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Introduction: Scope of the Book

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1.1 Introduction: Green Chemistry, Solvent-free Synthesis, and Nanocatalysts

Since the realization that the future of chemical/industrial processes primarily depends on their sustainable quotient, the path of modern science has shifted toward the improvement of processes/products following green chemistry principles [1, 2]. Green chemistry as a branch of chemistry primarily deals with developing chemical processes using environmentally benign protocols, including inexpensive renewable less-toxic precursors. In that respect, the "12 rules of green chemistry," first formally introduced by Anastas and Warner in their book "Green Chemistry: Theory and Practices" [3], play a pivotal role in identifying the areas that should be focused to achieve the expected sustainability goals [4]. For chemical processes, the main aim of introducing these 12 principles is to save the environment and society by reducing the usage of toxic and hazardous chemicals and solvents without affecting the product yield/selectivity. While the 12 principles are quite self-explanatory, as depicted in Figure 1.1, the emphasis in certain areas often depends on the convenience of implementing them for specific protocols and the outcome. Of these 12 principles, this book focuses on the historical and recent developments of strategies that minimize solvent use in a chemical process, often termed "solvent-free synthesis," and the associated catalytic procedures involving nanomaterials.

The use of a solvent in a reaction creates a homogeneous solution phase where the reactants can interact effectively. While ideally, any liquid can be used as a solvent, the focus is largely on solvents based on their polarity and protic nature (e.g. methanol, ethanol, chloroform, dichloromethane, dimethylformamide [DMF], dimethyl sulfoxide [DMSO], toluene). The primary reasons can be attributed to their ability to solubilize various organic reactants/products as well as to control the stability of the transition state/intermediates (leading to modifications of the thermodynamic and kinetic reaction parameters) [5]. However, with the growth of

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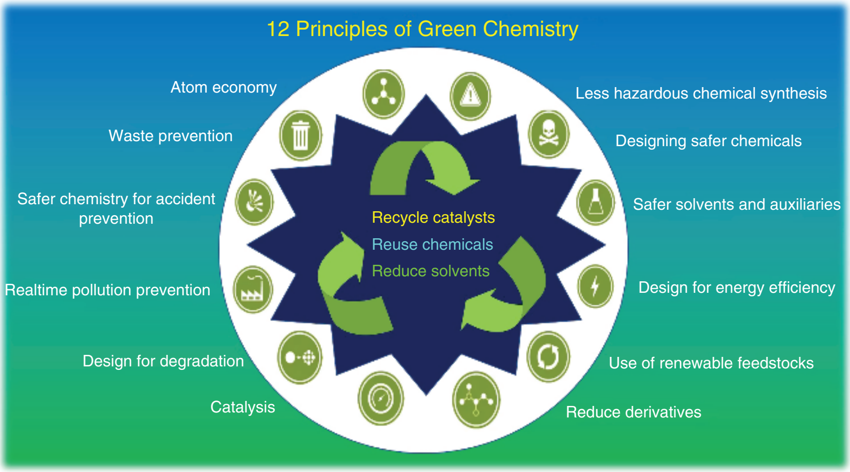

Figure 1.1 12 principles of green chemistry.

industrial chemical processes along with growing interest in developing sustainable protocols, emphasis has been shifted toward choosing the best solvent based on not only their solubilizing power but also their abundance, cost, and, last but not least, short- and long-term impacts on environment [6]. In that context, water has long been considered a sustainable choice. However, the poor solubility of organic species in aqueous solution has limited its wide use primarily at the industrial scale [7, 8]. While some of the current choices, such as ionic liquids (ILs), often come as rescue options, their selection has remained an area of concern for the processes related to bulk scale production of materials [9]. Around this debate regarding the choice of solvent, the idea of “no solvent is best solvent” was also considered. However, it did not receive its due because of the lack of initial appreciation, especially for industrial purposes. However, with the advent of eco-friendly and greener approaches, the idea of “solvent-free synthesis” resurfaced, and presently, it is being explored as one of the viable options for the synthesis of chemicals as well as various materials (Figure 1.2a) [10]. Initially, synthesis under solvent-free conditions was associated with the solid-phase synthesis where the reactants were made to react in the solid phase. However, recent advances in the area of materials syntheses (which include thermal treatment, plasma etching, etc.) have extended its scope significantly [11, 12]. Modern-day scientific and technological developments are primarily governed by the utilization of materials for specific purposes. Thus, the choice of their synthetic strategies is often determined by the type of materials, their subsequent use, and their sustainable quotient. Considering these, the class of “nanomaterials” has emerged as a crucial player. Hence, a brief introduction of nanomaterials with special emphasis on their catalytic applications seems timely before moving to a detailed discussion on their solvent-free synthetic procedures.

Nanomaterials are the class of materials size that falls under 1–100 nm in at least one dimension (Figure 1.2b) [13, 14]. The exceptional growth in the development

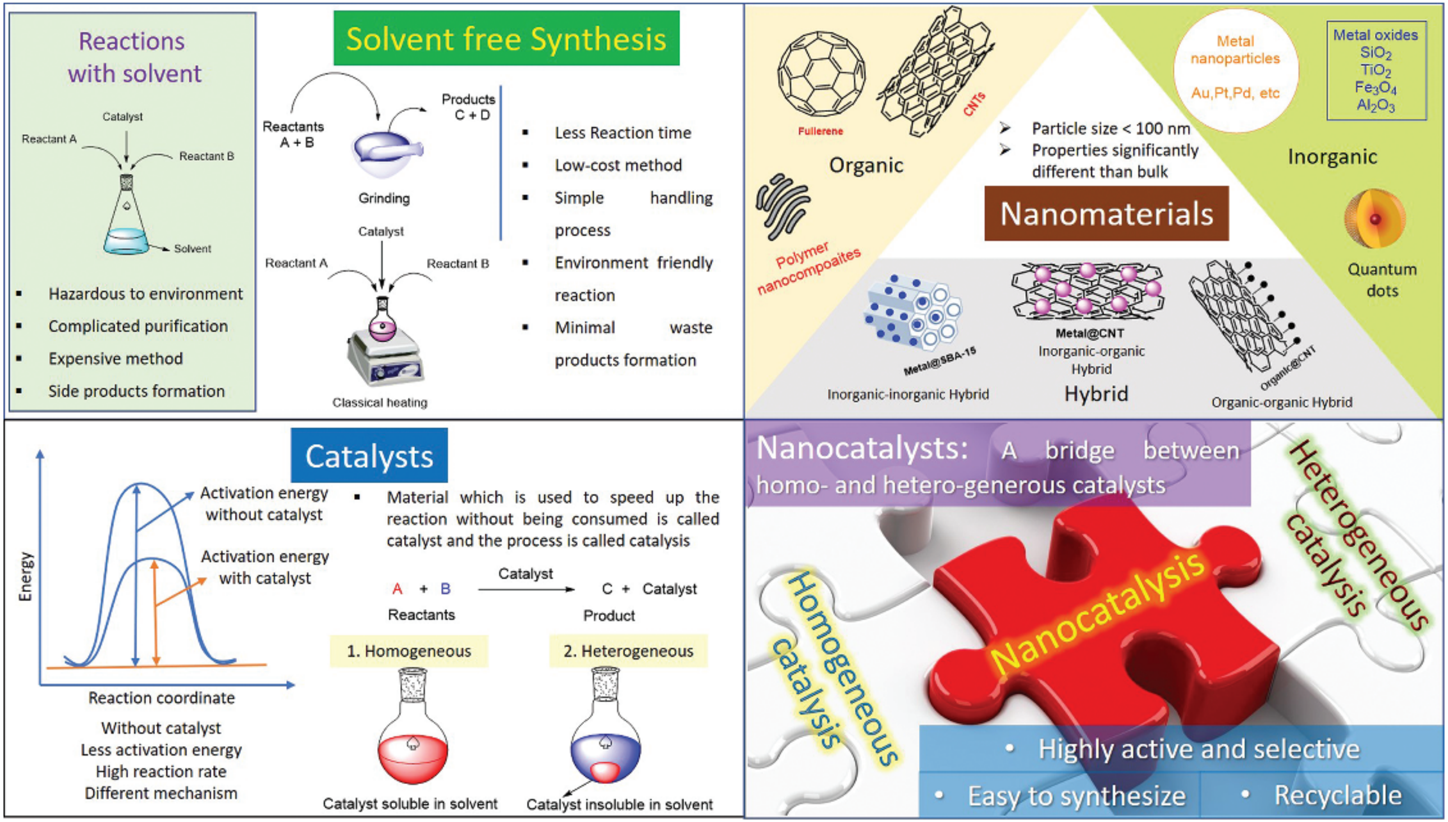

Figure 1.2 Introduction to (a) solvent-free synthesis, (b) nanomaterials, (c) catalysts, and (d) nanocatalysis. CNTs = Carbon nanotubes.

