Review Article**New Opportunities in Heterogeneous Catalysis**

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Nearly 80% of the processes involved in the chemical production of bulk or fine chemicals employ heterogeneous catalysts that are typically solids. The heart of the heterogeneous catalyst is the surface active site which must be highly active, selective and stable during several hundred cycles of reaction. Although it is not always possible to determine the structure of an active site in a heterogeneous catalyst, the emphasis of modern day research has not only been to understand the structure of an active site but also synthesize and study them. The article will describe some of the challenges from this perspective with examples from the authors research.

Keywords: Heterogeneous Catalysis; Multifunctional Catalysts; Hydrogenation; Dehydrogenation

Introduction

Catalysts are defined as chemical substances that transform reactants to products through uninterrupted and repeated cycles of elementary steps in which the catalyst is regenerated to its original form by the end of a cycle. Catalysts bind with reactants in a specific manner and cause an accelerated rate of transformation to products by lowering the activation energy. Heterogeneous catalysis involves studies of catalysts that are in a physical phase different from that of reactants and products. Typically, heterogeneous catalysts are solids, while the reactants and products are liquids or gases or a mixture of both. Heterogeneous catalyst science and technology is a matured branch in chemistry with several pivotal contributions to major economic transformations in

the human history. For example, iron oxide catalyst promoted with K_2O , CaO , SiO_2 or Al_2O_3 was used to produce fertilizers by converting N_2 to NH_3 . This reaction helped quadruple the productivity of agricultural lands which was desperately needed during the world war (Jacobsen *et al.*, 2001). Another important example is the refining of crude oil by hydrocracking, hydrodesulfurization, hydrodenitrogenation, hydrodechlorination over Mo based catalysts and zeolite catalysts to produce useful distillates. This reaction was responsible for the large scale production of fuel grade gasoline and diesel in addition to several low molecular weight hydrocarbons and aromatic compounds useful in chemical industry (Matar *et al.*, 1998). Besides large scale production of fuels and chemicals, heterogeneous catalysts are also extensively used in automobiles in catalytic converters

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that treat CO, unburnt hydrocarbons and NO_x from the engine exhausts to a less harmful composition. The ease of separation from the reaction mixture and robustness even under very harsh reaction conditions have given heterogeneous catalysts a competitive edge over its homogeneous counterparts (Khosla, 1997; Leadlay, 1997; Staunton and Wilkinson, 1997; Townsend, 1997; Bew *et al.*, 2015). Heterogeneous catalysts are very promising candidates to address emerging problems ranging from indoor sensors, purifiers to photocatalytic H₂ production.

The most important aspect of a heterogeneous catalyst is the active sites (or active centers) at the surface of the solid. The active site could be a specific crystallographic plane of the solid with an surface atoms in an under co-ordination environment, a defect in the crystallographic phase such as a vacancy, surface composition or an interface between metal and support (Gao *et al.*, 2016; Chen G 2016). The electron density at the active sites are usually different from rest of the surface affecting the chemisorption of the reactant and product molecules at these sites. The heterogeneous catalyst is typically a high-surface area material (e.g., 10-1000 m² g⁻¹), and it is usually desirable to maximize the number of active sites per reactor volume. A successful heterogeneous catalyst is a product of fine optimization of physical and electronic structure leading to an enhanced stability and performance. Such catalysts are characteristic of high turnover numbers (defined as the number of reactant molecules transformed per gram of the catalyst in a unit time), high selectivity, cost effectiveness, high stability and maximum reusability. Current research efforts in heterogeneous catalysis are focused on the understanding and development of highly selective chemical active sites on the surface of the catalyst. The challenge is not only to identify the most suitable active site on the catalyst for a reaction but also ensure its abundance and stability on the surface of the catalyst throughout the reaction.

In the current global scenario, development of sustainable catalysts for reactions that are highly relevant to the production of bulk or fine chemicals, pharmaceutical products, fuels and materials are receiving greater attention. In addition, raising concerns about the overall economy of a chemical process, environmental benignity and carbon foot print presses new demands on catalysts. This review article

will present some of the works of the authors in heterogeneous catalysis at CSIR National Chemical Laboratory in Pune in recent years (2013-2018). The review will highlight some of the important research outcomes related to the chemistry of catalyst materials in an attempt to address some of the emerging challenges mentioned above. The review is divided into three section. In the first section, our work related to multifunctionality in catalysts are discussed. Next generation catalysts are expected to have multiple catalytic sites on the same solid so that many reactions may be carried out in tandem. In the second section, we describe our attempts to produce single atom catalysts for organic transformation. We also discovered that unprecedented catalytic behavior could be observed by tuning the microstructure of the catalyst. In the last section, we describe our work related to Iron carbon alloy catalysts for hydrogenation of CO₂. The article provides a brief background in each of the works, novelty of the approach, detailed discussion of the materials and future challenges. The article is written in the light of challenges in catalyst materials in the context of different kinds of reactions.

