoporous carbon catalyst than the microporous one. This difference can be accredited to the mesoporous structure containing larger pores, meaning the effects of coking are less significant and take a greater timespan to build up.

In the fine chemical industry where activity and selectivity are paramount, the use of microporous carbon catalysts carries several advantages but, in most cases, these are outweighed by its disadvantages. Their large specific surface area is particularly beneficial for the adsorption of smaller molecules which can prove useful, in purification or pollutant-catching processes. Despite these advantages, however, the challenges posed by pore blockage are significant and cannot be overlooked, particularly when blockages can lead to a loss in activity and catalytic deactivation. The comparison with mesoporous carbon structures further underlines this issue, as it becomes clear that these larger pores offer higher overall conversions and slower deactivation rates. Considering these factors, it can be concluded that mesoporous carbon structures are generally more beneficial for applications in the fine chemical industry in processes whereby longer catalyst life and higher resistance to catalyst fouling and deactivation are required.

2.5.2.3. Aluminophosphate

There are several other microporous structures used as heterogeneous catalysts for both the production of fine chemicals and the chemical industry as a whole.

One of these commonly used structures is Aluminophosphate. Aluminophosphate usually comes in a crystalline structure formed by connecting oxygen atoms between alternating phosphorus tetrahedra and aluminium polyhedra. Aluminophosphates come in a variety of polymorphs that can create pore frameworks with varying dimensions. These crystalline aluminophosphates often feature uniform pores with diameters above 1nm, placing them in the category of extra-large microporous crystalline materials [175]. The structure of these frameworks provides a number of sites for chemical reactions to occur, which is essential for activity and their effectiveness as acid catalysts [176]. Often, aluminophosphates are doped with specific metals whereby the metal ions replace the aluminium ions within the framework. This process is often used in the manufacture of single-site catalysts [177], allowing for its use in particular reactions, such as in the oxidation of hydrocarbons [178] or the esterification of acetic acid [179]. One notable example of the use of the metal aluminophosphate being used in the fine chemical industry features in a research paper on the production of Biphenylurea [180]. Findings from the paper indicated Cobalt-aluminophosphate as the catalyst providing the highest yield of Biphenylurea. The paper also concluded that under mild conditions metal-aluminophosphate catalysts are a viable alternative to traditionally used environmentally hazardous and costly alternatives.

When compared to their crystalline counterparts, amorphous aluminophosphates are a more affordable and often more thermally stable catalyst [181]. They only require a straightforward co-precipitation step in their manufacture, whereas the synthesis of crystalline aluminophosphates requires the use of organic agents that direct structure, like trialkylamines or copolymers, which are then burned off after the synthesis is complete.

2.5.2.4. MOFs

Microporous MOFS, like mesoporous MOFs, consist of self-constructing cationic systems with polytopic organic ligands acting as linkers. In comparison to mesoporous MOFs, they possess a much larger specific surface area, making them more suitable for interactions requiring high surface contact [182]. As well as this, their smaller pore size becomes useful in situations where their ability to process and discriminate between smaller molecules proves advantageous. A notable feature microporous MOFs can possess is their ability to adsorb Carbon Dioxide [183]. This article was produced by Pal et. Al surrounding a co-MOF assesses its selectivity in terms of CO2 sorption Involving Aryl C–H···O═C═O Interactions. The study presents the use of microporous MOFs as an effective carbon capture solution, illustrating the Co-MOFs ability to selectivity predominantly adsorb carbon dioxide over other gases in the mixture. This can be explained by GCMC computer simulations on the Co-MOF structure showed how the CO_2 molecules had been electrostatically trapped as a result of interactions between oxygen atoms in the CO2 molecules and the hydrogen atoms attached to the pyridine rings in the framework's spacers. These results are supported by additional literature in this field of research, such as in this study similarly investigating the selective adsorption properties of microporous MOFs [184]. These findings prove microporous MOFs as valuable within the field of green chemistry, laying a foundation for further investigation into their CO_2 adsorption abilities, given their potential to actively reduce atmospheric greenhouse gas emissions.

