Synthesis of Advanced Nanomaterials: Catalytic and Sustainable Applications

Habilitation Thesis

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Dedicated to My Late Mother
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Synthesis of Advanced Nanomaterials: Catalytic and Sustainable Applications

1. Introduction

1.1. History of Catalysis

Heterogeneous catalysis dominates the chemical industry, and touches our daily life in various ways. More than 90% of all chemical synthesis is performed using various catalytic protocols, and catalysis contributes to nearly 35% of the world’s gross domestic product (GDP).[1] Catalytic transformations are sustainable way of producing chemicals and materials as they perform a fundamental role in energy applications (in oil refining, biofuel production, and fuel cells, etc.), in pollution control, in medical applications and in food manufacturing. Historically, it is well-known that catalysis increases the rates of the chemical reactions as was first introduced by Berzelius in 1835.[2] The early catalytic applications were introduced for simple but industrially significant reactions such as the oxidation of sulfur dioxide to sulfuric acid, the production of ammonia from N₂ and H₂ (the Haber process), and the synthesis of methanol and its oxidation to formaldehyde.[1, 3] However, in some recent applications, increasingly complex reaction networks are at play which dictates specificity traits to avoid the formation of undesirable byproducts. Thus, in order for catalysts to be viable, it is obligatory to enhance its reaction performance (conversion/yields/selectivity), to simplify the overall synthesis process, eliminating expensive product separation steps, and to minimize the generation of potentially polluting byproducts.[4, 5] Additionally, the stereoselective catalytic processes drive the field for the manufacturing of speciality chemicals for various industrial applications, especially pharmaceuticals.[6] This shift dictates properties of catalysts to be prominently selective with other constraints about its practical utility for specific chemical processes.[7]

Generally, catalysis occupies an important place in chemistry, which contained three different categories, namely heterogeneous, homogeneous, and enzymatic. Among them, homogeneous and heterogeneous catalysis are renowned as being two different areas depending on the phase of the reactant and the catalysts, while the main goal being the discovery of better catalytic activity. Both the catalysts have their advantages and drawbacks. For example, heterogeneous catalysts are easy to recover but in some cases harsh conditions as well as the inefficient mass transport limit its applicability. On the other hand, while homogeneous catalysts are
recognized for their higher activity and selectivity, the separation of expensive catalysts, especially transition metals, from substrates and products remains a key issue for industrial applications.[8] Heterogeneous catalysts are traditionally prepared by using simple synthetic routes with relatively limited control over the morphology. Furthermore, it becomes more difficult to control selectivity in such cases, especially when precise effects such as stereo- or enantioselectivities are concerned. Thus, considering its recyclability from a greener perspective, it becomes imperative to devote more efforts towards bridging the gap between homogeneous and heterogeneous catalysts thus capitalizing on the good attributes of both these systems. In this aspect, possibly, the seminal efforts were made between the 1970s to the early 1980s when the field witnessed a rapid growth in parallel with the growth of nanoscience. Pioneering works on surface molecular chemistry accomplished by J. M. Basset, M. Che, B. C. Gates, Y. Iwasawa, and R. Ugo, among others, to develop single-site catalysts, and/or reach a better understanding of conventional supported catalyst preparation through a molecular approach (molecular field). Chemists such as G. Ertl and G. Somorjai, contributed to the molecular understanding of surface chemistry associated with the catalytic processes. This paved the way for the development of novel nanotechnology pathways for the preparation of complex solids with well-defined characteristics, for applications in catalysis.[9-11]

In the intervening 20 years, there has been enormous development in the field of nanoscience and nano-catalysts especially at the interface between homogeneous and heterogeneous catalysis; catalyst development specifically from recyclability, selectivity, and environmental viewpoints have been emphasized.[12] The main focus is well-defined catalysts, which may include both metal/metal oxide nanoparticles possibly exploiting nanomaterial as a support. Specific reactivity can be projected due to the nanosize of the materials that display specific characteristics which are difficult to achieve with traditional, bulk materials (Figure 1).

The ability to produce materials with specific sizes or shapes, or to grow complex solid nanostructures, can be exploited to fulfill specific selectivity requirements in catalysis. The full understanding of the synergistic effects among the different parts of the nanocatalysts still in its infancy, but the field has already started to see many exciting developments, and promises that may revolutionize chemical manufacturing.
Figure 1. Nanoarchitecture: an avenue to superior precision. Axes are: A: composition of functional sites; B: ordering level of sites; C: functional properties of material. Adapted from ref. [13]

Additionally, an immense developments in the field of surface science at the molecular level was possible because of the advanced synthetic techniques (e.g., clean single crystal surfaces alternative energy inputs, ultrahigh vacuum techniques, etc.) and characterization techniques [e.g., (X-ray photoelectron spectroscopy (XPS), atomic emission spectroscopy (AES), low energy electron diffraction (LEED)].

In terms of nomenclature, the term ‘colloids’ has been loosely used for nanoparticles (NPs) in liquid-phase catalysis, termed ‘colloidal catalysis,’ while ‘nanoparticle’ is often referred to NPs in the solid state. The terms ‘nanostructured’ or ‘nanoscale’ materials (and by extension ‘nanomaterials’) are any solids that possess a nanometre dimension. Despite these differences in nomenclature, ‘nanocatalysts’ or ‘nano-catalysis’ summarize well all the different cases as discussed below in various sections.

1.2. The Impact of the Intrinsic Properties of Nanomaterials on Catalysis

The interatomic interactions affect the overall catalytic performance of solids or a cluster of atoms. Modification of the relative number of the under-coordinated surface atoms delivers an additional choice that allows one to tailor the properties of a nanosolid as compared to its bulk counterpart. Hence, from the knowledge about the under-coordinated atoms and the contribution of interatomic
interaction can bridge the gap between a single molecule and a bulk material in physical and chemical performances. The impact of reduction of atomic coordination (deviation of length, bond order and angle) is remarkable, which dictates the activity of a surface, a nanosolid, and a solid in amorphous state due to their difference in bond relaxation and its consequences on bond energy.[14]

Figure 2. The impact of the intrinsic properties of nanomaterials on catalysis. Adapted from ref. [13]

The uncommon nature of a surface and a nanosolid can be understood and thoroughly formulated as functions of atomic coordination reduction and its effects (size dependence) on the atomic trapping potential, crystal binding intensity, and electron–phonon coupling; this combination embodies the final activity of the nanomaterials. The physical quantities of a solid are generally classified as follows:

- Quantities that are directly associated to bond length, such as the mean lattice constant, atomic density, and binding energy.
Quantities that depend on the cohesive energy per discrete atom, such as thermal stability, critical temperature for phase transitions, and evaporation in a nanosolid and the activation energy for atomic dislocation, diffusion, and chemical transformations etc.

Properties that differ with the binding energy density in the relaxed continuum region such as the Hamiltonian that controls the entire band structure and is correlated with the characteristics such as core level energy, band gap, photoabsorption, and photoemission. Structural alteration has certainly given a new freedom that allows us to tune the physical properties that are initially nonvariable for the bulk portions by just modifications of the shape and size to effectively use the atomic coordination reduction. Thus, the intrinsic properties of nanomaterials especially size dependency, will directly or indirectly induce, significant effects on the catalytic activity (Figure 2).

1.3. How the Properties of Nanocatalysts can be Tailored?

The use of metal, metal oxides, and mixed metal oxides NPs in catalysis is critical as they mimic active metal surface at the nanoscale and thereby bring selectivity and efficacy to heterogeneous catalysis.[12] According to the literature, in order to obtain superior yet sustainable catalytic performance, NPs should at least: (i) have a specific size (1–10 nm); (ii) have a well-defined surface morphology; (iii) have reproducible syntheses and properties; and (iv) be amenable for easy isolation and possible reuse. In the cases where the nanoparticle is supported, query of specific control of its location, chemical and spatial surroundings play pivotal roles in determining its activity. Tailoring the properties of nanocatalysts thus entails exploration of NP characteristics such as morphology, crystalline structure and composition (surface state) using different synthetic techniques and/or post-synthetic modifications. To understand the characteristics of the nanocatalysts, it is crucial to clarify the chemical and physical properties of the materials, which include the size and shape of the nanoparticles, surface properties, and nature of surface coating and presence of any impurities/unreacted starting materials (Figure 3).
1.4. Nanocatalysis: Applications in Chemical Industry

Today, nanocatalysis is one of the fast growing fields, which essentially involves the use of nanomaterials as catalysts for a variety of important catalytic transformations. Heterogeneous catalysis signifies one of the commercial applications of nanoscience; nanoparticles of metals, semiconductors, oxides, and other compounds have been widely employed for significant chemical reactions. Since, most commercial catalysts are still manufactured by ‘mixing, shaking and baking’ mixtures of multicomponents, their nanoscale properties and structures are not well controlled and the synthesis–structure–performance interactions are poorly understood.

Key points of sustainable nanocatalysis research should include:

- Enhancement of selectivity and activity, low energy consumption, and long lifetime of catalysts.
- Replacement of precious metal catalysts through catalysts design at the nanoscale and use of earth-abundant and inexpensive metals, thus reducing preparation costs.
- Unique design of catalytic procedures which can eliminate/reduce the formation of the
undesirable molecules.

In order to fulfill all aforementioned benchmarks, precise control of the size, shape, surface composition and electronic structure, as well as thermal and chemical stability of the individual nano components is essential. Diverse impending benefits (Figure 4) can ensue via the use of nanocatalysts as has been testified by great academic and industrial research attention in recent times.

![Diagram](image)

**Figure 4.** (A) Expected benefits of nanocatalysis. (B) Catalyst market by end-use. Adapted from ref. [13]

Because of the wide-spread applications of catalysis (especially heterogeneous catalysis) in industry segments including petrochemical, pharmaceuticals, chemical, food processing sectors, among others, a recent valuation of the global catalysts market is as follows:

- The global market for nanocatalysts employed in catalytic applications increased from US $3.3 billion in 2002 to US $5.0 billion in 2009. It is expected to reach approximately US $10.0 billion by 2017.
- Commercially well-known catalysts such as industrial zeolites, enzymes, and transition metal catalysts, till date, accounted for about 98% of global sales.
- The use of nanocatalysts, such as transition metal oxides/mixed metal oxides, gold catalysts, carbon nanotubes and others have been continuously increasing their combined market share from 2009 onwards.
Not surprisingly, nanocatalysis is a growing business. The list of companies that have already patented and/or commercialized technologies relating to nanocatalysts is rising rapidly. The dominant global players include BASF Catalyst LLC, BASF SE, Argonide Corporation, Bayer AG, Hyperion Catalysis International, Johnson Matthey PLC, Catalytic Solution, Inc., Evonik Degussa GmbH, Genencor International, and Zeolyst International, etc. as they are steadily pushing the boundaries of the field in order to achieve better nanocatalysts.