Multi-functional Catalysts

Multi-step reactions are often encountered in organic synthesis wherein catalysts are required for each step of a reaction in the sequence. Sometimes, the catalysts required in successive steps of a sequence could not only be different but also chemically incompatible with each other (e.g. acid and base). In such cases, a traditional organic synthesis methodology would recommend several work up steps resulting in poor catalytic effect, low yield and 'low quotient' on greenness of the process. Achieving such sequential transformations in tandem is definitely an effective approach to overcome the problem. However, such tandem reactions will demand a catalyst with multiple catalytic functional sites on it. Each functional site must be capable of catalyzing at least one of the several steps in the synthetic sequence. Importantly, the catalytic sites must be spatially isolated and not interfere with the catalytic action of the other sites. One can imagine that a multifunctional catalyst can conveniently transform a synthetic intermediate into a desired product by pushing it into a subsequent catalytic cycle ultimately leading to the final desired product. Thus, the process intensification is achieved without isolating an unstable or toxic synthetic

intermediate (Tietze, 1996; Stankiewicz and Moulijn, 2000; Nicolaou *et al.*, 2006; Van Gerven and Stankiewicz, 2009; Dhakshinamoorthy *et al.*, 2014). Synthesis and applications of multifunctional catalysis is therefore an important area of research. Several recent reviews deal with the applications of multifunctional heterogeneous catalysts in tandem organic transformations (Huh *et al.*, 2005; Margelefsky *et al.*, 2008; Motokura *et al.*, 2008; Corma *et al.*, 2010; Liu *et al.*, 2012; Diaz *et al.*, 2013; Xu *et al.*, 2014; Jagadeesan, 2016).

Development of a multifunctional catalyst involve a careful choice of catalytic active sites required for the entire sequence of the transformation. Following this, a synthesis scheme needs to be designed to introduce the reactive sites on a solid. The ability of a multifunctional catalyst is usually tested by studying the conversion and selectivity in a two-step sequential transformation, for example, first step needs an acid catalyst and the second step needs a base catalyst. In fact, materials based on this idea were proven to be efficient to carry out sequential transformations in a single pot (Huh *et al.*, 2005). Ironically, the chemical approaches employed to introduce multiple functionalities on a catalyst themselves involved multiple steps involving surface functionalization, chemical protection and deprotection steps (Huh *et al.*, 2005; Margelefsky *et al.*, 2008; Motokura *et al.*, 2008; Corma *et al.*, 2010; Liu *et al.*, 2012; Diaz *et al.*, 2013; Xu *et al.*, 2014; Jagadeesan, 2016).

In this context, our group demonstrated for the first time the acid-base bifunctional reactivity in metastable transition metal oxyhydroxide phases (MOOH where M is usually a transition metal). In our opinion, inorganic metastable phases such as MOOH are ideal as they are robust, inexpensive and easily scalable materials. These materials are usually prepared by hydrolytic sol-gel methods and can be considered as intermediates between hydroxylated metal sol precursors and completely condensed dense oxide phases (Cornell and Schwertmann, 2004). The functional groups $-OH$ and their deprotonated conjugate base $-O^-$ groups are present in abundance on the surface and on the interiors of the materials exhibiting acidic and basic properties, respectively. Hence, the advantage with these materials is that there is no need for any surface functionalization to impart

acidic and basic bifunctional catalytic activity (Jolivet *et al.*, 2000; Yan *et al.*, 2014; Smith *et al.*, 2016). Interestingly, the surface hydroxyl groups on MOOH surface can exist in three different coordinated states. Under normal conditions MOOH surface can exist as 1) singly ($\equiv MOH$, $-OH$) 2) doubly ($\equiv M_2OH$, $\mu-OH$) and triply coordinated ($\equiv M_3OH$, μ_3-OH) (Song *et al.*, 2013). MOOH usually exists in multiple polymorphs such as α , β , γ , δ which arises due to difference in arrangement of $M(O)_6$ octahedra structural unit. These polymorphs have different crystal structure, morphology and also differ in densities of surface hydroxyl groups. One may expect the pK_a values of each of the $-OH$ and $-O^-$ species to be different depending on the coordination as well as structural arrangement of the basic structural unit giving rise to the possibility of tunable bifunctional property.

MOOH is an interesting class of material containing abundant surface hydroxyl groups than metal oxides along with M-O-M linkages and are more stable than Metal hydroxides. MOOH (M = Fe, Co, Ni, Mn, Cr & Al) have been widely explored for a variety of applications. For example, FeOOH and AlOOH have been used for adsorption of toxic metals, anions from water sources (Ostergren *et al.*, 1999; Horanyi *et al.*, 2003). CrOOH and FeOOH used as precursors for pigments due to their green, orange-brown colour (Liang *et al.*, 2014). CoOOH, NiOOH, FeOOH and a composite of these are extensively used for electrochemical applications such as Oxygen Evolution Reactions, Hydrogen Evolution reactions, supercapacitors and photochemical water splitting (Trotochaud *et al.*, 2014; Lim *et al.*, 2015; Feng *et al.*, 2016; Huang *et al.*, 2016; Kim *et al.*, 2016). The predominant advantage of using MOOH for these applications is due to the nano size and presence of dissociable hydroxyl groups. However, MOOH as active catalyst for organic transformations has been not studied so far except for the use of AlOOH as a passive support for organic reactions where $-O_3H$ functionalized SiO_2 was coated on AlOOH (Ghorbani-Choghamarani *et al.*, 2016). Another example used AlOOH as a support for Pt nanoparticles for formaldehyde synthesis, where the surface hydroxyl groups of AlOOH help in adsorbing the reactant molecules (Xu *et al.*, 2015). We explored MOOH as an active material for acid-base bifunctionality, redox base bifunctionality and compared them with those

available in literature which often require complex functionalization or use of expensive noble metals. Our work brings out the novel bifunctional aspect of Metal Oxyhydroxides and emphasizes a better substitute for the present state of art catalysts.

Acid-Base Bifunctional Catalytic Activity

MOOH ($M = \text{Fe, Co, Mn, Cr and Al}$) were synthesized by “Soft Chemistry” routes at room temperatures or less than 300°C in hydrothermal process. Experimental parameters such as concentration, pH, temperature, nature of anions can be modified to control size, texture and purity of various polymorphs in high yields. They are intermediates between metal hydroxides and highly condensed metal oxides. Metal is in trivalent state and surrounded by three O^{2-} and three OH^- thereby making $\text{M}(\text{O})_6$ octahedra as the basic structural unit. The $\text{MO}(\text{OH})$ has surface hydroxyl groups as in metal hydroxides along with condensed M-O-M linkages found similar in metal oxides. The structure offers MOOH stability as well as reactivity making it an interesting catalyst.