In terms of their catalytic applications, particularly in the fine chemical industry, they can be employed in the Hantzsch reaction to produce polyhydroquinolines, whereby its derivates are utilised in the pharmaceutical industry due to its medicinal functions, as discussed in [185]. In this paper [186], the Zn-MOF conveyed high efficiency as a result of its hierarchical microporous structure, which provided a large surface area for reactions to occur on the structure. As well as this, the paper discussed how the Zn-MOF catalyst could be reused multiple times with only a moderate decrease in performance, demonstrating its stability and potential long-term financial viability. Notably, however, the intricacies of the potential deactivation mechanisms (such as coking) were not extensively discussed. The potential for deactivation of the catalyst is a pivotal factor in terms of its suitability for such a reaction over traditional catalysts, as such drawbacks would be crucial on an industrial scale. Similar experimental work conducted on the use of microporous Zn-MOFs as heterogeneous catalysts has been conducted by Roy et al., whereby its impact on various organic

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transformations has been explored [187]. The Zn-MOF studied in this paper exhibited high catalytic efficiency during reactions such as the cycloaddition of CO2 with epoxides to form cyclic carbonates (a valuable intermediate in the fine chemical industry). One advantage to using the MOF structure was highlighted as its ability to catalyse reactions under mild conditions. This could prove particularly beneficial for large-scale industrial reactions as the sector shifts towards more sustainable and eco-friendly chemical processes. Further to this, the paper addresses the low price associated with Zinc metal, linking this to its large surface area to volume ratio and divalent oxidation state. This presents the Zn-MOF catalyst as an overall suitable alternative for several organic processes, including high temperature reactions and during the involvement of hazardous materials.

2.5.2.5. Metal oxides

Microporous metal oxide structures feature metal centres of either single ions, clusters, or mixed-metal clusters, linked together through oxygen atoms. These linkages, which contribute towards its stability, can then form a variety of structures such as rings, chains, and layers, which lead to the formation of its porous structure. Similar to other microporous structures, they can be organised in either a crystalline or amorphous structure. Zeolites are a type of metal oxide; however, other types of metal oxides do exist yet are used much less frequently in the fine chemical industry. Other types of metal oxides used as microporous catalysts include MoVNbTeOx [188] and surface-phosphate nickel oxide [189] which can be used in the dehydrogenation of ethane to ethylene. An alternative avenue for future exploration would be the use of heterogeneous transition metal oxide catalysts, which have applications in several areas, including the conversion of hydrocarbons to value-added chemicals and geochemical redox processes [190]. Their production has been explored in [191], where MoO_3 and WO_3 catalysts have been synthesised. The paper draws comparisons between them and traditional zeolites, explaining how these transition metal oxides combine the molecular-sieve attributes of Si-zeolites with the enhanced acidic strength and redox properties of metal cations. Combining these properties into one structure provides versatility in terms of catalytic performance, which is highly sought after in the fine chemical industry. The drawbacks of transition metal oxide catalysts were discussed, with the most significant being structural stability issues and synthesis complexity. These issues provide a hindrance to the practical implementation of transition metal oxides, indicating significant further validation both experimentally and practically would be required to fully leverage their advantages and result in widespread industrial implementation.

2.5.2.6. Polymer-supported catalysts

Alkene epoxidation is a vital chemical reaction utilised in the fine chemical industry to produce various compounds, including epoxides, a valuable intermediate in the synthesis of pharmaceutical and agrochemical products [192]. The potential use of polymer-based structures as catalyst supports for these reactions has been the subject of focus in recent years as they have exhibited greater potential in terms of stability, as well as providing a potentially greener production route. Subsequently, new, modern methods have been developed and patented, including several patents regarding liquid phase epoxidation and incorporated heterogeneous catalysts, [193–195]. These polymer structures provide a support matrix that facilitates and subsequently immobilises the catalyst. A study conducted on the epoxidation of alkenes using a polymer-supported Mo(VI) catalyst [196] evaluated the stability and activity as well as catalytic leaching under a range of conditions. It highlighted current industrial concerns regarding the potential leaching during the use of long-term heterogeneous catalysts, mentioning the recent research conducted into the use of alternative inorganic catalyst structures and their lack of suitability [197–199], underlining the need to develop and scale up a stable method utilising a polymer-based structure instead. Whilst this research consisted of a batch process, the focus was to investigate the catalyst structure for its future uses in continuous processes. Findings from the paper include enhanced reaction stability and efficiency as well as the potential for reuse of the catalyst. One drawback to note included the importance of utilising optimal conditions in the process to ensure efficiency was optimal. Such a drawback exists with almost all chemical reactions regardless of sector however, outlining the weighting of the benefits of using a polymer structure as a heterogeneous catalyst can possess over any negative aspects. Similar studies investigating the preparation of epoxides using a polybenzimidazole-supported Mo(VI) catalyst [200,201] produced similar results. Whilst the alkene being epoxidized varied between the studies, the findings illustrated that a polymer-based catalyst structure (in this case polybenzimidazole) is active in these reactions, and exhibits particularly high activity under reaction-specific optimized conditions. Both studies showed greater reaction efficiency, with a notable catalyst leaching recorded in [201]. However, these studies were conducted under batch conditions, and it has been suggested that when transferred to a continuous process leaching and loss in catalytic activity would no longer be an issue. This is of great importance in terms of scale up and adoption of these processes on a larger scale, particularly in the fine chemical industry whereby both prolonged catalyst activity and lifespan are highly desirable.