1.5. Nanocatalysts and Sustainable Chemistry

Nanocatalysis is the key constituent of “sustainable nanomaterials and organic transformations” relevant to nearly all types of catalytic organic transformations [16-19]. Among nanocatalysts, several forms such as magnetic nanocatalysts, nano-mixed metal oxides, core-shell nanocatalysts, nano-supported catalysts; graphene-based nanocatalysts have been successively used in diverse applications [15, 20-22]. Magnetic nanocatalysts stand apart in this group because of their low preparation cost, excellent activity, great selectivity, high stability, efficient recovery, and good recyclability (Figure 5).

![Figure 5. Advantages of nanocatalysts over simple homogeneous and heterogeneous catalysts.](image)

These versatile semi-heterogeneous nanocatalysts (with high surface area) are the best alternatives to conventional catalysts, the highest catalytic activity, selectivity, and stability can be achieved by
their shape, size, composition, and nature of nanocatalyst structure.[27-29] These noteworthy advantages of nanocatalysts are attributed to the nanosized effect and the catalytic performance generally increases with decreasing size of nanostructures. Though, when the size of the active site is reduced to nanoscale dimensions, the surface free energy increases, resulting in the aggregation of the particles into small branches and reducing the catalytic productivity. Also, the isolation and recovery for the catalysts become difficult as their size decreases; in most cases, separation through traditional filtration is not an easy task. Therefore, it is important to use the appropriate support materials/nanomaterial to design an effective, reusable and recyclable nanocatalysts.[30]

In this thesis, I emphasize sustainable organic transformations catalyzed by earth-abundant iron-based catalysts, supported catalysts and core-shell nanocatalysts. Our emphasis is on identifying the driving forces for the design of specific catalysts, a concrete mechanistic knowledge on the desired reaction that defines the requirements from nanotechnology in the manufacturing of useful catalysts. It is our belief that only via this synergy between nanotechnology and basic mechanistic studies, aided by the knowledge from surface science[31] and computational simulations,[32] developments of efficient, greener nanocatalysts can be successfully achieved.[20]

2. Iron-oxide-based Nanocatalysts

The progressive development of “green chemistry” has made catalysis field even more innovative and inspiring, as it leads to effective and sustainable synthetic protocols that evade the use of volatile organic solvents, toxic reagents, severe reaction conditions, and time-consuming, uneconomical separations.[33-37] In a homogeneous catalysis system, the catalytic species and the reactants are in the same phase, which allows facile interaction between the components and, hence, results in better activity/selectivity, higher turnover numbers and the possibility to tune the chemo-, and enantioselectivity of the catalyst by amending the active catalytic molecules.[38] Consequently, these catalytic systems are extensively used for various important chemical transformations in a large number of industries. However most of them have not yet been commercialized, because of trouble encountered in isolating the catalyst from the final reaction mixture, making the overall process cumbersome.[39] On the other hand, there have been considerable developments in heterogeneous catalysis over recent decades, owing to the associated advantage of easy separation notwithstanding having low activity and selectivity.[40] In order to overcome the difficulties associated with both types of catalytic systems, heterogenization is typically achieved, either via entrapment or covalent grafting of the active catalytic species on
surfaces or inside the pores of a solid support, including magnetite, graphene, silica, alumina, zeolite, ceria, and so forth.[41-46]

Among these, iron oxides are inexpensive earth-abundant materials and they are ideal replacement of scarce, and expensive noble metals. In the last few years, various forms of iron oxides namely Fe$_3$O$_4$ (magnetite), FeO (wüstite), Fe$_2$O$_3$ (Iron III oxides), α-Fe$_2$O$_3$ (hematite), β-Fe$_2$O$_3$ (beta phase), and γ-Fe$_2$O$_3$ (maghemite) have been used in catalysis.[47-51] Magnetite and maghemite are ideal oxide supports, easy to prepare, having a very active surface for adsorptions or immobilization of metals and ligands. In addition, they can be separated by magnetic decantation after the reaction, thus making it a more sustainable and economic catalyst.[52, 53]

Based on their crystal structure, magnetite contains cubic inverse spinel structure (space grouping of Fd3m).[54] The unit cell has interesting magnetic properties due to the presence of nonequivalent cations in two valence states; Fe$^{2+}$ and Fe$^{3+}$ in the crystal structure forms (Figure 6a).[55] The unit cell also comprises of 32 O$^{2-}$ ions which are systematic cubic close packed along the [110] direction. Generally, Fe$_3$O$_4$ crystals are dispersed with octahedral and mixed octahedral/tetrahedral layers along the (111) direction.[56]

The crystal structure of α-Fe$_2$O$_3$ (hematite) is described within the space group with lattice parameters a = 5.034 Å and c = 13.752 Å (Figure 6b). Hematite exhibits two magnetic transitions, i.e., one at ~950 K (known as the Néel temperature) from a paramagnetic to weakly ferromagnetic state and other at ~265 K (known as the Morin transition temperature) from a weakly ferromagnetic to a perfect antiferromagnetic state. Hematite is also best alternative and active catalysts/support for various types of catalytic and environmental applications. Even though it is not magnetic in nature, it can be totally isolated by simple filtration or centrifugation.

γ-Fe$_2$O$_3$ (maghemite), on the other hand, contains cubic structure of an inverse spinel type with a = 8.351 Å (Figure 6c).[57-59] In crystal structure of maghemite, two crystallographically nonequivalent cation sites (tetrahedral (T) and octahedral (O)) are documented, and γ-Fe$_2$O$_3$ is a strong ferrimagnet with the Curie temperature projected in the range from ~780 to ~980 K; the direct determination of its Curie temperature is not possible due to the γ-Fe$_2$O$_3$ -to- α-Fe$_2$O$_3$ polymorphic transformation upon heating. If the size of γ-Fe$_2$O$_3$ nanoparticles falls below a certain value (~30 nm), it displays a superparamagnetic nature with a strong magnetic response under small applied magnetic fields.

In this section, I mainly focused on non-magnetic (hematite) and magnetic (magnetite and maghemite) nanocatalysts, (either as supports and/or catalytically active species) for catalytic and
environmental applications.

Figure 6. a) Crystal structure of Fe$_3$O$_4$, green atoms are Fe$^{2+}$, brown atoms are Fe$^{3+}$, grey atoms are oxygen. Reproduced from ref. [55] with copyright permission from The Royal Chemical Society. b) Crystal structure of hematite (α-Fe$_2$O$_3$). c) Crystal structure of maghemite (γ-Fe$_2$O$_3$). Adapted from ref. [60]

2.1. Morphology-dependent Nanooiron Oxides - Synthesis and Catalytic Applications

In the past few decades, extensive studies have demonstrated that the size and shape of a catalyst, at the nanometre scale, greatly affect its reaction performance. Especially, control of the particle morphology permits a selective exposure of a larger fraction of the reactive surfaces on which the active sites can be developed and tuned. This anticipated surface coordination of catalytically active atoms or domains considerably helps to improve catalytic performance, selectivity, and stability, resulting into “morphology-dependent nanocatalysts”.[61] For example, Mou et. al.
achieved rod-shaped $\alpha$- and $\gamma$-Fe$_2$O$_3$ particles from of $\beta$-FeOOH nanorods using appropriate dehydration procedures (Figure 7).\[62-64] The $\beta$-FeOOH nanorods of 30–50 nm in diameter and 400–500 nm in length were obtained by aqueous-phase precipitation of ferric chloride with sodium carbonate in polyethylene glycol (PEG) at 120 °C. The calcination of this $\beta$-FeOOH precursor at 500 °C in air produced $\alpha$-Fe$_2$O$_3$ nanorods (diameter ~ 30–40 nm and length was 400–500 nm). The $\alpha$-Fe$_2$O$_3$ nanorods were walled by two (001) side planes, two (001) side planes, and two (010) top planes. The side planes were Fe-ended surfaces without O anions, whereas (010) planes concurrently displayed the presence of both Fe and O ions. Notably, when, rod-like $\beta$-FeOOH precursor refluxed in PEG at 200 °C created $\gamma$-Fe$_2$O$_3$ nanorods of 30–40 nm in diameter and 400–500 nm in length. Each nanorods contained (110) side planes, (001) side planes, and (110) top planes and were all terminated by iron cations and oxygen anions.

Figure 7. (A, B) TEM/SEM images of $\beta$-FeOOH nanorods. (C, D) TEM images of $\gamma$-Fe$_2$O$_3$
nanorods of 30–40 nm in diameter and 400–500 nm long. (E) Atomic illustration of cubic $\gamma$-Fe$_2$O$_3$, and the real shape of nanorods that preferentially expose the (110) and (001) planes. (F) The selective reduction of NO by NH$_3$ as a function of temperature. TPD profiles of (G) NH$_3$ and (H) NO/O$_2$ using the $\gamma$-Fe$_2$O$_3$ nanorods. Reproduced with permission from ref. [63]. Copyright 2012, WILEY-VCH Verlag GmbH & Co.

In the following sub-section, I have highlighted rod-shaped hematite and its applications for environmental remediation and catalytic applications. Hematite ($\alpha$-Fe$_{III}$O$_3$), one of the most common natural iron-bearing soil minerals in the earth,[65] has been extensively studied for treating environmental contaminants due to its high natural abundance, stability, and nontoxicity.[66, 67] Hematite is also very well-explored form of iron oxide and used in numerous catalytic reactions and energy-related applications.[68-70]

2.1.1. Synthesis of Micro-mesoporous Iron Oxides and its Environmental Applications

In the case of heterogeneous catalysis, the materials surface area and porosity plays often an important role because of better interactions between the catalysts and the reagents. Recently, mesoporous iron oxides are prepared via the aid of soft and hard templating approaches.[71-76] However, both methodologies lead to a somewhat poor control of the morphological development of the iron oxide materials-an asset that is often compromised during the calcination procedure. Thus, for chemists, it is a great challenge from the synthetic viewpoint to accomplish well-ordered morphology of iron oxide in a superficial and environmentally friendly protocol. The template-free conversion of metal oxalate precursor trailed by thermal decomposition of the intermediate materials may certainly offer a direct way to obtain such preserved morphology for the preparation of porous metal oxides.[77, 78] There are some reports from our group for the template-free thermally induced solid-state decomposition of iron oxalate precursor that can provide iron oxide nanoparticles control of the particle size, structure, morphology, surface area and crystallinity, upon varying the reaction conditions and precursor properties.[79-82] Herein, I describe a unique mild solid-state methodology for the preparation of morphologically controlled highly ordered hematite ($\alpha$-Fe$_2$O$_3$) nanocatalysts, which are further employed for hydrogen peroxide decomposition ($1.43\times10^{-1}$ min$^{-1}$); one of the highest rate constant on iron-based catalysts so far.[83] Furthermore, synthetic protocol using iron (II) oxalate as a
precursor has been documented, preserving its unique morphology, which represents a unique strategy towards a new class of micro-mesoporous nanocatalysts with an amazing efficiency in degradation of organic pollutants.