The crystalline nature of MOOH materials were characterized using X-ray Diffraction. The polymorphs were identified using Infrared absorption spectra. The microstructure of the materials were studied under Transmission Electron Microscopy. Surface acidic and basic sites were studied using Temperature Programmed Desorption of CO_2/NH_3 and IR absorption spectra of the samples adsorbed with pyridine. We tested the materials for a model acid catalyzed deacetylation reaction followed by a base catalyzed condensation reaction in a single pot to probe the behavior of these solids (Fig. 1).

Fig. 1: Equations of acid-base catalyzed reactions (A) Deacetylation-Knoevenagel reaction (B) Deacetalization-Henry reaction

In Fig. 2, the general mechanism of acid-base reaction on a hypothetical MOOH surface is represented. The reaction involving acid catalyzed hydrolysis of benzaldehyde dimethylacetal followed by base catalyzed condensation is carried out in the presence of MOOH. In the first step, the surface of the metal oxyhydroxide surface gets deprotonated by externally added water. In the presence of acidic sites, benzaldehydedimethylacetal (1) gets protonated and proceeds via subsequent loss of MeOH molecules to form benzaldehyde (2). In the next step the deprotonated hydroxyl groups act as active bases to abstract protons from the active methylene malononitrile forming a carbanion, which attacks the adsorbed benzaldehyde molecule on the surface as shown, ultimately leading to benzylidenemalononitrile (3) by loss of water molecule.

Our group reported the bifunctional acid-base property in FeOOH for the first time and also the difference in the catalytic activity in different polymorphs of FeOOH (Vernekar and Jagadeesan, 2015). Acid-base bifunctional nature of MOOH was found to differ with respect to the polymorphs in the case of FeOOH . We synthesized four polymorphs of FeOOH namely, α , β , γ and δ . Bifunctional catalytic activity in FeOOH polymorphs were demonstrated in a tandem reaction deacetalization—Henry reaction in one-pot. The first step involved an acid catalyzed hydrolysis of benzaldehyde dimethylacetal to benzaldehyde and the second step was the base catalyzed condensation of benzaldehyde with nitromethane to give trans- β -nitrostyrene. A chemical

Fig. 2: The possible acid and base centers on metal hydroxides and metal oxyhydroxides

Fig. 3: (A) Conversion for the various polymorphs for deacetylation-Henry reaction (B) Yields of the products for the polymorphs. Reproduced by permission of The Royal Society of Chemistry

equilibrium between OH and O⁻ groups on the surface of the catalysts was proposed as acidic and basic sites, respectively in the presence of H₂O as shown in Eq. (1).

Difference in the density and strength of acid-base sites on the surface facets differed with polymorphs causing a difference in the catalytic activity. The OH group on the surface of FeOOH can either be single, doubly or triply coordinated to Fe atoms and hence lead to difference in the relative values of acidity and basicity. The four polymorphs of FeOOH (α , β , γ and δ) exhibited different bifunctional activity towards the reaction (Fig. 3).

α -FeOOH with a conversion of 50% behaved as a weak acid catalyst with a high selectivity to benzaldehyde. The other three polymorphs (α , γ and δ) gave a conversion of more than 90% with a very high yield of trans- β -nitrostyrene. However β -FeOOH showed an odd behavior with the formation of a base catalyzed Michael addition product namely, trans- β -nitrostyrene with nitromethane to form a dinitro product indicating stronger basic sites. The chloride ions in the channels of β -FeOOH could be responsible for the dinitro product (3). The presence of water was found to be crucial to the formation of bifunctional sites on FeOOH as γ -FeOOH gave just 52% conversion in the absence of water as compared to 97% in the presence of water. Stability and recycle studies show the catalyst was stable even after five recycles and the activity was maintained.

The nature of acidic and basic sites were probed using pyridine IR and Hammett titrations. Pyridine being a base can get easily adsorbed to acid sites and can be identified using Infrared spectroscopy (Fig. 4).

Fig. 4: Pyridine-IR data probing the acidic sites i) α -FeOOH ii) β -FeOOH iii) γ -FeOOH and iv) δ -FeOOH. Reproduced by permission of The Royal Society of Chemistry

All the polymorphs showed three prominent bands centered around 1560, 1541 and 1508 cm⁻¹ which are due to the interaction of the Brønsted acid sites with pyridine forming pyridinium ion. The Lewis acidic interaction of Fe³⁺ was also observed at 1457 cm⁻¹. These results gave qualitative information on the acidic sites. Acid-base titrations using Hammett indicators having different H₀ values provided with

Fig. 5: Hammett titration data for the FeOOH polymorphs showing acid and base sites

the strength of acidic and basic sites on FeOOH polymorphs (Fig. 5). The acidity value is represented as the number of acidic sites (mmol g^{-1}) whose acid strength is equal to or less than the H_0 value (of the indicator) and the basicity value as the number of basic sites (mmol g^{-1}) whose base strength is equal to or greater than the H_0 value (of the indicator). Acidity and basicity are tabulated on a common H_0 scale in the Fig. 3. A low H_0 value was indicative of a strong acid sites whereas high H_0 value represented a strongly basic site. The polymorphs showed a high number of acid sites of various strengths ($H_0 = -3.3, 1.5, 3.3, 4.0, 6.8$). The numbers of acid sites were comparatively higher than the number of basic sites. All the polymorphs showed a higher percentage of acid sites with $H_0 = 1.5$ & 3.3 . This showed the FeOOH polymorphs are moderately acidic. As expected from the catalysis data α -FeOOH showed high acid value and a low base sites as it gave the acid catalyzed product in high yield. All other polymorphs showed moderately strong base sites as well. However, the base site density was less as compared to acid sites.

