

Chapter 2

Green Chemistry and Catalysis

Abstract Green chemistry has always been a lively research field. In the time period, the emphasis of catalysis research has significantly shifted and spread from traditional applications in green chemistry. This chapter gives an introduction to overall theme of green chemistry and catalysis emphasizing the concepts such as homogeneous and heterogeneous catalysts, preparation and characterization of catalysts. Readers will find coverage of some important types of green catalysts namely nanocatalysts and perovskite type catalysts with an emphasis on their preparation and characterization. The section on catalyst preparation is concerned with the preparation of bulk catalysts and supported catalysts, with an emphasis on general principles. For the supported catalysts the relation between the method of preparation and the surface chemistry of the support is highlighted. The section on catalyst characterization summarizes the most common techniques in four subtitles: Structural Analysis, Thermal Analysis, Spectroscopic Techniques and Microscopic Techniques.

2.1 Green Chemistry

Green chemistry also named as sustainable chemistry is defined as the practice of chemical science and manufacturing in a manner that is sustainable, safe, and non-polluting and that consumes minimum amounts of materials and energy while producing little or no waste material (Sheldon et al. 2007).

Anastas and Warner also defined Green Chemistry as “*The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances*” (Anastas and Warner 1998).

The design of environmentally benign chemicals and processes are guided by the 12 Principles of Green Chemistry developed by Anastas and Warner.

These 12 principles of green chemistry can be described in detail as follows:

1. **Prevention**
It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy**
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis**
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals**
Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries**
The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency**
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks**
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives**
Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**
Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-Time analysis for Pollution Prevention**
Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention**
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

These principles have been used as guideline and criteria for the scientists and hence the researches are mainly focusing around the principles of green chemistry. Consequently, it can be said that the modern society has an ever increasing demand for environmentally friendly processes.

It is well known that catalysts have an enormous impact on the chemical industry because they enable reactions to take place and make reaction processes both more efficient and environmentally friendly. A suitable catalyst can enhance the rate of a thermodynamically feasible reaction but cannot change the position of the thermodynamic equilibrium. Most catalysts are solids or liquids, but they may also be gases (Julkapli and Bagheri 2015).

2.2 General Considerations on Catalysts: Homogeneous versus Heterogeneous Catalysts

Catalysis is generally divided into two types, homogeneous and heterogeneous. Heterogeneous catalysis is where the catalyst and the reactants are in the different physical phases, while homogeneous is where both are in the same phase.

2.2.1 Homogeneous Catalysis

The field of homogeneous catalysis can be characterized as a source of easily arranged, selective catalysts with high activity.

In homogeneous catalysis, the catalyst is in the same phase as the reactants and products. In general, homogeneous catalysts exhibit excellent catalytic activities with high selectivities in particular. But, it is difficult for the homogeneous catalyst to be separated from reaction media.

2.2.2 Heterogeneous Catalysis

Heterogeneous catalysts also offer many advantages, some of which are not displayed by their homogeneous counterparts, including recyclability, ease of separation from the reaction mixture and use in continuous flow processes. It is highly desirable to develop new systems that blend the many advantages of heterogeneous catalysis with the versatility of homogeneous catalysts.

Heterogeneous catalysts have several advantages compared to other catalytic processes (Tang 2007):

- they avoid formation of inorganic salts
- they are regenerable

- easy to handle, safe to store and has long life time
- easy and inexpensive of recovery and recycling
- the selectivity and activity of homogeneous catalysts under mild reaction conditions is unbeaten by their heterogeneous counterparts.

2.2.3 *Green Catalysts*

Recently, growing attention is being directed towards the development of innovative catalytic systems with high performance from the point of environmentally greener processes, economical efficiency and minimum consumption of resources. The application of catalysis to reduce toxicity and renewable energy systems, and efficiency makes it a central focus area for green chemistry research.

Green Catalysis is a subtitle of green chemistry but the most important one and one of the urgently needed challenges facing engineers now is the design and use of environmentally benign catalysts. Green and sustainable catalyst should possess, higher activity, higher selectivity, efficient recovery from reaction medium, durability or recyclability, cost effectiveness.