Various literature portrays polymers as suitable catalyst supports as a result of them being inert, insoluble and non-toxic [202,203]. In particular, being inert is an essential characteristic to maximise the efficiency of catalytic reactions. This reduces the risk of catalyst poisoning and facilitates the reuse and recovery of the catalyst, providing a potential economic advantage in the long run in terms of cost savings in process scale-up. Their non-toxic properties are essential in the fine chemical industry in terms of safety assurance and regulatory compliance, particularly in industries where products may subsequently face human consumption. These findings are further supported in [204] whereby a Ps·AMP·Mo catalyst has been used in the epoxidation of 1-hexene and 4-vinyl-1-cyclohexene. Continuous and batch operations were analysed, with the catalyst exhibiting high activity and selectivity in both circumstances. In addition to this, epoxidation in a FlowSyn continuous flow reactor illustrated noticeable time savings, highlighting the benefits and potential streamlining of operations that the use of a polymer-based catalyst structure can provide.

The importance of optimising these processes to fully reap the benefits has been a consistent theme throughout most literature regarding the epoxidation of alkenes using polymer-based catalyst structures. The increased catalytic activity and efficiency are diminished under non-ideal reaction conditions, regardless of the polymer structure used, as evidenced in [205]. In this research paper, the catalyst used was a polystyrene 2-(aminomethyl) pyridine-supported Mo(VI) catalyst, yet the importance of optimising the reaction conditions was further stressed, regardless of whether it was a batch or continuous process. Further to this, optimisation of a process reduces environmental impact as well as operating and energy consumption costs. To further verify results produced during the physical optimisation of a polymer-based catalytic epoxidation reaction, an Artificial Neural Network model has been employed and compared to those results produced experimentally [206]. This has highlighted not only the importance of optimising a process in terms of cost savings and efficiency but also the benefits it supplies in terms of continuous epoxidation experiments as an elaboration from those carried out in batch reactors. The importance of greener epoxidation processes has been explored in [207], with the main benefits of developing greener methods including reduced waste, further potential savings on energy and material costs, as well as exhibiting progressive movements towards more environmentally conscious processes and tighter emissions regulations.

2.6. Comparison between mesoporous and microporous structures and their uses as catalysts in the production of fine chemicals

After reviewing existing literature on various types of mesoporous and microporous catalysts, one key takeaway would be that many of these structures can alternate between mesoporous, microporous, or sometimes both (hierarchical). For example, both micro- and mesoporous zeolites exist, yet their uses differ, dependent on the reaction or process in question. A similar case exists for MOFs and carbon-based structures along with many others. Despite this, in the context of fine chemicals, some pore structures with specific materials are significantly more suited. A clear example of this would be the carbon-based structures. According to the definition provided by the International Federation of Pure and Applied Chemistry (IUPAC), porous carbon-based materials can be split into three categories based on their pore diameter size: microporous carbon (<2 nm), mesoporous carbon (between 2 and 50 nm), and macroporous carbon (> 50 nm) [208]. Much of the

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literature on microporous carbon-based structures falls into the field of electrochemistry, as opposed to the industry of fine chemicals. One explanation for this may be due to its strong conductive abilities over other heterogeneous catalysts. Apart from this, many of the other advantages that it provides are shared with other catalytic structures. Despite this, its properties are not often harnessed in fine chemical production, yet in its mesoporous form its use is significantly more common.