Challenges and Opportunities

One of the important challenges in the use of MOOH is its preparation. Since MOOH exist in polymorphs,

synthesizing a pure polymorph invariably includes presence of impurities from its other polymorph. Hence the conditions needed for their synthesis must be careful. As MOOH as metastable intermediates, they tend to transform into their corresponding oxides and lose their active surface hydroxyl groups when subjected to temperatures above $350\text{--}400^\circ\text{C}$. Thus, MOOH cannot be used for extreme high temperature reactions. Our ongoing research also involves probing similar acid-base bifunctional activity in other MOOH such as Co, Al, Mn and Cr. We are also working on the trends in acid-base bifunctional activity in metal hydroxides, MOOH and metal oxides. More fundamentally, it is necessary to establish the chemical equilibrium between surface OH and O^- groups and change in the strength of catalytic activity with metals. Our group is currently focusing on the spectroscopic technique to monitor the surface concentration of OH and O^- and their role in the catalytic sequence. In spite of these challenges MOOH can serve wonderfully well and provide great activity for organic transformations where the temperatures do not exceed the degradation temperature of MOOH. An interesting idea is to combine different catalytic sites such as redox, hydrogenation, acidic, basic properties onto the same MOOH platform for a sequential organic transformation involving oxidation, condensation and coupling reactions. It would also be interesting to probe the synthesis of mixed MOOH where doping a heavier metal ion in a MOOH matrix could alter the geometric and electronic properties and use them for catalyzing industrially important oxidations.

Heterogeneous Catalysts with Isolated Active Sites

Apart from new multifunctional MOOH catalysts, we worked on developing an efficient synthesis strategy to prepare advanced catalysts. Porous materials have been conventionally used as supports for active metals and metal oxides. The role of porous materials in such cases is inactive except for the prevention of agglomeration of active metal catalysts supported on them by sintering at high temperatures. Although metal components are generally finely dispersed on the porous supports, only a small portion is actually involved in catalysis. Heterogeneity in metal size and shape produces difference in reactivity among the metal particles affecting the efficient utilization of metal active sites and thus reduces selectivity toward

a specific product. Size reduction of metal particles partially overcomes such heterogeneities, in addition to benefiting the performance of catalysts due to low-coordination environment of metal centers, quantum size effects and enhanced metal-support interactions. Recent theoretical and experimental studies have shown that sub nanometer-sized metal clusters can sometimes exhibit better catalytic activity than nanometer-sized catalysts (Lei *et al.*, 2010, Qiao *et al.*, 2009, Turner *et al.*, 2008, Kaden *et al.*, 2009). There have been recent research efforts to decrease the size of the active metal or oxide component down to the extent of isolated single atom or ion level (Yang *et al.*, 2013). Porous materials containing isolated metal active sites are an emerging class of catalysts due to unique reactivity (He and Antonetti, 2002). Synthesis of such porous materials containing isolated metal active sites is challenging as there is a high tendency to the formation of nanoparticle due to the aggregation of isolated atoms.

Titanium containing silicate (TS-1) catalysts, where Ti^{4+} substitutes Si^{4+} of crystalline silicates is a remarkable catalyst for the epoxidation reactions (Taramasso *et al.*, 1983). The occurrence of a uniform and homogeneous distribution of Ti^{4+} active sites in silica matrix has been shown to be essential for the performance of the catalyst (Saikia *et al.*, 2007). The potential of Ti- substituted mesoporous molecular sieve to catalyze the selective oxidation of organic compound was realized by its successful incorporation in different mesoporous silica framework like SBA-15, MCM-41, MCM-48, KIT-6 and HMS (Luan *et al.*, 1999). Various synthesis and postsynthesis attempts have been made to synthesize Ti-substituted silica matrix. The postsynthesis path was found to be more effective over direct synthesis. However, such an approach was found to lessen the structural and textural properties of the mesoporous matrix (Fukuda *et al.*, 2015). The sol-gel method based on the hydrolysis/condensation of alkoxide precursors, received wide attention as an efficient procedure for the synthesis of metal oxide materials and considerable effort was focused in order to obtain homogeneous samples featuring a high concentration of Ti-O-Si hetero atom linkages. These efforts concentrated on fine-tuning the hydrolysis rates for the titanium and silicon precursor alkoxides, or by use of single precursor or via prehydrolysis of the silicon precursor (Zhang *et al.*, 2002). However, uniform distribution

of the active site in silica matrix in high concentration by sol-gel chemistry was elusive. A general synthetic approach for incorporation of heteroatom on silica catalysts while maintaining single-site behavior was considered as a major advancement.

Our group explored the Ti-complexation method to produce a precursor that is stable and can condense with silica precursor for yielding a homogeneously distributed isolated Ti centers on a silica matrix. Ethylenediamine (ED) was used as a ligand to complex with Ti, which co-condensed with hydrolysed silica precursors. ED acted as the protecting group for Ti centres and did not allow the formation of Ti-O-Ti species during the entire course of synthesis (Gupta *et al.*, 2015). In addition, we also showed through various systematic characterization studies that the catalyst material synthesized using ED ligand did not contain any phase-separated TiO_2 either in crystalline or in amorphous form for Si/Ti ratio as high as 10. This mesoporous SiO_2 containing isolated Ti centres catalyst was used in the oxidation of cyclohexene, which is an industrially important chemical reaction.