The synthesis of micro-mesoporous Fenton nanocatalysts includes template-free protocol based on the direct precipitation of iron(II) oxalate precursor from an equimolar mixture of oxalic acid and Fe(II) chloride in N,N-dimethylacetamide (DMA) at room temperature (step I), followed by solid-state isothermal treatment at 448 K for 12 h in air (step II).

The as-prepared iron oxide-DMA catalyst was characterized using several characterization techniques, which is very well described.[83] Here, I would like to give brief information about field-emission scanning electron microscopy (FE-SEM) image of iron oxide-DMA (Figure 8a). Remarkably, the catalyst reserved the flower-like morphology of the oxalate precursor along the entire synthesis even after the thermal treatment (Figure 8b). Structurally, the flower-like organization of the crystallites in the iron oxide-DMA sample comprises several rods, further composed of nanosized particles (5-7 nm), representing the smallest building units in this complex 3D nanoarchitecture.[83]

It is noted that iron oxide-DMA is very much comparable to previously reported mesoporous and nanocrystalline iron-oxide-based heterogeneous catalysts, which exhibit variable catalytic activity in the hydrogen peroxide decomposition with rate constants ranging from $10^{-5}$ to $10^{-2}$ min$^{-1}$, depending on the particles size/shape, crystallinity, porosity, and surface area.[83]

In this research work, it is noted that various characteristics such as chemical composition, size, surface area, pore volume, crystal structure, crystallinity of the catalyst, and 3D nature of nanoparticles play pivotal roles in the materials’ catalytic performance to $\text{H}_2\text{O}_2$ decomposition, and degradation of organic contaminants (Figure 8c).
Figure 8. a) FE-SEM micrographs of the iron oxide  b) Flower like morphology  c) Iron oxide-DMA catalyzed H₂O₂ decomposition, and degradation of organic contaminants. Reproduced from ref. [83] Copyright 2016 Royal Society of Chemistry.

2.1.2. Micro-mesoporous Iron Oxide Catalyzed Transfer Hydrogenation of Nitroarenes

After successful applications for the decomposition of hydrogen peroxide and morphology driven catalysis for degradation of organic pollutants, we realized that this material has excellent active sites for the catalysis. So, we decided to continue to evaluate the same material for other catalytic applications. Keeping in mind the acidic nature of iron oxide and on the basis of previous literature, we have performed transfer hydrogenation of nitroarenes using formic acid as a reducing agent.[84] It is well-known that research towards the design and development of highly efficient and benign catalysts for the transfer hydrogenation is a required goal from the viewpoint of sustainable chemistry. The iron-catalyzed reactions are of significant interest to limit or avoid the use of precious and toxic metals, as it is abundant, benign by nature and inexpensive.[85-88] There are various studies performed on different forms of iron for selective reduction of nitroarenes.[89-
For example, the transfer hydrogenation of α,β-unsaturated ketones with trihydride iron complex and using cyclopentanol or 2-propanol as hydrogen source without any base showed excellent activity and reactivity.[92-94] Recently, the use of first well-defined iron complexes as an effective homogeneous catalyst for the reduction of nitroarenes employing formic acid as the reducing agent was reported by Beller and co-workers.[95] It is noted the catalytic activity of this iron catalysts is influenced by metal-ligand combination. In the literature, some reactions had been performed using formates as hydrogen donors, however with other metal-based catalytic systems.[96, 97] In this research work, we have reported for the first time, micro-mesoporous iron oxide (MMIO) with high surface area (360 m²/g) as well-designed catalyst for transfer hydrogenation of nitroarenes using formic acid as a reducing agent, tris[(2-diphenyl-ethyl)phosphine] as ligand without any additional base (Figure 9).[84] The MMIO catalyst has been well characterized by FE-SEM, HRTEM, XRD, N₂ adsorption-desorption isotherm measurements and Mössbauer spectroscopy. It is noted that the recyclable catalytic system permits the reduction of a broad range of substrates and exhibit high tolerance to sensitive functional groups to deliver good to excellent yields of the corresponding products. In this research work, we did not use any noble and transition metals which make this protocol more sustainable. We consider that the tuning of the combination of micro-mesoporous iron oxides with different phosphine ligands could be used for several other industrially important hydrogen transfer reactions.

**Figure 9.** MMIO catalyzed transfer hydrogenation of nitroarenes.
2.1.3. Synthesis of Flower-shaped Magnetite for the Reduction of Nitroarenes

Following the reported micro-mesoporous iron oxide (hematite) as versatile materials for various kinds of catalytic applications in earlier section, we embarked on the synthesis of magnetite from iron oxalate via a simple two-step methodology.[98] In the first step, thermally induced solid state decomposition of iron oxalate was employed to prepare ultra-small iron(III) oxide nanoparticles; in the second step, the ensuing thermally-induced reduction of prepared iron(III) oxide in hydrogen atmosphere afforded magnetite (Figure 10a). The stepwise conversion of iron(III) oxide to magnetite by hydrogen reduction process via in-situ monitoring by XRD (Figure 10b). The two shoulder peaks (around 40° and 74° of 2θ) are clearly visible in the diffraction patterns up to 210 °C and suggest that the material is iron(III) oxide with ultra-small nanoparticles. At 220 °C, the diffraction lines belonging to fcc structure of magnetite/maghemite start to appear and their intensities gradually improved during the 60 min period of isothermal treatment. Therefore, we choose temperature 220 °C for 2 hours as the optimal condition for the synthesis of magnetite from iron(III) oxide with ultra-small particles via a tube furnace under hydrogen atmosphere. Notably, the flower/rod like morphology of the precursor is well-maintained even after the hydrogen treatment. The as-synthesized magnetite is characterized by several techniques including XRD, FE-SEM, TEM, N₂ adsorption-desorption isotherm and Mössbauer spectroscopy.

Figure 10. a) Synthesis of magnetite b) Evolution of X-ray diffraction patterns during in-situ monitored thermally induced transformation of iron(III) oxide with ultra-small particles to magnetite in hydrogen gas atmosphere.[98]
Figure 11a shows the XRD pattern of magnetite and all of the diffraction lines can be evidently attributed to standard face-centered cubic (fcc) structure of Fe$_3$O$_4$ (space group: Fd3m (227), JCPDS card No. 01-089-3854). Subsequently, Mössbauer spectroscopy was used for direct identification of iron oxide form (Figure 11b). The acquired spectrum is clearly composed of two magnetically split subspectra (i.e., sextets). The first sextet component with an isomer shift (δ) value of 0.27 mm s$^{-1}$, quadrupole shift ($\varepsilon_Q$) value of $-0.01$ mm s$^{-1}$, and hyperfine magnetic field (B$_{hf}$) value of 49.0 T corresponds to Fe$^{3+}$ ions occupying all the tetrahedral positions in the Fe$_3$O$_4$ crystal structure and with a contribution from Fe$^{3+}$ ions sitting in the octahedral sites having Fe$^{3+}$ ions as the nearest neighbours (i.e., Fe$^{3+}$-O-Fe$^{3+}$ pathway).

![XRD pattern](image1.png)

![Mössbauer spectrum](image2.png)

![SEM image](image3.png)

![TEM image](image4.png)

**Figure 11.** a) XRD pattern and b) Mössbauer spectrum of magnetite c) SEM and d) TEM image of magnetite.[98]

On the other hand, the second sextet with $\delta = 0.67$ mm s$^{-1}$, $\varepsilon_Q = 0.00$ mm s$^{-1}$, and B$_{hf} = 46.0$ T is ascribed to Fe$^{2+}$ and Fe$^{3+}$ ions occupying the octahedral positions in the Fe$_3$O$_4$ crystal structure among which the electron hopping occurs (i.e., an Fe$^{2+}$ ion with a neighbouring Fe$^{3+}$ ion and *vice versa*; Fe$^{2+}$-O-Fe$^{3+}$ pathway) with a frequency faster than the characteristic time of the Mössbauer
technique and thus manifested as component with $\delta$ value lying in the range typical of an average valence state of +2.5.[99] Relative spectral area of $\text{Fe}^{3+}$ and $\text{Fe}^{2.5+}$ sextet is 41 and 59%, respectively.

The SEM image (Figure 11c) of magnetite revealed the retention of rod/flower like pattern as found in the case of iron(III) oxide.[83] From the TEM image (Figure 11d), it can be seen that the individual nanorods possess an average size 300 nm and the self-assembled floral pattern has diameter of about 3 $\mu$m. The efficiency of the catalyst was then tested for the reduction of nitro moieties under microwave (MW) irradiation and with ethanol as a solvent.

![Chemical reaction equation and product structures](image)

**Figure 12.** Reduction of nitroarenes with magnetite.

First to scrutinize the reaction conditions, various parameters including effect of temperature, catalyst loading, solvent, and various hydrogen sources including the amount of hydrazine hydrate were investigated by selecting the nitrobenzene as model substrate. Different iron catalysts for the reduction of nitrobenzene with hydrazine hydrate were also inspected under the optimized
conditions. It is noted that commercial Fe powder, FeSO₄·7H₂O, FeCl₃·6H₂O did not show any activity under these conditions while FeCl₃·4H₂O, Fe(acac)₃ and magnetite exhibit 18%, >99 % and >99 % conversion respectively. Furthermore, these optimized reaction conditions were then applied to a selection of 15 substituted nitroarenes containing additional reducible groups to determine the chemoselectivity of the catalyst (Figure 12). In most of the cases, quantitative (>99%) conversion of the substrates to the desired amine derivatives was obtained within 15 min. The catalyst recycling is certainly essential in heterogeneous catalytic reactions. Therefore, we examined the recyclability of our developed catalyst for reduction reaction using nitrobenzene as a model substrate under the optimized conditions. After completion of the reaction, the catalyst could be easily separated using an external magnet. The separated catalyst was then washed with ethanol and dried before reuse. This process was repeated 10 times successfully without noticeable decrease in catalytic activity (Figure 13).