Leading on from this, several materials explored in this review can possess either a crystalline or amorphous structure, such as microporous MOFs. However, the crystalline structure often features more in catalytic research whereas in industry, amorphous structures are typically used more often due to their lower cost and greater flexibility [209–211].

In terms of determining the most efficient or most suitable catalyst, it could be argued that this is nothing but a trivial matter. Despite some structures featuring more advantages over others, it is solely a matter of the process in question. For example, compared with the most used catalyst support structures such as silica and zeolites, carbon-based materials possess several advantages, such as stability in both basic and acidic mediums. As well as this, activated carbon obtained from biochar can yield a highly porous structure with surface areas reaching as high as 2000 m^2/g (dependent on the source and synthesis/activation method). This is significantly larger in comparison to other common material-specific surface areas, for example, silica can only reach 750 m^2/g and zeolites up to 800 m^2/g [157]. However, in the case of an acid catalysis reaction in the petrochemical industry, the use of a zeolite structure would be strongly preferred due to its strong Brønsted and Lewis acid sites, something that a carbon-based catalyst could not offer on its own.

2.7. Synthesis and modification

Often, during the production of fine chemicals, a large number of preparation steps are required. This has been reviewed above for specific processes with certain materials. This section, however, will analyse these modification and preparation methods more generically. Often, the reactants being used must be altered or treated before use. Furthering this, the catalyst being used will often require some prior steps, be it modification with alternative compounds, thermal treatment, a form of synthesis or application to support [212]. According to [213], the approach taken to synthesise and prepare the catalyst structure will heavily influence the formed structure in terms of the dispersion of the catalyst, as well as its surface area and concentration. These findings are also supported by [214–216], indicating the method used in catalyst development and preparation is crucial in dictating the reaction's performance and outcome. The additional costs incurred during any preparation in terms of additional materials and energy requirements further add to the value of the final product being manufactured, hence the choice of catalyst is not to be taken lightly.

The majority of literature in this field often focuses on the effectiveness of the catalyst used for a specific process, with the type of processes being analysed varying heavily. Often, the processes being investigated consist of either Hydrogenation, dehydrogenation, hydrocracking, and decarbonylation (which occur on metal sites) or dehydration, isomerization, and hydrogenolysis (which occur on acid sites) [217]. A significant amount of literature has been produced in recent years with a focus on modifying and enhancing existing micro and mesoporous catalysts to improve performance. The primary focus of research in this field has been the synthesis, characterization and applications of acidic, noble and transition metal modification.

In the context of heterogeneous catalysts, modification occurs when the base catalyst substance is combined or added to an alternative substance, often a liquid or solid, to alter and extrude specific properties it can exhibit that may be desired for a reaction. Unlike the direct synthesis of a catalyst, it is not being generated solely from reactants but exists already and is being both chemically and physically altered. For example, in the case of the synthesis of Florol, as explored by [218], the H-USY-30 catalyst was modified via treatment with an aqueous NaOH alkaline solution. This modification consisted of combining the two in an Easymax 106 reactor for a specific period, followed by ion exchange to convert it to its protonic form. There are countless other examples of catalyst modification across all aspects of the chemical industry, for example in [45], Kumar investigates the ring opening of decalin using MCM-41, modified with Ru. Leading on from this, according to [213], the most common methods of mesoporous catalyst preparation or modification (Zeolites, mesoporous silicas etc.) are ion exchange and impregnation, with in-situ synthesis being hardly used owing to it being a relatively new method.

There are a range of ways in which catalysts can be modified, depending on their existing structure and the desired outcome. These include ion exchange, impregnation of catalyst as well as In-situ and composite methods. These will be explored in further detail below, with their relevance in the production of fine chemicals assessed and reviewed across existing literature and experimental papers/journals.

2.7.1. Ion-Exchange

The ion exchange method is a widely used technique in catalysis particularly for materials with micro and mesoporous structures. It involves the replacement of ions within the material's framework with other ions from a solution. This method is often employed for catalysts with low metal loadings [45], allowing for the controlled introduction of specific ions or molecules to modify the catalytic properties of the material. In the context of catalyst preparation, the ion exchange method helps put certain metal ions into the molecular sieve's structure. This exchange process in most cases is crucial for tailoring the surface properties as well as enhancing the catalytic activity of the material. The reasoning behind using ion exchange in this way is to control the types and concentrations of ions introduced, so the acidity and selectivity of the catalyst can be managed, enabling it to be used in specific chemical reactions more efficiently. As mentioned previously, preparing a catalyst in this way often requires many steps to ensure the properties of the catalyst are controlled. Even slight deteriorations from the correct process can lead to a change in the catalyst, rendering it inefficient or perhaps no longer viable. Further to this, ion exchange can be an energy-intensive process, leading to the conclusion that an ion exchange method possesses both pros and cons. This explains its popularity in the use of heterogeneous catalysts but points towards the use of other modifications and preparation steps to obtain a more ideal catalyst.

2.7.2. Evaporation Impregnation

Metal precursors are dissolved in distilled water and added to the microporous zeolites or mesoporous materials in a flask. Metal modifications are carried out for 24 h in a rotatory evaporator equipped with a water bath. After completion of synthesis, the aqueous phase is evaporated and the catalyst is removed from the flask, followed by drying and calcination in a muffle oven [219].

2.7.3. Deposition precipitations

In the deposition precipitation method, the pH of dissolved metal precursor and microporous zeolites or mesoporous materials is enhanced to 9-10 and synthesis is carried out for 24 h in alkaline media. After completion of synthesis, the catalyst is filtered, washed with distilled water, dried, and calcined in a muffle oven.

2.7.4. Physico-chemical characterization

Physico-chemical characterization of catalytic materials applied in the production of fine chemicals is of immense importance for understanding the reaction mechanism. Furthermore, physico-chemical characterization results are utilized in the development of new efficient and stable catalysts with high selectivity to desired fine chemicals. Instruments and techniques applied in the physico-chemical characterizations are as follows: X-ray powder diffraction (XRD) used for structure and phase purity determination; scanning electron microscopy (SEM) for determination of morphological features such as crystal shape, size and distributions; Energy Dispersive X-ray Analyses (EDXA) for measurement of the chemical compositions. Textural properties such as surface area, pore volume and pore size distributions, of the pristine solid acid, transition and noble metal modified heterogeneous catalysts are determined using N_2-physisorption. The amounts and strength of Brønsted and Lewis acid sites in the catalytic materials are measured using FTIR-Pyridine.

Transition and noble metal nanoparticle size, shape and distributions are measured using transmission electron microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM). Furthermore, HRTEM and TEM are also applied for measurements of pore dimensions, periodicity of pores and channel systems in structured microporous and mesoporous materials utilized for fine chemical synthesis. Framework Al and extra-framework Al important for the creation of Brønsted and Lewis acid sites are measured using ^{27}Al-NMR and ^{29}Si MAS NMR spectroscopies. Oxidation states of transition and noble metals are important for the production of fine chemicals using heterogeneous catalysts. X-ray photoelectron spectroscopy (XPS) is used for the determination of oxidation states of metal-modified catalysts.

2.7.5. Acid preparation

Acids can play a crucial role in the development, modification, or synthesis of catalysts. They can perform several roles, with the main objective being to chemically alter the catalyst to increase conversion and promote greater selectivity towards the desired products of a reaction. Common ways in which acids are used in this process include template removal, pore diameter adjustment and forms of surface modification.

Template removal incorporates the use of an acid to remove organic templates or surfactants from the synthesized catalysts. The acids are used to dissolve or remove the organic components from the synthesized material, leaving behind the desired porous structure. It must be noted however that paying close attention to the removal process is crucial to maintaining the material's structure and desired qualities. Incomplete or improper removal could lead to structural flaws, blocked pores, or unwanted contaminants, ultimately impacting the catalyst's performance.

Pore size adjustment allows for the diameter of the pores within the material to be altered. By doing so, the ability of reactant molecules to enter the structure and contact active sites can be modified, providing the ability to change the catalyst's conversion and selectivity.

Altering the surface of the material using an acid can not only change its structure and the number of active sites available for a reaction, but it can enhance the catalyst's stability and reduce the risk of catalyst contamination or deactivation. This is vital in extending the life of the catalyst, meaning it can be recovered and reused more often, reducing catalytic costs in the long term.