The role of Ti-ED complex in the synthesis of porous SiO_2 with isolated Ti^{4+} sites is shown in Fig. 6. ED can form monomeric and dimeric complex with Ti and Si by acid-base interaction, which is more favorable with Ti. In addition, ED also triggers the hydrolysis and condensation process of metal and Si precursors. The formation of complex with ED prevent the formation of phase segregated TiO_2 . The Ti-ED complex species assemble over CTAB micelles, which when removed at high temperature will yield porous structures. The non-phase separated nature of materials were confirmed using various spectroscopic techniques. UV-vis spectroscopy and UV Raman spectroscopy showed the formation of isolated Ti centres without phase separated TiO_2 . Solid UV-vis DRS spectra analyzed for different Ti /Si ratio shown in Fig. 7. The absorption band at 220 nm correspond to tetrahedrally coordinated Ti species and band at 260 nm represent the multiple coordination of Ti in silica framework (Guo *et al.*, 2012). The sample prepared without ED complex (TSC-25) showed a broad band at 330 nm confirming the presence of TiO_2 species. Importantly, the absorption band at 330 nm is absent in the sample prepared by using Ti-ED precursor, which suggest majority of tetrahedral and

Fig. 6: The formation ED complexes of Ti and Si (Ti-ED and Si-ED) and its self-assembly over the CTAB micelles. During calcinations in air TSC-ED-X samples with isolated Ti^{4+} species incorporated on SiO_2 matrix is obtained. Copyright permissions are obtained

Fig. 7: UV-vis DRS spectra of (i) TSC-ED-25 (ii) TSC-ED-10 and (iii) TSC-25. Reproduced by permission of The Royal Society of Chemistry

multiple coordinated Ti species were present in samples prepared using ED ligand, without appearance of phase segregated TiO_2 .

In order to confirm the absence of amorphous TiO_2 species, we analyzed the UV Raman spectra

(Fig. 8A, 8B). In all ED complex samples (TSC-ED-10, 25 and 40), band at 495 cm^{-1} and 1115 cm^{-1} are observed due to tetrahedral Ti species, while a sharp band around 690 cm^{-1} indicated the octahedral coordinated Ti species. These tetrahedral and multiple coordinated species are highly important in selective oxidation process. Phase separated amorphous TiO_2 species which represent by 710 cm^{-1} band was not found in Ti-ED complex samples, which proves the importance of ED-Ti complex in the generation of homogeneous isolated active sites. Isolated Ti sites on silica support are highly active for various oxidation reactions.

The as-prepared materials were tested for the oxidation of cyclohexene using various oxidants such as H_2O_2 , TBHP, O_2 . Ti-ED complex derived catalyst gave higher conversion and selectivity for epoxide which clearly indicated the presence of high number of isolated Ti^{4+} centres and high surface area. Among different Si/Ti ratio, Si/Ti 25 showed a higher activity, with 52% conversion of cyclohexene and 73% selectivity towards epoxide. At low concentration of Ti^{4+} , number of crucial active site are less while at higher concentrations decomposition of the H_2O_2 and TBHP oxidants occur rapidly. The catalyst showed stability for 5 cycle of oxidation reaction without drastic change in activity.

Encouraged by the success of making isolated metal catalysts by the decomposition of the metal complex, we explored extension of this method to other transition metals. Our group reported the first heterogeneous catalyst for an efficient acceptorless dehydrogenation of several bio-derived substrates such as alcohols, amines, N-heterocycles to various aldehyde, imines and quinoline derivative without using any oxidants or hydrogen acceptors Scheme 4 (Jaiswal *et al.*, 2017; Jaiswal *et al.*, 2016). The active catalyst Fe-L1@EGO-900 was prepared by depositing the molecular complex of iron and phenanthroline on different supports such as exfoliated graphene oxide and silica and calcined at higher temperature in inert atmosphere as per the Fig. 9 (Jaiswal *et al.*, 2017; Jaiswal *et al.*, 2016).

The crystalline nature and the microstructure of the catalyst was characterized using powder X-ray diffraction technique (PXRD), electron microscopy (TEM and SEM). The surface chemical

Fig. 8: UV-resonance Raman spectra of (i) TSC-25, (ii) TSC-ED-10, (iii) TSC-ED-25, and (iv) TSC-ED-40 excited at 273.8 nm between regions 400-800 cm^{-1} (A) and 1050-2000 cm^{-1} (B) of Raman shift. Reproduced by permission of the Royal Society of Chemistry

Fig. 9: Synthesis of Fe-L1@EGO-900

species were analyzed using X-ray Photoelectron Spectroscopy (XPS). Elemental composition was analyzed using Energy dispersive X-ray analysis (EDX). In PXRD data, peaks were indexed to multiple phases of Fe_3O_4 , Fe_3N , $\beta\text{-Fe}_2\text{O}_3$ and Fe_7C_3 .

Fig. 10: SEM image of Fe-L1@EGO-900 catalyst

The morphology of the active catalyst was analyzed using scanning electron microscopy in Fig. 10. It is clear from the SEM image that iron-rich nanoparticles were well separated and supported on graphene layers. The microstructure of iron catalyst was analyzed using TEM and shown in Fig. 11. Iron-rich nanoparticles were spherical in shape having size in the range of 4 to 100 nm with majority of the particles in the range of 11-20 nm as shown in the histogram (Fig. 11A). It was found that nanoparticles were having unique core-shell type of microstructure. High-resolution transmission electron microscopy (HRTEM) image of the above catalyst showed lattice fringes of 2.02 Å corresponding to the d spacing of (211) plane of Fe_7C_3 at the core and 2.42 Å corresponding to the d spacing of (222) plane of Fe_3O_4 phase. STEM analysis in Fig. 12 also supports presence of iron nanoparticles supported on graphene.

The iron catalyst (Fe-L1@EGO-900) was investigated for the acceptorless dehydrogenation of partially saturated *N*-heterocycles, alcohols and amine.