![Figure 13](image)

*Figure 13.* Reaction condition: Nitrobenzene (1 mmol), Hydrazine hydrate (200 µL), Fe₃O₄ (60 mg), EtOH (3 mL), temperature (90 °C), MW.

Overall, a robust, chemo-selective and flow-shaped magnetite reusable nanocatalyst has been developed for the reduction of industrially valuable nitroarenes substrates in the presence of other sensitive reducible functional groups. A diverse range of amines derivatives were obtained in excellent yields under the MW heating conditions at 90 °C using hydrazine hydrate as hydrogen source within 15 minutes that precludes the use of a precious metal catalyst and hydrogen gas in the preparation of amines derivatives.
2.1.4. Conclusion and Perspectives

The use of nanoparticles in catalysis is a rapidly growing field due to its important influences to both materials science and chemical transformations. Wide-ranging investigations on nanocatalysis, employing both metal and oxide particles, have enthusiastically established that the size and shape of the catalyst on the nanometre scale greatly affect catalytic activity. The particle size effect has characteristically been clarified on the basis of differences in the number of active sites; small particles with high surface-to-volume ratios display more active sites containing low-coordinated atoms in defect sites such as terraces, edges, or vacancies. Increasing attention now proposes that the shape of the catalyst particle is equally imperative for obtaining the anticipated catalytic performance and selectivity. This morphological necessity becomes more important with decreasing size along specific dimensions as shown in previous examples.

We believe that not only morphology-dependent hematite and maghemite can be prepared but, also other active forms of iron oxides; even other metal oxides could be prepared in unique morphology, which will show better activity/selectivity than their powdered form counterparts. Such methods would allow us to directly and intensely control the size, shape, and interfacial structure of individual nanoparticles and to recognize the dynamic temperature- and gas-induced structural deviations at the active sites.

2.2. Magnetic-supported Nanocatalysis - Applications in Sustainable Organic Transformations

Magnetic iron oxide nanoparticles stand out to be very attractive candidates as support materials in view of their easy availability, and cost-effective nature.[100-105] These nanoparticles can be effortlessly recovered with an external magnet due to the paramagnetic behaviour resulting in remarkable catalyst recovery without using difficult filtration/separation processes.[30, 106-109] This could significantly improve the catalytic efficiency and decrease the operational cost which is crucial for practical applications.

2.2.1. Synthetic Strategies of Magnetic Catalysts

A large number of synthetic strategies have been executed for the preparation of the magnetic nanoparticles involving oxides, such as magnetite (Fe₃O₄), maghemite (Fe₂O₃), spinel-type ferromagnets (e.g., MgFe₂O₄, MnFe₂O₄, and CoFe₂O₄ etc.) pure metals (Fe and Co), alloys (CoPt₃ and FePt).[20, 52, 110] Amongst all the magnetic NPs, magnetite has been studied most extensively for a variety of applications in multidisciplinary fields. The common synthetic
methodologies include chemical methods (namely co-precipitation, thermal decomposition, microemulsion, hydrothermal, solvothermal processes), [20, 52, 110, 111] and physical methods (such as electron beam lithography, gas phase decomposition, pulsed laser ablation). [112, 113] Chemical methods are extensively employed by industries and research laboratories owing to the ease of synthesis and involvement of less stringent conditions. However, with the rising environmental concerns and the current emphasis on adopting greener pathways, friendly procedures for the synthesis of metal nanoparticles (MNPs) have been advanced; various advantages and drawbacks of the various synthetic protocols are described.

In this section, I would report mostly on magnetite and maghemite supported nanocatalysts and its applications in various important organic transformations. Since, few years, we are working on the field of “magnetic nanocatalysts” and to date we had reported noble- and transition metal-supported magnetic nanocatalysts, magnetic supported-sulfonic acid, and magnetite-supported L-cysteine and its applications in several important reactions including Mannich type reactions, C-C, C-S, and C-O coupling reactions, oxidation, reductions, and Ritter reaction etc. (Figure 14)

**Figure 14.** Magnetic-supported Nanocatalysts.

So far our efforts have resulted into more than 15 publications in the field of magnetic nanocatalysis,[20, 30, 40, 52, 53, 109, 114-125] but to due space limitation, we have selected 6-8 papers for inclusion in this habilitation thesis, highlighting the importance of our works; all published papers are cited in this thesis.
2.2.2. Magnetic-supported Pd Nanocatalysts

Recently, there are various reports on the synthesis of magnetic-decorated metal nanocatalysts (e.g., Pd, Cu etc.,) and its applications in important organic transformations. In most of these reported protocols, various types of linkers and ligands have been used that often require multistep synthesis procedure, which renders them more expensive. So, it is important to design and develop such inexpensive protocols for the catalytic applications. As described in Figure 15, the magnetic supported-Pd nanocatalyst was prepared by simple co-precipitation method from inexpensive precursors, and without resorting to cumbersome linkers or ligands and was used for several organic transformations. First, we reported magnetite-supported palladium nanocatalyst for Buchwald reactions for arylation of amines and amides using Xantphos as ligand and cesium carbonate as base.[122] Due to sturdy interaction between Pd and ferrite MNPs, the catalyst could be reused and recycled without any significant loss in catalytic activity and any noticeable Pd leaching.

![Figure 15](image-url)

**Figure 15.** Synthesis of maghemite-Pd nanocatalyst and its catalytic applications for Buchwald-Hartwig reaction.

A nanocatalyst comprising ultra-small Pd/PdO nanoparticles (<5 nm, 3.2wt%) supported on maghemite was prepared by co-precipitation protocol using inexpensive raw materials and was deployed successfully in various significant synthetic transformations, namely Heck-Mizoroki olefination (up to 95%), Suzuki reaction (60-95%), and allylic oxidation of alkenes under milder conditions (Figure 16).[120] The chemical nature, morphology, size, and loading of palladium nanoparticles over the magnetic support were studied by TEM/EDX, HAADF-STEM chemical mapping, XPS, AAS, and in-field $^{57}$Fe Mössbauer spectroscopy.[120] Notably, XPS analysis
confirmed the presence metallic palladium (Pd) and palladium oxide (PdO) of both forms; though it is noted that after the first cycle catalysts display the exclusive presence of Pd$^0$.\cite{120} The combination of DMF and water with K$_2$CO$_3$ plays an important role in the reaction, as it serves as dual function of a solvent and a reducing agent (PdO to Pd$^0$) under heating conditions.\cite{120} The reported systems display several greater features matched to previously reported catalysts.
including very short time required for the reaction completion (1-2 h), very high yield and conversion, excellent selectivity as well as good recyclability.

2.2.3. Magnetic-supported NiO Nanocatalysts

In transfer hydrogenation reactions, 2-propanol is often preferred as the hydrogen donor. However, glycerol has recently gained increased attention as an alternative sustainable solvent for catalytic and non-catalytic organic transformations,[126] because of its unique combination of physical and chemical properties, such as polarity, low toxicity, high boiling point, and biodegradability.[127, 128] The reduction of nitro as well as carbonyl compound with transfer hydrogenation reagents is a much safer and more benign process than reactions involving molecular hydrogen, metal hydrides, or soluble metals. In this research work, we reported the combination of glycerol and magnetic nanocatalysts (magnetite-NiO) as heterogeneous catalysts for hydrogen transfer reactions (Figure 17).[129] Glycerol acts as a hydrogen donor as well as solvent in the reduction of nitro and carbonyl compounds catalysed by magnetite-NiO nanoparticles.

![Figure 17. Reduction of nitroarenes and carbonyl compounds.](image)

2.2.4. Magnetic-supported CuO Nanocatalysts

Cu is one of the most important 3d transition metals because of its range of oxidation states (Cu$^0$, Cu$^I$, and Cu$^{II}$) helping the smooth electron transfer either via one or two-electron routes, interesting physical and chemical characteristics.[130] Owing to such distinctive properties, Cu-based
nanomaterials as catalysts have well-deserved place in the multidisciplinary research including nanotechnology, catalytic reactions, electrocatalysts, photocatalysis, etc.[131, 132] However, because of their propensity for oxidation, the main challenges in Cu-based nanocatalysts for various chemical transformations remains the synthesis of highly active and selective, stable, robust, and inexpensive catalytic materials.[133, 134] Immobilizing Cu-based NPs (e.g. Cu, CuO and Cu₂O) on various solid supports (e.g. iron oxides, SiO₂, carbon material, polymer, etc.) is a sustainable strategy for scheming advanced Cu-based NPs for catalysis applications. Among these supports, magnetic iron oxide is an ideal support for the immobilization of Cu species, because of it is inexpensive and highly recyclable through magnetic separation.

Following the same strategy as before, we developed a magnetite-supported copper (nanocat-Fe-CuO) nanoparticles for the synthesis of 4-methoxyaniline, pyrazole derivatives, and Ullmann-type condensation reaction under benign reaction conditions.[124] We were able to prepare nearly 20-30 nm magnetic-CuO nanoparticles via simple impregnation method in aqueous medium from readily available inexpensive starting materials. In this study, we reported nanocat-Fe-CuO catalyzed expedient and facile synthesis pyrazole aldehydes with malononitrile and dimedone via Knoevenagel condensation under solvent-free conditions. Various substituted 1,3-diphenyl pyrazole aldehydes were prepared via Vilsemeier–Haack reaction of the corresponding hydrazine. Furthermore, the catalytic activity of nanocat-Fe-CuO catalyst was established for the synthesis of 4-methoxyaniline and an Ullmann-type condensation reaction (Figure 18).

The reaction of the 4-methoxybromobenzene with nanocat-Fe-CuO, and aqueous ammonia in a mixture of acetone and water was performed to obtained the 4-methoxyaniline in good yield. Ullmann condensation reaction, between 4-methoxyphenol and iodobenzene performed in DMSO at 120 °C, afforded the corresponding condensation product in 75% yield.

Significant efforts have been made concerning the carbon-heteroatom (C-O, C-N, and C-S) bond formation reactions using transition metal catalysts.[135] These reactions are reflected as influential tools for the synthesis of important substrates/intermediates that are of biological, pharmaceutical, industrial, and material interests. The cross-coupling reactions of diverse nucleophile with aryl halide have been achieved by the most widely used protocols namely Ullmann, Buchwald, Hartwig, Evans, and Chan.[136, 137] Of these, the standard and possibly oldest Ullmann condensation reaction has been an efficient exercise, since it includes Cu as catalyst, which often delivers high catalytically activity similar to expensive, toxic and noble metal such as palladium.[138]
In continuation of our study using magnetic-copper nanocatalyst, we reported the synthesis of maghemite-copper nanocomposites from inexpensive precursors, and showed their efficacy as efficient nanocatalysts for carbon-heteroatom (C-O, C-N, and C-S) bond formation reactions (Figure 19).[123] These cross-coupling reactions progressed effectively and found to be superior in terms of yield. This may be credited to the nano size of the maghemite solid support material (30-40 nm) which permitted the immobilization of a higher amount of Cu nanoparticles on its surface and improved the dispersion of the catalytic active sites in the reaction medium, thus improving their accessibility to the substrate. While the presence of electron donating group such
as -Me, -OMe and -Bu on phenols at ortho and para positions delivered good to excellent yields; for the substituents at meta position of phenols comparatively less moderate yields were achieved. Remarkably, naphthalene homologues of phenol such as 2-Naphthol afforded excellent yield of desired coupling product.

**Figure 19.** Maghemite-Cu catalyzed cross-coupling (C-O, C-S and C-N) reactions.

### 2.2.5. Magnetic-supported Au Nanocatalysts

Metal/metal oxide-supported nanocatalysts especially with noble metal (Pd, Pt, and Au) have created tremendous interest among the chemists and they are becoming an important part of organic synthesis and catalytic transformations. Gold nanoparticles and supported-gold nanocatalyst have attained an important place among noble metals, because of their unique reactivity and selectivity in various catalytic activities.[139] Metal oxide-supported Au NPs (Au/MgO or TiO₂ or iron oxides, etc.) with controllable shape can be synthesized by the adsorption or deposition-precipitation methodologies among others.[140, 141]

Inspired by such approach, we reported synthesis of Au nanoparticles supported on iron oxides and their effective utilization for the hydrogenation of aromatic nitro compounds and oxidative esterification of aldehydes under benign conditions (Figure 20a).[118] HRTEM images and elemental mapping revealed that the hybrid material is composed of well-defined stoichiometric maghemite support (20-30 nm) adorned with ultrasmall (5-6 nm) gold nanoparticles (Figure 20b). Under optimization reaction conditions for oxidative esterification of aldehydes, the catalytic performance of catalyst was further discovered with other substrates bearing and electron withdrawing and electron donating groups to obtain good to excellent yield. Notably, even with the deactivating substituents p-nitro- and m-bromo-, the reaction afforded 84% and 40% yields,
respectively.[118] Encouraged by this admirable catalytic activity of nanocat-Fe-Au for oxidative esterification of aldehydes, the catalyst was further used for hydrogenation of nitrobenzene in benign reaction medium. It was noted that under the transfer hydrogenation reaction condition, nanocat-Fe-Au displays excellent activity and selectivity (83-94%) with various functional groups (Figure 20). We also performed control experiments with bare iron oxide (without Au) which produced no/low yields of the corresponding products.

![Catalytic applications of maghemite-Au nanocatalyst](image)

**Figure 20.** a) Catalytic applications of maghemite-Au nanocatalyst, b) elemental mapping image of maghemite-Au. Reproduced from ref. [118]. Copyright 2014 Royal Society of Chemistry.

It is noted that the reaction progressed via heterogeneous catalysis as we could not detect the soluble species (Fe and Au) by ICP-AES analysis in the supernatant. The benefits offered by this general procedure are effective simplicity, applicability to oxidative esterification and the reduction reaction, and high yields of products with diverse substrate scope. This greener protocol enables easy recyclability of the catalyst, restrained up to five times without loss of efficiency, and deployed benign reaction medium.

### 2.2.6. Magnetic-supported Sulfonic Acid

The Ritter reaction is a traditional acid-catalyzed reaction between a carbocation precursor, namely substituted olefin or alcohol, and nitriles to produce amides.[142] It has useful applications for the preparation of pharmaceuticals intermediates and heterocycles.[143, 144] Generally, sulfuric acid, trifluoromethane sulfonic anhydride, triflic anhydride, 2,4-nitrobenzenesulfonic acid, and I$_2$/H$_2$O are often used for this reactions.[117] Since, in most of these reactions, homogeneous catalysts (expensive and not reusable) are often involved, an efficient protocols based on heterogeneous
catalysts is always welcome.[145]
Sulfuric acid and related protic acids are the important catalyst for the manufacture of industrial chemicals and pharmaceutical intermediates. More than 15 million tons of sulfuric acid is annually spent as “not recyclable catalysts” which involves costly and unproductive separation of the catalyst from homogeneous reaction medium for the synthesis of industrially essential chemicals, thus resulting in an enormous waste of energy and waste products. The sustainable approach for the chemical processes has inspired the practice of recyclable strong solid acids as substitutes for such unrecyclable “liquid acids” catalysts. Though the technology has been extensively discovered and well-developed, yet to invent new methodologies for the immobilization of sulfonic acid, exclusively for economically and industrially attractive concerns requires employing less toxic and readily available precursors as well as benign supports, simple and non-energy-intensive protocols for recovery and reuse of catalyst.[146]
In this research work, we focussed on a highly effective Nanocat-Fe-SO$_3$OH (sulfonic acid supported iron oxide), a magnetically separable and reusable nanocatalyst for the Ritter reaction under solvent-free conditions (Figure 21).[117] Notably, the reactions carried out with the bare magnetite (without sulfonic acid group appended) delivered no desired product. The reaction between a hindered aromatic nitrile and a hindered alcohol also led to the corresponding amide formation in good yield. In general, the mechanism apparently involves the formation of the carbocation by the acid catalysis of the Nanocat-Fe-OSO$_3$H at the alcohol carbocation precursor, which reacts with the nitrile to form a nitrilium ion. Water hydrolysis and a series of proton transfer steps then produce the final amide product. After obtaining the excellent activity for Ritter reaction, we explore the Strecker reaction and the quinoline synthesis, which has important interest in medicinal chemistry because of its application in the pharmaceuticals.[147] The multicomponent reaction between 4-flurobenzaldehyde, piperidine and TMSCN under solvent-free conditions delivered the corresponding product in 93% yield and the condensation reaction between 2-amino benzophenone and 5,5-dimethyl-1,3-cyclohexandione under MW delivered in 92% yield (Figure 21).
2.2.7. Other Magnetic-supported Nanocatalysts

Additionally, we reported on magnetic-supported nanocatalysts including magnetite-Co nanocatalysts employed for oxidation of alcohols,[116] magnetite-cysteine was synthesized without any additive or additional source of linkers and successfully used for the synthesis of β-amino carbonyl and hydroquinoline compounds.[148] Furthermore, magnetite–Mo was used in the oxidation of benzyl alcohol and a series of examples of important organic reactions including A3 couplings, hydrogenations and hydrations.[109] Also, some other silica-coated magnetite namely silica-based magnetic manganese nanocatalyst were employed for the applications in the oxidation of organic halides and alcohols.[53] Lately, silica-based magnetic palladium nanocatalyst has been

Figure 21. Synthesis and catalytic applications of Nanocat-Fe-OSO$_3$H.
used for copper-free, phosphine-free, direct coupling of acyl chlorides with terminal alkynes to prepare a variety of ynones under aerobic conditions at room temperature without the use of any additives and inert conditions.[149] Due to some limitation of pages and keeping in mind length of habilitation thesis, the above mentioned articles are not explained in details, but their electronic copies are appended to this thesis.

2.2.8. Conclusion and Perspectives
In recent years, nanotechnology-based advances have allowed the growth of economic and sustainable synthetic pathways to produce highly active catalytic nanomaterials. Efforts have been engaged towards the preparation of magnetic materials for the design of magnetic nanocatalytic systems owing to their exceptional physico-chemical characteristics and fast response to the applied magnetic field. Moreover, these magnetic-based nanocatalysts are robust, easy to prepare, non-toxic, and can be reused numerous times for several reaction cycles. Therefore, they have occurred as the feasible replacements to existing solid-supported heterogeneous catalysts. Though remarkable progress has been accomplished in the area of nanocatalyst research, yet the major challenge lies in the comprehensive understanding of the mechanistic features of the catalytic procedures that would ultimately help in tuning and tailoring the properties of the newly designed catalysts. In predictable future, the strategy of novel magnetic nanocatalysts with multiple components and well-controlled interactions will find major applications in industrially important organic transformations.

3. Core-shell Nanoparticles – Applications in Catalysis
Core-shell nanoparticles (CSNs) are generally nanostructured materials consisting of inner core and outer layer(s). Owing to the possible different types of core and shell materials with various composition, structure and thickness, core-shell nanoparticles can be easily varied to encompass different materials, properties, and functionalities into a single system; this can often provide the multifunctional materials with enhanced synergistic properties. Moreover, the possible unique properties arising by the interfacial effect between the core and the shell could also render unique properties. For instance, the cooperative effect by Ni core and ZnO shell in Ni@ZnO core-shell can give rise to nonlinear dielectric resonance and excellent microwave (MW) absorption property in the material.[150]
Depending on the compositions and provisions of the two components in the materials, core-shell nanomaterials can be divided into several classes, including inorganic/inorganic, organic/inorganic, inorganic/organic, and organic/organic type CSNs.[151-153] Due to their multifunctional and/or enhanced properties, core-shell nanostructures are gradually attracting attention because of their conducive and versatile compositions to accomplish these anticipated outcomes.[154-157] In many cases, core-shell nanostructures offer synergistic and cooperative properties that are much more than the simple sum of the characteristics of the cores and the shells, thus concluding in improvement in specific physical and chemical properties.[158-162]

The development of highly active and selective, robust, inexpensive and benign catalytic protocols is the great challenge for chemists. This problem as a whole or in part is proven to be addressed by making catalytic systems with core-shell structural features. For instance, using noble metals (e.g., Au, Pt or Pd), which have high catalytic ability, to prepare only a monolayer on the surface of non-precious/inert base nanometal (e.g., Ni, Fe, or Co) is an sustainable strategy for designed synthesis of core-shell nanoparticles with good catalytic efficacy.[163] For example, carbon-supported Pd@Co core-shell nanoparticles were prepared for electrocatalysts for oxygen reduction reaction.[164]

By including magnetic materials, multifunctional core-shell nanoparticles with catalytic as well as magnetic properties (the latter for ease of recyclability of the CSNs after the reaction under the power of a magnetic field) can easily be prepared with similar synthetic approaches.[165] This synthetic strategy has been widely applied for the construction of various bifunctional nanomaterials, e.g., magnetic and optically/photocatalytically active Fe₃O₄@ZnS nanoparticles.[166] Recently, this has been one of the inspirations behind worldwide research in the synthesis and investigation of bifunctional core-shell nanoparticles for catalysis of various chemical reactions (Figure 22).[15, 167, 168]
3.1. Synthetic Strategies to Various Core-shell Nanomaterials and Catalysts

CSNs have been recognized for their enormous potential in various applications owing to their unique structural, physical and chemical properties. Subsequently, the field has perceived a rapid growth in the synthetic strategies described for making such particles, and literature which enclosed some of the sub-topics.[169, 170] In general, the techniques that have been used for the synthesis of nanomaterials can often be extended to synthesis of either/both the core and/or shell components of CSNs. These synthetic methods can generally be classified as 1) “top-down” or 2) “bottom-up”. The main difference between these two synthetic methods lies in the types of starting materials that are used and the ways by which the nanoscale materials are formed. The “top-down” method starts from bulk materials and utilizes external controls like microfabrication techniques, mechanical stress, etc. to obtain the required nanomaterials with desired shapes and sizes. Instead, the “bottom-up” technique starts from molecular or atomic building blocks and mostly relies on the intrinsic chemical properties of individual elements and their mutual interfaces (via, e.g., sol-gel synthesis, chemical vapor deposition, etc.) to form the preferred nanomaterials. We have extensively abridged different synthetic strategies for the preparation of core-shell nanoparticles in our recent review (Figure 23).[171]
3.2. Transfer Hydrogenation Reactions with Ag@Ni Core-shell Nanocatalyst

As a part of our recent endeavors in the field of nanocatalysts focusing on core-shell nanoparticles, we have reported on magnetic core-shell Ag@Ni core-shell nanocatalyst that can be prepared by simple one-pot procedure, where oleylamine was employed both as solvent and reducing agent for the Ag⁺ and Ni²⁺ ions and triphenylphosphine was used as a surfactant.[172] The TEM image of the nanocatalyst shows nanoparticles with spherical morphology with a diameter of *ca.* 14.9 nm and with a narrow size distribution (Figure 24a). The selected area electron diffraction (SAED) pattern acquired for the NPs displays diffraction rings, which can be indexed to face-centered cubic (fcc) corresponding to both Ni and Ag.[172]

It is well-known that Ni and Ag metals are best catalysts for reduction of nitro, and carbonyl group reactions. So, we have used magnetic core-shell Ag@Ni nanocatalysts for the reduction of functional groups including nitro, azido, and carbonyl compounds which are of great significance.
for common applications in organic synthesis and in the synthesis of biologically active compounds for medical applications. Specifically, the Ag@Ni core-shell nanoparticles were used for the transfer hydrogenation of aromatic nitro compounds using isopropyl alcohol (IPA) as hydrogen donor (Figure 24b); electron withdrawing as well as donating groups such as -Cl, -Br, -F, and -OCH$_3$ were found to have no substantial influence on the reaction. In addition, the catalytic activity of the CSNs was tested for the reduction of carbonyl compounds nanoparticles and reduction of a variety of ketones to the corresponding alcohols was achieved in good to excellent yields (90-94%).

![Figure 24](image_url)

**Figure 24.** a) TEM image of Ag@Ni core-shell nanocatalyst, b) Hydrogen transfer reactions of aromatic nitro compounds and carbonyl compounds on Ag@Ni core-shell nanocatalyst. Reproduced from ref. [172].Copyright 2013 Royal Society of Chemistry.

### 3.3. Pd@Pt Core-shell Nanoparticles for Olefin Reduction

In recent years, effective tuning the functionalities (core and shell) of metallic nanocrystals especially Au-, Pd-, and Pt-based core-shell colloids are becoming interesting because of their exceptional optical and catalytic activities. Au@Pd, Au@Pt, Pt@Pd, and Pd@Pt core-shell structured nanoparticles have showed superior catalytic performance properties which are not achievable by their monometallic counterparts.[173, 174]. For instance, a Pt monolayer supported on Pd surface display an enhanced activity for oxygen reduction reaction (ORR), when established against a pure Pt surface.[175, 176] Heterointerface between the Pd core and the Pt shell of Pd@Pt CSNPs delivers a favorable environment for metal hydride formation making this material useful for catalytic applications. There are several choices for the synthesis of Pd@Pt core shell NPs including seed-mediated growth, co-reduction, and galvanic replacement.[177-185]
Recently, fabrication of bimetallic core-shell NPs with highly branched/porous structures garnered special attention because of their promising catalytic and electronic properties. These assemblies display a high index crystal facets on concave pore surface defined as a set of Miller indices \((hkl)\) with at least one integer higher than the unity permitting an easier access to active sites. More importantly, the porous framework allows the interface or accessibility of reactants with more active surfaces due to the abundance of pores enabling the overall kinetics of reaction.[186-188]

Herein, we describe a facile one-pot preparation of porous and highly branched Pd@Pt core-shell NPs at room temperature without any organic solvents or without adding pre-synthesized seeds.[189] Interestingly, these nanoarchitectures showed superior catalytic activity towards the reduction of olefins, an important reaction in organic chemistry, which is normally carried out using flammable hydrogen gas and heterogeneous transition metal catalysts.[190, 191] Complementary to catalytic hydrogenations with hydrogen gas, the use of inexpensive liquid hydrogen donors like formic acid, ethanol, propanol, hydrazine hydrate, ammonium formate etc. (transfer hydrogenation) allows the reduction process under ambient conditions without the use of high pressure condition.

Recently, we reported, the catalytic efficacy of branched porous Pd@Pt NPs for the reduction of various olefins using hydrazine hydrate as a reducing agent at room temperature (Figure 25).[192] The Pd@Pt NPs displayed evidently high catalytic activity than Pd NPs, Pt black and Pd+Pt NPs indicating the superior synergistic effects between Pd core and Pt shell (Figure 25). Overall, a facile one-pot aqueous synthetic method has been established for the assembly of highly branched micro-mesoporous Pd@Pt core-shell NPs with unique dandelion-like morphology. This unique catalytic protocol could be accomplished by the sequential development of the Pd core followed by the Pt shell due to the modification in their reduction kinetics associated with the use of ascorbic acid as a weaker reducing agent. A wide range of olefins, with several functional groups namely 4-fluorostyrene, 4-methoxy styrene were reduced in good to excellent yields. The comparison of catalytic efficacy with individual metals (Pd NPs and commercial Pt black) and their physical mixture (Pd/Pt=1/1) for the reduction of styrene displayed that the established branched core-shell Pt@Pt NPs stand out as the best contestant in terms of conversions due to the synergy arising from the combination of Pd and Pt. We consider that unique micro-mesoporous structure with a high contribution of mesopores is one of the crucial parameters accountable for the superior catalytic effect.
Figure 25. Olefins reduction using Pd@Pt NPs and effect of various catalysts, Pt black, Pd NPs, physical mixture of Pd and Pt NPs (1:1) and branched core-shell Pt@Pd NPs (1:1), on the degree of conversion in hydrogenation of styrene to ethylbenzene. Reproduced from ref.[192] Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.4. Synthesis of Pd@Pt/rGO and its Catalytic Applications
For catalytic purposes, Pd@Pt core-shell nanostructures (with a Pt shell on a Pd core) have exhibited higher catalytic performance compared to their individual components.[175, 176, 192, 193] However, in spite of having great potential, the wider applications have been somewhat limited to the field of electrocatalysis and the activity of such heterogeneous nanocatalytic systems for sustainable and recyclable organic/organometallic transformations has yet to be fully investigated. One of the possible reasons for such restrictions has been claimed to be challenges associated with the large scale production of such core-shell nanoparticles and in this case core-shell nanomaterials (Pd as core and Pt as shell), supported on heterogeneous support offered significant promises but remained largely unexplored.
In heterogeneous catalysis, the catalyst supports are indeed critical to i) anchor the catalytically active species, ii) avoid particle agglomeration by maintaining the well-dispersion, iii) minimize the leaching, iv) interact with the reactants/products to offer a possible synergism among all three components (core, shell and the supports). In this case, graphene - a two-dimensional atomic layer of carbon shows promises because of its high specific surface area, high electrical conductivity and good chemical/thermal stability;[194] the only problem being the hydrophobic nature of graphene surface due to the lack of surface functionalities. Alternatively, the other relatively more hydrophilic graphene derivatives, namely graphene-oxide (GO) and reduced graphene oxide (rGO), can be envisioned as better support materials for the immobilization of the nanoparticles.[194]

In most cases, the support and the nanoparticles are synthesized in two different steps and then require an additional step of “final” immobilization. Hence, a one-pot strategy for the synthesis of the final supported nanocatalysts is always welcome. In addition to the development of the support as well as the core-shell nanoparticles, the recent upsurge in the field of alternative energy outputs (namely MW, sonochemical etc.), also offers significant advantages for the synthesis of such nanomaterials especially under one-pot conditions. Intrigued by the combination of such ideas, coupled with the recent reports on “metal-free carbocatalysis” as well as our ongoing research on nanocatalysts, and supported nanoparticles, we developed a one-pot microwave (MW)-assisted approach to prepare the reduced graphene oxide (rGO)-supported Pd-Pt core-shell nanoparticles (Pd@Pt/rGO) (Figure 26A) and applied the nanocatalysts successfully for the aromatic dehalogenation and reduction reaction.[195]

In this approach, initially, the Pt and Pd precursors were well mixed with graphene oxide, pH was adjusted to 9 and L-ascorbic acid was added as reductant. The reaction mixture was then treated under MW for 3 min. During the MW treatment, not only the Pd and Pt precursors change to Pd@Pt core-shell nanoparticles, but also the graphene oxide gets reduced to reduced graphene oxide (rGO) to finally obtain the core-shell nanoparticles supported on reduced graphene oxides; the spherical core-shell nanomaterials (~95 nm) with Pd core (~80 nm) and 15 nm Pt shell were nicely distributed on the rGO matrix.
Figure 26. (A) Schematic illustration of the synthesis of Pd@Pt/rGO NPs. (B) HRTEM images of the final particles showing its core-shell nature. (C) PXRD pattern of Pd@Pt/rGO showing the Pd and Pt crystalline phases after Rietveld refinement.

The materials were characterized using different techniques like TEM, HRTEM, XRD, XPS, etc. While the TEM/HRTEM clearly exhibits the core-shell nature of the nanoparticles (Figure 26B), the XRD pattern indicates the presence of rGO and Pd and Pt on the surface (Figure 26C). The information about the metallic state of both Pd (in this case, we also found little amount of oxide) and Pt and the different functionalities on the rGO surface was obtained through XPS analysis. The well-characterized supported nanomaterial was then successfully employed for the aromatic dehalogenation and olefin reduction reaction.
Figure 27. Catalytic aromatic dehalogenation and catalytic reduction of olefin using Pd@Pt/rGO as nanocatalysts.

In case of catalytic aromatic dehalogenation one of the most important reactions for the synthesis of various pharmaceuticals and value-added products the Pd@Pt/rGO catalysts showed high yield (>98%) and high selectivity (>98%) when MW-assisted method was applied at 90 °C for 15 mins using EtOH as solvent (Figure 27). Additionally, the synergism between the core-shell can be established as both, Pt/rGO and Pd/rGO and even their physical mixtures showed relatively lower conversions in dehalogenation of 3-bromoaniline. The catalysts showed high substrate scope and can be recyclable (up to 5 times) without losing its activity and also maintaining its integrity. The mechanism of dehalogenation reactions with Pd@Pt/rGO catalyst is discussed. We believe that the rGO matrix facilitates the adsorption of the reducing agent/reactants thus increasing the local concentration leading to higher activity. Before our disclosure, this MW-assisted strategy encompassing the synergistic effect of core-shell nanoparticles on a graphitic support is unprecedented for such reaction.

Similarly, in the reduction of styrene to ethylbenzene, while Pt@Pd core-shell nanoparticles (without rGO support) possess considerably lower conversion (60%), compared to Pd@Pt/rGO, the supported catalyst system shows near quantitative conversion under the same reaction condition (EtOH as solvent, 60 °C, 30 mins) exhibiting the superior synergism among the support and core-shell nanoparticles. The versatility of the catalyst has been well demonstrated for the reduction of various olefins/alkynes under hydrothermal conditions (Figure 27). We strongly believe that catalysts like Pd@Pt/rGO will be beneficial for a variety of sustainable organic
transformations because of their activity, selectivity, diverse-substrate-scope, recyclability and most importantly synergistic action of individual components.

3.5. Summary and Future Perspectives
Core-shell nanoparticles have emerged as unique and diverse nanomaterials for catalysis, because of their additive or complementary improved characteristics compared to their component counterparts. The strain and ligand effect between the core and the shell are to be utilized to modify the catalytic action and selectivity of core-shell nanocatalysts. The recent advances in the synthesis of core-shell nanoparticles and their applications in various chemical transformations including hydrogenation reactions, oxidation reactions, cycloaddition reactions, ammonia decomposition, coupling reactions, etc., have been studied well.

In spite of their comprehensive application in catalysis, there are still some unexplored areas which require further research: the knowledge (or lack thereof) about the type of interaction between the core and the shell is possibly the most important among them.

Core-shell nanoparticles seem to have extraordinary potential in vapor phase reactions (e.g., hydrogenation, oxidation, and alkylation) including gas phase reactors. The emerging areas of flow chemistry and MW-assisted organic reactions may be major beneficiary of advances in core-shell nanocatalysis. The combination of two metals (bimetallic) as core and shell have emerged as a new generation of nanocatalyst systems, which can be discovered for a number of significant chemical transformations and the tuning of two metals may permit selective organic transformations with ease and offer additional tools for chemists to attain sustainability. These advancements in core-shell nanocatalysts will provide a solid and stable platform for heterogeneous catalysis, organic transformations and sustainable procedures in the near future.

4. Sustainable Organic Transformations
The field of sustainable organic synthesis witnessed huge progress in past years with numerous advanced scientific discoveries attended by improved and effective synthetic protocols which evade the use of toxic reagents.[196-198] Green chemistry includes a multifaceted approach in the design of environmentally benign protocols focusing on the relevant topics such as energy consumption, atom efficiency, and sustainability. Concepts such as “atom-economy,[199, 200] which involves the efforts towards minimization of supplementary chemicals, form the pillar of material efficacy in chemical productions. A foremost point in the design of sustainable processes
relates to the efficiency of the procedures which have to take into account numerous parameters including energy, material consumption, and man-power and reactor (flow versus batch reactions) usage.

For example, in chemical transformations, solvents play a very significant role in extractions, reactants solubility, washing, and separation of final products. In the past decades, scientists have dedicated a tremendous efforts for the substitution of toxic and harmful solvents by more environmentally benignalternates;[201] polyethylene glycol (PEG)[202], supercritical carbon dioxide (scCO\textsubscript{2}),[203] and water[204] are amongst the most broadly used benign replacements in recent years.

Moreover, inexpensive byproduct from biofuel industry, glycerol is also a useful solvent which has been quite used in several benign organic transformations.[205] Because of the choices of alternative protocols due to advancement of technology, additionally, the strategy of more environmentally benign and low influence procedures has become a highly extended practice in organic synthesis. The use of magnetic nanocatalysts,[20, 30] ionic liquids,[206] scCO\textsubscript{2},[207] solvent-free reactions,[24] MW-assisted synthesis,[9] and reactions in aqueous media,[34] among others, are important alternatives to improved efficiency of sustainable protocols.

Escaping the use harmful/toxic solvents and catalyst in chemical reactions is a highly challenging task. In chemical transformations the ideal synthesis should be a combination of a number of eco-friendly, safe, non-waste generating and economic procedures (Figure 28) which evidently entails a rational design of the target process based on fundamental understanding to address several green chemistry principles in an inclusive manner.

In this section, I describe the development of various environmentally benign protocols including the Fmoc protection, synthesis of 2-amino-4H-chromene, and triazoles in aqueous media. In addition, other benign methods like reduced graphene oxide decorated gold nanoparticles for Suzuki reaction in water and oxidative esterification, continuous flow hydrogenation of nitroarenes, azides, and alkenes and lastly magnetic ZSM-5 zeolite catalyzed valorization of furfuryl alcohol to γ-valerolactone, alkyl levulinates or levulinic acid, have also been included.
4.1. Organic Transformations in Aqueous Media

4.1.1. Catalyst-free Fmoc Protections of Amines in Aqueous Media

The development of selective and mild procedures for the protection of amines is important for organic transformations and has been shown to be mainly useful for reactions that include multistep synthesis. In this perspective, carbamates have become one of the most appealing protecting group for amines. Consequently, several kinds of protecting groups have been effectively employed. Among them, the 9-fluorenylmethoxycarbonyl (Fmoc) group has become one of the most adaptable protecting groups because of its important features like lability in basic media and stability in acidic media.[208] The Fmoc group has been particularly used for orthogonal protection of organic molecules, transprotection, and in cascade elimination reactions.

In the field of organic chemistry such as peptide, nucleoside, or combinatorial synthesis easily accessible amine protecting groups are often required. The groups should be stable under a wide range of reaction conditions and both easily and selectively cleavable.[2] The Fmoc group has grown enormously in reputation since its introduction as a protecting group for primary and secondary amines and particularly for amino acids. It is used in most existing solid and solution phase peptide synthetic synthesis because of its stability in acid and liability in base, being the chloroformate ester (Fmoc-Cl) usually engaged for its incorporation.[208]

There are several reported examples of Fmoc protection of amines that employed acid and base reagents in stoichiometric quantity and also, costly reagents or catalysts and organic/toxic solvents.

**Figure 28.** The ideal green synthesis. Reproduced from ref. [23]. Copyright 2013 Royal Society of Chemistry.
Until the publication of our paper, there was no report of catalyst-free Fmoc protection of amines in aqueous medium. We reported a very simple and highly efficient approach for the Fmoc protection of amines under catalyst-free conditions in aqueous medium.[209]

![Chemical reaction diagram]

**Figure 29.** Catalyst-free Fmoc protection of amines in aqueous media.

Several aromatic, aliphatic, cyclic amines as well as heterocyclic amines were transformed into the N-Fmoc derivatives in good to excellent yields (Figure 29). Excellent chemoselectivity was perceived in case of 3-amino phenol, ethanol amine, and dopamine chloride, as no bis Fmoc derivatives were observed. Furthermore, considering its importance in solid phase synthesis as well as in nucleoside, or combinatorial synthesis, Fmoc protection of amino acid was also explored.[209] This protocol can be used for the protection of amino acids, a crucial step in solution and/or solid phase synthesis.

### 4.1.2. Mg/Al Hydrotalcite Catalysed Synthesis of 2-Amino-4H-Chromenes in Aqueous Medium

2-Amino-4H-Chromenes have an extensive range of biological activities, including, antiproliferative, sex pheromone, antitumor, cancer therapy, and central nervous system activity. Various protocols have been reported for the production of 2-Amino-4H-Chromene and its derivatives using malononitrile, resorcinol and aldehyde. Numerous catalysts have been reported including piperidine, triethyl amine, aqueous K$_2$CO$_3$, cetyltrimethylammonium bromide (CTAB), Ca(OH)$_2$ as well as basic ionic liquids. We have reported Mg/Al hydrotalcite (HT) heterogeneous catalyst for three component reaction among aldehyde, resorcinol, and malononitrile under mild
and aqueous medium (Figure 30). Among the heterogeneous basic catalysts, hydrotalcite is a versatile material employed as catalyst for various organic transformations such as multicomponent reaction, aldol and Knoevenagel condensation, polymerization, Michael reaction, and Bayer-Villiger oxidation, etc.[210]

\[
\begin{align*}
\text{OH} & \quad \text{O} \quad \text{CN} \\
\text{OH} & \quad \text{R} \quad \text{CN} \\
\text{MgAl/ HT} & \quad \text{H}_2\text{O, 60 °C} \\
\text{Yields} & = 75-95\% \\
R & = \text{H, 2-Cl, 3-Cl, 4-Cl, 4-NO}_2, 3-\text{NO}_2, 2\text{-thiophene, 4-Me, 4-OMe, 4-OH, 2,5-(OMe)\text{}_2, 3,4-(OMe)\text{}_2, 4-F, 4-Br}
\end{align*}
\]

**Figure 30.** Synthesis of chromenes using hydrotalcite in aqueous medium.

We have reported hydrotalcite catalyzed one-pot synthesis of 2-amino-4H-chromenes with resorcinol, malononitrile and aldehyde in aqueous medium.[211] This protocol compromises numerous benefits including benign reaction conditions, reusability, and high yield of desired products.