2.7.6. Base preparation

Utilising a base either in the preparation or synthesis of a catalyst generally achieves similar objectives as using an acid, however it progresses along a different chemical route. They can be used to control the pH of the catalyst, as well as perform surface adjustments to the catalytic material. This includes adding or removing specific functional groups from the catalyst surface, which can in turn lead to a different chemical structure and so altered reaction parameters. They effectively allow for the customization of the structural characteristics of the catalyst, providing an enhancement to its efficiency, selectivity and conversion. In comparison to the route followed by an acid, the alkaline route features both hydrolysis and condensation, leading to a significantly more compact and refined structure [220].

The use of either a base or acid as a heterogeneous catalyst has featured in extensive research recently, with attempts made to generate a hybrid catalyst featuring both. Such a catalyst has been growing in popularity due to its faster reaction times and lower corrosion or deactivation potential as evidenced in [221,222].

2.7.7. Comparison

A comparison between using an acid, a base and an ion exchange resin as a heterogeneous catalyst during the production of biodiesel have been explored in [32]. Advantages of using an acid heterogeneous catalyst have been listed as the recovery and reuse aspect of the catalyst, with the main drawback being a loss of catalyst due to leaching, as well as a high temperature being required and prolonged reaction time. This has also been mentioned in a similar context in [223], [224] and [225].

Conversely, the paper suggests that using a base as a heterogeneous catalyst produces a higher reaction rate. However, there was also a loss of catalyst experienced due to leaching, as well as it being sensitive to materials used during the reaction. Finally, the paper compares these to the use of an ion-exchange resin. The ion-exchange resin featured the complete removal of by-products, as well as easy product separation from the reactants and catalyst, in addition to its ability to catalyse the reaction as either a base or an acid. Its drawbacks however included its resin active sites suffering from deactivation, as well as a slow reaction rate.

2.7.8. Impregnation

The technique of impregnation features the absorption and/or penetration of an active catalyst species into the pores of a solid support material, such as activated carbon, alumina, or silica. The impregnated catalyst can be in the form of a solution, dispersion, or suspension, and is deposited onto the supporting structure through several physicochemical interactions.

This method of preparation allows for a relatively high concentration of active species on the support material, providing greater catalytic activity and selectivity. This is done through careful control of the active species and the impregnation time.

A key advantage of the impregnation method is its flexibility in accommodating a range of active species, including metals, metal oxides, and metal complexes.

Potential drawbacks to the use of impregnation as a catalyst synthesis method include possible uneven distribution of the active catalyst within the porous structure of the support material, which can affect the overall catalytic performance and stability. One proposal to solve this issue would be to employ careful control of the impregnation parameters and post-impregnation treatments e.g., drying and calcination. The use of some form of post-treatment would ensure uniform distribution as well as strong adhesion of the active species within the structure of the support material.

The porous structure undergoing impregnation can vary, depending on the specific reaction. Often the structure must undergo a form of preparation or treatment before the impregnation step, usually calcination [226,227]. Following this, the impregnation occurs either through wet impregnation or incipient wetness impregnation. In some specific cases, for example [226], impregnation of a catalyst occurs in a solvent-less environment, leading to what is known as “precursor dry impregnation”. Alternatively, evaporation-impregnation can be used, such as in the preparation of ceria-supported catalysts [228]. Here, evaporation-impregnation was achieved by stirring in a rotary evaporator, followed by water evaporation under vacuum.

One important aspect of the impregnation method to note is the preparation of a precursor solution and the following drying and/or calcination that occurs. This pre-step is like the methodology used in the ion-exchange method. However, the impregnation method is regarded to be more straightforward and is claimed to be one of the most popular methods, as per [229].

2.7.9. Oxygen doping

Oxygen doping is an approach used on mesoporous carbon bases to improve the hydrophilicity of the surface. This can then serve as active sites in catalytic reactions or in the selective adsorption of cationic compounds. Furthering this, it can aid in the dispersion of metals within the structure [230,231]. In general, oxygen doping can introduce additional active sites to the structure, increasing activity, as well as increasing thermal stability which in some cases can prevent sintering, extending the life of the catalyst.