Fig. 11: Bright field TEM images of Fe-L1@EGO-900 catalyst. (A), at the scale bar 50 nm with inset showing an histogram of size of 100 nanoparticles, (B) at the scale bar 20 nm, (C) a single nanoparticle at the scale bar 5 nm and (D) shows the high resolution lattice fringes

Dehydrogenation reactions are one of the most important organic transformations used in petrochemical and pharmaceuticals industries. Usually dehydrogenation reactions take place in the presence of strong oxidant or oxygen pressure which generates lot of copious waste (Yamaguchi *et al.*, 2009; Balaraman *et al.*, 2017, Xu *et al.*, 2015). Recently, researchers have started using a sacrificial organic acceptor molecule to carry out the dehydrogenation reaction. A greener, environment friendly and efficient alternative can be to carry out the reaction without the use of acceptor molecules (Dobereiner and Crabtree 2010; Johnson *et al.*, 2010; Wu *et al.*, 2013; Fujita *et al.*, 2014, Xu *et al.*, 2015). Such a process is called acceptorless dehydrogenation in which hydrogen will be the only sole side product. Mostly noble metal based homogeneous catalysts are explored for the acceptorless dehydrogenation reaction (Dobereiner and Crabtree 2010; Johnson *et al.*, 2010; Wu *et al.*, 2013; Fujita *et al.*, 2014; Xu *et al.*, 2015). The disadvantages of such catalytic systems are high price, sophisticated synthesis of ligand, sensitive handling and poor recovery.

Fig. 12: (A) STEM image of Fe-L1@EGO-900 catalyst, (B) Line profile of Fe (blue), O (green) and N (Red) passing through the line, (C) STEM image of single particle and (D) Line profile of single iron nanoparticle passing through the particle in the given area single particle (Fe (blue), O (green) and N (red))

Replacement of noble metals with cheaper 3d transition metal-based catalyst especially that of iron, cobalt and the manganese-based heterogeneous catalyst is an area of contemporary interest (Bähn *et al.*, 2011; Gunanathan and Milstein, 2013; Ketcham *et al.*, 2014; Obora 2014). The challenges in this area is to improve the conversion and selectivity of the catalysts to match up those of noble metal-based catalysts. Iron-catalyzed synthetic organic transformations are highly demanding primarily due to its earth abundance.

Fe-L1@EGO-900 catalyst actively converted alcohols to aldehydes, amine to imine and partially saturated *N*-heterocycles to saturated *N*-heterocycles with the liberation of hydrogen. In order to probe the active site of the catalyst the reactivity of the active catalyst and individual pure phases were tested for the selective acceptorless dehydrogenation of alcohols. As it is clear, from the Fig. 13, only Fe-L1@EGO-900 catalyst was active for the selective conversion of alcohols, individual single phases of iron are not active for the catalysis.

Entry	Catalyst (8 mol%)	Conversion (%)	Selectivity (%)
1	Fe-L1@EGO-900	95	93
2	Fe ₃ O ₄	15	55
3	Fe ₂ O ₃	38	40
4	Fe ₂ N	15	80
5	Fe ₃ C	12	70

Fig. 13: Table showing the conversion and selectivity of various pure inorganic phases in comparison to the mixed phase catalyst FeL1@EGO-900 in the selective dehydrogenation of alcohol

Hence, it is possible that the mixture of the phases or the interfaces of different phases of iron having specific core shell morphology is showing catalytic activity. In the similar way acceptorless dehydrogenative coupling (ADC) of alcohols with amines is also very important reaction for pharmaceutical and industry (Gnanaprakasam B. *et al.*, 2010, Xu *et al.*, 2010, Ho *et al.*, 2010, Maggi *et al.*, 2010, Li *et al.*, 2010). We have reported ADC of alcohol and amines using a heterogeneous Fe-catalyst as per the Fig. 14.

The reaction operates under mild conditions with

Fig. 14: Schematic representation of acceptorless dehydrogenation of alcohols, amines and *N*-heterocycles

the liberation of dihydrogen and water as the byproducts. The developed ADC strategy is simple, efficient, exhibits wide functional group tolerances and can be scaled up. The molecular hydrogen generation was qualitatively analyzed by gas chromatography. Hydrogen generated during the reaction was also quantified with dual catalysis (Fig. 15).

Fig. 15: Schematic showing the dual catalysis reaction where the H₂ evolved from the dehydrogenation reaction was used to hydrogenate cyclohexene to cyclohexane

For Dual catalysis model reaction with tetrahydroquinoline substrate was conducted and connected with cannula to another reaction tube containing cyclohexene and a catalytic amount of Wilkinson's catalyst in benzene. After the completion of reaction, 45% of cyclohexane was produced in the second reaction tube demonstrating that the hydrogen gas was generated which is responsible for the hydrogenation of cyclohexene. The active catalyst can be magnetically separated as per given in Fig. 16. The important highlight of our work is that only the core shell structure of the complex mixed phase catalyst that is synthesized under specific conditions

Fig. 16: Picture showing the separation of the catalyst from the reaction medium in the presence of external magnetic field

is catalytically active. A number of control experiments suggested that the inorganic iron phases when sharing the interface become catalytically active. It is still not clear if these interfaces alter the electronic structure of the surface or create defects that are active in the catalysis of the reaction.

Challenges and Opportunities

Synthesis strategy of thermally decomposing a molecular complex of a metal yielded isolated metal atom catalysts in the case of Titanium silicate. The approach is important in the case of noble metal based catalysts, where high activity at decreased concentration of metals is highly desirable. It may be highly important to investigate and improve the activation of small molecules such as H_2 , CH_4 and O_2 on these catalysts so that sustainable greener catalysts may eventually be developed. Interestingly, a similar method also yielded a core shell structure with mixed phase that showed unique catalytic property. It is necessary to understand the role of ligands, concentration, surface of the support and decomposition kinetics to predict the structure that we may get. The future scope of the work would be to understand the mechanism of formation of the active core shell structure from the molecular precursor and the nature of active sites. In the future other 3d-transition metal based catalyst can also be synthesized and explored for different kind of organic transformation.