of nanomaterials can be attributed to high surface area, quantum confinement effect, and the possibility of fine-tuning their surface properties utilizing relatively straightforward methods. While the natural origin of nanomaterials can be traced back to the time of big-bang, Prof. Feynman, in his great lecture series "There is plenty of room at the bottom," first introduced the enormous potential of nanomaterials [15, 16]. Since then, progress in nanomaterials has been significant, and in the modern world, it is nearly impossible not to encounter nanomaterials in daily lives [17, 18]. Among the various fields in which nanomaterials have been explored, one of the areas involves their catalytic applications due to their unique size and shape-dependent surface properties [19, 20].

The term "catalyst" (or "catalysis") was first introduced in 1835 by Swedish chemist J.J. Berzelius [21, 22]. Since then, the catalyst is defined as a substance/material that improves the reaction rate by minimizing the activation energy of the process without being consumed during the process (Figure 1.2c). The initial developments in catalysis were concentrated on relatively expensive transition metal–derived systems primarily due to their intrinsic catalytic properties. However, the need for sustainable results has allowed the recent advancements to focus on less-toxic, low-cost, and highly abundant and recyclable catalytic alternatives [23, 24]. Though the categorization of catalysts may vary depending on the classification criteria, catalysts are commonly divided into two classes: homogeneous and heterogeneous [25]. Homogeneous catalysts are the compounds that remain in the same phase as reactants/products during the catalytic reactions (mostly in the presence of a suitable solvent). While homogeneous catalysts often exhibit higher catalytic activity, poor separation and recyclability appear significant challenges. In contrast, heterogenous systems involve different reactants/products and catalyst phases and ideally have better separation and reusability. However, due to various mass transfer and diffusion limitations, the catalytic activity of heterogeneous catalysts remains inferior to their homogeneous counterparts. Thus, a combination of advantageous factors for both systems is essential to overcome the existing challenges of both sides to achieve the desired goals. In that context, the utilization of nanomaterials (often termed "nanocatalysts," [NCs], Figure 1.2d) either as catalysts or as support materials for various homogeneous/heterogeneous catalytic entities has opened newer avenues as they often exhibit the potential to overcome the respective challenges in homo- and heterogenous catalysts [26].

The synthesis of NCs does not deviate too much from the synthesis of nanomaterials. It hence can primarily be classified into "top-down" and "bottom-up" approaches [27, 28], each of which can further be divided based on specific techniques. In "top-down" approaches, NCs are prepared from the bulk using various "cutting" techniques, whereas the "bottom-up" approaches involve synthesis of NCs from their atomic and/or molecular precursors. Both approaches have their own advantages and disadvantages, and often, the choice of synthetic methods is dictated by the NCs' specific properties and applications. For instance, while various "top-down" strategies are preferred for carbon-based nanomaterials (e.g. graphene, nanotubes), metal-oxide nanoparticles (NPs) are generally synthesized using "sol–gel" techniques [29]. Irrespective of the synthetic processes, "solvent-free" methods are always preferred as they can be directly related to the goals of green and sustainable transformations.

This brief introduction provides a general idea about various related topics interlinked with a common theme of sustainability and hopefully allows the readers to have a smooth transition in the remaining parts of the chapter.

1.2 Topics Covered in this Book

The chapters in this book are carefully designed to provide a very in-depth idea about NCs and their applications using solvent-free methods. In Chapter 2, Gawande and coworkers provide an illustrative overview of the syntheses of nanocatalysts using solvent-free methods. The idea of introducing this chapter is to make readers aware of various synthetic techniques and their advantages and disadvantages that can be used for the solvent-free preparation of nanocatalysts. The remaining part of the book (except the conclusion chapter, Chapter 9) primarily deals with catalytic applications of nanocatalysts using solvent-free methods. In Chapter 3, Prof. Zamani introduce the topic of solvent and catalyst-free organic transformations with specific examples of academic and industrial importance to set up the stage for the next chapters. While Manyar and coworkers describe various solvent-free organic transformations, catalyzed by metal/metal-oxide nanocatalysts in Chapter 4, a separate chapter is dedicated to silica-based nanomaterials as catalysts/support for solvent-free organic reactions (Chapter 5). In Chapter 6, Prof. Torad emphasizes the importance of carbon-based nanomaterials either as supports or as nanocatalysts for solvent-free organic reactions, focusing on doped and functionalized nanocarbons. In Chapters 7 and 8, concentration has been deliberately steered toward current developments in the areas of solvent-free reactions using nitride-based and ionic liquid-based nanocatalytic systems, respectively, because they have been explored recently as potential sustainable choices in comparison to the existing ones. In the book's concluding chapter (Chapter 9), Prof. Pieta summarizes the present status of solvent-free synthesis of nanomaterials and solvent-free nanocatalytic transformations, emphasizing their relevance with green chemistry and sustainability. The author also provides a brief account of the challenges related to current approaches and some possible solutions as an outlook. Starting from the introductory chapter to the concluding one, the primary focus of this book has been on providing readers with insights into the background, recent advances, and future possibilities regarding solvent-free synthesis of nanocatalysts as well as solvent-free nanocatalytic methods. We, as contributors, strongly feel that this book will be helpful to students and researchers who want to gain knowledge about these topics and pursue their research in those areas. Following that thought, the next sections highlight some solvent-free methods used in the synthesis of NCs, followed by their specific catalytic applications.

1.3 Solvent-Free Synthesis of Nanocatalysts

As the name suggests, solvent-free methods for preparing uniform, monodisperse solid NCs essentially follow the synthetic protocols that do not use any solvent [27, 30]. The size and shape of the synthesized NCs vary depending on the methods and the reaction conditions. While the approaches used in these syntheses can also be considered as a part of traditional “top-down” or “bottom-up” based classification, the present literature examples tend to categorize them in terms of specific procedures. In that context, primarily four types of procedures along with their subclassifications have been reported: (i) mechanochemical, (ii) thermal, (iii) plasma-assisted, and, last but not least, (iv) deposition techniques (Figure 1.3).

The mechanochemical process for the synthesis of nanomaterials primarily involves grinding of bulk precursors into nanoscale materials using mechanical force [31, 32]. In that category, the traditional “ball-milling” approach has widely been used [33–35]. For example, Barcellos and coworkers synthesized CuO NCs using high-energy ball milling, and the synthesized NCs were used for nitroarene reduction under aqueous media [36]. Recently, solid-phase synthesis that involves grinding the precursor materials using a mortar and pestle has also generated much interest owing to its simple operational procedure [37]. For instance, gram-scale synthesis of Au/chitosan was reported by Reddy et al. recently using a mortar and pestle. The nanocatalyst was used for catalytic homocoupling of phenylboronic acid and the aerobic oxidation of benzyl alcohol in water [38].

One of the most widely used and well-studied approaches for the synthesis of NCs includes the preparation of NCs using heat as an energy source, and this strategy (often termed “thermal treatment”) primarily involves heating of molecular precursors at high temperatures under an oxidative or reductive environment to obtain nanomaterials [39–41]. For example, various metal oxides are routinely synthesized from their precursors using heat treatment under an oxidative environment (e.g. air, O_2) [42]. However, for synthesizing carbon-based nanomaterials, precursors are often pyrolyzed under an inert atmosphere (N_2, Ar, etc.). The product yield, extent of doping, and degree of graphitization depend on the nature of precursors, temperature, heating rate, etc. [43, 44]. Goswami et al. showed that a hydrogen-assisted thermal treatment could be used to convert metal precursors into metal NPs [45]. As opposed to conventional heating treatment, to make the synthetic process greener and more sustainable, alternative energy sources (such as microwave (MW) or ultrasound) or bio-derived precursors/processes have also been used to prepare metal nanoparticles NPs [46–48].

With the advent of instrumental developments, several sophisticated “top-down” approaches have been developed to synthesize NCs. Among them, plasma-assisted strategies have shown great promise due to their environmentally benign nature, no additional requirements of solvent or stabilizing agents, etc. [49]. In this case, “feed materials” are transformed into atoms or molecules through vaporization with the help of plasma and thus NPs/NCs are formed. The size, morphology, and properties of the final materials are generally dependent on the absolute temperature of plasma, the kinetics of plasma formation, quenching process, and the size and

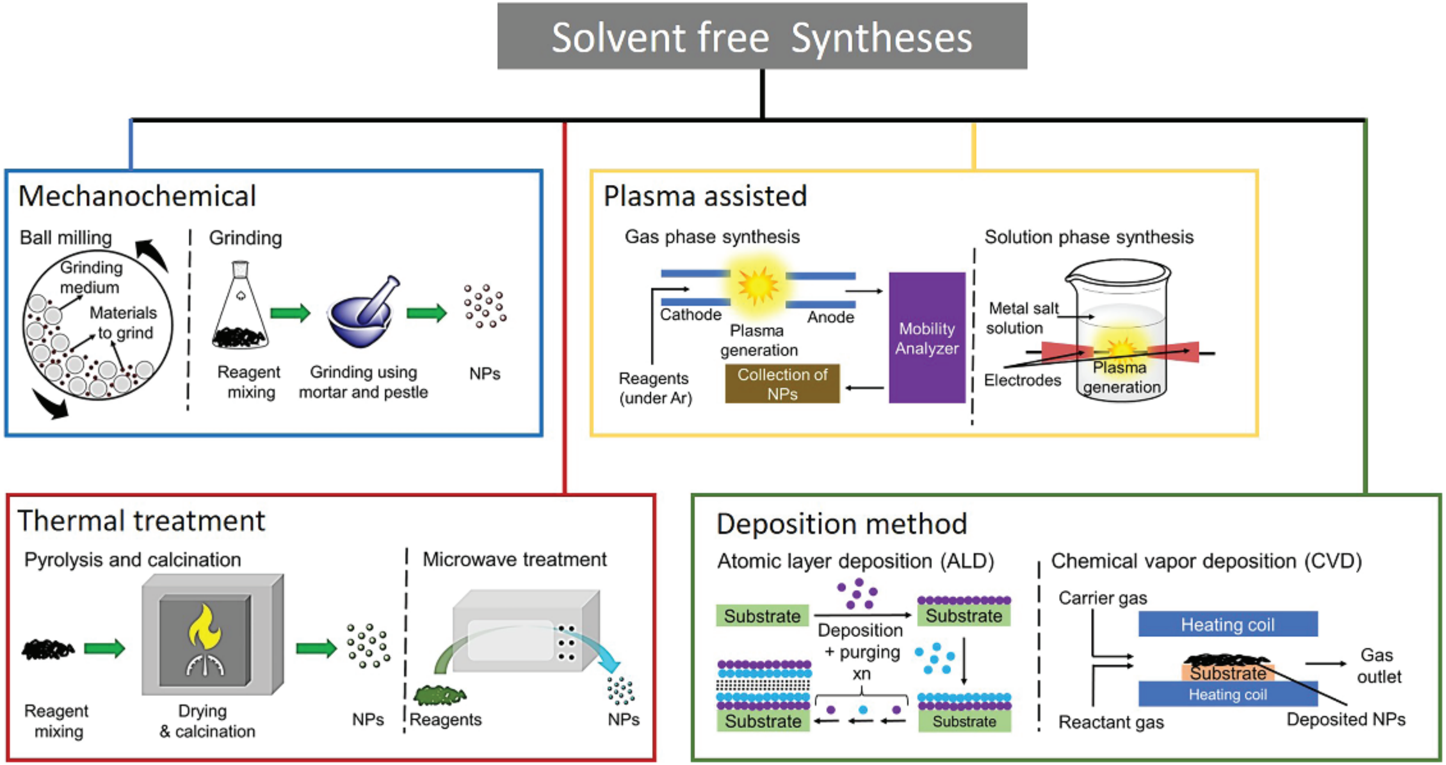

Figure 1.3 Representative solvent-free methods used for the synthesis of NCs. NPs = Nanoparticles.

composition of feed materials. Based on the internal energy of electrons used for plasma generation, this can be classified into two categories: (i) thermal plasma and (ii) cold-plasma methods [50]. While plasma is used to generate an intense heat source in both cases, the significant difference between these two processes lies in the operating temperature. In the case of thermal plasma, feed materials are atomized at an operating temperature of a few thousand degrees. Nanomaterials/NCs are formed during the cooling process. For example, NiO nanocubes were prepared from bulk Ni metal utilizing thermal plasma with oxygen as a carrier gas [51]. On the other hand, cold plasma uses a low-pressure, low-temperature method where NCs can be synthesized even at room temperature [52]. This energy-efficient method is primarily used to synthesize noble-metal NPs (e.g. Pd, Ag, Au), as exemplified by recent reports [53–55]. Recently, Haye et al. have also utilized this method to synthesize non–noble-metal-based FeNPs (more precisely Fe_3N) embedded on carbon support [56].

Another solvent-free method for the synthesis of nanomaterials/nanocatalysts that gained tremendous attention is deposition techniques (more precisely, vapor deposition techniques) [57, 58]. In this method, nanomaterials/nanocatalysts are deposited on a substrate in the form of thin films from their atomic precursors. Depending on the nature of deposition, they can further be classified into physical and chemical vapor deposition (CVD), and among them also several subclassifications are made. In the context of solvent-free synthesis of NPs, CVD techniques [59] and atomic layer deposition (ALD) techniques [60] have been widely explored. For instance, carbon-based support materials such as carbon nanotubes (CNTs) and graphene are routinely synthesized using the CVD method [61–63]. In addition, metal NPs have been embedded onto a carbon matrix using the CVD method [64, 65]. On the other hand, the precursors copper(II)-hexafluoroacetylacetonate [$Cu(hfac)_2$] and diethylzinc [DEZ, $(C_2H_5)_2Zn$] were used to synthesize Cu/ZnO-50 nanocatalysts using the ALD method [66].

The aforementioned examples are the only selected ones chosen from the vast pool of synthetic strategies employed for the preparation of NPs while these are primarily representative of the solvent-free protocols; a detailed discussion on this topic is included in Chapter 2.

1.4 Solvent and Catalyst-Free Organic Transformations

To have a smooth transition from the solvent-free synthesis of NCs to solvent-free processes utilizing NCs; as an intermediate, a separate section has been devoted to solvent and catalyst-free organic transformations (Figure 1.4). As opposed to the use of relatively toxic catalytic entities and solvents, solvent- and catalyst-free organic transformations can be considered among the classes of reactions that aim to follow sustainability goals [78]. While these straightforward protocols have shown great promise, the desired success of these procedures is often restricted

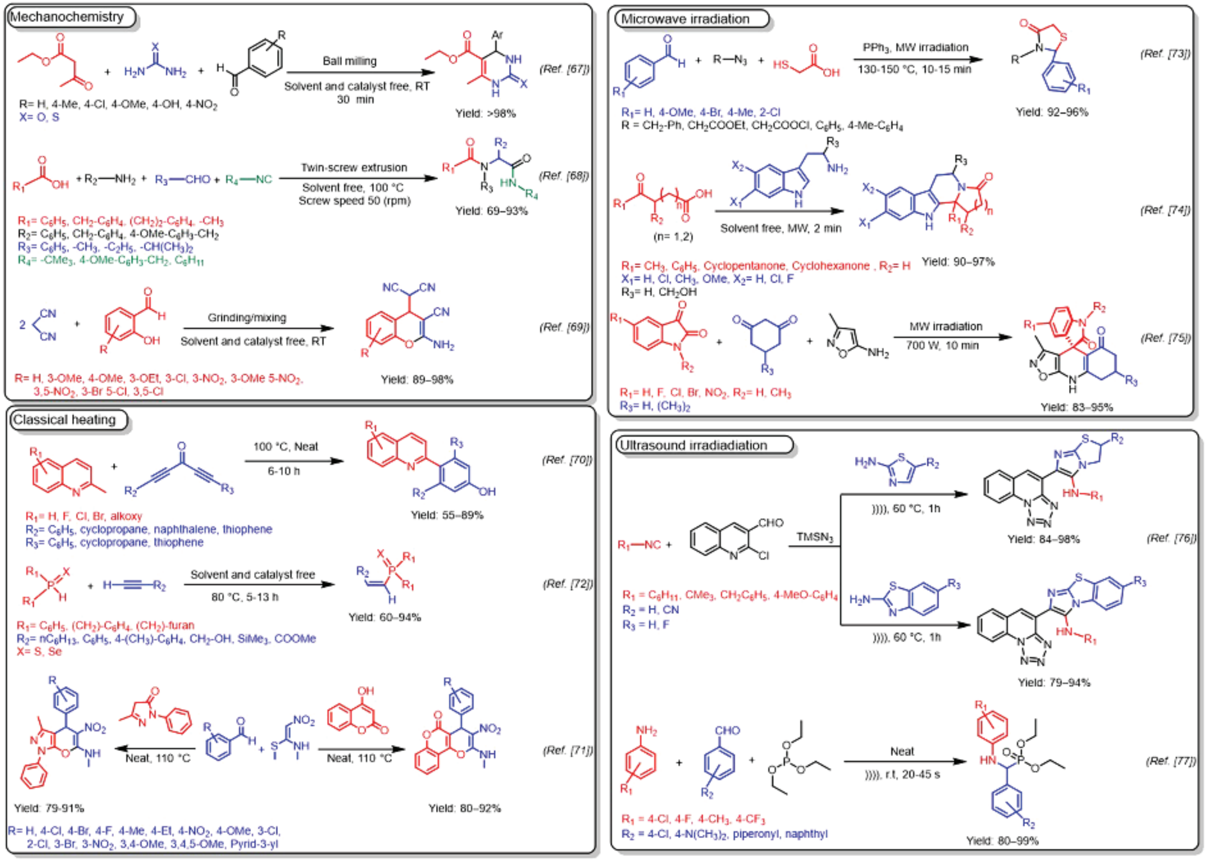

Figure 1.4 Representative examples of solvent and catalyst-free organic transformations. Source: Adapted from the references given in parentheses.

due to poor yield, significant energy investment, etc. However, in recent years, the advancement of alternative energy sources and increasing knowledge of fundamental reaction mechanisms enable them to get closer to the expected ideal outcome.

Among other processes, mechanochemical processes hold a special place because of the utilization of simple mechanical force/energy to drive the reactions forward and its underexplored potential for large-scale production of organic compounds without complicated purification steps. Different types of mechanical processes have been developed depending on the types of reactions and their outcome, among which ball-milling, twin-screw, mortar and pestle methods have become very popular. For example, thiourea derivatives were synthesized using ball-milling within 10–20 minutes [67], and various multicomponent reactions (MCRs) such as Ugi, Biginelli have been carried out using twin-screw extruder (TSE) [68]. Additionally, mortar and pestle method has also been exploited for the synthesis of fused heterocycles [69]. These are representative of the enormous possibility of mechanochemical synthesis.

Conventional thermal heating under solvent- and catalyst-free conditions is often considered the classical way of achieving the desired product for any chemical transformations. Despite the challenges related to the product selectivity and energy efficiency that have impacted the long-term use of the process negatively, several heterocycles (including imidazoles [70], pyrazoles [71]), phosphonates [72] have been synthesized under solvent- and catalyst-free thermal heating methods.

To tackle the challenges related to the conventional thermal heating process, alternative energy sources such as MW and ultrasound have given a fresh impetus to make the synthetic methods more energy efficient and greener [73, 74]. The use of MW under solvent- and catalyst-free conditions has been explored to synthesize spiro compounds [75], N-containing heterocycles [79], etc. The employed protocols have shown faster kinetics, better reactivity, higher selectivity, and broader substrate scope. The utilization of ultrasound irradiation to drive a chemical reaction is also considered one of the green approaches. In this context, a combination of solvent- and catalyst-free method with ultrasound irradiation stands unique because of safer energy inputs, waste reduction, higher yields/selectivity, etc., compared to other traditional approaches [80]. Starting from simple formylation [76] or protection of amines [77] to multicomponent coupling of heterocycles [81], the use of ultrasound irradiation has proven to be highly efficient, as exemplified in recent examples.

The aforementioned methods provide a glimpse of solvent- and catalyst-free approaches that have shown great promise compared to traditional ones. More details about these procedures/approaches are provided in Chapter 3.

1.5 Solvent-Free Reactions Using NCs

Most of the solvent-free reactions using NCs are largely focused on three major classes: (i) metal or metal-oxide NPs (Figure 1.5), (ii) silica-based NCs (Figure 1.6),

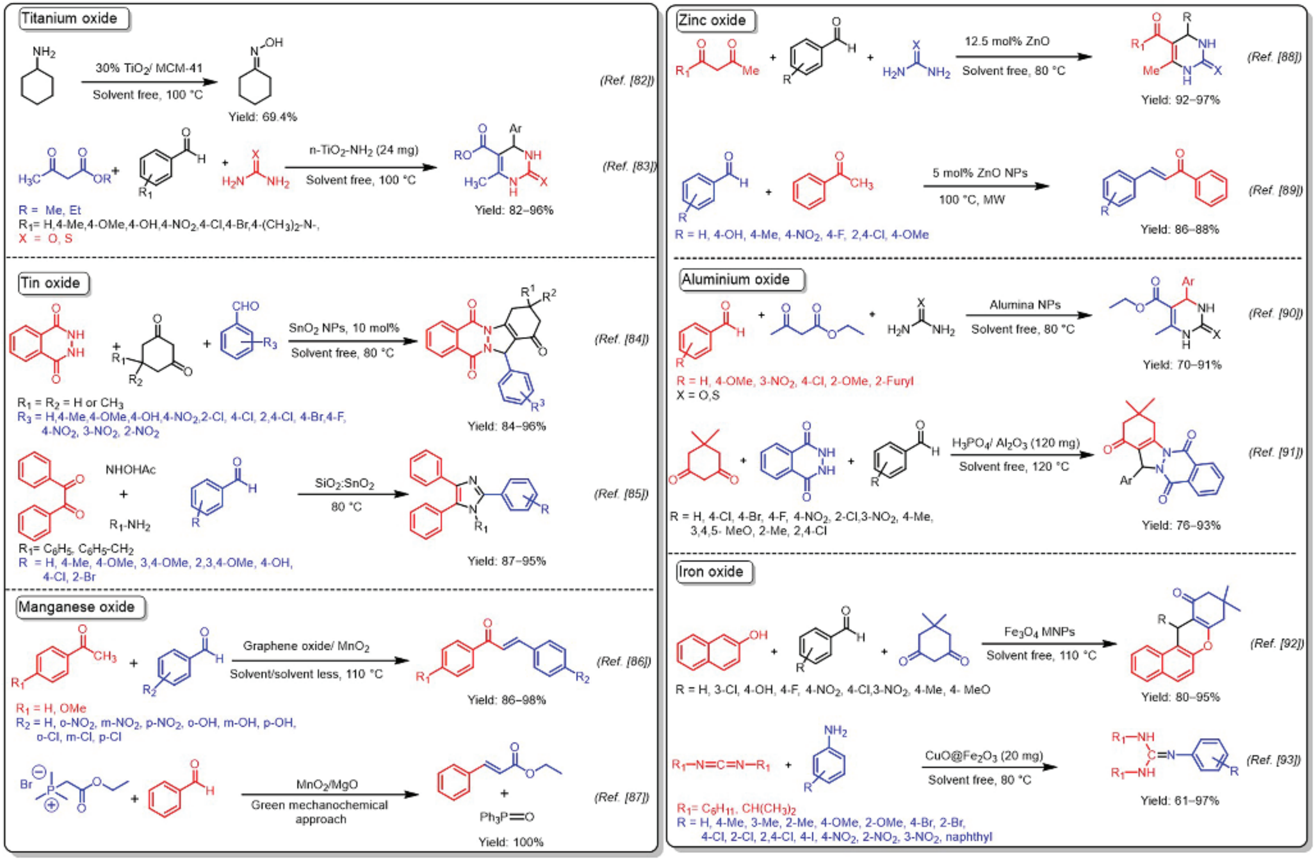

Figure 1.5 Representative examples of solvent-free nanocatalytic procedures using metal-oxide NPs as catalysts/supports. Source: Adapted from the references given in parentheses. MNPs = Magnetic nanoparticles.

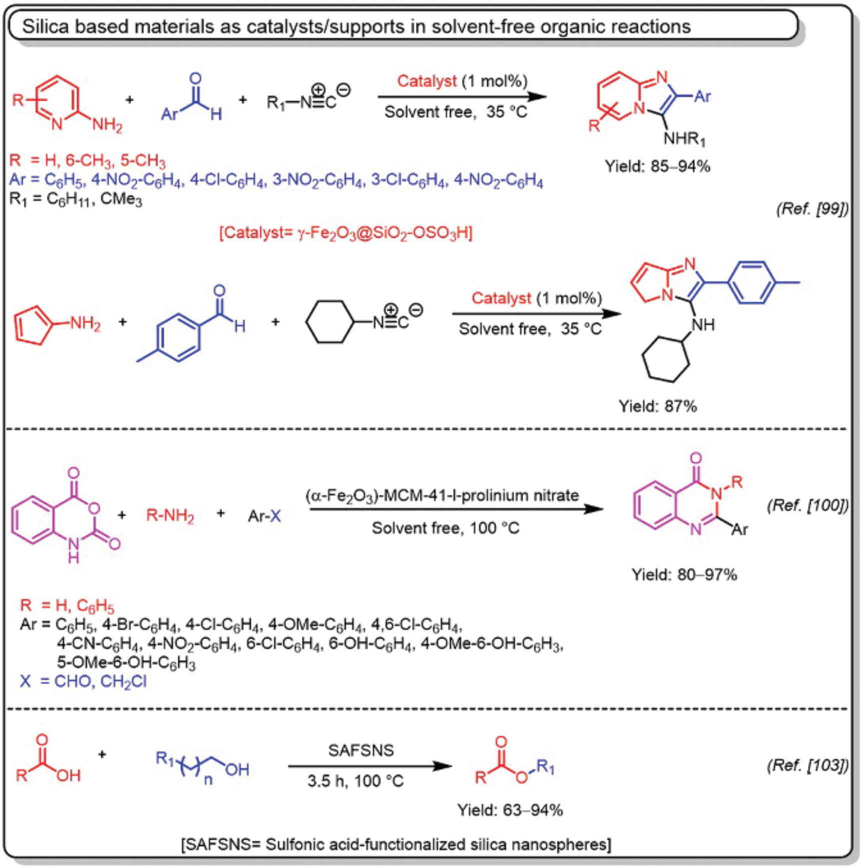

Figure 1.6 Representative examples of silica-supported nanocatalytic systems for organic transformations. Source: Adapted from the references given in parentheses.

and (iii) carbon-based nanosystems as catalyst/support (Figure 1.7). Additionally, nitride-based (Figure 1.8) and ionic liquid (IL)-based NCs (Figure 1.9) have recently been reported. While such topics will be discussed in detail in subsequent chapters, several such reactions are highlighted to exhibit a variety of the responses that can be performed using these NCs.

1.5.1 Different Metal Oxides as a Catalyst/Support in Solvent-Free Reaction

1.5.1.1 Titanium Oxide

Titanium oxide (TiO_2) and titanium oxide–supported catalysts are used for organic reactions, including solvent-free methods, because of their unique properties and catalytic activity. In 2007, M. Hosseini-Sarvari et al. reported TiO_2 as a new and reusable nanocatalyst for the Knoevenagel condensation reaction, which exhibited good to excellent yields [100]. For efficient conversion of cyclohexylamine into cyclohexanone oxime (78.4%) with high selectivity (89.1%) under solvent-free

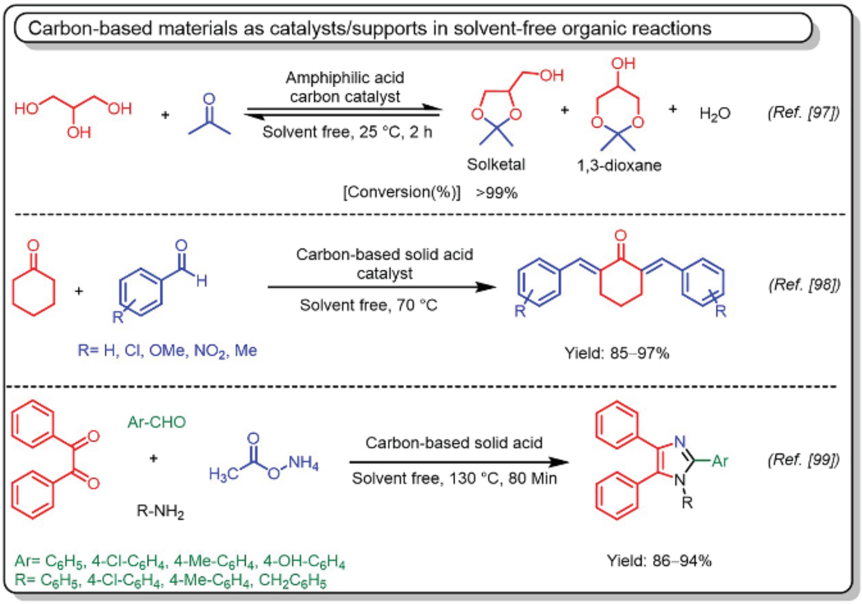

Figure 1.7 Saluted examples of carbon-based nanocatalysts for organic transformations under solvent-free conditions. Source: Adapted from the references given in parentheses.

conditions, Liu et al. used mobil composition of matter (MCM)-41-supported TiO_2 NCs [82]. After using for five cycles, no significant change was observed in catalytic efficiency, and characterization data showed the hydroxyl groups on titania acted as catalytic sites. Recently, Amoozadeh and coworkers synthesized nickel(II) Schiff base complex supported on nano-titanium dioxide, and the supported NCs were used for the synthesis of 3,4-dihydopyrimidin-2(1*H*)-ones through Biginelli reaction under solvent-free conditions [83]. The catalytic activity was found to be superior to previous catalytic systems and showed diverse substrate scope.

1.5.1.2 Tin Oxide

Tin oxide nanoparticles (more specifically SnO_2 NPs) exhibit excellent catalytic properties in various organic reactions to synthesize organic compounds. In addition to the high catalytic activity/selectivity of SnO_2, the possibility of easy separation (or reusability) has made this oxide unique as exemplified in several instances, including ones that use solvent-free conditions. SnO_2 NPs as NCs were utilized to synthesize 2*H*-indazolo[2,1-*b*]phthalazine-triones using an MCR of aromatic aldehydes 1,3-cyclohexanedione and phthalhydrazide under solvent-free conditions [84]. The catalytic results showed that the final products can be obtained in good yields with high selectivity. While initial research was more focused on the catalyst and yields, with more advancements in the catalysis, recyclability came into the picture. For example, 1,2,4,5-tetra substituted imidazoles were prepared using silica-supported tin oxide under solvent-free conditions [85]. In addition to high catalytic performance (yield: 84–97%), the catalyst can be separated easily from the reaction mixture and recycled up to five cycles without any significant change in the catalyst's activity and/or composition. In another example, Ahmed et al. synthesized nanocrystalline sulfated tin oxide. They used them as NCs to synthesize coumarin derivatives under solvent-free conditions using acetoacetate and *m*-cresol as reactants [101].

1.5.1.3 Manganese Oxide (MnO_x)

Manganese metal is widely used in catalysis because it is inexpensive, is easily available, is less toxic, and shows variable oxidation states ranging from +II to +VII. Its various oxides are also available in different forms such as 3D structure, chain-like structures, layered or sheet structures. These materials are routinely used as heterogeneous catalysts for numerous chemical transformations. In that respect, graphene oxide–supported manganese oxide (GO/MnO_2) was used as a catalyst for synthesizing chalcogens under solvent and solvent-free conditions [86]. The NCs showed superior catalytic activity than their counterparts, confirming the synthesis between each compound. In another example, manganese oxide–doped magnesium oxide (MnO_2/MgO) was employed as a NC to prepare ethyl cinnamate (mostly known as a flavoring agent) using a Witting reaction between benzaldehyde and tri-phenyl phosphonium salts following a green mechanochemical solvent-free approach [87].

1.5.1.4 Zinc Oxide

Zinc oxide (ZnO) NPs have also been routinely explored in various applications, including optoelectronic field, photoluminescence devices, and solar cells. In addition, the recent research efforts are also engaged in tuning the shape, morphology, and properties of ZnO NPs for their utilization in electronic and antibacterial applications. In the case of nanocatalysis (especially for organic transformations), ZnO NPs have also been exploited as novel and reusable catalysts. In the present context of solvent-free reactions, ZnO-NPs-catalyzed Biginelli reaction was reported to synthesize dihydropyrimidinones using aromatic aldehydes, urea, or thiourea and acetoacetic esters under solvent-free conditions [88]. The catalyst showed excellent catalytic activity (94–97% of yields). In another study, a wide range of chloroesters were synthesized from cyclic ethers and acyl chlorides using ZnO NPs as nanocatalysts under solvent-free conditions at room temperature [102]. The catalyst can provide good yields (87–95%) and be recycled easily up to three cycles. The ZnO nanoflowers, derived from the peel of *Musa balbisiana* and zinc nitrate, were used as catalysts for synthesizing chalcones via the Claisen–Schmidt condensation reaction using MW irradiation under solvent-free conditions [89]. The ZnO-decorated GO nanocomposite acts as a highly efficient reusable catalyst for synthesizing xanthenedione from 1,3-dicarbonyl compounds and aromatic aldehydes under neat reaction conditions [103]. The final products were obtained in excellent yields, and the catalyst can be used up to five cycles.

1.5.1.5 Aluminum Oxide

Aluminum oxide (Al_2O_3, commonly known as alumina) has been extensively employed in the separation and purification of organic compounds primarily due to the insolubility of aluminum oxide in both water and organic solvents and variable interactions between the alumina surface and the eluting compounds with different polarities. Moreover, due to alumina's high Lewis acidic nature, catalytic applications of aluminum oxide and supported aluminum oxide-based materials have also been explored for various organic transformations. For example, alumina NPs were used for the MCR to synthesize dihydropyrimidinones under solvent-free synthesis through the Biginelli reaction [90]. ZrO_2-stabilized aluminum oxide was also reported as recyclable NCs (up to six cycles) for O-methoxymethylation reaction between substituted alcohols and dimethoxymethane under solvent-free conditions [104]. In another case, Shetarian et al. synthesized phosphoric acid–supported aluminum oxide (H_3PO_4/Al_2O_3), which could be used as an efficient catalyst for MCRs to synthesize 2*H*-indazolo[2,1-*b*]phthalazinetriones, 2,3-dihydroquinazoline4(1*H*)-ones, and benzo[4,5]imidazo[1,2-a]pyrimidines under solvent-free conditions [91].

1.5.1.6 Iron Oxide

Iron oxide NPs exist in various forms depending on the oxidation states of iron, oxygen vacancy, etc., among which maghemite, magnetite, and hematite are the prevalent ones. Because of the magnetic nature of some of the iron oxide NPs, the magnetic separation of the catalyst from the reaction mixture becomes easy, resulting in better catalyst recovery for recyclability. In 2015, Habibi et al. used iron oxide NPs as catalysts for the synthesis of benzoxanthenes using the reaction between aryl aldehydes, dimedone, and 2-naphthol [92]. The catalyst worked effectively with excellent yields (80–95%) and was reusable up to 20 cycles. Magnetic iron oxide NPs as support were also explored extensively for anchoring catalytic entities on them. For example, Abbasi et al. synthesized $CuO@\gamma\text{-}Fe_2O_3$ (copper oxide–supported magnetic NPs) to synthesize substituted guanidines via the simple addition of amines to carbodiimides [93]. The separation of the catalyst was straightforward by applying an external magnetic field, and it was confirmed that the presence of copper improved the activity of the catalyst and produced the desired products in good yields (60–97%) under solvent-free conditions. The catalyst could be reusable for four cycles without any significant loss of its activity.

1.5.2 Silica-Based Materials as Catalysts/Supports in Solvent-Free Organic Reactions

The use of silica and/or silica-based nanomaterials as either NCs or supports mainly stems from their exceptional thermal and chemical stability, high surface area, straightforward synthetic protocols, and the possibility of surface functionalization to incorporate various organic and/or inorganic functionalities [94, 105]. Among the different silica materials, two major types are extensively used for catalytic applications either as catalysts or as support: (i) nonporous and (ii) porous silica. While nonporous silica is historically important, the high surface area of porous silica offers a significant advantage due to the enhanced accessibility of catalytically active sites. As the catalytic activity of silica-based materials depends on the functionalities present on the surface, controlling the amount, distribution, and nature of surface functionalities is essential. Irrespective of the materials, most of the synthetic and/or functionalization strategies utilize “sol–gel” methods. Hence, the synthesis of silica-based nanocatalysts hardly follows solvent-free protocols [95]. However, post-synthetic modifications are often performed under solvent-free conditions to introduce and control surface functionalities [106]. In terms of catalytic activity, surface silanol groups with their Lewis acidic character assist the active catalysts whenever needed. In addition, surface functionalization, i.e. incorporating catalytically functional groups, becomes a pivotal step in developing better NCs. In general, organic functionalities are grafted on the silica surface using organosilanes, and they have been used as recyclable organocatalysts for organic transformations [107]. These supported NCs have been used in various organic transformations, including solvent-free ones (Figure 1.6). For example, a sulfonic acid-functionalized silica nanosphere (SAFSNS) catalyst was prepared and used under solvent-free conditions to synthesize carboxylic acid ester [96]. To incorporate metal/metal-based NPs on silica surface, suitable organic functionalities are grafted that act as anchoring sites for the metal precursors. Depending on the requirements, metals can be further reduced to their nanoparticle forms or oxidized to oxide forms. In that respect, selective oxidation of toluene was achieved using silica-supported Au NPs where the performance of the nanocatalysts improved through a mild reductive deprotection strategy [108].

1.5.3 Carbon-Based Materials as Catalysts/Supports in Solvent-Free Organic Reactions

Carbon-based NCs are often considered highly promising due to their high thermal stability, higher surface area, and low cost. The traditional “organocatalysts” are excluded in this category as they have already been considered under “small molecule” homogeneous catalysis rather than a heterogeneous one. In most cases, acid- or base-functionalized carbon-based materials can be used as catalysts. Alternatively, carbon materials can also act as support for anchoring other catalytic entities. Recent progress in this area indicates that carbon materials can be synthesized by pyrolysis of biodegradable waste materials such as corn, coconut shells at higher temperatures [43, 109]. The amphiphilic carbon has been used as a recyclable catalyst for the reaction between glycerol and 2-propanone to form solketal under solvent-free conditions [97]. Zali et al. used a carbon-based solid acid catalyst for the solvent-free aldol condensation of aromatic aldehydes with ketones to obtain the desired products in good yields; the catalyst can be reusable up to five times without a decrease in yields [98]. The carbon-based catalyst has also been explored for various MCRs. For instance, Tavakoli-Hoseini et al.

reported a carbon-based solid acid catalyst for the synthesis of tetra-substituted imidazoles via one-pot reaction using benzil, primary amines, aromatic aldehyde, and ammonium acetate as starting materials [99]. Figure 1.7 represents some examples where carbon-based nanocatalysts have been explored under solvent-free applications.

1.5.4 Nitride-Based Materials as Catalysts/Supports in Solvent-Free Organic Reactions

The functionalized or modified graphitic carbon nitrides (g-C_3N_4) are used as catalysts to synthesize several organic compounds under solvent-free green synthetic methods. In 2021, Azizi and coworkers synthesized xanthene derivatives using sulfonic acid–functionalized graphitic carbon nitride under solvent-free condition using the ball-milling method (Figure 1.8) [110]. The catalyst showed excellent catalytic activity with high yields and short reaction time and can be easily separated and reused up to four cycles.

Sonogashira coupling reaction is well known for the formation of the carbon–carbon bond. Commonly, palladium-based catalytic systems are used for Sonogashira coupling reactions. However, efforts have been devoted to finding a sustainable solution to replace expensive and scarce palladium-based catalysts. In that context, Akhlaghinia group reported a new catalyst, i.e. cobalt oxide (Co_3O_4) embedded in a triplet shelled carbon nitride (TSCN) for the Sonogashira–Hagihara cross-coupling reaction between aryl halides and substituted acetylenic compounds under solvent-free conditions (Figure 1.8) [111]. Though some of the reactions took place in water, the catalyst exhibited good performance under solvent-free conditions. The catalyst can be reusable up to five cycles without significant change in their conversion and rate.

In 2021, Liu and coworkers reported hexagonal boron nitride (h-BN) nanoflakes and a titanium dioxide hybrid photocatalytic system for the oxidation of cyclohexane with oxygen to form cyclohexanone with better selectivity than cyclohexanol under solvent-free conditions. The catalyst showed excellent catalytic activity up to four cycles without any change in the yield and selectivity (Figure 1.8) [112].

For controlling environmental pollution, conversion of carbon dioxide (CO_2) into useful products is an efficient way of mitigating the hazardous impact of CO_2. Chand et al. developed a catalytic system for converting carbon dioxide into cyclic carbonates at atmospheric pressure using boron-doped graphitic carbon nitride as a catalyst under solvent-free conditions [113]. The catalyst was synthesized using thermal condensation method (Figure 1.8). The catalyst's performance with respect to yield, selectivity, and turn-over number (TON) was superior to the previously reported catalytic systems. The catalyst can be reusable for eight cycles without any change in the activity and efficiency. A similar work was previously reported by Yin's group in 2016 (Figure 1.8) [114]. They synthesized phosphorous-modified carbon nitride and used it as a catalyst (in the presence of tetra butyl ammonium bromide [Bu_4NBr] as cocatalyst) for the cycloaddition reaction between carbon dioxide and epoxides to obtain the cyclic carbonates in excellent yields. The catalyst was readily separated

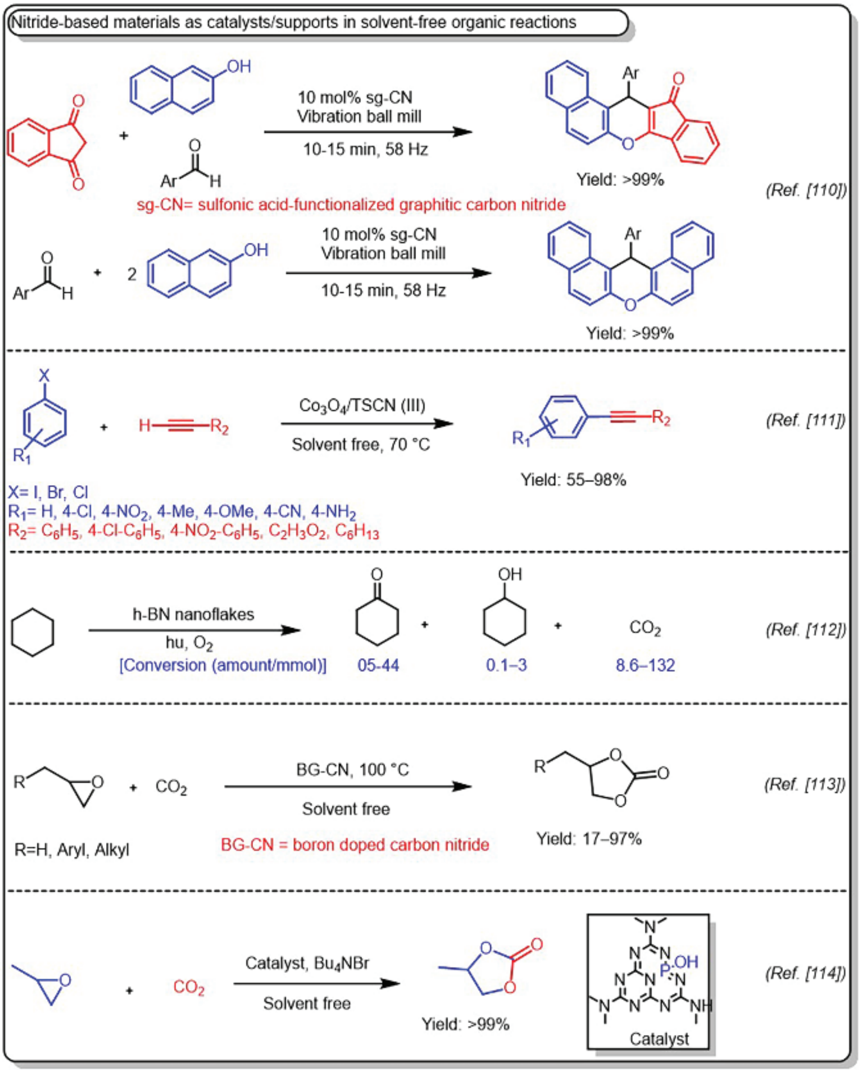

Figure 1.8 Representative examples of nitride-based materials as catalysts/supports in solvent-free organic reactions. Source: Adapted from the references given in parentheses. TSCN = triplet shelled carbon nitride.

from the reaction mixture via centrifugation. After washing and drying, the catalyst could be recycled up to five cycles with above 90% yields and 100% selectivity of the product.

1.5.5 Ionic Liquid-Based Materials as Catalysts/Supports in Solvent-Free Organic Reactions

Ionic liquids (ILs) are organic salts that exist under ambient conditions. Generally, they are made of polyatomic inorganic anions and organic cations and used

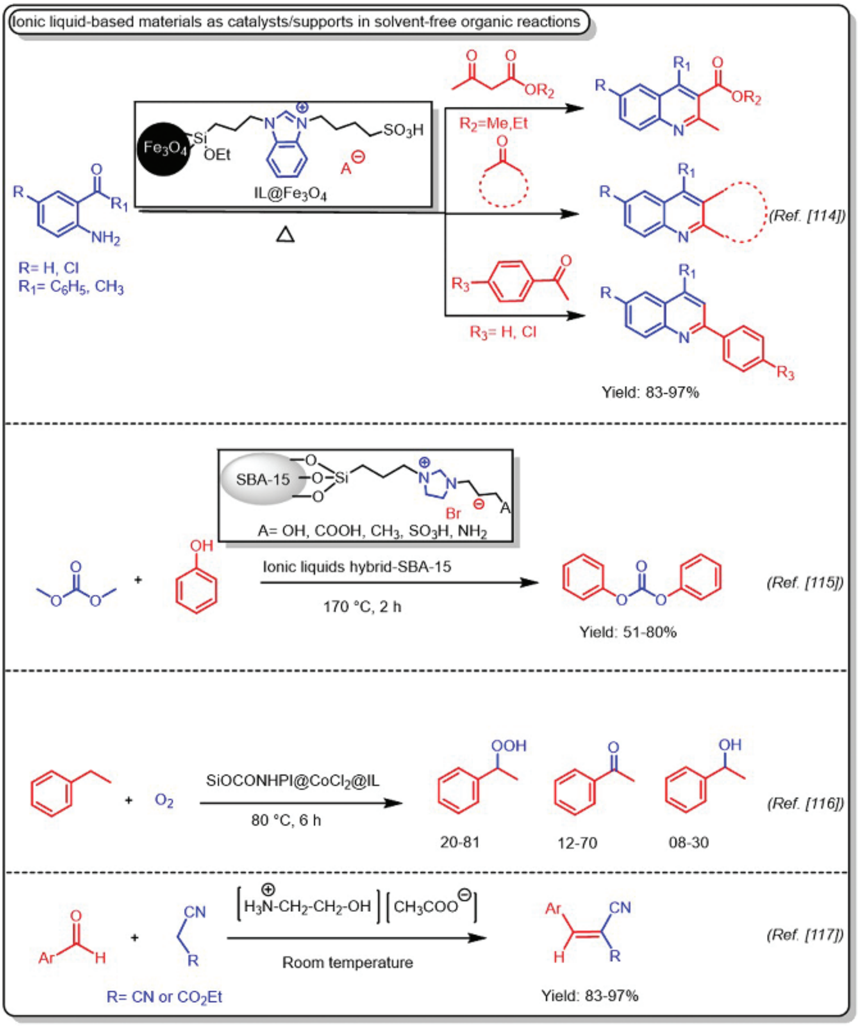

Figure 1.9 Representative examples of ionic liquid (IL)-based materials as catalysts/supports in solvent-free organic reactions. Source: Adapted from the references given in parentheses.

as solvents because of their wide range of solubility. Recently, they (either in their original forms or as functionalized derivatives) have been used as catalysts, especially under solvent-free conditions. For example, Dadhania et al. prepared iron oxide nanoparticle-supported acidic ionic liquid catalyst to synthesize quinolines and fused polycyclic quinolines by the Friedlander reaction under solvent-free conditions (Figure 1.9) [115]. The catalysts can be used up to six cycles without any loss of efficiency.

In recent years, synthesis of diphenyl carbonates has become extremely important due to their diverse applications, including the preparation of polycarbonates. Recently, Wang et al. reported that diphenyl carbonates could be successfully synthesized using a metal-free, Santa Barbara Amorphous (SBA)-15 IL hybrid catalyst under solvent-free conditions [116]. By changing the functional groups, they prepared 14 different catalysts, among which [SBA-15-IL-OH]Br with hydroxyl-terminated groups showed superior performance than the previously reported transition metal–based catalysts. The catalyst was reused up to the sixth cycle without significant changes in conversion, yield, and selectivity.

The oxidation of hydrocarbons plays a crucial role in organic synthesis. Instead of using metal-based compounds as catalysts (Co, Mn, etc.), Dobras et al. synthesized a catalyst using commercially available silica gel immobilized with *N*-hydroxyphthalimide (NHPI), followed by a coating with ILs [117]. The catalysts have been used for the oxidation of ethyl benzene (EB) under solvent-free conditions, resulting in three different products, namely, acetophenone (AP), ethylbenzene hydroperoxide (EBOOH), and 1-phenylethanol (PEOH). The selectivity of the product changes with the reaction conditions. To the best of their knowledge, this was the first time this class of catalyst was used under solvent-free conditions and recycled for three cycles [117].

IL-catalyzed Knoevenagel condensation reaction between different types of aromatic aldehydes and malononitrile or ethyl cyanoacetate under solvent-free conditions was reported by Yue et al. in 2008 [118]. With a minimal amount of the catalyst, the reactions were completed within less than an hour, and the catalysts exhibited high reactivity/selectivity and substrate scopes. The easy separation of the catalysts via simple filtration allowed the NCs to be recycled up to five cycles without any noticeable changes in the activity [118].

1.6 Present Status and Future Direction

Rapid progress in NCs can be attributed to their shape- and size-dependent properties (which are very different from their bulk counterparts), tunable surface functionality, higher surface area, ease of synthetic protocols, and a better understanding of their reaction mechanisms due to the rapid growth of sophisticated instrumentation. During the developmental phase of nanocatalysis, the main focus was devoted to making them more efficient and selective, and, in that process, sustainability parameters were often overlooked. However, since the formulation of “12 principles of green chemistry” to make processes more sustainable, the field of nanocatalysis has also reorganized its importance and started to develop accordingly. In that respect, both solvent-free synthesis of catalyst and solvent-free catalytic processes using NCs have taken up a central stage.

The idea of a solvent-free process undoubtedly pushes the boundaries of the existing synthetic strategies to achieve the required goal of sustainability. While the recent thrust in this area accompanies delivering catalytically improved active species, the term “solvent-free” refers to any solventless process either during the preparation of NCs or during the catalytic processes. Since both parts are recognized as equally important for developing sustainable procedures, the chapters in this book emphasize both aspects.

The question of how solvent-free procedures can be applied to the synthesis of NCs depends on the structure of nanomaterials and the target of use. In that respect, any form of energy that can replace the conventional thermal methods has the potential of making the synthetic steps more energy efficient and economically viable. The processes ranging from mechanochemical approaches to relatively sophisticated plasma-based strategies have been exploited for the solvent-free preparation of NCs. In addition, the synthesis of NCs has also been widely investigated using energy-efficient alternative energy sources. Moreover, for the catalytic systems where the primary synthetic strategies do not necessarily involve solvent-free approaches (e.g. silica), several post-synthetic solvent-free modifications are adopted to incorporate additional functionalities to further modify surface properties. The advancement of solvent-free deposition techniques has been beneficial for preparing various 1D and 2D nanomaterials. Briefly, the present status of solvent-free methods of NCs preparation indicates a brighter future where more precise control can be achieved.

As far as the solvent-free catalytic processes are concerned, the potential of NCs has been investigated in various reactions. Though gas-phase catalytic reactions are beyond the scope of the present discussion, it is worth mentioning that significant development has been observed. This progress can be attributed to the drive from industrial sectors to utilize green-house gases to produce value-added chemicals and also to convert the stored chemical energies into other forms of energies [119]. Nanomaterials' involvement in catalyzing organic reactions has been extensively studied because NCs offer the advantages of both heterogeneous and homogeneous catalysts [120]. The solvent-free organic reactions utilizing NCs often deliver further assistance to improve the catalytic activity and selectivity by providing a conducive reaction environment. In this respect, metal-oxide-based NCs are routinely explored for solvent-free catalytic organic transformations, ranging from simple Knoevenagel and Michael condensation reactions to the complicated synthesis of heterocycles or multicomponent reactions with a particular emphasis on bioactive target molecules. Other classes of NCs that have also gained tremendous attention include silica-based and carbon-based nanosystems. Different types of oxidation, reduction, coupling, multicomponent reactions are catalyzed using these materials under solvent-free conditions. While both are predominantly used to anchor/support other catalytically active species onto their surface to improve catalytic stability and recyclability, the presence of surface functional groups (e.g. silanols for silica and various organic functionalities for carbon-based nanomaterials) has also been reported to act as catalytic entities. In that context, "Carbocatalysis" has also emerged as an active area of research where defects and surface functionalities play an essential role in determining the catalytic outcome [121, 122].

Despite the significant attention the solvent-free methods (either NCs synthesis or nanocatalytic organic transformations) have received in recent years, the expected growth is often limited due to the various challenges. Some of the existing hurdles that need to be overcome to make the field more acceptable are as follows:

1. The solvent-free methods for the synthesis of NCs are still at their developmental phase due to a lack of knowledge of energy-transfer processes. Thus, to make these processes more economically viable and universally acceptable, more experimental and theoretical studies are essential for a fundamental understanding of the mechanism under solvent-free conditions.
2. Despite several literature precedents where nanomaterials are effectively used as catalysts, barring energy industries, the industrial uses of NCs have been limited, which is particularly pronounced in pharmaceutical industries where hardly any step in the synthesis of potential drug candidates uses NCs. The difficulties in scaling up the catalysts, existing well-established protocols for homogeneous catalysts, inferior activity of nanocatalysts compared to the homogeneous ones, poor understanding of nanocatalytic mechanism, etc. are identified as the reasons behind the lack of interest from such industries. Thus, more serious efforts are needed to explore the possibility of using similar NCs for industrially relevant challenging transformations.
3. Till date most studies involving NCs under solvent-free conditions focus on finding out the efficiency of NCs and establishing the superiority of the solvent-free methods in terms of reactivity and selectivity. However, other parameters including short-term and long-term effects of NCs on the health and environment, the compatibility between the highly concentrated reactants and NCs, the reasons for catalyst poisoning are often ignored and hence need to be thoroughly investigated.

Undoubtedly, these challenges are multifaceted and require sincere efforts from every discipline. Fortunately, the researchers who work in these areas have already acknowledged these gaps and have actively been engaged tackling these issues. More details about these concerns and their potential solutions are discussed in the subsequent chapters. To the best of our knowledge, no available books have dealt with these issues yet. We do hope readers, especially those who want to know the present status and future opportunities of solvent-free nanocatalytic processes, will find this book essential and relevant. It will motivate them to pursue their research in the exciting multidisciplinary area.

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