3. Conclusions

Overall, this literature review has explored the complex and wide-ranging field of microporous and mesoporous catalysts within the fine chemical industry. The efficiency, selectivity, and sustainability of the chemical reactions involved are strongly influenced by the catalyst of choice, regardless of its mesoporous or microporous nature. Because their pores are smaller (< 2nm), microporous materials — like zeolites, aluminophosphate and some metal-organic frameworks

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(MOFs) — offer excellent selectivity and are especially well-suited for reactions involving smaller molecules. They often require significantly fewer steps during their manufacture and synthesis, resulting in fewer harmful emissions and a lower cost of production. The most used microporous structure as a heterogeneous catalyst is zeolites. However, the rise of MOFs and other alternatives that provide a wider range of customisability in terms of pore size and volume are under development every day, with their significance rapidly growing as a result of their potential promise as better heterogeneous catalysts.

Mesoporous materials, including various silica-based structures, Zeolites, ZIFs and some MOFs, provide the advantage of accommodating larger molecules and demonstrating enhanced diffusion. This makes them ideal for a broader range of reactions. Further to this, they possess the ability to have adaptive pore shapes and sizes, meaning the catalytic structure can be tailored to the needs of individual reactions, massively increasing its effectiveness due to its high selectivity and activity. The most popular mesoporous catalysts in the industry include organo-silica-based MCM-41 as well as mesoporous zeolites. In a similar fashion to microporous materials, however, the use of MOFs in place of traditional mesoporous catalysts is growing. Reasoning for this trend includes the almost infinite number of possible structures MOFs can take, meaning they can be tailored for almost every reaction and there is always the possibility of developing a catalytically improved structure. Further to this, industrial catalytic use of ZIF structures as heterogeneous catalysts is beginning to rise, not just in the fine chemical industry but across a range of chemical sectors. This is a result of their high specific surface areas, coordination topology features, and in some cases nitrogen-rich structures leading to a high density, uniform distribution of active sites.

This review has also demonstrated the importance of catalyst modification and preparation, showing how techniques like ion exchange, impregnation, and oxygen doping can significantly alter the properties of these catalysts, making them suitable for certain uses in the fine chemical industry. These modifications can enhance properties such as surface area, pore volume and chemical functionality, therefore improving the catalytic activity and selectivity of a reaction.

In conclusion, the field of heterogeneous catalysis for fine chemical production is a dynamic and ever-changing area of research. Continued research in micro and mesoporous catalyst design, combined with a clearer understanding of structural impact on activity, will significantly advance the field. This deeper insight into catalytic behaviour and material properties will lead to the production of more efficient, selective, and sustainable processes in the fine chemical industry. It is noteworthy to mention that solid acid, transition and noble metal modified heterogeneous catalysts during the production of fine and speciality chemicals undergo catalyst deactivation. However, most of the spent catalytic materials after the reaction could be regenerated and reused.

The findings from this literature review provide a solid foundation for further exploration and a critical review in this field of fine chemical production using micro- and mesoporous heterogeneous catalysts.

4. Future Directions

A key area for future research in this field would involve investigation into bridging the gap between lab-scale experiments through to industrial-level applications of meso- and microporous heterogeneous catalysts. It is evident through existing literature that a case for various porous catalyst structures including MOFs and ZIFs, exists. However, a lack of experimental work focused on increasing utilisation scale and production volumes is outstanding, indicating further work in this field is required before widespread adoption of porous catalysts in the fine chemical industry becomes a possibility.

Further to this, a future exploration into innovative synthesis methods to enhance selectivity, stability and efficiency and additional work on the alteration of catalyst structures both physically and chemically to modify specific properties if highly recommended. Doing so would open a gateway into not just greater adoption of the catalyst structures reviewed but more environmentally and economically beneficial processes, which is something that would be highly valuable in a sector such as the fine chemicals industry whereby even marginal gains and advancements would prove instrumental.

Finally, the incorporation of computational modelling and machine learning into catalyst design would provide further optimization of reactions and chemical processes, providing the opportunity to enhance the efficiency and sustainability of fine chemical production. Such optimisation could lead to reduced chemical waste, experimentation costs and development times, all of which are critical for maintaining competitiveness and meeting regulatory standards in the fine chemical industry.

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Abbreviations: MT - Megatonnes; TOF - Turnover frequency; TON - Turnover number; MOF - Metal organic framework; ZIF - Zeolitic imidazolate framework; GCMC - Grand Canonical Monte Carlo; IUPAC - International Federation of Pure and Applied Chemistry.

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