In recent years the development of catalysts for processes to replace conventional ones has made a significant contribution to the reduction of environmental pollutants. Thus, there is an increasing interest on the topic of green catalysis recently. It not only includes developing new catalysts which can offer stable, highly effective catalytic performances, but considers the application of environmentally friendly catalyst preparations.

Numerous studies have been focused on green catalysts. In this book, among these catalyst categories, it will be mainly focused on nanocatalysts, perovskite type catalysts and green catalysts used in several types of advanced oxidation processes.

2.2.3.1 *Nanocatalysts*

Nanomaterials have structured components with at least one dimension less than 100 nm. Nanomaterial is expected to be fruitful area for green chemistry catalysis due to the increasing ability to design in nano state and the high surface areas found in nano materials.

Employing green chemistry principles for the production of nanoparticles can lead to a great reduction in waste generation, less hazardous chemical syntheses, and an inherently safer chemistry in general (Bhattacharya et al. 2013).

Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). A material such as gold,

which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales (Chaturvedi et al. 2012).

Nanostructured materials are potential candidates for the innovative catalyst because of the unique properties such as enormous surface areas they exhibit compared to their bulk counterparts (Glaser 2012).

The nano sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing the contact between reactants and catalyst dramatically and mimicking the homogeneous catalysts. However, their insolubility in reaction solvents renders them easily separable from the reaction mixture like heterogeneous catalysts, which in turn makes the product isolation stage effortless. Also, the activity and selectivity of nano-catalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology (Polshettiwar and Varma 2010).

In the emerging regime of nano-catalysis the synergetic effect of the nanosized catalyst is known to be important for the overall performance, where global processes such as the transport of the reactant atoms to the catalyst could play an important role in the overall reaction kinetics (Xie et al. 2013). In general, it can be concluded that due to rapid $\cdot\text{OH}$ radical based oxidation reactions, AOP by nanocatalysts is characterized by high reaction rates and hence short treatment times. In addition it is known that less toxic intermediate products are formed and pollutants can be degraded in ppb level.

Nanotechnology can step in a big way in lowering the cost and hence become more effective than recent techniques for the removal of pollutants from water in the long run. In this perspective nanoparticles can be used as potent sorbents as separation media, as catalysts for photochemical destruction of contaminants; nano-sized zerovalent iron used for the removal of metals and organic compounds from water (Bhattacharya et al. 2013).

Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or diminished by using nanosorbents, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, nanotubes (Bhattacharya et al. 2013).

Nanomaterial properties desirable for water and wastewater applications include high surface area for adsorption, high activity for (photo)catalysis, antimicrobial properties for disinfection and biofouling control, superparamagnetism for particle separation, and other unique optical and electronic properties that find use in novel treatment processes and sensors for water quality monitoring (Qu et al. 2013).

Nanosized metal oxides, including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, are classified as the promising ones for wastewater treatment systems (Hua et al. 2012).

Consequently, the catalysts that are prepared by methods of nanotechnology used in advanced oxidation processes are of particular interest because of their environmentally friendly features.

2.2.3.2 Perovskites

The most of the catalysts used in modern chemical industry are based on mixed metal oxides. Among the mixed metal oxides, perovskite-type oxides are attracting much scientific application interest owing to their low price, adaptability, and thermal stability, which often depend on bulk and surface characteristics (Guiotto et al. 2015; Gupta et al. 2015).

In its ideal form, perovskites are described by the generalized expression ABX_3 . They have a cubic structure, where each of the cubes consists of three different chemical elements A, B and X present in a 1:1:3. Atoms A and B are metal cations (positively charged ions) and the X atoms are not metal anions (negatively charged ions, usually oxygen). The cation A is the largest atomic radius is the hub center, the cation B occupies the eight vertices and in the center of the edges of the cubic cell are centered anions X (Yazdanbakhsh et al. 2011).

Although the most numerous and most interesting compounds with the perovskite structure are oxides, some carbides, nitrides, halides, and hydrides also crystallize in this structure.

Perovskite materials exhibit many unusual properties that may also furnish practical applications. Such phenomena as high magnetoresistance, ferroelectricity, superconductivity, charge ordering, spin-dependent transport, high thermopower and the interleaving of structural, magnetic and transport properties are those typically observed from this family of materials. Perovskites with transition metal ions (TMI) on the B site show an enormous variety of intriguing electronic or magnetic properties. This variety is not only related to their chemical flexibility, but also and to a larger extent related to the complex character that transition metal ions play in certain coordination with oxygen or halides (Lemmens and Millet 2004).

The Perovskite-type catalysts are promising candidates for the advanced oxidation of wastewater in environmental catalysis applications because:

- wide range of elements that can be incorporated into the structure, combination of elements with different oxidation states.
- high temperature resistance.
- it is a good alternative as it is possible to produce metal particles high dispersion, thus reducing the formation of coke in reaction.

2.3 Fundamentals in Catalyst Preparation

The catalytic process is realized on the catalyst surface. Therefore, the catalyst surface should be as large as possible, but moreover, surface must be accessible to the reactants.

The design of a catalyst covers all aspects from choice of the active phases to the method of forming the particles.

The desired structures of the catalysts and the criteria for a good catalyst are

- homogeneity
- often nano-structured, but not necessarily
- adapted pore structure
- uniform particle size distribution
- suitable shape and mechanical stability
- activity
- selectivity
- cost

and generally all these structures depend on the preparation method.

Generally, the catalysts may be classified according to the preparation procedure as: bulk catalysts or supports and impregnated catalysts. According to the preparation methods the catalytic active phase is generated as a new solid phase or the active phase is introduced or fixed on a pre-existing solid by a process which intrinsically depends on the support surface (Campanati et al. 2003).

2.3.1 Basic Preparation Techniques for Bulk Catalysts and Supports

2.3.1.1 Precipitation and Co-precipitation

In the process the desired component is precipitated from the solution. The precipitation process is used for preparation of bulk catalysts and support material. Co-precipitation is used for simultaneous precipitation of more than one component. Catalysts based on more than one component can be prepared easily by co-precipitation.

In the co-precipitation procedure the solutions containing the metal salt and a salt of a compound that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxides and/or carbonate. After washing, these can be transformed to oxides by heating (Pinna 1998).

Metal salt solutions and support precursors are combined together, and then calcined. It was widely used method, due to simplicity, economic and reproducibility.

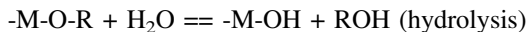
Co-precipitation method offers some advantages. These are:

1. produces nanoparticles in large quantities in a relatively short amount of time
2. utilizes inexpensive and readily available chemicals as precursors
3. easy control of particle size and composition and
4. various possibilities to modify the particle surface state and overall homogeneity.

2.3.1.2 Sol-Gel

Sol-gel processing is one of the routes for the preparation of porous materials by solidification (without precipitation) from a solution phase.

The reaction proceeds in two steps:



The sol-gel methods show promising potential for the synthesis of mixed oxide catalysts. The versatility of the sol-gel techniques allows control of the texture, composition, homogeneity, low calcination temperatures (minimizing the undesired aggregation of the particles), and structural properties of solids, and makes possible production of tailored materials such as dispersed metals, oxidic catalysts and chemically modified supports (Brinker and Scherer 1990; Prasad and Singh 2011).

The main advantages of sol-gel technique are versatility, low temperature process and flexible rheology allowing easy shaping. The procedure involving sol-gel technique is as follows (Kandasamy and Prema 2015).

- preparation of homogeneous solution by dissociation of metal organic precursor in the organic solvent or in organic salt solution,
- transformation of precursor oxide into a highly cross linked solid,
- hydrolysis leads to sol, dispersion of colloidal particle in liquid done by suitable reagents (generally water),
- further condensation leads to gel, a rigid inter connected organic network.

Citric acid (CA) complexing approach

Citric acid (CA)-assisted sol-gel method (namely Pechini approach) is a facile synthesis for producing homogeneous nanocomposites. In this method the citric acid is used as chelating agent to ensure the formation of homogeneous transparent metal-citrate gels (Wei and Hua 2007; Prasad and Singh 2011).

Alkoxide sol-gel method (Pechini Method)

The Pechini method based on polymeric precursors, is used to prepare spinels and it does not require high temperature calcinations. The method has good stoichiometric control as well as reproducibility. This method consists of the formation of a polymeric resin between a metallic acid chelate and polyhydroxide alcohol by polyesterification. The method involves relatively easy synthesis route when compared to the other conventional processes. Low operating temperature and control over the end stoichiometry are the main advantages of this technique (Lessing 1989; Pimentel et al. 2005; Prasad and Singh 2011).

Non-alkoxide sol-gel route

Non-alkoxide sol-gel process, involving hydrolysis and condensation of metal salts, avoids the disadvantage of alkoxide sol-gel process (high sensitivity to moist

environment), however, has still the disadvantage of different hydrolysis susceptibilities of the individual components (Cui et al. 2005). One of the advantages of this method is the important reduction of the required calcination temperatures, minimizing the undesired aggregation of the particles (Prasad and Singh 2011).

2.3.1.3 Solvothermal Reaction

In this reaction, precursors are dissolved in hot solvents. If the solvent is water then the process is referred to as hydrothermal method. Solvent other than water can provide milder and friendlier reaction conditions.

2.3.1.4 Solid-State Reaction

The solid-state reaction route is the most widely used method for the preparation of polycrystalline solids from a mixture of solid starting materials. Solids do not react together at room temperature over normal time intervals and it is necessary to heat them to much higher temperatures (1000–1500 °C) in order for the reaction to occur at an appropriate rate.

The factors on which the feasibility and rate of a solid state reaction depend include, reaction conditions, structural properties of the reactants, surface area of the solids, their reactivity and the thermodynamic free energy change associated with the reaction (West 2005).

2.3.1.5 Flame Spray Pyrolysis

Flame spray pyrolysis is a novel one step method for preparation of especially nano-sized particles. In the process a liquid feed metal precursor dissolved in an organic solvent is sprayed as micrometer sized droplets with an oxidizing gas into a flame zone. The spray is combusted and the precursor is converted into nanosized metal or metal oxide particles, depending on the metal and the operating conditions (Høj 2012).

2.3.2 Basic Preparation Techniques for Supported Catalysts

Many industrial catalysts consist of metals or just as a carrier but it may actually contribute catalytic activity. Further, the interaction between the active phase and the support phase can affect the catalytic activity

2.3.2.1 Impregnation

Impregnation method appears to be simple, economic and able to give a reproducible metal loading which is however limited by the solubility of the metal precursor. In the procedure the support is contacted with a certain amount of solution of the metal precursor, usually a salt (e.g. metal nitrate, chloride), then it is aged, usually for a short time, dried and calcined.

According to the amount of solution used, there are two types of impregnation: incipient wetness or wet impregnation.

In the wet type of impregnation an excess amount of solution with respect to the pore volume of the support is to be used. The system is left to age for a certain time under mixing, filtered and dried (Pinna 1998).

In incipient wetness impregnation, the volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support. The maximum loading is limited by the solubility of the precursor in the solution (Campanati et al. 2003).

Ion exchange

Ion exchange process consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species. The support containing ions (X) is immersed into an excess volume (compared to the pore volume) of a solution containing other ions (Y). Ions Y gradually penetrate into the pore space of the support, while ions X pass into the solution, until equilibrium is reached (Campanati et al. 2003).

2.3.2.2 Deposition–Precipitation

This method includes two steps:

- precipitation from bulk solutions or from pore fluids and
- interaction with the support surface.

The dissolution of the metal precursor is followed by adjustment of the pH to achieve a complete precipitation of the metal hydroxide which is deposited on the surface of the support. The hydroxide formed is subsequently calcined and reduced to the elemental metal (Campanati et al. 2003). The main problem is to allow the precipitation of the metal hydroxide particles inside the pores of the support: therefore the nucleation and growth on the support surface will result in a uniform distribution of small particles on the support (Pinna 1998).

2.3.2.3 Inert Gas Condensation

The inert gas condensation technique, in which nano particles are formed by the evaporation of a metallic source in an inert gas, had been extensively used to produce fine nano particles.

Methods:

- Physical Vapor Deposition (PVD)-(no catalytic interaction)
- Chemical Vapor Deposition (CVD)-(with catalytic interaction)

Chemical Vapour Deposition (CVD) is a well known process in which a solid is deposited on a heated surface via a chemical reaction from the vapour or gas phase. In thermal CVD, the reaction is activated by a high temperature above 900 °C. A typical apparatus comprises of a gas supply system, a deposition chamber and an exhaust system (Malik and Singh [2010](#); White et al. [2009](#)).

2.3.2.4 Inert Structured Media

Preparation of particles in structured medium by imposing constraints in form of matrices such as

- zeolites
- layered solids
- molecular sieves
- micelles/microemulsions
- gels
- polymers
- glasses

Imposing the structure in form of matrices the growth kinetics can be slowed down and directed and the size can be limited leading to nanoparticles with well defined structures (Overney [2010](#)).

2.4 Catalyst Characterization

To investigate the fundamental relations between the state of a catalyst and its catalytic properties several approaches can be adopted. By using the appropriate combination of analysis techniques, the desired characterization on the atomic as well as bulk scale is certainly possible.

A heterogeneous catalyst is a composite material, characterised by:

- the relative amounts of different components (active species, physical and/or chemical promoters, and supports)
- shape
- size
- pore volume and distribution
- surface area

In this section some of the characterization techniques that are most commonly used will be discussed.

These techniques will be summarized in four subtitles:

- Structural analysis
- Thermal analysis
- Spectroscopic techniques
- Microscopic techniques

(a) **Structural analysis**

In heterogeneous catalysis, the reaction occurs at the surface. Catalysis and catalytic surfaces, hence, need to be characterized by reference to their physical properties and by their actual performance as a catalyst. The most important physical properties are those relating to the surface because the catalyst performance is determined by surface parameters.

Surface area—Brunauer, Emmet and Teller (BET) method

In heterogeneous catalysis, since most of the reactions occur at the surfaces, investigating the surface area is very significant. Surface area measurements are mainly performed by Brunauer, Emmet and Teller (BET) method.

The BET theory is based on various hypothesis:

- the adsorption is supposed to be localized on well defined sites; all the sites have the same energy (homogeneous surface) and each of them can only accommodate one adsorbate molecule
- a multilayer adsorption is supposed to occur even at very low pressure. The adsorbed molecules in the first layer acting as adsorption sites for the molecules of the second layer and so on; there is no lateral interaction between adsorbed molecules.
- an adsorption–desorption equilibrium is supposed to be effective between molecules reaching and leaving the solid surface.

The BET equation describes the relationship between volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage. BET equation can be written in the form:

$$\frac{V}{V_m} = \frac{C(P/P_0)}{(1 - P/P_0)(1 - P/P_0 + C(P/P_0))}$$

$$\frac{1}{V[(P_0/P) - 1]} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \left(\frac{P}{P_0} \right)$$

where P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, V is the adsorbed gas quantity (for example, in volume units), and V_m is the monolayer adsorbed gas quantity. C is the BET constant,

$$C = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

where E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction. R is ideal gas constant and T is the absolute temperature.

If a plot of $\frac{1}{V[(P_0/P)-1]}$ versus $\left(\frac{P}{P_0}\right)$ is drawn, it will yield a straight line with slope $\frac{C-1}{V_m C}$ and intercept $\frac{1}{V_m C}$ if the BET model holds true. Knowing slope and intercept, V_m can be calculated which is used for the calculation of specific surface area using the following equation

$$S_g = a \frac{V_m N_A}{V}$$

S : total surface area

N_A : the Avagadro constant

V : molar volume of the adsorbent gas

a : adsorption cross section of the adsorbing species,

Pore analysis—The Barrett-Joyner-Halenda (BJH) method

Since a catalytic reaction occurs at the fluid-solid surface a large interfacial area can be helpful or even essential in attaining a significant reaction rate. This area is provided by a porous structure, the solid contains many fine pores, and the surface of these pores supplies the area needed for the high rate of reaction.

A catalyst that has a large area resulting from pores is called a porous catalyst. Sometimes pores are so small that they will admit small molecules but prevent large ones from entering.

In general, catalyst consists of pore in the range of, micropore, mesopore or macropore depending on the preparation conditions and compositions.

Not all catalyst need the extended surface provided by a porous structure, however, some are sufficiently active so that the effort required to create a porous catalyst would be wasted. For such situations one type of catalyst is the monolithic catalyst. They can be porous or non porous.

The pore analyses consist of determining the average pore size, average pore volume and pore size or pore volume distribution.

The Barrett-Joyner-Halenda (BJH) method for calculating pore size distributions is based on a model of the adsorbent as a collection of cylindrical pores. The theory accounts for capillary condensation in the pores using the classical Kelvin equation, which in turn assumes a hemispherical liquid-vapor meniscus and a well-defined surface tension.

X-Ray Diffraction (XRD)

X-ray diffraction is the most powerful and successful technique for determining the structure of crystals. It also gives some idea regarding crystallinity, crystal grain size, lattice parameters, phase composition, lattice defects etc.

The instrument used for this analysis is called an X-ray diffractometer. In the diffractometer, an X-ray beam of a single wavelength is used to examine the specimens. By continuously changing the incident angle of the X-ray beam, a spectrum of diffraction intensity versus the angle between incident and diffraction beam is recorded.

The major applications of XRD are phase identification and average crystallite size determination.

Phase Identification

The catalysts are generally composed of mixture of several phases. Phase identification is based on the comparison of the diffraction pattern of the specimen with that of pure reference phases or with a database.

Average crystallite size determination

The average crystallite size can be determined by Scherrer formula using elementary line broadening analysis.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where

D = Crystallite size, Å

K = Crystallite-shape factor

λ = X-ray wavelength, Å

θ = Observed peak angle, degree

β = X-ray diffraction broadening, radian

(b) Thermal analysis

Temperature Programmed Reduction (TPR)

Temperature programmed reduction is used to determine the reducibility of the catalysts.

Temperature Programmed Desorption (TPD)

Temperature programmed desorption technique measures the desorbed molecules from the sample surface as function of temperature.

Thermo Gravimetric Analysis (TGA)

In thermogravimetric analysis, the change in mass of samples is monitored with an increase in temperature at specified gas environment and heating rate. TGA

characterization is used to determine the thermal stability, content of moisture and volatile material, if any, or decomposition of inorganic and organic material in the catalysts.

Differential Thermal Analysis (DTA)

DTA consists of heating a sample and reference material at the same rate and monitoring the temperature difference between the sample and reference.

(c) Spectroscopic techniques

Infra Red Spectroscopy

Infra red spectroscopy is a vibrational spectroscopy as it is based on the phenomenon of absorption of infrared radiation by molecular vibrations. IR spectroscopy gives information about the molecular structure of the materials and bonds. Both inorganic and organic materials can be analyzed. By the help of this, compounds are identified and sample composition can be investigated.

Raman Spectroscopy

Raman spectroscopy is used to analyze the internal structure of molecules and crystals. It is based on scattering phenomenon of electromagnetic radiation by molecules.

(d) Microscopic techniques

Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a widely accepted technique to extract structural and chemical information point-by-point from a region of interest in the sample. It is generally employed to examine the surface morphologies of the material at higher magnifications. In SEM, image is formed by focused electron beam that scans over the surface area of specimen.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a powerful tool that provides information about the morphology, crystallography and elemental composition for advanced materials. It is also an electron microscopic technique with high resolution to extract structural information.

References

- Anastas PT, Warner JC (1998) Green chemistry: theory and practice. Oxford Science Publications, Oxford
- Bhattacharya S, Saha I, Mukhopadhyay A, Chattopadhyay D, Ghosh UC, Chatterjee D (2013) Role of nanotechnology in water treatment and purification: potential applications and implications. *Int J Chem Sci Technol* 3(3):59–64

- Brinker CJ, Scherer GW (1990) Sol–Gel science: the phys chem sol–gel proces. Academic Press, Boston
- Campanati M, Fornasari G, Vaccari A (2003) Fundamentals in the preparation of heterogeneous catalysts. *Catal Today* 77(4):299–314
- Chaturvedi S, Dave PN, Shah NK (2012) Applications of nano-catalyst in new era. *J Saudi Chem Soc* 16:307–325
- Cui H, Zayat M, Levy D (2005) Sol–Gel synthesis of nanoscaled spinels using spropylene oxide as a gelation agent. *J Sol–Gel Sci Technol* 35:175–181
- Glaser JA (2012) Green chemistry with nanocatalysts. *Clean Technol Environ Policy* 14:513–520
- Guiotto M, Pacella M, Perin G, Iovino G, Michelon N, Natile MM, Glisenti A, Canu P (2015) Washcoating versus direct synthesis of LaCoO_3 on monoliths for environmental applications. *Appl Catal A* 499:146–157
- Gupta VK, Eren T, Atar N, Yola ML, Parlak C, Karimi-Maleh H (2015) $\text{CoFe}_2\text{O}_4@ \text{TiO}_2$ decorated reduced graphene oxide nanocomposite for photocatalytic degradation of chlorpyrifos. *J Mol Liq* 208:122–129
- Høj M (2012) Nanoparticle synthesis using flame spray pyrolysis for catalysis one step synthesis of heterogeneous catalysts. Doctoral Thesis, Technical University of Denmark
- Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q (2012) Heavy metal removal from water/wastewater by nanosized metal oxides: a review. *J Hazard Mater* 211–212:317–331
- Julkapli NM, Bagheri S (2015) Graphene supported heterogeneous catalysts: an overview. *Int J Hydrogen Energy* 40(2):948–979
- Kandasamy S, Prema RS (2015) Methods of synthesis of nano particles and its applications. *J Chem Pharm Res* 7(3):278–285
- Lemmens P, Millet P (2004) Spin—orbit—topology, a triptych, in “quantum magnetism”. Springer, Heidelberg
- Lessing PA (1989) Mixed-cation powders via polymeric precursors. *Am Soc Ceramic Bulletin* 68 (5):1002–1007
- Malik H, Singh AK (2010) Engineering physics. Tata McGraw Hill Education Private Limited, New Delhi
- Overney R (2010) Nanothermodynamics and nanoparticle synthesis. Lecture Notes
- Pimentel PM, Martinelli AE, de Araújo Melo DM, Pedrosa AMG, Cunha JD, da Silva Júnior CN (2005) Pechini synthesis and microstructure of nickel doped copper chromites. *Mater Res* 8 (2):221–224
- Pinna F (1998) Supported metal catalysts preparation. *Catal Today* 41(1–3):129–137
- Polshettiwar V, Varma RS (2010) Green chemistry by nano-catalysis. *Green Chem* 12:743–754
- Prasad R, Singh P (2011) Applications and preparation methods of copper chromite catalysts: a review. *Bull Chem React Eng Catal* 6(2):63–113
- Qu X, Brame J, Li Q, Alvarez PJJ (2013) Nanotechnology for a safe and sustainable water supply: enabling integrated water treatment and reuse. *Acc Chem Res* 46(3):834–843
- Sheldon RA, Arends I, Hanefeld U (2007) Green chemistry and catalysis. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
- Tang Z-R (2007) Green catalysts preparation using supercritical CO_2 as an antisolvent. Doctoral Thesis, Cardiff University
- Wei L, Hua C (2007) Synthesis and characterization of Cu–Cr–O nanocomposites. *Solid State Sci* 9 (8):750–755
- West AR (2005) Solid state chemistry and its applications. Wiley, New York
- White RJ, Luque R, Budarin VL, Clark JH, Macquarrie DJ (2009) Supported metal nanoparticles on porous materials. Methods and applications. *Chem Soc Rev* 38:481–494
- Xie W, West DJ, Sun Y, Zhang S (2013) Role of nano in catalysis: palladium catalyzed hydrogen desorption from nanosized magnesium hydride. *Nano Energy* 2:742–748
- Yazdanbakhsh M, Tavakkoli H, Hosseini SM (2011) Characterization and evaluation catalytic efficiency of $\text{La}_{0.5}\text{Ca}_{0.5}\text{NiO}_3$ nanopowders in removal of reactive blue 5 from aqueous solution. *Desalination* 281:388–395

Novel Catalysts in Advanced Oxidation of Organic
Pollutants

Atalay, S.; Ersöz, G.

2016, X, 60 p. 2 illus. in color., Softcover

ISBN: 978-3-319-28948-9