### 4.1.3. Nano-γ-Fe\textsubscript{2}O\textsubscript{3}/HAP Catalyzed Synthesis of Triazoles in Water

Triazoles are imperative class of heterocyclic compounds and have comprehensive range of biological activity including anti-infective agent, anti-HIV activity, and anti-bacterial.[212] Various synthetic protocols are reported for the development of triazoles using numerous catalytic systems and benign reaction conditions.[213]

Among the various methods for the synthesis of triazoles, the most often used metals are copper and ruthenium.[213] Though, these metals are very advantageous for the regioselective preparation of triazole derivatives, the developments of novel transition metal catalysts and environmentally benign catalytic procedures for cycloaddition of alkynes to in situ generated azides aqueous medium is still a dynamic area of research. In this research, we reported γ-Fe\textsubscript{2}O\textsubscript{3} nanoparticles supported on hydroxyapatite (HAP) for the one-pot synthesis of 1,2,3-triazoles in aqueous medium (Figure 31). Notably, this was the first report of copper free iron nanoparticles based cycloaddition reaction for synthesis of triazoles.
Various aromatic and aliphatic halides and alkynes gave moderate to good yield in the aqueous medium. The use of an iron-based heterogeneous catalyst instead of the commonly used copper or ruthenium ones renders the reported methodology relatively more sustainable, and, therefore, interesting for industrial use. The catalyst can be reused up to five cycles and after each cycle recovery of the catalyst can be accomplished using a simple external magnet.

Furthermore, we investigated hexagonal mesoporous silica (HMS) supported copper oxides (CuO/HMS) prepared by sol-gel method. The catalytic efficacy of CuO on the HMS support with varying Cu loadings (1, 3, 5, 10, and 15 wt%) was investigated for the transformation of aldehydes to primary amides; 3 wt% CuO/HMS displayed good catalytic performance in good to excellent yields of amides (60-92%) in aqueous medium.[214]

Figure 31. Cycloaddition reactions among alkyne, halide and azide in aqueous medium.
4.2. Au/rGO Nanocomposites for Suzuki-Miyaura Coupling Reaction and Oxidative Esterification Reactions under Benign Conditions

Carboxylic acid derivatives are significant analogues of pharmaceuticals, polymers, agrochemicals, and building blocks for natural products.[215-217] In general, they are prepared from acid or acid halide using stoichiometric amount of catalyst with oxygen-based nucleophiles.[218] Alternative operative technique is oxidative esterification of the readily available aldehydes or alcohols. But some of these processes use stoichiometric amounts of heavy-metal oxidants.[219] So, it is prudent to discover sustainable benign conditions for the oxidative esterification of aldehydes.

![Figure 32. a) Au/rGO nanocomposites b) Elemental mapping of Au/rGO showing uniform dispersion of Au NPs. c) Catalytic applications of Au/rGO for Suzuki Miyaura coupling reaction and oxidative esterification reactions. Reproduced from ref. [220]. Copyright 2016 Elsevier.](image)
In continuation of our sustainability research, we reported Au/rGO nanocomposites for the aerobic oxidation of aldehydes to esters.[220] Synthesis of Au/rGO composite was attained using sodium citrate as a reducing and stabilizing agent which yielded nanometer-sized Au particles well-dispersed on rGO support (Figure 32a and b). The as-synthesized and well-characterized Au/rGO catalyst was also investigated for Suzuki-Miyaura in aqueous medium. The choice of water as solvent was designated to improve a low-cost approach and sustainable reaction conditions. Electron donating and withdrawing groups affected the reaction progress and yield towards the product formation.[220]

Moreover, the catalytic performance of Au/rGO nanocatalyst was explored for the aerobic oxidative esterification of aldehydes (Figure 32c). In summary, we have effectively established that gold nanoparticles (mean diameter ~12 nm) deposited homogeneously on the surface of reduced graphene oxides which displayed excellent catalytic activities. The optimized Au/rGO catalyzed reaction protocol was successfully applied to both activated and deactivated aryl halides for Suzuki reactions in aqueous medium and aerobic oxidation of aldehydes to esters using environmentally friendly O₂ as oxidant. The excellent reusability results confirm very well prospect of Au/rGO catalyst in Suzuki-Miyaura coupling and aerobic oxidative esterification reactions.

4.3. Maghemite-Pd Catalyzed Flow Hydrogenation of Nitroarenes, Azides, and Alkenes
Flow chemistry and continuous synthesis have become increasingly popular as feasible and, in several cases, superior substitute to batch reactions.[221] Continuous flow protocols normally offer better safety, energy efficiency, scalability, and reproducibility. Notably, heterogeneous catalysis and photochemistry, performing reactions in flow offers further benefits that cannot be matched in a round-bottom flask or a stirred tank.

The application of continuous flow protocol on a process scale has recently seen a rapid increase, representing that these advantages are tangible and impactful.[222] It is distinguished that chemoselective and partial catalytic hydrogenation of hydrocarbons with multiple C=C and C≡C bonds is very significant and a prerequisite in the pharmaceutical and petrochemical industries.[223] Mostly, the catalytic transfer hydrogenation are performed by various transition and noble metals containing heterogeneous catalysts under continuous flow conditions.[224] However, most of these catalysts are not recyclable and show leaching to large extent due to high pressure and related reaction parameters in flow reactor.[225] In this context magnetic nanocatalysts are great alternative as they are cost-effective, and
recyclable. Herein, we have reported maghemite-supported ultra-fine Pd (Maghemite-Pd, 1-2 nm) nanoparticles, for flow hydrogenation of nitroarenes, azides, and alkenes (Figure 33).[121] The corresponding products were achieved in good to excellent yield, without any need of filtration. The heterogeneous environment and stability of nanocatalyst were found to be intact with the added advantage that it is recyclable more than 10 times without any noticeable loss of its catalytic activity. To chemical nature of palladium in fresh and reused maghemite-Pd catalyst analyzed by XPS analysis; notably XPS spectra of both samples display dominantly Pd(0) and PdO species with no change in the nature of Pd.[121] The obtained results are of importance for the improvement of benign progresess for fine-chemicals and, especailly for the larges-scale reactions.

![Diagram](image)

Figure 33. Maghemite-Pd catalyzed continuous flow hydrogenation of nitroarenes, azides, and alkenes.

4.4. Magnetic ZSM-5 Zeolite: Valorization of Furfuryl Alcohol

The manufacture of new, resourceful, carbon-based building blocks from biomass resources is the sole alternate to prevent the massive use of petroleum-based chemicals. The conversion of
lignocellulosic biomass into fuels and chemicals signifies various scientific and technical experiments, covering diverse arena including catalysis and chemical engineering. Importantly, numerous composites obtained from the lignocellulosic biomass have found wide-ranging applications not only as precursors for the preparation of fuels and value-added chemicals, but also for straight use as environmentally benign solvents and fuel additives.[226]

In this context, platform molecules namely γ-valerolactone (GVL), alkyl levulinates (AL) and levulinic acid (LA) are of huge interest because of their fascinating characteristics and the prospect to be further transformed into highly desired building blocks (Figure 34).[227]

**Figure 34.** Conversion of furfural into chemical building blocks and fuels.

Generally, the production of GVL entails in the stepwise hydrogenation of levulinic acid or its esters in the presence of Lewis acids followed by cyclization.[228] Herein, we projected the preparation of a magnetic nanocatalyst that exhibits both Brønsted and Lewis acid properties, a characteristic that allows the direct domino transformation of FA to GVL reconciled by a single catalyst. Additionally, we explored the opportunity of producing other highly valued platform chemicals by the fine tuning of the catalytic protocol. To prepare such multifunctional catalytic system, we chose ZSM-5 zeolite as the active phase and magnetic microspheres as the support.[125]

First, levulinic acid (LA) or alkyl levulinates (AL) are obtained from FA through a hydrolysis (Figure 35, Path a) or alcoholysis (Figure 35, Path b) reaction catalyzed by Brønsted acids in the presence of water or alcohol, respectively. Further the obtained
LA or AL products are transformed to 4-hydroxypentanoic acid or alkyl 4-hydroxypentanoate, respectively, via a transfer-hydrogenation reaction catalyzed by a Lewis acid in the presence of a secondary alcohol which also acts as a hydrogen donor. Lastly, the 4-hydroxypentanoic acid or alkyl 4-hydroxypentanoate suffer an acid-catalyzed cyclization reaction, making the GVL product.

**Figure 35.** Reaction pathway for the synthesis of γ-valerolactone from furfuryl alcohol. Inset elemental mapping of Fe, Si, and Al from magnetic ZSM-5 zeolite catalyst. Reproduced from ref. [125]. Copyright 2016 Royal Society of Chemistry.

Overall this procedure permits the synthesis of various high-valued chemicals by simply varying the solvent employed in the reaction; for example, with 2-butanol, the major product was 2-butylation, and a mixture of water/2-butanol provided levulinic acid as the key product. Also the catalysts could be recycled for several cycles with small changes in the conversion and selectivity.

### 4.5. Conclusion and Perspectives

Organic transformations using benign and more efficient approaches are essential for the exploration of more sustainable practices. This involvement has been expected to highlight the significance of water-promoted as well as solvent- and catalyst-free protocols in organic synthesis, with the inclusion of a complete range of examples that demonstrate the significant developments transpired in the research area over the past ten years.[23, 24] However, it is nearly impossible to perform every reaction under water and/or solvent- and catalyst-free conditions, because of the intrinsic chemical properties of materials as well as the activation parameters of the process. In this regards, nanomaterials have emerged as sustainable catalysts for several organic reactions under
benign conditions including the use of water as a solvent or even under solvent-free conditions. Additionally, alternate energy sources inducing microwave- and ultrasound irradiation also act as favorable benign choices with various benefits compared to conventional protocols. In this context, further developments of benign protocols are increasingly expected in the coming decade including rise of flow chemistry for various important organic transformations, biofuel synthesis, photocatalytic reactions, biocatalysis, and advanced applications of magnetic nanocatalysis. In the light of these principles, it is obvious that the partnership between benign reaction conditions with sustainable nanomaterials can offer numerous advantages in the design of future synthetic protocols.

5. References