CO_2 Hydrogenation Using Iron-carbon Alloy Catalyst

Another important area of research that caught our attention was the development of non-noble metal

based heterogeneous catalysts for hydrogenation of CO_2 . The molecular transformation of CO_2 into value-added products has fascinated researchers for a long time (Arakawa *et al.*, 2001; Jagadeesan *et al.*, 2015). In particular, conversion of CO_2 to hydrocarbons by catalytic hydrogenation will help in producing carbon neutral fuels, thus addressing both environmental pollution as well as energy shortage. However, hydrogenation of CO_2 can produce a wide range of hydrocarbons from C_1 to C_{20} depending on the reaction conditions. In fact, one of the major challenges in CO_2 hydrogenation is the lack of selectivity in the product formation. Conversion of CO_2 to lower olefins such as ethylene or propylene is considered important as they are useful as starting materials for the production of several bulk chemicals in polymer and fine chemical industries (Gao J *et al.*, 2017).

The high temperature reactions such as CO_2 hydrogenation are conventionally catalyzed by supported metal catalysts to withstand harsh reaction conditions. There are many factors concerning supports such as pore size, structure of supports, surface chemistry and metal-support interaction that can influence the performance of metal catalysts in achieving the desired selectivity of products (Corma, 1997; Melaet *et al.*, 2014; Gupta *et al.*, 2016). The activity and selectivity of these catalysts are sensitive to the interaction between the active metals and oxide supports. Previous studies suggested that the reduction of CO_2 requires the cooperation of metal which can dissociate H_2 , and the metal-support interface which can activate CO_2 (Rodriguez *et al.*, 2015). Several examples can be found in literature where, nanoparticles of Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt supported on SiO_2 , TiO_2 , Al_2O_3 , ZrO_2 , CeO_2 and mixed oxides can convert CO_2 to value added products (Dorner *et al.*, 2010; Wang *et al.*, 2011; Drab *et al.*, 2013). Although many catalysts like supported Fe, Co and Ru nanoparticles show activity in CO_2 hydrogenation, activity of noble metals were superior in the reaction. Development of inexpensive heterogeneous catalysts based on Fe or Co is attractive due to competitive advantages such as low cost and earth abundance and high tolerance to impurities (Zhang *et al.*, 2010).

Our group contributed to the iron carbon catalysts system for hydrogenation reactions and in particular CO_2 hydrogenation. Our approach to this problem was inspired by the challenges that CO_2 hydrogenation

reaction conditions posed on the iron based catalysts which will be described shortly. Iron carbon alloy system is an interesting class of materials where the carbon is often found in the interstices of Fe lattice resulting in the interstitial iron carbides. The relevance of iron catalysts as a potential catalyst gained support when the search for a non-noble metal based catalysts for hydrogenation reactions intensified (Smit *et al.*, 2008). Iron based catalysts are known to be active in Fischer Tropsch process (FTS), where the catalyst is usually a mixture of oxide, metallic and carbide phases. Extensive studies were carried out on Fe_3O_4 based catalysts for FTS was undertaken in Germany and South Africa to convert syngas to fuel grade hydrocarbons during the world war (Anderson, 1956). Iron oxide phase is responsible for water gas shift activity, while iron carbide phase is essential for chain propagation leading to the formation of hydrocarbons. The results relating to the prominent role of carbide phases in both the reaction as well as deactivation were confirmed and contradicted by several surface spectroscopic studies. However, it is well established that Fe_3O_4 forms phases of carbides such as Fe_7C_3 , Fe_5C_2 and Fe_3C during the course of the reaction. Various modifications were carried on iron-based catalysts that are known to catalyse both RWGS and FTS reactions. Improvement of the CO_2 hydrogenation performance of Fe catalysts were achieved by the addition of chemical promoters, such as alkali and transition metals, and structure promoters such as Al_2O_3 , TiO_2 , CeO_2 and SiO_2 . Fe_3O_4 nanocatalysts supported on graphitic carbon have emerged as a promising class of nanocatalyst for CO_2 hydrogenation in recent years (Büchel *et al.*, 2014; Minett *et al.*, 2014). A review article dealing with the preparation, electronic properties and catalytic performance of Fe_3O_4 /carbon nanocatalysts in the conversion of CO_2 to value-added products may be found (Sun *et al.*, 2012; Tu *et al.*, 2015). Furthermore, the FTS reaction was found to start when the iron carbiding process was almost finished. We developed an iron carbon core shell nanocatalyst system containing pre active iron carbide and oxide phases and used it for CO_2 hydrogenation reaction.

We synthesized the carbide-containing iron oxide catalyst by starting from a core shell catalyst. Although Fe_3O_4 @carbon core shell catalysts were known in the literature (Xuan *et al.*, 2007). Several chemical routes were developed to synthesize carbon

encapsulated Fe_3O_4 nanostructures. But the main disadvantage is blockage of active site by complete graphitic carbon shell, which alters the catalytic activity. Fe_3O_4 /carbon nanocatalyst reported in our work was synthesized from a precursor which formed amorphous carbon in the shell (Chen *et al.*, 2008). During pyrolysis at a high temperature, the amorphous carbon not only diffused into the core to form a mixture of Fe_3O_4 and Fe_5C_2 core but also created a partially graphitized shell. Our synthesis protocol offered a carbon precursor shell that was reactive and formed the active phase of Fe_5C_2 during annealing by reacting with Fe_3O_4 core. A chemical composition of Fe, Fe_5C_2 and Fe_3O_4 encapsulated inside partially graphitized carbon shell were necessary for better efficiency of catalytic activity in CO_2 hydrogenation in terms of higher FTY and higher O/P ratio in C_2 - C_4 range of hydrocarbons. The carbon shell also prevented the rapid deactivation of the catalyst due to aggregation of particles.

Fe_3O_4 nanoparticles (IO NPs) was coated with a shell of amorphous carbon derived from the hydrothermal treatment of aqueous solution of glucose to form IO@aC-1 nanoparticles (Fig. 17). The as synthesized IO@aC-1 was heated in argon atmosphere at 550 °C to form IO@gC-1 (where 'g' refers to the graphitization of amorphous carbon shell). The synthesis method allowed control over the thickness of the carbon shell by varying the concentration of glucose solution which in turn controlled the chemical composition of the core. Additionally, size of 100 nm microspheres of Fe_3O_4 (IO- μ) coated with graphitized carbon (IO- μ -gC-1) were synthesized using similar procedure. Fig. 18A shows a TEM image and inset shows the HRTEM image of an IO NP with lattice fringes of 3.5 Å corresponding to the d spacing of (311) planes of magnetite Fe_3O_4 . The size distribution of IO NPs is represented as a histogram for 200 particles shown in Fig. 18B. The majority of particles distributed in the range of 10 to 15 nm. Fig. 18 C, D, represent the TEM images of IO@aC-1 and IO@gC-1. The particle size distribution was not affected by hydrothermal conditions and high temperature treatment suggesting the effectiveness of carbon coating. The inset of Fig. 18C and Fig. 18D represent the HRTEM images of IO@aC-1 and IO@gC-1, where crystalline lattice fringes correspond to the Fe_3O_4 core and Black dashed lines indicate the interface of iron rich core

Fig. 17: Schematic representation to explain the preparation of the samples (A) IO@gC x, (B) IO μ@gC 1 and c) cartoon representation showing the structure of a representative IO@gC x sample after activation in H₂

Fig. 18: (A) TEM image of IO NPs, (B) Histogram showing the size distribution of IO NPs (N=200 nanoparticles) and (C) TEM image of IO@aC 1 and d) TEM image of IO@gC 1

and carbon shell. In Fig. 18D, the magnified image of IO@gC-1 revealed parallel layers of discontinuous graphitic carbon in the shell with a thickness of around 1-1.5 nm.

Fig. 19: Raman spectra of IO NPs, IO@aC-1, IO@gC-1 and IO@gC-800

The chemical nature of carbon shell was studied by Raman spectroscopy using 514 nm excitation (Fig. 19). The graphitization of carbon studied by Raman spectra showed G band at 1593 cm⁻¹ representing in-plane vibrations of graphitic carbon. The G band appeared in higher intensity for IO@gC-1 than IO@aC-1. The presence of relatively higher intense D-band at 1350 cm⁻¹ indicated the presence of defect centres. These defects probably originate in form of micropores on the shell making the accessibility of reactant molecules to the active iron centre feasible.

Fig. 20: Catalytic activity of IO@gC-0.5, IO@gC-1, IO@gC-1.5, IO@gC-2.0, IO μ and IO- μ @gC-1.0 in hydrogenation of CO₂ showing FTY and O/P ratio. Reproduced by permission of the publisher.

Fig. 21: From left to right: Catalytic activity of (i) IO NPs, (ii) IO@aC-1, (iii) IO@gC-1 in hydrogenation of CO₂ showing FTY and O/P ratio. Reproduced by permission of the publisher

Systematic catalytic studies of the hydrogenation of CO₂ at 1 atm pressure showed that the unique nanostructure showed excellent selectivity to C₂-C₄ olefins and high thermal stability in comparison to other catalysts. The catalytic results showed that both the composition of the nanocatalysts and the extent of graphitization of the carbon shell played important roles in the catalytic performance. Partially graphitic carbon encapsulated nanoparticles (IO@gC-1) showed Iron time yield (FTY) value $11.7 \times 10^{-5} \text{ mol g}^{-1} \text{ s}^{-1}$, compared to bare Fe₃O₄ (IO NPs) nanoparticles (FTY = $6 \times 10^{-5} \text{ mol g}^{-1} \text{ s}^{-1}$). FTY may be described as the number of moles of CO₂ reduced per gram of catalyst in one second. With increasing the thickness of carbon shell (from IO@gC-0.5 to IO@gC-2) the olefin to paraffin

selectivity decreased due to hydrogen spillover effect on carbon shell (Fig. 20, 21). Also the thickness of carbon shell plays a crucial role in catalytic activity. IO@gC-1.5 catalyst showed a highest FTY of $16 \times 10^{-5} \text{ mol g}^{-1} \text{ s}^{-1}$ while IO@gC-0.5 showed only $8 \times 10^{-5} \text{ mol g}^{-1} \text{ s}^{-1}$ and that of IO@gC-2 decreased to $12.5 \times 10^{-5} \text{ mol g}^{-1} \text{ s}^{-1}$. Increase in FTY observed with increase in carbon content upto optimum level. Further increase in carbon shell thickness results decrease in activity due to the blockage of access to Fe active sites.

Challenges and Opportunities

Converting CO₂ into CO via RWGS has attracted considerable attention since CO product can be used as feedstock material for Fisher Tropsch synthesis which efficiently converts CO and hydrogen mixture into hydrocarbons. However, the major obstacle in the catalytic conversion from CO₂ to CO is chemical inertness of CO₂ molecule and its thermodynamic stability. Noble metal based catalyst such as Pt, Pd and Ir are commonly used for RWGS reaction, but high cost of these metals retards its application in large scale industrial process. