Handbook of Greener Synthesis of Nanomaterials and Compounds

VOLUME 1

Fundamental Principles and Methods

> <mark>Edited by</mark> Boris I. Kharisov Oxana V. Kharissova



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Volume 1: Fundamental Principles and Methods

Edited by

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Contents

Contributors	xiii
Preface	xxi

Part 1 Fundamentals of greener synthesis

1	The Fundamental perspectives of greener synthesis	3
	Avtar Singh, Nirmaljeet Kaur, Anupama Parmar, Harish Kuma	r Chopra
	1.1 Introduction	3
	1.2 General synthetic methods in green chemistry	4
	1.3 Green solvents in synthetic methods	15
	1.4 Conclusions	26
	Acknowledgments	26
	References	26
2	The importance of green chemistry metrics	37
	Ana P.C. Ribeiro, Luísa M.D.R.S. Martins, David E.N. Bastos,	
	Ana F. Cristino, Rui Galhano dos Santos	
	2.1 Introduction	37
	2.2 Green metrics parameters	39
	2.3 Final remarks	59
	References	60
3	Greener synthesis at different scales	63
	Anandarup Goswami, Chandrasekar Kuppan, Shajeeya Amren	
	Shaik, Murthy Chavali	
	3.1 Introduction	63
	3.2 Synthesis at macroscale	64
	3.3 Greener synthesis at nanoscale	73
	3.4 Possibilities of the synthesis at industrial scale	89
	3.5 Summary and final remarks	91
	References	92
4	Role of greener syntheses at the nanoscale	107
	S. Gobalakrishnan, N. Chidhambaram, Murthy Chavali	
	4.1 Introduction	107
	4.2 Green syntheses	108

	4.3 4.4 4.5 Refer	Role of green synthesis Possibilities of the synthesis at industrial scale Conclusion and outlook ences	109 128 128 129
Par	rt 2	Greener methods: Physical and chemical methods	
5	One-	pot synthesis of nanomaterials	137
•		e Hameed, Amjad Hameed, Habibullah Nadeem, Tahir Farooq	10.
	5.1	Introduction	137
	5.2	General applications of nanomaterials	137
	5.3	**	141
	5.4		164
	Refer	ences	164
6	Ultra	sound assisted reactions	177
	Saure	ibh Puri, Anupama Parmar, Harish Kumar Chopra	
	6.1	Introduction	177
	6.2	Synthesis of heterocyclic compounds	179
	6.3	Condensation reactions	187
	6.4	Addition reactions	194
	6.5	Substitution reactions	196
	6.6	Reductions	200
	6.7	Photochemical reactions	204
	6.8	Coupling reactions	205
	6.9	Alkylation and acylation reactions	208
	6.10	Polymerisation reactions	210
	6.11	Oxidation reactions	212
	6.12	Miscellaneous	215
	6.13	Conclusion	234
	Refer	ences	234
7		sound-assisted process: Applications in reactions, extraction, surface modifications	247
	Aidé	Sáenz-Galindo, Adali O. Castañeda-Facio, José J. Cedillo-Portillo,	
	Paola	F. Vera-García, Patricia A. De León-Martínez, Raúl Rodríguez-Herrera	
	7.1	Introduction	247
	7.2	Basics of ultrasound	248
	7.3	Green chemistry and ultrasound	249
	7.4	Organic reactions assisted by ultrasound	251
	7.5	Ultrasound-assisted extraction of bioactive compounds	254
	7.6	Ultrasound application in food	257
	7.7	Surface modifications of nanostructures by ultrasound	258
	7.8	Conclusion	265
	Ackn	owledgments	265
	Refer	ences	265

8	"Synthesis of carbon nanomaterials by chemical vapor deposition		
	method using green chemistry principles"	273	
	Diana Litzajaya Garcia-Ruiz, Francisco Gabriel Granados-Martinez,		
	Carmen Judith Gutierrez-García, Jael Madai Ambriz-Torres, José de Jesús		
	Contreras-Navarrete, Nelly Flores-Ramirez, Francisco Mendez,		
	Lada Domratcheva-Lvova		
	8.1 Introduction	273	
	8.2 Chemical vapor deposition	276	
	8.3 Carbon nanotubes and related structures	279	
	8.4 Graphene	286	
	8.5 Carbon nanospheres	291	
	8.6 Carbon nanobeads	293	
	8.7 Graphene quantum dots	295	
	8.8 Carbon dots	296	
	8.9 Porous carbon nanomaterials	297	
	8.10 Conclusions and future perspective	299	
	Acknowledgments	300	
	References	300	
9	Synthesis of nanomaterials and compounds via microwave		
	irradiation as a greener alternative	315	
	Ana Sofia Ortega-Villarreal, Eugenio Hernández-Fernández, Israel López		
	9.1 Introduction	315	
	9.2 Microwave fundamentals	316	
	9.3 Microwave equipment	323	
	9.4 Features of microwave irradiation <i>versus</i> conventional heating	330	
	9.5 Special considerations in microwave-assisted synthesis	333	
	9.6 Microwave-assisted synthesis of nanomaterials	335	
	9.7 Microwave-assisted synthesis of organic compounds	343	
	9.8 Outlook and perspectives	350	
	References	350	
10	Ionic liquids as alternative greener solvents and catalysts in		
	organic transformations	359	
	Roli Mishra, Satyendra Mishra, Snehkrishna A. Chaubey, Yash B. Barot		
	10.1 Introduction	359	
	10.2 Application of ionic liquids in organic transformations	359	
	References	399	
11	Synthesis of nanomaterials by mechanochemistry	405	
	Ghada A.Al Bazedi, Aiman Eid Al-Rawajfeh, Mona A. Abdel-Fatah,		
	Ghada A.Al Bazedi, Aiman Eid Al-Rawajfeh, Mona A. Abdel-Fatah, Mohammad R. Alrbaihat, Ehab AlShamaileh		
	Ghada A.Al Bazedi, Aiman Eid Al-Rawajfeh, Mona A. Abdel-Fatah,	405 406	

	11.4 Mechanochemical synthesis of metal nano-particles	409
	11.5 Mechanochemical synthesis of complex ceramic oxides	410
	11.6 Mechanisms and kinetics of mechanochemical reactions	411
	11.7 Aldol condensation	413
	11.8 Mechanochemical synthesis of carbon nanotubes	414
	11.9 Mechanochemical dry synthesis of nanocrystalline semiconductors	414
	11.10 Mechanochemistry in the preparation of nanosized pharmaceutical	
	drugs	415
	11.11 Conclusions	415
	References	415
12	Greener catalysis for sustainable development of fine chemicals: An	
	environmentally benevolent approach	419
	Ateeq Rahman, Daniel Likius, Veikko Uahengo, V.S.R. Rajasekhar Pullobhotla	
	12.1 Introduction	419
	12.2 Zeolites	424
	12.3 Alkylation reactions promoted by molecular sieves	427
	12.4 S-Alkylation reaction for introducing peptide modification	427
	12.5 Benzylation of arylcyanamides performed via acid catalysis	
	of zeolites	429
	12.6 Synthesis of polysubstituted cyclopropanes catalyzed by basic zeolite	430
	12.7 Ni/SiO ₂ catalyzed organic transformations	431
	12.8 Hydrotalcites	433
	12.9 Biocatalysis	434
	12.10 The key points addressed in the introduction section are	437
	12.11 Conclusions	437
	Acknowledgements	438
	Funding	438
	Conflicts of interest	438
	References	438
13	Nanocatalyst: As Green Catalyst	445
	Shalini Chaturvedi, Pragnesh N. Dave	
	13.1 Introduction	445
	13.2 Green nanocatalyst	447
	13.3 Green reactions with nanocatalyst	451
	13.4 Conclusion	454
	References	454
14	Greener synthesis and applications of hybrid sol-gel-processed	
	materials	459
	Rita Bacelar Figueira	
	14.1 Introduction	459
	14.2 Sol–Gel method	460
	14.3 Research challenges on organic-inorganic hybrid sol–gel materials	476

	14.4 Concluding remarks	478
	Funding	479
	Acknowledgments	479
	Conflicts of interest	479
	References	479
15	Microwave assisted organic syntheses (MAOS): The green synthetic	
	method	491
	Leonardo Xochicale-Santana, C.C. Vidyasagar,	
	Blanca M. Muñoz-Flores, Víctor M. Jiménez Pérez	
	15.1 Introduction	491
	15.2 Microwave organic synthesis in the last two decades	491
	15.3 Solvent-free and green solvent in microwave organic synthesis	498
	15.4 Conclusion	518
	15.5 Multi component reactions under microwave irradiation	518
	References	531
16	Recent advances in microwave assisted syntheses of organometallic	
	and coordination compounds	543
	Jesús A. Lara-Cerón, C.C. Vidyasagar, Blanca M. Muñoz-Flores,	
	Víctor M. Jiménez Pérez	
	16.1 Introduction	543
	16.2 Complexes of group 5 metals (Vanadium)	544
	16.3 Complexes of group 6 metals (Cr, Mo, W)	544
	16.4 Complexes of group 7 metals (Mn, Tc, Re)	548
	16.5 Complexes of group 8 metals (Fe, Ru, Os)	552
	16.6 Complexes of group 9 metals (Co, Rh, Ir)	557
	16.7 Complexes of group 10 metals (Ni, Pd, Pt)	562
	16.8 Complexes of group 11 metals (Cu, Au, Ag)	564
	16.9 Complexes of group 12 metals (Zn, hg, cd)	567
	16.10 Complexes of group 13 metals (B and Ga)	570
	16.11 Complexes of group 14 metals (Sn, Ge, Pb)	572
	16.12 Lanthanides	574
	References	578
17	Glycerol: The liquid support for nanocatalysts	585
	David E.N. Bastos, Rui Galhano dos Santos, Luísa M.D.R.S. Martins,	
	Ana P.C. Ribeiro, Ana F. Cristino	
	17.1 Introduction	585
	17.2 Nano in chemistry/catalysis	587
	17.3 Synthesis of nanomaterials using greener protocols	588
	17.4 Other metals	605
	17.5 Conclusions	608
	References	608

Part 3 Greener methods: Biological methods

18	Gree	ner synthesis of nanomaterials and compounds from	
	biom	ass sources	615
	Prage	nesh N. Dave, Shalini Chaturvedi	
	18.1	Introduction	615
	18.2	Diverse modes of nanoparticle synthesis	618
	18.3	Principles of green biosynthesized chemistry	619
	18.4	Solvent system- based "green" synthesis	620
	18.5	Summary	621
	Refer	ences	625
19	Biosy	nthesis of bioactive zinc oxide nanoparticles	631
	Bubu	n Banerjee, Gurpreet Kaur	
	19.1	Introduction	631
		Biosynthesis of ZnO nanoparticles	632
	19.3	Applications of biosynthesized ZnO nanoparticles	652
		Conclusions	654
	Ackn	owledgements	655
	Refer	ences	655
20		n synthesis of nanocomposites using plant extracts and their	
		cations	663
		hit Ameta, Avinash Kumar Rai, Shubang Vyasb, Jayesh P. Bhatt,	
		h C. Ameta	
		Introduction	663
		Composites	664
		Green synthesis	666
		Conclusion	678
	Refer	ences	678
21		materials fabrication: bacteria-assisted synthesis	683
		m M. Saleh, Amal I. Hassan	
	21.1	Introduction	683
		Traditional methods of preparation	684
	21.3	Sol-gel techniques	684
	21.4	Manufacturing nanomaterials from nature	686
	21.5	Biosynthesis via bacteria	686
	21.6	Extreme importance of bacteria in the manufacture of	
		nanomaterials	689
	21.7	Nanotechnology in medicine	691
	21.8	Future applications of nanotechnology	692
	21.9		694
	Refer	ences	695

22	-	e-, fungi-, and yeast-mediated biological synthesis of nanoparticle	
		heir various biomedical applications	701
		sh Kumar Bachheti, Limenew Abate, Deepti, Archana Bachheti,	
		Madhusudhan, Azamal Husen	701
	22.1	Introduction	701
	22.2	Biological synthesis of nanoparticle using algae, fungi, and yeast	702
		Biomedical applications Conclusion	709
		ences	721 721
23	Indu	strial useful bioproducts and devices development from	
	micro	obial strains assisted nanosystems or nanoparticles	735
	Rajes	h K. Srivastava, Boris Ildusovich Kharisov,	
	Oxan	a Vasilievna Kharissova	
	23.1	Introduction	735
	23.2	Nanotechnology	737
	23.3	Application of nanotechnology in life sciences	741
	23.4	Conclusions	748
	Refer	ences	748
24	Plant	extracts: a key ingredient for a greener synthesis of plasmonic	
	nanoparticles		
	Carlo	os Puente, Israel López	
	24.1	Plasmonic materials	754
	24.2	Plant biology and secondary metabolites	757
	24.3	Chemistry of the plant-mediated synthesis	761
	24.4	Plant-mediated nanostructures obtainment	764
	24.5	Plant tissues in nanoparticles synthesis	768
	Refer	ences	779
25		-assisted biological methods for greener synthesis of nanomaterials	785
	Srinivasan Krishnan, Sheetal K. Bhardwaj, Shanhu Liu, Ruimin Xing,		
		hy Chavali	
	25.1	Introduction	785
	25.2	Bio-assisted green synthesis of nanomaterials	788
	25.3	Virus-mediated biosynthesis of NPs	789
	25.4	Synthesis of NPs by M13 bacteriophages	795
	25.5	Synthesis of Fe-based nanocomposite by a T4 bacteriophage virus	798
	25.6	Synthesis of gold NPs by virus-mediated reduction	800
	25.7	Conclusion	800
	Confl	ict of interest	801
	Refer	ences	801

26	Sustainable valorization of the abundant biodiesel byproduct-	
	The glycerol	807
	Sanaa Shehayeb, Samira Zaher, Leila Ghannam, Hassan Srour, Ali Kanj,	
	Janah Shaya, Iyad Karamé	
	26.1 Introduction	807
	26.2 Hydrogenolysis to propanediols (PDOs)	808
	26.3 Acetalization	815
	26.4 Etherification	821
	26.5 Esterification	823
	26.6 Carboxylation: carbonates of glycerol	824
	26.7 Catalytic dehydration of glycerol to acrolein	831
	26.8 Catalysts used for the glycerol dehydration	832
	26.9 Glycerol conversion into epichlorohydrin, mono-	
	chloropropane-diol and dichloro-propanol	834
	26.10 Polymerization and oligomerization of glycerol	836
	References	845
27	Fungi and metal nanoparticles	861
	Mitesh Patel, Malvi Surti, Arif Jamal Siddiqui, Mohd Adnan	001
	27.1 Introduction	861
	27.2 Biogenic synthesis of nanoparticles	862
	27.3 Fungi-mediated synthesis of nanoparticles	865
	27.4 Different nanoparticles synthesized by fungi	873
	27.5 Methods employed for the characterization of NPs	875
	27.6 Recent developments and applications of green synthesized	070
	myco NPs	876
	27.7 Conclusion	883
	References	884
28	Supercritical fluids as green solvents	891
	Amita Chaudhary, Ankur Dwivedi, Sreedevi Upadhyayula	
	28.1 Introduction	891
	28.2 Summary	913
	References	913
29	Artificial photosynthesis system for the reduction of carbon dioxide to	
	value-added fuels	917
	Waseem Raza, Khursheed Ahmad	
	29.1 Introduction	917
	29.2 Basic principles for understanding of CO_2 photoreduction	919
	29.3 Designing and engineering of photocatalytic materials for CO_2	/ 1/
	reduction	923
	29.4 Conclusion	930
	Acknowledgments	932
	References	932
Ind	ex	939

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Preface

Modern techniques to produce nanoparticles, nanomaterials, and nanocomposites are based on physical and chemical (of zerovalent (elemental) metals, their oxides and salts), various nanomaterials and nanocomposites are examined. Main (of zerovalent (elemental) metals, their oxides and salts), various nanomaterials and nanocomposites are examined. Main methods for green synthesis include the use of *natural products* (*i.e.*, tea, banana, coffee, wine, glucose, sugar, extracts of various plants or parts of plants, simple amino acids), acting as capping, chelating agents, and/or reductants (mainly polyphenols) in these processes. Indeed, a variety of plant biomolecules (vitamins, alkaloids, sugars, enzymes/proteins, etc.) can contribute to the formation and stabilization of nanoparticles. These techniques are environmentally friendly, simple, and mainly one-step method as a part of biosynthesis applies several bacteria for nanoparticle formation. The yield of final products, size and method as a part of biosynthesis applies several bacteria for nanoparticle formation. The yield of final products, size and morphology of nanoparticles, extraction of biologically produced metal nanoparticles will be discussed.

Currently, in addition to the biological methods above, several *physical* and *chemical* routes for nanomaterials fabrication can be considered as green methods, for example UV-irradiation, ultrasound- or microwave-assisted reactions (dry media synthesis), use of special microreactors, water, liquid and supercritical CO_2 , some ionic liquids, supercritical fluids, glycerol and polyethylene glycols as nonharmful solvents, green catalysis (or catalyst-free reactions) in organic synthesis, incorporation of reactants in clays, zeolites, silica, or alumina. Methods of green synthesis are frequently simple, inexpensive, and efficient, without hazards for the environment.

We are extremely grateful to all authors for their hard work in creation of the present Handbook and hope that this collection will be a useful guide for developing novel materials and reaction routes for a sustainable and clean future.

Editors Boris I. Kharisov Oxana V. Kharissova

Synthesis of nanomaterials by mechanochemistry



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11.1 Introduction

During the previous decades, several achievements in the creation of nanomaterials have pulled in tremendous considerations in multidisciplinary research areas along with commercial [1], agricultural [2] and medicinal [3] packages. Moreover, nanomaterials usually possess great mechanical, magnetic and electrical residences etc., which lessen the impurity on fabric surfaces and lead to superior functional advantages [4].

Nano-size particles of less than 100 nm in diameter are currently attracting more attention for the wide range of new applications in many fields and industries because of some effects like small particle dimension, high surface to volume ratio and their quantum confinement [5,6].

Nano chemistry is the understanding and control of matter of sizes roughly in the range of 1 to 100 nanometers. If one of the dimensions is in this range, it is considered a nanoparticle. Bulk materials when reduced to the nanoscale show some properties (melting point, physical strength, surface area, penetration power, electric conductance, optical effect, magnetism etc.) which are different from what they exhibit on a macro scale enabling unique applications. These materials can be either natural or engineered.

At nanoscale, gravity would become less important, whereas surface tension and van der Waal forces would become more important [7]

In the meantime, the remarkable surface properties of nanomaterials enrich them as special materials with better practical exhibitions material to progressively sensitive conditions [8,9].

The name mechanochemistry became carried out to the kind of reactions accomplished via mechanical strength. A narrower area, tribochemistry, became used for reactions generated by way of friction at some point of the milling

Mechanochemistry deals with chemical transformations induced by mechanical means such as compression, shear, or friction. In mechanochemical processes, the energy required for the activation of chemical reactions is usually provided by mechanical force as similar to thermochemistry, photochemistry, or electrochemistry, where energy is provided by heat, light, or electrical potential, respectively.

Mechanochemical processes have a long history and continue to be of high importance because these can quantitatively and rapidly promote solid-phase reactions only using nominal amounts (wet milling or liquid-assisted grinding). In conventional chemical synthesis, the solvent often plays a key role in energy dispersion, dissolution/solvation and transportation of chemicals.

Mass and energy transport may be hampered in solvent-free reactions. The efficient mixing process under ball milling or grinding can offer an effective way out from this problem, enabling the reactions between solids or solidified reagents in solvent-free conditions. Despite these advances in solvent-free molecular synthesis, solvents remain prevalent for the isolation of products in satisfactorily pure forms. "Liquid-assisted grinding" (LAG) has been introduced to provide a potential alternative to minimize the use of solvents in (nano)materials syntheses.2 In contrast to "dry milling" mechanochemical processes, LAG may offer advantages such as greater time efficiency, proper usage of materials and energy and can result in the discovery of new or improved reactivity and products [10].

The first part of the chapter is devoted to this subject and discusses various topics, including the theoretical background for Mechanochemistry and relation between milling conditions and phase formation, the course of mechanochemical reactions including amorphization and nucleation phenomena triggered by high-energy milling, the formation of intermediate phases during a reaction, the evolution of the crystal-lite size and the particularities of the nanocrystalline products and the preparation of nanosized pharmaceutical drugs.

11.2 Theoretical background

Generally, the mechanochemical treatment of solids leads to a positive influence on the solid – liquid kinetics [11,12]. It has been documented by [13] that the breaking of bonds in the crystalline lattice of solids brings about a decrease (ΔE^*) in the activation energy and an increase in the rate of leaching

$$\Delta E^* = E - E^* \tag{11.1}$$

$$k^* = k \exp\left(\Delta E^* / RT\right) \tag{11.2}$$

where E is the apparent activation energy of the non-disordered solid, E* is the apparent activation energy of the disordered solid k, R and T stand for the rate constant of leaching for the non-disordered solid, (the pre-exponential factor) gas constant and reaction temperature, respectively; k* is the rate constant of leaching for the disordered solid.

If $E > E^*$, then exp ($\Delta E^*/RT$) > 1 and thus it follows from eq. (11.2) that $k^* > k$, i.e., the rate of leaching of a disordered solid is greater than that of an ordered mineral.

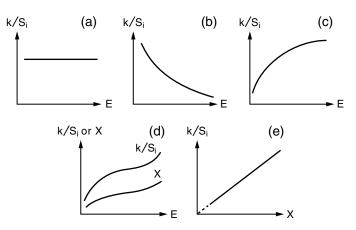


Fig. 11.1 Schematic diagrams representing the mutual dependence of physicochemical characteristics and reactivity of mechanically activated solids: k – the rate constant of leaching, S_i – surface area, X – structural imperfections, E – applied energy [14].

Senna have analyzed the effect of surface area and the structural disordering on the leachability of mechanically activated solids [14]. In order to solve the problem, whether the surface area or structural parameters are predominant for the reactivity the rate constant of leaching was divided by the proper surface area and plotted against the applied energy by milling (Fig. 11.1).

For example, if the rate constant of leaching divided by the surface area remains constant with respect to the applied energy, as shown in Fig. 11.1A, then the measured surface area may be the effective surface area and at the same time, the reaction rate is insensitive to structural changes. If, on the other hand, the value k/Si decreases with applied energy, as shown in Fig. 11.1B, then the surface area is probably not the effective surface area. In the third case where k/Si increases with increasing applied energy, as shown in Fig. 11.1C, the surface area Si, may be again the effective surface area, with an overlapping effect of the structural imperfection as a result of mechanical activation. Alternatively, when k/Si and X vary parallel to each other with E, as shown in Fig. 11.1D, or the value k/Si is proportional to X, as shown in Fig. 11.1E, it seems more appropriate to accept the chosen Si as an effective surface area [15].

11.3 Mechanochemical reactors

Processing in mechanochemical reactors can be completed in an assortment of ways. The most straightforward is the laboratory mortar and pestle. This hand processing forms can incite countless mechanochemical responses, which do not require the outperforming of a high-vitality hindrance. Ball plants are utilized when higher vitality is included and when the processing time requires hours or even days. Research center vibrators of the Wiggle-Bug type are exceptionally productive in processing small

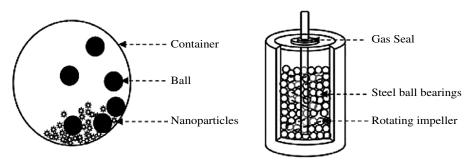


Fig. 11.2 A ball mill consists of a hollow cylindrical chamber [17].

samples. Exceptionally high-vitality vibrators, for example, fast attritors or treated steel ball plants of high effect are utilized for delayed high vitality processing as in mechanical alloying or amorphization of hard crystalline solids. This area features a portion of the significant utilizations of mechanochemistry in natural blend utilizing mortar and pestle, high speed ball milling (HSBM) process, high intensity grinding (HIG) [16].

11.3.1 Ball milling

This mechanical method of production of nanomaterials works on the principle of controlled impact. The size reduction is achieved through the impact caused when the balls drop from the top of the chamber containing the source material.

A ball mill consists of a hollow cylindrical chamber (Fig. 11.2) which rotates about a horizontal axis, and the chamber is partially filled with small balls made of steel, tungsten carbide, zirconia, agate, alumina, or silicon nitride having diameter generally 10 mm. The inner surface area of the chamber is lined with an abrasion-resistant material like manganese, steel, or rubber. The magnet, placed outside the chamber, provides the pulling force to the grinding material, and by changing the magnetic force, the milling energy can be varied as desired. The ball milling process is carried out for up to approximately 150 h to obtain uniform-sized fine powder (Fig. 11.3).

In high-energy ball milling, vacuum or a specific gaseous atmosphere is maintained inside the chamber. High-energy mills are classified into attrition ball mills, planetary ball mills, vibrating ball mills, and low-energy tumbling mills. In high-energy ball milling, formation of ceramic nano-reinforcement by in situ reaction is possible.

It is an inexpensive and easy process which enables industrial scale productivity. As grinding is done in a closed chamber, dust, or contamination from the surroundings is avoided. This technique can be used to prepare dry as well as wet nano powders. Composition of the grinding material can be varied as desired. Even though this method has several advantages, there are some disadvantages. The major disadvantage is that the shape of the produced nanoparticles is not regular. Moreover, energy consumption is relatively high, which reduces the production efficiency. This technique is suitable for the fabrication of several nanocomposites, which include Co- and Cu-based nanomaterials, Ni-NiO nanocomposites, and nanocomposites of Ti, C [18].

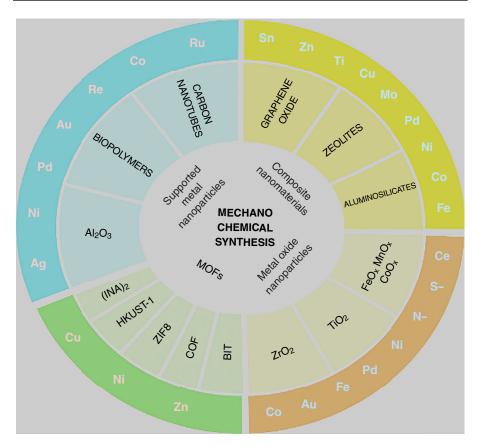


Fig. 11.3 Pictorial representation of different types of mechanochemically synthesized (nano) materials [25].

11.4 Mechanochemical synthesis of metal nano-particles

Mechanochemical reduction could be an effective route for the synthesis of metal nanoparticles (generally noble metals) with improved structural and catalytic properties. Mechanochemically prepared Ag/Al₂O₃ nanomaterials have been prepared and tested in the selective catalytic reduction (SCR) of NOx using hydrocarbons in the presence and absence of hydrogen [19,20].

The catalyst exhibited a remarkable increase in activity at lower reaction temperatures as compared to traditional catalysts prepared via standard wet impregnation methods. The enhanced activity of the mechanochemically synthesized catalyst was related to surface modifications that provided an increased affinity towards hydrocarbons relative to water, consequently reducing the activation barrier for the reduction of NOx. The straightforward two-step process involved a dry mixing of a precursor metal salt (e.g., a metal acetate) with carbon nanotubes (single- or multiwalled) followed by heating in an inert atmosphere in the absence of any solvent, reducing agent or electric current. The proposed methodology can be, in principle, scalable to multigram quantities and generally applicable to various other carbon substrates (e.g., Carbon nanofibers, expanded graphite and carbon black) and many metal salts (e.g., Ag, Au, Co, Ni and Pd acetates) [21].

Generally, mechanochemical synthesis has attracted considerable scientific and technical interest in recent years as a consequence of the unique nanostructures and properties developed by this process. High-energy milling can be used to induce a wide variety of solid-solid and even solid-liquid reactions [22,23]. A chemical reaction is believed to occur at the interfaces of the nanometer sized grains that are continually regenerated during milling. As a consequence, reactions, that would normally require high temperatures to occur, due to separation of the reacting phases by the product phases, can occur at lower temperatures in a ball mill. An important feature of the mechanochemical synthesis is the rapid refinement of the particle microstructure, i.e. grain size or crystallite size, during milling. While powder particle sizes generally decrease only to the micrometer level, a nanometer grain size can develop within each particle [23].

Farit Kh. Urakaev 2012. Have studied the mechanochemical synthesis of nanoparticles by a dilution method. The results showed that studying the kinetics of mechanochemical processes can be recommended to find the specific features for the numerical estimation of the mass transfer coefficient in a mechanochemical reactor [24].

C.-F. Zhou et al., 2009 studied the synthesis of polyaniline nanofibers, by a simple solid-state mechanochemical reaction and template-free method. Another study by Venkatesha Narayanaswamy et al., 2019 regarding the synthesis of Graphene oxide-Fe₃O₄ nanocomposites by a mechanochemical method to yield extremely heterogeneous particles. The nanocomposites milled for deferent extents of time have shown deferential behavior for magneto thermic heating. The magnetic composites synthesized by the ball milled method were able to retain the functional groups of graphene oxide [25].

From supported metal nanoparticles, composite nanomaterials to metal oxide nanoparticles and metal organic frameworks (MOFs) including covalent organic frameworks (COF). Examples of relevant materials include zinc-based ZIF-8 structures (BIT-11), Cu (INA)₂ and Cu-containing HKUST-1 as well as supported noble metals on aluminosilicates, and graphene [26].

11.5 Mechanochemical synthesis of complex ceramic oxides

In general, complex ceramic oxides exhibit a variety of properties, making them attractive for a diversity of different applications. The main effects associated with each direct mechanochemical synthesis (regarding the formation of the final product at once at some stage in milling) and the mechanochemical activation-based synthesis (relating to excessive-electricity milling, used to increase the reactivity of the powders, which is accompanied through an annealing step to set off the formation of the very last product) of complex oxides with a variety of properties is investigated [27].

Ferroelectric, antiferroelectric, piezoelectric, relaxor and multiferroic oxides as well as oxides with magnetic, semiconducting and catalytic properties are highlighted, in particular the influence of mechanochemical activation on both the phase formation during subsequent annealing and the preparation of the final ceramics, the influence of milling conditions, such as humidity, and the effect of the hydration state of the reagents on the course of the mechanochemical reaction as well as the issue of contamination during milling [27].

In metallic–ceramic composite powder formation, the preparation of metals and alloys by reducing their salts or oxides with more reactive metals is commonly known as metallothermic reduction. This reaction is expressed in general by the equation:

$$M_A X + M_B > M_A + M_B X \tag{11.3}$$

where a metal M_A is reduced by a more reactive metal M_B (reductant) to the pure metal M_A . $M_A X$ and $M_B X$ are oxides, chlorides, sulphides and other salts.

Metallothermic reactions are characterized by a large negative free-energy change and therefore they are thermodynamically feasible at room temperature [27].

Mechanochemical synthesis has recently received a lot of interest for processing ceramic powders, opening up better approaches for creating mechanically significant oxides with complex compositions one of the most significant research regions is the investigation of the mechanisms and kinetics of mechanochemical reactions, which structure the basis of the further advancement of mechanochemical synthesis [19,21,27].

11.6 Mechanisms and kinetics of mechanochemical reactions

Based on the theory of glancing collision of rigid bodies, the theoretical calculation of t–P–T conditions and the kinetics of mechanochemical processes are possible for the reactors that are intended to perform different physicochemical processes during mechanical treatment of solids. According to the calculations, the 'physicochemical' effect of mechanochemical reactors is due to short-time impulses of pressure ($\Delta P = \sigma \sim 1010-1011$ dyn cm–2) with shift, and temperature $\Delta T(x, t)$. The highest temperature impulse $\Delta T \sim 103$ K are caused by the 'dry friction' phenomenon.

Typical spatial and time parameters of the impact–friction interaction of the particles with a size R ~ 10–4 cm are as follows: localization region, $\Delta x \sim 10-6$ cm; time, $\Delta t \sim 10-8$ s. the effect of short-time contact fusion of particles treated in various can play a key role in the mechanism of activation and chemical reactions for wide range of mechanochemical processes.

The spatial and time characteristics of the fused zone are such that quenching of non-equilibrium defects and intermediate products of chemical reactions occurs; solidification of the fused zone near the contact point results in the formation of a 'nanocrystal or Nano amorphous state'. The calculation models and the kinetic equations permit quantitative estimates of rate constants to be performed for any particular processes of mechanical activation and chemical transformation of the materials in ball mills [28].

The main merits of applying mechanochemistry to various functional materials are charge transfer across a boundary of dissimilar solids with simultaneous polarization, size reduction and homogenization without external heating. This could prompt development in organic syntheses starting from the solid state, involving solvent-free and subsequently green chemical processes. Affordable metals could be used instead of noble metals in catalysis process since the mechanical stress applied brings excited state. Mechanochemical processes is expected to be applied further in different fields including biocompatible complexes and pharmaceutics [29,30].

Seyedia et al.,2015 clarified that Nano-size particles of less than 100 nm in diameter are currently attracting more attention for the wide range of new application in many fields and industries because of some effects like small particle dimension, high surface to volume ratio and quantum confinement, [31–33] Mechanochemical processing is a new method involving the mechanical activation of solid-state chemical reactions displacement during ball milling which has been widely researched in the recent years and were used to synthesize of metallic, oxide and sulfide nanoparticles, [31,32]. The other competitor methods that have been developed to synthesize nanoparticles include sol-gel, vapor phase condensation, sputtering, wet chemical precipitation and hydrothermal synthesis.

The main advantage of mechanochemical synthesis is that in this method the process carried out in solid state and agglomeration did not occur in comparison to the above methods. In addition, the control of the overall particle size distribution in this method is easier, Yang et al. (2004). During milling fracture, deformation and welding of the reactants take place. Chemical reactions occur at the interface of reactants, consequently the chemical reactions that require high temperature will occur at low temperature without any external applied heat, [31, 35,36]. Mechanochemical synthesis was done by displacement reaction according to the following reaction:

$$AxC + yB = xA = ByC$$
 (11.4)

where AxC and B are the reactants, A is favorable product and ByC is by-product of the reaction. By choosing suitable conditions such as milling parameters, suitable BPR and the stoichiometric ratio of starting materials, mechanochemical processing can be used to synthesize nanocrystalline particles. After the milling process, the nanoparticles will be surrounded with by-product materials which are dispersed within this soluble salt matrix, selective removal of the matrix phase must be done by washing the resulting powder with appropriate solvents.

After that nanoparticles will be formed as small as 5 nm, [34,36]. Nowadays fabrication of iron oxide nanoparticles has attracted a lot of attention due to their unique properties and industrial capability.

11.7 Aldol condensation

The reaction of two carbonyl compounds, one as a nucleophile (in the form of an enol or enolate derivative) with another acting as an electrophile, gives rise to a b-hydroxycarbonyl compound. This on dehydration produces an a,b-unsaturated carbonyl compound which is commonly referred to as the aldol condensation reaction. These reactions are utilized to underivative ketones and aldehydes with simple acid or base catalysis, the reaction is usually carried out using preformed enolates which serve both to increase the driving force of the reaction and to ensure that the desired chemoselectivity is achieved [30].

11.7.1 Reformatsky reaction

Toda et al. demonstrated that Reformat sky reactions proceed efficiently in the absence of solvent. The solvent-free reaction was carried out by mixing aldehyde or ketone, a-bromo ester and Zn-NH₄C1 in an agate mortar and pestle while keeping the mixture at room temperature for several hours. Treatment of the aromatic aldehydes with ethyl bromoacetate and Zn-NH₄C1 gave the corresponding Reformatsky reaction products in very high yield (80–94 percent) (Fig. 11.4).146 The reaction yield was found to be much better than that obtained by the reaction in dry benzene–ether solution (61–44 percent); the additional advantage of solvent-free Reformatsky reaction is that it does not require the use of an anhydrous solvent [30].

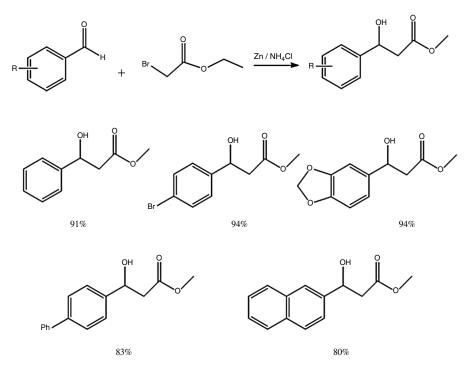


Fig. 11.4 Synthesis of b-hydroxy ester [30].

11.7.2 Luche reactions

Toda and coworkers also found the Luche reactions proceed efficiently in the absence of solvent, although Grignard reactions under similar conditions are not very efficient and give more reduction product than the normal carbonyl addition product. The solvent-free Luche reactions can be carried out by a very simple procedure and give very high yield in comparison to the reaction under conventional reaction conditions using solvent [30,35–36].

11.8 Mechanochemical synthesis of carbon nanotubes

In a more recent report, carbon nanotubes were also utilized as support for Pd NPs using a similar solvent less dry milling method in the absence of any reducing agent or electric current [25]. 16 Pd NPs (1–3 nm size) could be uniformly dispersed on the support and the mechanochemically prepared Nano catalyst exhibited excellent activities in Suzuki cross coupling reactions with high turnover numbers (TON) and turnover frequencies (TOF). Pd NPs prepared by thermal annealing (300 °C) formed larger NPs due to agglomeration as compared to Pd NPs prepared at room temperature, thereby leading to reduced catalytic activities. A similar mechanosynthesis technique can be utilized to prepare functionalized ultra-small Au NPs in gram scale using a bottom-up approach [17]. The size of AuNPs could be controlled by varying the ligand/precursor ratio, milling time and/or the nature of the ligand [25].

Along these lines, a simple and scalable method for the preparation of supported gold, palladium and gold–palladium bimetallic catalysts via the physical mixing of the acetate salts of metals followed by a simple heat treatment was also recently described.

11.9 Mechanochemical dry synthesis of nanocrystalline semiconductors

Nanocrystalline semiconductors, also called quantum dots, appear to be interesting objects for studying basically novel properties of matter. In general, reducing the size of semiconductors down to the nanometer length scale is expected to increase the energy gap of the semiconductor structure and, consequently, to give rise to shorter wavelengths optical emission spectra relative to that of bulk semiconductors [1].

Tatykaev et al., have successfully prepared nanoparticles of silver chloride dispersed within a soluble salt matrix by means of powders grinding in a mortar (z = z2 = 3:64) and in rotating laboratory mill (z = z1 = 7:22) via reaction NH₄Cl + A gNO₃ + zNH₄NO₃ = (z + 1)NH₄ NO₃ + AgCl. The synthesis of silver chloride by soft mechanochemical reaction, revealed by XRD, and that the sizes (L) of synthesized particles are L(z2) = 132 nm, L(z1) = 151 nm. The SEM examination of the reaction products suggests the formation of silver chloride particles with wide ranges of size distribution, commonly less than 200 nm. Thermal analysis allowed identification of the optimal temperature range to yield nanoparticles of a desired phase [37].

11.10 Mechanochemistry in the preparation of nanosized pharmaceutical drugs

During KOFST project at the College of Pharmacy of Pusan National University, Baláž et al. clarified that "Mechanochemical preparation of nano – sized pharmaceutical drugs for the application in cancer therapy". The obtained results are good starting point for the future research activities. Arsenic sulphides belong to the very progressive compounds in pharmaceutical applications. In medicine, there is a great need for an effective treatment of cancer, particularly haematological cancer including leukaemia and lymphomas. Further, there is a great need for orally active anticancer agents. Drugs with arsenic sulphides as active components are good candidates for such demands [15].

11.11 Conclusions

Mechanochemistry has made significant progress during the recent decade. The accessible hypothetical, experimental and applied results are outlined in this chapter. The distinguished hallmarks of mechanochemistry include: impacting reactivity by creating interphases (particularly in composite and multi/phase systems), abandons in solids and by presence of relaxation phenomena, making great crystalized cores of nanoparticles with disordered near surface shell regions, performing simple, dry, time-convenient one-step syntheses, preparing nanomaterials with properties set in advance, scaling up to industrial production, and empowering work under environmentally friendly and essentially waste-free conditions.

In general, there is still a long way to go in mechanochemistry. Mostly the clarification of the mechanism of the reactions and industrial application of mechanochemistry in nanotechnology are the issues. However, there is no doubt that mechanochemistry should be incorporated in textbooks of not only solid-state, but additionally other branches of chemistry. A similar idea was proposed by Wilhelm Ostwald (The Nobel Prize in Chemistry 1909) long time ago.

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Index

Page numbers followed by "f" and "t" indicate, figures and tables respectively.

A

Acceptable green analysis, 50 Acidification potential (AP), 57 Acoustic cavitation, 4 Actinomycetes, in NP synthesis, 76 Advanced oxidation process (AOPs), 251, 419 Aldol condensation, 413 Algae, 702–703 Algae-mediated synthesis, 77 Alkylation reactions, 427 2-alkyl-2-oxazolines, 67 Amidino ligand, 548 Amino acid ionic liquids (AAILs), 370 Analytical Eco-Scale, 50-51, 50t Analytical Method Volume Intensity (AMVI), 53, 55f Antibacterial agent, 880 Antibacterial Mn(II) complexes, synthesis of, 551f Antifungal activity, 880 Antiviral activity, 880 Aqueous epoxide ring-opening polymerization (AEROP), 66 Arene-iron complexes, microwave synthesis of, 552f Arylazoimidazoles ruthenium complexes, formation of, 556f ASDIC system, 177 Aspartame, 435f Astatine radiopharmaceuticals, microwave synthesis of, 561f Atom economy (AE)39-40 Atom utilization, 40 Attenuated total reflectance (ATR), 643 Azole-metal complexes, microwave synthesis of, 561f

B

Bacteria-mediated synthesis, 76 Baran'spercent ideality metric, 59 Benzonitrile, 65 Benzothiazole, 544

chromium complex, 546f mixed nickel, microwave synthesis of, 562f vanadium complex synthesis of, 544f Benzylation of arylcyanamides, 429 Betti reaction, 528 Biaryl and alkynes, 65 Biginelli reaction, 527 Bimetallic nanoparticles, 607 Bioactive compounds and ultrasound, 254, 254fBio-assisted synthesis of nanoparticles, 790f Biocatalysis, 434-436 Biomedical applications, 709, 719f antimicrobial activity, 709 antioxidant property, 720 cytotoxicity activity, 720 Biosynthesis and bacteria, 686 Biosynthesized ZnO nanoparticles, application of, 652 acaricidal activity, 653 antibiofilm activity, 654 anticancer activity, 653 antidiabetic, 654 antiinflammatory activity, 653 antimicrobial activity, 653 antioxidant activity, 652 antiproliferative, 654 antituberculosis, 654 larvicidal activity, 654 photocatalytic activity, 654 Bis(indolyl)methanes, 71 Bis (2-hydroxyethyl) terephthalate (BHET), 264 Boronates ester, 570 Boron Schiff bases (BOSCHIBA), 571 synthesis of, 571f Bovine papilloma virus (BPV), 794 Bronsted acidic ionic liquid, 389 Brønsted acidity of zeolites, 426 Buchwald-Hartwig amidation reaction, 519

С

Cancer treatment, nanotechnology in, 691 Carbon-based NHs, 89 Carbon dots (CDs), 296 Carbon economy, 42-43 Carbon footprint, 57 Carbon nanobeads, 293, 294f Carbon nanomaterials, 276 Carbon nanospheres, 291 Carbon nanotubes (CNTs), 279, 286f functionalization of, 160 MWCNTs. 159-160 one-pot synthesis of, 158 bio-inspired, 160 Carbon spheres., 293f Carboxylation, 823 Carboxyl-functionalized poly(ionic liquid) (CFPIL), 392, 393f Catalysts, 419, 437 Catalytically assisted Chemical Vapor Deposition (CCVD), 291 Cavitation process, 177, 248f Cell apoptosis, in cholesterol synthesis, 254. See also Ultrasound Cellulose nanocrystals (CNC), 71 Chemical vapor deposition reactor, 277f Chemoenzymatic peptide synthesis (CEPS), 72 CHeteroatom bond, 497 types of, 498t Chitosan (CS), 151 Cinnamate ligands, 574 Cinnamic acid, synthesis of, 575f Ciprofloxacin (CIP), 671 Cisplatin, formation of, 563f Claisen reaction, 492 Cobalt complex, microwave synthesis of, 557f-558f metallocene, ORTEP diagram of, 560f Collagen, 664 Colorimetric method, 605 Composites, 664 advantages, 665 ceramic/mineral-based, 676 defined, 664 graphene-based, 673 limitations, 665 matrix-type, 665f

metal-based, 666 natural, 664 polymer-based, 671 Computational nanotechnology, 615 Conjugated linoleic acid (CLA), 64 Conventional sol-gel technique, 253 Copper, 598 Copper-based MOF (Cu-MOF-74), 70 Cost-effective extraction method, 758 Coumarin-3-carboxylic acid, 72 Coupling reactions, 492 Cowpea chlorotic mottle virus (CCMV), 792 Cowpea mosaic virus (CPMV), 792 Cr-based MOF, 70 Cresol isomers, 419, 420t, 422t Cresols catalytic oxidation, 423f Cross-coupling reactions, 497 Cyanocobalamins, 256. See also Ultrasound Cyclodextrin-based MOF, 69 Cysteine sulfhydryl group, 427

D

Diels Alder reactions, 373, 373f-374f, 514f AlCl₃, 376f of 1,4-benzoquinone with isoprene and 2,3-dimethyl-1,3-butadiene, 378, 379f with [Bmim] [NTf₂] as reaction media, 377, 378f borenium ionic liquid as catalyst, 378, 380f chiral indium complex, 376f chiral indium complex with, 376, 376f with chiral ionic liquid, 377, 377f chlorometallate (III), chlorogallate (III) and chloroaluminate (III) as catalysts, 378, 379f domino reactions, 378 hydrogenbutylimidazolium tetrafluoroborate, 375f Lewis acidic catalysts for, 378 with MacMillan catalyst, 380, 381f of N-phenyl imine with 1-methoxy-3-(trimethylsilyl) oxybuta-1,3-diene, 374, 374f with pyridinium based ionic liquids [EtPy] as solvent, 375 of Spiro [cyclohexane-1,3-indolin], 381f between substitute cyclopentadiene and methyl methacrylate, 375 water and RTILs, 376, 377f

Diethyl maleate, 419 Diffuse reflectance spectra (DRS), 638 Diffusion, 904 Dihydropyridines, 527 Dimethyl carbonate (DMC), 69 1,1-diphenyl-2-picrylhydrazyl (DPPH), 652 Dipolar polarization, 498 Dipyrromethanes, 66 Dirhenium paddlewheel complexes, synthesis of, 550*f* Disease detection, nanotechnology in, 691 Doebner-Miller reaction, 526 Dry nanotechnology, 615

Е

Eco-friendly" techniques, 787 Effective mass yield (EMY), 43-44 Electrochemical double-layer capacitors (EDLCs), 159 Electrophilic substitution, 263 Endothermic reactions, 498 Energy consumption (EC), 57 Engineered nanomaterials (ENM), 663 Environmental assessment tool for organic syntheses (EATOS), 40, 41f Environmental (E) factor, 40-41, 41t, 43t difficulties with, 42 Environmental Protection Agency (EPA), 249 Epichlorohydrin, 834 Essential oil of ginger (EO-G), 667 Ester solvents, 913 Ethylene oxide, preparation of, 39 Ethyl oxalate benzylidene hydrazides, 65 European Technology Platform for Zero Emission Fossil Fuel Power Plants. 917 Eutectic solvents, 256. See also Ultrasound Eutrophication potential (EuP), 57 Exothermic reactions, 498 Extracellular synthesis, 701

F

Fac-tris-ortho-metalated iridium(III), microwave-assisted synthesis of, 562f
Fe-based nanocomposite, 798
Fenton reaction, 251
Fe₃O₄/Chitosan NPs, 437
Fibroblast growth factor (FGF), 879
Fluoranthenes, 65
Folin-Ciocalteu reaction, 762 Food, ultrasound application in, 257 Fourier-transform infrared spectroscopy (FTIR), 736, 876 Fullerenes, 684 Functional ionic liquids (FILs), 360 Fungi, 702–703 Fungi-mediated synthesis, 77 Furfural, 67

G

Gas chromatography (GC), 905 Germanium (IV) complexes, synthesis of, 574f Global warming potential (GWP), 57-58, 57f-58f Glucamine, 68 Glyceraldehyde radicals, 606 scavenging effect of, 606f Glycerol, 64, 505 ball and stick representation of, 588f catalyst-free synthesis of thiazole derivatives, 508f catalysts, 833t catalytic dehydration of, 831 for chemical reduction of silver and gold, 605 dehydration mechanism of, 832, 832f gold nanoparticles synthesis by, 607f metal ions in. 605 oligomerization process, 837, 839 polymerization and oligomerization of, 836 polymerization process, 839 synthesis of, 606f and transition metal, 601 Glycerol acetalization, 815, 820 Glycerol esterification, 823-824 Glycerol etherification of, 821 Glycerol transformations, 808f Glycopolymers, 72 Gold. 607 complexes, syntheses of, 567f Gold NPs (AuNPs), 144-145 Golgi bodies, 683 Graphene, 258, 259f Graphene oxide, 286, 291 Graphene Quantum Dots (GQDs), 295 Green analytical chemistry (GAC), 47, 49 Green Analytical Procedure Index (GAPI), 53, 53f, 54t

Green aspiration level (GAL), 58-59 Green biosynthesized chemistry, 619 principles of, 619 Green Certificate, 51-52, 52f Green chemistry, 445, 447 defined, 615 principles, 3, 37, 38f synthetic methods in, 4 and ultrasound, 249 Greener synthetic strategies, 75f, 63 at industrial scale, 89-91 advantages, 91f large-scale, 90 scaling-up, 90 at macroscale, 64 biomaterials, 71–72 metal oxides, 67-69 organic compounds, 64-66 organometallic complexes and MOFs, 69-71 pharmaceuticals, 72-73 polymers, 66-67 at nanoscale, 73, 82t actinomycetes, in NP synthesis, 76 algae-mediated synthesis, 77 bacteria-mediated synthesis, 76 bottom-up approach, 74 carbon-based NHs, 89 factors affecting, 79 fungi-mediated synthesis, 77 green polymer NCs (GPNC), 89 nonbiogenic greener approaches, 80-81 polymer NPs, 89 production of nanomaterials, nanocomposites (NCs), and hybrids, 81 sustainable synthetic approaches, 74 top-down approach, 74 using biogenic resources, 75-76 using microorganisms, 79-80, 79f using nonbiogenic conditions, 75 using plant extracts, 78 virus-mediated synthesis, 78 Green metric parameters, 38t analytical chemistry metrics, 47 analytical Eco-Scale, 50-51, 50t Analytical Method Volume Intensity (AMVI), 53, 55f Green Analytical Procedure Index (GAPI), 53, 53f, 54t

Green Certificate, 51-52, 52f National Environment Methods Index (NEMI), 48-49, 48f-49f industry metrics acidification potential (AP), 57 carbon footprint, 57 energy consumption (EC), 57 eutrophication potential (EuP), 57 global warming potential (GWP), 57-58, 57f-58f green aspiration level (GAL), 58-59 Life Cycle Assessment (LCA), 55-56, 56f ozone formation potential (OFP), 57 solid waste production (SWP), 57 organic chemistry metrics (OCM), 39 atom economy (AE), 39-40 atom efficiency (AEf), 40 atom utilization, 40 carbon economy, 42-43 effective mass yield (EMY), 43-44 environmental assessment tool for organic syntheses (EATOS), 40 environmental (E) factor, 40-41, 41t, 43t mass intensity (MI), 44 product mass intensity (PMI), 44-45 reaction mass efficiency (RME), 44 solvent and catalyst environmental impact parameter, 47 stoichiometric factor, 45-47, 46t-47t Green nanocatalyst, 447, 448t aluminum oxidenanoparticles, 450 gold nanoparticles, 449 iron nanoparticles, 450 nickel-platinum nanoparticles, 450 palladium-gold nanoparticle, 449 palladium nanoparticles, 447, 448 platinum nanoparticles, 449 rhodium nanoparticles, 450 silica nanoparticles, 447 silver nanoparticles, 449 titania nanoparticles, 449 zinc oxide nanoparticles, 450 Green Nanoscience, 787 Green nanotechnology, 446f Green polymer NCs (GPNC), 89 Green solvents, in synthetic methods, 891, 911 $AgClO_4, 22$ fluorinated salts of Ag, 23

ionic liquids, 15-16 IL, 22 Fe₂O₃@[EMIM][BF₄] IL, 20 2-hydroxyethanaminium formate IL, 18 IL-carrying PdNPs, 17 nitrile functionalized ILs, 16 OH-functional ILs (FILs), 16 phosphonium and imidazolium-based ILs. 21 polymeric ILs (PILs), 22 supercritical carbon dioxide (scCO₂), 15, 23 formation of Ru- and Rh-based NPs, 24 properties of, 23 in synthesis of bimetallic NPs, Pt-rich NPs. 23 in synthesis of CuNPs, 25 in synthesis of flower-like ZnONPs, 25 in synthesis of PdNPs, 24-25 in synthesis of PtFe/ordered mesoporous carbon (OMC) catalyst, 24 in synthesis of Pt-W nanocomposite, 24 Green syntheses, 107, 108f, 110f advantages, 109, 109f economic and environmental benefits, 110 at industrial scale, 128 metal NPs, 110, 112t copper NPs, 111 iron NPs, 111-112 titanium NPs, 111 using Allium eriophyllum leaves extract. 111 using Eclipta prostrata leaves extract, 111 using Garcinia mangostana leaf extract,111 using Vaccinium floribundum extract, 112 metal oxide NPs, 120 mesoporous ZnO nanocrystals, 121 monodispersed CuONPs, 122 nano-sized nickel oxide (NiO) photocatalyst, 122 nickel oxide (NiO) nanorods, 122 using Abelmoschus esculentus (okra) mucilage, 121 using aloe vera extract solution, 122 using Annona muricata, 122 using Calliandra haematocephala dry leaves, 121 using Cinnamomum tamala, Cinnamomum verum, Brassica oleracea var. Italica plant extracts, 121

using flaxseed (Linum usitatissimum), 121 using Limonia acidissima Christmas juice, 122 using Psidium guajava leaf extract, 122 ZnONPs, 120-121 nanocomposites, 126t AgNPs decorated P-doped g-C3N4 (Ag/ PCN) composites, 124 chitosan cross-linked silver NCs (CSHD-Ag NC), 123 Cu/MgO NC from CuCl₂ and MgO, 124 Fe₃O₄ NPs over N-doped porous carbon (Fe₃O₄/NPC), 124 few-layer graphene/silver NPs, 125 graphene-Ag (GAg) NC, 123 graphene metallic NPs, 123 lichen-reduced graphene oxide (LrGO)bimetallic NP (LrGO-AgAu) NCs, 125 RS-AgNPs, 123 silver-chitosan NC, 125 silver/polystyrene (AgNPs/PS) nanocomposite (NC), 123 Zeolite/Fe₂O₃ NCs, 125 nanohybrids, 127 GSGNPs, 127 of reduced graphene oxide/Fe3O4/Ag ternary nanohybrid (rGO/ Fe₃O₄/ AgNH), 127 of sheet-like cellulose nanocrystal-zinc oxide (CNC-ZnO) nanohybrids, 127 of tea polyphenol-assisted Ag-nanodiamond (Ag-TPND) hybrid, 127 noble-metal NPs of Palladium (Pd) NPs, 119 of Platinum (Pt) NPs, 120 using aqueous ethanol and methanol extracts of Achillea millefolium (family Asteraceae), 119 using aqueous ethanolic extract of black pepper, 119 using Coffea arabica seed (CAS) extract, 117-118 using Euphrasia officinalis leaf extract, 119 using Ononidis radix extract, 120 nonmetal NPs, 118t from ascorbic acid, 116 biogenic sulfur NPs, 115

Green syntheses (Continued) of fluorescence carbon dots (CDs), 115 - 116from folic acid, 116 selenium NPs, 112-114 spice-derived C-dots, 116 sulfur NPs, 114 using carrot juice, 115 role of, 109 using plants or plant parts, 108 Green synthesis, 666 ceramic/mineral-based composites, 676 graphene-based composites, 673 metal-based composites, 666 of nanoparticles, 615 paths in, 620 polymer-based composites, 671 Green synthesis methods., 788f Green synthetic method, 503f Groebke-Blackburn-Bienaymé, 520 Group 6 metals, 544 Group 7 metals, 548 Group 8 metals, 552 Group 9 metals, 557 Group 10 metals, 562

H

Hantzch reaction, 525*f* Hantzsch dihydropyridine synthesis, 524 Heteroleptic copolymer complexes, synthesis of, 555*f* High-resolution transmission electron microscopy (HRTEM), 643 Humic acid, 64 Hydrotalcites, 433, 433*f* Hydroxides, 433 2-hydroxyethanaminium formate IL, 18

I

Ibuprofen-nicotinamide (IBP-NCT), 73 IL-carrying PdNPs, 17 Imidazolidin-4-one, 380 Intracellular synthesis, 701 3-iodine-1-methyl-1H-indoles, 252 Ionic conduction, 498 Ionic liquids, 15–16, 510 [AD]PO₄, 18 aldol condensation in, 360, 361*f*–364*f*, 364 appel reactions in, 364–366, 365f–367f conversion of alcohols, 366, 366f diphenylphosphinite (IL-OPPh₂) for, 367, 369f halogenating agents [Hmim] X for, 367, 368f phosphonium-based halide exchange reaction, 367, 368f pyridinium based ionic liquid for, 367, 367f application of organic transformations, 359 Baylis-Hillman reaction in, 369 of aldehydes and acrylates, 372f of aliphatic, aromatic, and α , β -unsaturated aldehydes, 370 f presence of AAILs as catalysts, 371f presence of chiral ILs, 369f, 371f quinuclidine functionalized ionic liquids in, 372f selenium functionalized IL with DABCO in, 373, 373f Diels Alder reactions in, 373, 373f-374f AlCl₃, 376*f* of 1,4-benzoquinone with isoprene and 2,3-dimethyl-1,3-butadiene, 378, 379f with [Bmim] [NTf₂] as reaction media, 377, 378f borenium ionic liquid as catalyst, 378. 380f chiral indium complex, 376f chiral indium complex with, 376, 376f with chiral ionic liquid, 377, 377f chlorometallate (III), chlorogallate (III) and chloroaluminate (III) as catalysts, 378, 379f domino reactions, 378 hydrogenbutylimidazolium tetrafluoroborate, 375f Lewis acidic catalysts for, 378 with MacMillan catalyst, 380, 381f of N-phenyl imine with 1-methoxy-3-(trimethylsilyl) oxybuta-1,3-diene, 374, 374f with pyridinium based ionic liquids [EtPy] as solvent, 375 of Spiro [cyclohexane-1,3-indolin]?3en-2-ones, 381f

K

Ketoxime, reaction of, 564f Knoevenagel condensations, 380, 429-430 of aldehydes and ketones, 383, 383f of aromatic aldehydes, 384, 385f between benzaldehyde derivatives and ethyl cyanoacetate, 387, 387f 1-(4-chlorophenyl) amino)-1-oxopropan-2-aminium perchlorate as catalyst, 386, 386f of diethylmalonate, 384 green recyclable alternatives as catalysts, 382 Lewis acidic catalysts, 382 of p-nitrobenzaldehyde with malononitrile, 384f of p-nitrobenzaldehyde with malononitrile, 384*f*

L

Laccases, 71 Lanthanides, 574, 603 Leaves-based nanoparticles, 768 Life cycle assessment (LCA), 55–56 Liquid-assisted grinding (LAG), 406 Lonza, 436 Luche reactions, 414 Lycopene, 254

M

Macrocyclic Co(II) complex, microwave synthesis of, 557*f* Magnetic NPs (MNP), 150 Mannich base, 387, 392 rate of reactions of, 389 Mannich reactions, 252, 387 of aromatic aldehydes, aromatic ammines and acetophenones, 392–393, 393*f* in [bmim] [BF₄], 387, 388*f* in [bmim] [PF₆], 391*f* Bronsted acid DMMI HSO₄-catalyzed, 393, 393*f*

catalysts for, 388, 391, 388f, 391f-392f of cyclic ketone and N-(pmethoxyphenyl)-protected iminoglyoxylate, 392 [DDPA] [HSO₄] and [TMBSA] [HSO₄] catalyzed, 390, 390f 1-methylimidazolium trifluoroacetic acid ([Hmim]⁺Tfa₂) catalyzed, 388, 388f RuCl₂(PPh₃)₃ catalyzed, 388, 389f using imidazolium ionic liquids, 392f using proline functionalized catalyst, 392, 392f M13 bacteriophage, 794 m-cresol oxidation, 420f, 421, 424 Mechanochemical processes, 406 mechanisms and kinetics of reactions, 411-412 rate of leaching, 406-407 of solids, 406 synthesis of carbon nanotubes, 414 complex ceramic oxides, 410-411 metal nano-particles, 409-410 nanocrystalline semiconductors, 414 nanosized pharmaceutical drugs, 415 Mechanochemical reactors, 407, 409f ball milling, 408, 408f high-energy, 408 Medicine, nanotechnology in, 691 Metal-embedded MOFs, 70 Metal-free material, 927 Metallic nanoparticles (MNP), 586 Metallocene, synthesis of, 559f Metallothermic reactions, 411 Metal oxide NPs, 110, 120, 112t, 923 copper, 111 iron, 111-112 mesoporous ZnO nanocrystals, 121 monodispersed CuONPs, 122 nano-sized nickel oxide (NiO) photocatalyst, 122 nickel oxide (NiO) nanorods, 122 titanium NPs. 111 using Abelmoschus esculentus (okra) mucilage, 121 using Allium eriophyllum leaves extract, 111 using Annona muricata, 122 using Calliandra haematocephala dry leaves, 121

Metal oxide NPs (Continued) using Eclipta prostrata leaves extract, 111 using flaxseed (Linum usitatissimum), 121 using Garcinia mangostana leaf extract, 111 using Limonia acidissima Christmas juice, 122 using Psidium guajava leaf extract, 122 using Vaccinium floribundum extract, 112 ZnONPs, 120-121 Metal oxides. Metal sulfide, 926 Microreaction technology (MRT), 616 Microreactor-assisted synthesis, of colloidal solutions, 15 Microwave-assisted bond, 492 Microwave-assisted nanoparticles synthesis, 7 of AgNPs, 9 of AuNPs from chloroauric acid, 10 from HAuCl₄, 10 of AuNPs from HAuCl₄, 10 of Au@TiO2NPs from HAuCl4, 10 of CuO and Fe₂O₃NPs, 12 gold/silver NPs from HAuCl₄/AgNO₃, 9 of metallic alloy (Pt-Au) NPs, 8 monometallic and monodispersed PtNPs, 8 of noble metal NPs (Au, Pt, Pd), 10 of PdNPs, 8-9 of PtNPs from H₂PtCl₆, 7 of PVP-stabilized monometallic (Pt, Pd, Rh, Ru) NPs, 8 reduction of AgNO₃ to AgNPs, 9-10 Ru-based NPs, 10 Ru-perovskites, 11 of TiO₂/AuNPs, 10 of ZnO-based NPs, 11 from ZnCl₂, 11 from Zn(NO₃)2.6H₂O, 11 Microwave-assisted organic synthesis (MAOS), 491 Microwave-assisted reactions, 492t MIL-91(Ti), 70 Mixed-Valent Oxide Catalytic Carbonization (MVOCC), 292 Mizoroki-Heck reaction, 252 Molybdenum oxide, Schiff base complexes of, 547*f* Morita-Baylis-Hillman reaction, 372 Multicomponent reactions (MCR), 572 Multiwalled carbon nanotubes (MWCNT), 258

Ν

Nanobiocatalysts (NBCs), 743 in pesticide degradation, 745 Nanobiotechnology, 736-737, 740 application of, 741 Nanocatalysts, 445, 447 green reaction acetylations, 452 arylations and diarylations, 452 conversion of organosilanes to silanols, 453 deoxygenation of epoxides, 451 deoxygenation reaction, 452 esterification of alcohols, 451 Heck cross-coupling reaction, 452 hydration of nitriles, 451 hydrogenation reactions, 452-453 lactonization of diols, 451 oxidation reactions, 454 oxidative coupling of alcohols, 451 reduction of p-nitrophenol to p-aminophenol, 451 Sonogashira cross-coupling reactions, 453 Suzuki cross-coupling reactions, 454 Ullmann reaction, 453 Nano chemistry, 405 Nanocomposites (NCs), 126t, 664 AgNPs decorated P-doped g-C3N4 (Ag/ PCN) composites, 124 chitosan cross-linked silver NCs (CSHD-Ag NC), 123 few-layer graphene/silver NPs, 125 graphene-Ag (GAg) NC, 123 graphene metallic NPs, 123 lichen-reduced graphene oxide (LrGO)bimetallic NP (LrGO-AgAu) NCs, 125 one-pot synthesis, 150, 154t bioinspired, 152 palladium (Pd)@graphene NCs (SP-HRG-Pd), 123 RS-AgNPs, 123 silver-chitosan NC, 125 silver/polystyrene (AgNPs/PS) nanocomposite (NC), 123 using Cassytha filiformis L. extract, 124 using Jatropha Cordata plant extract, 125 using Rhubarb stems, 123 using Salvadora persica L., 123 Zeolite/Fe₂O₃ NCs, 125

Nanoflowers one-pot synthesis of, 161, 164t bio-inspired, 162-163 for SERS applications, 161 Nanohybrids, 127 GSGNPs. 127 of reduced graphene oxide/Fe3O4/Ag ternary nanohybrid (rGO/Fe₃O₄/ AgNH), 127 of sheet-like cellulose nanocrystal-zinc oxide (CNC-ZnO) nanohybrids, 127 of tea polyphenol-assisted Ag-nanodiamond (Ag-TPND) hybrid, 127 Nanomaterials applications of, 137, 139f as catalysts, 140 for energy storage/production, 141 in healthcare, 141 as sensors, 140 wastewater treatments, 140 bacteria in manufacture of, 689, 690t bio-assisted green synthesis of, 788 classification of, 138f defined. 663 manufacturing, 686 one-pot synthesis, 144, 144f size and shape, 145 preparations, 141, 142f-143f biological methods, 142 bottom-up approach, 142 chemical methods, 142 physical methods, 142 vapor-phase methods, 142 synthesis of M13 bacteriophages, 795 synthesis of, 588 bimetallic nanoparticles, 607 copper, 598 gold, 607 lanthanides, 603 nickel, 590 palladium, 591 platinum, 593 silver, 605 zinc. 601 zirconium, 602 virus-mediated biosynthesis of, 789 Nanoparticles (NPs), 252, 683 biogenic synthesis of, 862

biological synthesis of, 702 algal species, 703, 710 fungal species, 705, 714 yeast species, 718 fungi-mediated synthesis of, 865 green synthesis of, 615 HRTEM images of, 765f inorganic, 684 one-pot bio-inspired synthesis of, 147-148, 149t one-pot synthesis, 144 synthesis, 586f methods in, 618f modes of, 618 Nanosilver, in medicine, 667 Nanotechnology, 273, 585, 615, 785 computational, 615 defined, 683 diverse, 616f dry, 615 future applications of, 692 in medicine, 691 wet. 615 Nanowires and nanofibrous mats, 882 National Environment Methods Index (NEMI), 48-49, 48f-49f classification, 49 requirements, 48-49 National science foundation fund (NSFF), 741 Native cyclodextrins (NCD), 111 Natural composites, 664 1-n-butyl-4-methyl-pyridinium bromide [1-n-B-4Mpyr] Br, 366 Nelson-Riley (N-R) analysis, 111 Nickel, 590, 590 Ni-luminol complex, microwave synthesis of, 563f Ni/SiO₂ catalyzed organic transformations, 431, 431*f*-432*f* Nitrile functionalized ILs, 16 Nitrone cycloaddition, 517f, 563f 3-(N,N dimethyldodecylammonium) propanesulfonic acid hydrogen sulfate ([DDPA] [HSO₄]), 390, 390f noble-metal NPs of Palladium (Pd) NPs, 119 of Platinum (Pt) NPs, 120 using aqueous ethanol and methanol extracts of Achillea millefolium (family Asteraceae), 119

noble-metal NPs (Continued) using aqueous ethanolic extract of black pepper, 119 using Coffea arabica seed (CAS) extract, 117-118 using Euphrasia officinalis leaf extract, 119 using Ononidis radix extract, 120 1-n-octyl-methylpyridiniumbromide [1-n-O-4-Mpyr]Br using 4-methylpyridine, 366 nonbiogenic greener approaches, 80-81 nonmetal NPs, 118t from ascorbic acid, 116 biogenic sulfur NPs, 115 of fluorescence carbon dots (CDs), 115 - 116from folic acid, 116 selenium NPs, 112-114 spice-derived C-dots, 116 sulfur NPs, 114 using carrot juice, 115 using Clausena dentata plant leaf extract, 113 using eutrophic algal blooms, 115 using fenugreek seed extract, 113, 117 using Ficus bengalensis leaf extract, 115 using hawthorn fruit extract, 113 using lemon juice, 117 using *Punica granatum* peels aqueous extract, 114 using saponin, 114 using Withania somnifera leaves extract, 114 Norfloxacin (NOR), 671 NPs-based system, 736 Nucleophilic substitution, 263

0

Octahedral chromium complexes, 547*f* Octenyl succinic anhydride (OSA), 253 OH-functional ILs (FILs), 16 Oligomerization mechanism, glycerol basedcatalyzed, 841*f* Olive leaves, 668 One-pot synthesis nanocomposites (NCs), 150 of nanoflowers, 161 nanoparticles (NPs), 144 quantum dots (QDs), 154 Onium ion-tagged proline catalysts in, 361 Organically-modified montmorillonite (OMMT), 279 Organic chemistry metrics (OCM), 39 Organic compounds. summary of microwave, 493f Organic-inorganic hybrid (OIH) materials, 463f, 459, 466 multifunctional and smart, 476, 476 sol-gel materials, 471-472, 475 research challenges, 476-478 Organic reactions and ultrasound, 251 Organotin (IV) complexes, synthesis of, 573f Organotin (IV) Schiff bases complexes, synthesis of, 573f Osmium synthon, microwave synthesis, 556f Oxadiazine, 73 Oxazole, 73 Oxidation reactions, 421 Oxodiperoxo molybdenum complexes, 546, 547f Ozone formation potential (OFP), 57

Р

Palladium, 591 Passerini reaction, 521–522, 522f p-cresol oxidation, 424, 425f Penicillin G, 434, 435f Pentamethylcyclopentadienyl rhodium, microwave-assisted synthesis of, 561f Peroxide, 65 Peroxo molybdenum complexes, 546 Petasis reaction, 529 Petroleum products, 909 Phenanthroline chromium complex, 546f Phenanthroline mixed nickel, microwave synthesis of, 562f Phenanthroline vanadium complex, synthesis of, 544f Phosphonium and imidazolium-based ILs, 21 Phthalocyanine zinc complexes, synthesis of, 568f Pinacol boron-ate ester, synthesis of, 570f Plant-based (green) synthesis of nanomaterials, 110 Plant extracted solvents, 912 Plant-mediated nanostructures, 764 Plant-mediated synthesis, 761

Plasmonic materials, 754 Plasmonic nanoparticles, 772 Platinum, 593 PMMA/Fe₃O₄ nanocomposites, 6 Polyaniline (PANI), 150 PANI-Au NCs, 150 PANI/Fe₃O₄ NCs, 150 PANI-NPs, 150 Polyaniline emeraldine base (PANIEB), 672 Polyanilines, 71 Polyethylene terephthalate (PET), 259 Polyimine, solvent-free synthesis of, 516f Polymeric amphiphiles, 67 Polymeric ILs (PILs), 22 Polymer-inorganic NCs (PINCs), 152 Polymer NPs, 89 Polyol, 588 process, 588 advantages of, 589f Polyoxazolines, 67 Polypyridine-ruthenium complexes, 554 microwave synthesis of, 554f Polysodium 4-styrene sulfonate, 263 Polystyrene sulfonic acid (PSSA), 501 Polysubstituted cyclopropanes, sythesis of, 430, 430f Polyvinyl alcohol (PVA), 263 Polyvinylpyrrolidone (PVP), 607 Porous carbon nanomaterials, 297 Porous carbon nanosheet like structures

(PCNS), 297 Product mass intensity (PMI), 44–45 Propionibacterium acnes isomerase (PAI), 64 Protein glycosylation, 152 Pulsed electric energy (PEE), 255 Pyrazolylrhenium complexes, synthesis

of, 549f

Q

Quantum dots (QDs) applications of, 157 bioinspired one-pot synthesis of, 156–157 one-pot synthesis of, 154, 158*t* water-soluble and biocompatible, 156 Quinuclidine and hydroxyl ionic liquid (HIL)-immobilized quinuclidine, 372

R

Reaction mass efficiency (RME), 44, 45t Reactor technology, in NP synthesis, 12 of Ag and AuNPs, 13 of AgNPs, 12-13, 13f of AuNPs, 14 of AuNPs from HAuCl₄, 12 cobalt ferrite NPs, 15 cobalt/reduced graphene oxide (Co/rGO) nanocomposites, 15 of colloidal solutions, 15 of magnetic iron-oxide NPs, 14 of NiNPs, 14 of PdNPs using NaBH₄, 15 of platinum NPs by reduction of H₂PtCl₆, 15 of ultrafine, uniformly distributed, and highly crystalline α -alumina NPs, 15 of ZnONPs, 14, 14f Reduced graphene-oxide (rGO) based NPs, 148 Reformat sky reactions, 413 of b-hydroxy ester, 413f Re(I) complexes, multicomponent microwave assisted synthesis of, 548f-549f Retro Diels-Alder reaction, 517, 517f Rhenium complexes, importance of, 548 Rhizome, 774 Ribosomes, 683 Riboswitches, 149 Ring-closing-metathesis reaction, 493, 495f RNA-based NPs, 149 Ruthenium complexes microwave synthesis of, 555f synthesis of, 555f

S

Salen-type chromium complexes, synthesis of, 546*f*S-Alkylation reaction, 427, 428*f*Scanning tunneling microscope, 738
Schiff base cadmium complexes, synthesis of, 569*f*Schiff base vanadium complexes, microwave synthesis of, 544*f*Secondary metabolites, 757
Selected-area electron diffraction (SAED), 705
Silk fibroin fibers (SFF), 671
Siloxane surfactants, 68

Silver NPs (AgNPs), 146-147 Single-molecule magnet, structure of, 551*f* SiO₂ catalysts, 421, 424 Sn(II)-based MOF, 71 Sodium borohydride-cellulose sulfuric acid (CellSA) catalyst system, 73 Sol-gel process, 459, 473t fundamentals, 466-467, 468t, 469-470 acidic catalysis, 469 alkaline catalysis, 470 condensation reaction of Si(OR)4- $_{n}(OH)_{n}, 470$ historical perspective and applications, 460-461, 462f, 464t steps, 467f Sol-gel techniques, 684, 685f mechanical installation, 685 mechanical preparation, 685 monitoring and glazing, 685 Solid-liquid phase transfer catalysis, 515 Solid-phase peptide synthesis, 72 Solid waste production (SWP), 57 Solubility, 900 Solvent-free reactions, 515 Solvents Polarity index, 500t Solvent system- based "green" synthesis, 620 Sonochemistry, 4 Soxhlet extraction, 256. See also Ultrasound Soxhlet system, 759 schematic diagram, 760f Stan model reaction, 436f Staudinger reaction, 530 Stoichiometric factor, 45–47, 47t 5-substituted 1H-tetrazoles, 64 Supercritical carbon dioxide ($scCO_2$), 15.23 formation of Ru- and Rh-based NPs, 24 properties of, 23 in synthesis of bimetallic NPs, Pt-rich NPs, 23 CuNPs. 25 flower-like ZnONPs, 25 PdNPs, 24-25 PtFe/ordered mesoporous carbon (OMC) catalyst, 24 Pt-W nanocomposite, 24 in synthesis of imetallic NPs, Pt-rich NPs, 23

Supercritical fluid, 895 chromatography (SFC), 905 extraction, 910 technique, 907 Suzuki coupling and C-C coupling reactions between benzhydrol and aromatic compounds, 396*f* continuous microflow system, 397, 397*f* Heck reactions, 398, 398*f* of N-contained heterocyclic chlorides, 395 palladium catalyst, 394–395, 394*f*, 397*f*, 398 Suzuki Cross-coupling reaction, 514, 514*f*

Т

Tandem reaction process, 530
Temsirolimus, 73
Terbium (III) complex, synthesis of, 575*f*Thermal gravimetric-differential thermal analysis (TG-DTA), 638
Tobacco mosaic virus (TMV), 793
Transesterification reaction, 45, 46*f*, 826
Transformation GAL (tGAL), 59
Triaryl phosphates, 65
Tribochemistry, 405

U

Ugi reaction, 518, 519f Ultrasonic and microwave technologies, 759 Ultrasound, 248 application in food, 257 bioactive compounds, 254, 254f green chemistry and, 249 organic reactions and, 251 surface modifications of nanostructures, 258 Ultrasound-assisted nanoparticle synthesis, 4 of AgNPs from AgNO₃, 5 of bimetallic Hg/ PdNPs, 6, 7f of crystalline ZnONPs from zinc acetate, 5 Cu-doped TiO2NPs using sol-gel method, 6 of Fe₃O₄, 6 of flower-like ZnONPs, 5 Heck reaction between iodobenzene and ethyl acrylate, 4 of MnFe₂O₄ NPs, 6 of nanodisperse NiNPs over ZrO₂, 6 Pt-graphene oxide-TiO2 nanosized photocatalyst, 6

of rod-like zinc oxide nanocrystals, 5

of silver and iron oxide NPs using fenugreek seed extract, 5 of spherical AuNPs, 5 of spindle-like silver/zinc oxide nanomaterials, 6 of starch-stabilized AgNPs, 4-5 of substituted-pyridopyrimidines, 6 Ultrasound assisted reactions addition reactions of 3,3-di(heteroaryl)indolin-2-one derivatives, 194, 195f of 2,3-epoxyl-1,3-diaryl-1-propanone, 195, 196f of ferrocenyl substituted 1,5-diketone and cyclic α , β -unsaturated ketones, 194, 194f of 2-((1H-indol-3-yl)(aryl)methyl) malononitriles, 196, 196f of β -indolylketones, 194, 195f of ortho-benzoquinones with furan, 194, 195f alkylation and acylation reactions of 2-alkyl-2-alkoxy-1,2-di(furan-2-yl) ethanone, 209, 210f C-alkylation of benzyl cyanide, 209, 209f of δ -chloroesters, 209, 209*f* of dioximes, 210, 210f of 2-methoxynaphthalene, 209, 209f of N-alkoxyphthalimides, 210, 210f N-alkylation of pyrrole, 208, 208f of phenylacetonitrile, 208, 208f bromination of acetophenones, 228 conversion of n α -urethane, 221, 222f coupling reactions of α-amino phosphonates, 207, 207f-208f of biaryls, 206, 207f of β -iodoethers, 206, 207f of propargylamines, 206, 206f Suzuki reaction, 206, 206f of z and e stilbenes, 205, 205f 1,1-diacetate preparation, 215, 215f diarylmethanes preparation, 216, 216f esterification of bile acids, 213, 214f of palmitic acid, 213, 214f iodination of unactivated aliphatic hydrocarbons, 229 nitroalkenes preparation, 216, 216f organic electrosynthesis, 224, 224f

oxidation reactions of alkylarenes, 215, 215f of α -benzoylbenzyl cyanide & alkylphenyl ketone, 212, 212f of dihydropyrimidinones, 212, 212f epoxidation of cyclohexene, 215, 215f glucose oligomerisation and sucrose oxidation, 213, 213f of isatoic anhydrides, 214, 214f of phenols, 213, 213f photochemical reactions of bromotrichloromethane, 205 of cyclohexanone, 204, 205f of 1-Iodocyclohexene, 204, 205f polymerisation reactions dimerization of pivalic acid, 211, 211f of poly-organosilanes, 210, 210f of siloxanes, 211, 212f sonochemical polymerization, 211, 211f protection of alcohols, 233, 234f radical cyclisation of o-allyl benzamides, 227, 229f reaction of 5H,5Cl-dibenzo[a,d]cyclohept atriene, 224, 225f rearrangement of methylbutynol, 224, 224f reduction of arylalkanones, 201, 201f asymmetric transfer hydrogenation of ketones, 204, 204f chemo-enantioselective hydrogenations, 203, 203fclemmensen-type reduction, 201, 202f of enones, 201, 202f of fluorinated alkanes and cycloalkanes, 200, 200fof 1α , 7α , 10α H-guaian-4-11-dien-3-one and hydrocolorenone, 201f of 1α , 7α , 10α H-guaian-4-11-dien-3-one and hydrocolorenone, 201 of histrionicotoxin, 202, 202f hydrogenation of trifluoromethyl ketones, 203, 203f hydrosilylation of alkyl substituted cyclohexanones, 203, 203f indirect electroreduction of benzyl chlorides, 204, 204f regioselective nitration of phenols, 229 regioselective synthesis of ketones, 216, 217f

Ultrasound assisted reactions (Continued) sonochemical excitation in reactions, 222, 223f sonochemical reactions of genistein derivatives, 225, 226f in solution, 221, 222f of triphenylmethane and triphenylmethylcarbinol, 223, 224f substitution reactions of 4-alkyl-(aryl)aminobenzaldehydes, 196, 197*f* anchoring of carboxylic acids to merrifield resin, 198, 198f of arylacetylenes, 198, 198f of bis(indolyl)methanes, 200, 200f of diaryl ethers, 199, 199f of ferujol, 196, 197f nitration of phenols, 200, 200f of oximes, 196, 196f sonochemical reaction of bromothiophenes with chlorotrimethylsilane, 199, 199f of trimethylsilyl pseudohalides, 198, 198f supported catalysis, 225, 225f synthesis of alkynyl sulfonate esters, 228 of bis(substituted pyrazol-4-ylcarbonyl)-Substituted thioureas, 221, 221f of 5,9-Dimethylpentadecane and 5,9-Dimethylhexadecane, 233 of disteryl ethers, 222, 223f of 2,3-epoxy-1-phenyl-3-aryl-1propanone, 227, 227f of 2H-indazole derivatives, 219, 219f β -lactams and β -aminoesters, 228, 230f of mandelic acid, 231, 232f of metal-1,3-diketonates, 233, 233f of 2-Methoxy-6-alkyl-1,4benzoquinones, 231, 232f of N-benzyl-N-arylcyanamides, 220, 220f of new pyridinium ionic liquids, 227, 227f of α -oximinoketones, 226, 226*f* of Pyrazolo[1,5-a]pyrimidines, 217, 217f of pyridinium ionic liquids, 233, 233f of pyrido[2,3-d:6,5-d]dipyrimidines, 219, 219f of pyrrolizidines, 229 of spiro[indoline-3,4'-pyrano[2,3-c] pyrazole] derivatives, 218, 218f

of substituted coumarins, 216, 217f of 3-substituted coumarins, 220, 220f of substituted phenanthrene-1,4quinones, 227, 228f of 2-substituted-3-(phenylamino)dihydroquinazolin-4(1H)-ones, 219, 220f of 1-substituted tetrazoles, 219, 219f of sulfonamides, 217, 218f of 3-(Thiophen-2-yl)-4,5-dihydro-1H-pyrazole-1-carboximidamides, 221, 221f synthetic organic chemistry, 178-179 of 2-(alkylamino)benzoic acids, 191, 191f of 1-amidoalkyl-2-naphthols, 192, 193f of 2-amino-4-aryl-3-carbalkoxy-7,7dimethyl- 5,6,7,8-tetrahydrobenzo[b] pyran derivatives, 191, 192f of 2-amino-2-chromenes & 2H-chromen-2-ones, 184-185, 184f-185f of β -aminoketones, 190, 191fof aminopyrazoles, 183, 183f of aryl-hydrazones, 188, 189f of arylmethylenemalononitriles, 191, 191f of benzo[b]furans/nitro benzo[b]furans, 187, 187f of 1,5-benzodiazepinic heterocyclic rings, 181, 181f of benzotriazoles and 1-Acylbenzotriazoles, 181, 181f of α, α '-bis(SubstitutedBenzylidene) cycloalkanones, 192 of α, α' -bis(SubstitutedBenzylidene) cycloalkanones, 192f of chalconoids, 189, 189f-190f of 1,5-diaryl-1,4-pentadien-3-ones, 189 of 1,4-dihydropyridines, 182, 182f of 3,4-dihydropyrimidin-2-(1H)-ones, 182, 183f of 1,8-dioxo-octahydroxanthene derivatives, 185, 185f of 5,5-disubstituted hydantoins, 184, 184f of ferrocenyl substituted 3-cyanopyridine derivatives, 187 of β -hydroxyl ketones, 187, 187*f* of 5-hydroxy-5-trihalomethyl-4,5dihydroisoxazoles and β-enamino trihalomethyl ketone, 185-186, 185f-186f

of imidazolines, 180, 180*f*–181*f* of imines, 187, 188*f* of ketoximes, 193, 193*f* of 4-Oxo-2thioxohexahydropyrimidines, 192, 192*f* of pyrazoline derivatives, 179 of pyrido[2,3-*d*]pyrimidine derivatives, 193, 193*f* of pyrroles, 186, 186*f* of vitamins, 184, 184*f* thiocyanation of aromatic and heteroaromatic compounds, 226, 226*f*

V

Valance band (VB), 920 Vanadium, 544 Vanillylmandelic acid (VMA), 69 Van Leusen reaction, 523, 525*t* Vascular endothelial growth factor (VEGF), 879 Vegetable oils, 504 Viral-mediated reduction, 800*f* Virus-mediated synthesis, 78 Viscosity, 903 Viscosity (Pas) parameters, 904*t* Volatile organic compounds (VOCs), 419 Vulcan carbon (VC), 259

W

Water, pressure-Temperature phase diagram of, 899*f*Water-soluble polyaniline, 71Wet nanotechnology, 615

Y

Yeasts, 702

Z

Zeaxanthin dipalmitate (ZDP), 255 Zeolites, 424, 427f acid, 426, 429 dehydrated, 426 Zeolitic imidazolate framework (ZIF) family of MOF. 70 Zerovalent organometallic carbonyl compounds, synthesis of, 545f Zinc. 601 complexes, synthesis of, 568f luminol derivative, synthesis of, 569f Zirconium, 602 ZnAl₂O₄ spinels, 67 ZnO nanoparticles, biosynthesis of, 632 microbes, 647 plant leaf extracts, 632, 642f, 644f, 646f

Handbook of Greener Synthesis of Nanomaterials and Compounds **VOLUME 1**

Fundamental Principles and Methods

Edited by Boris I. Kharisov and Oxana V. Kharissova

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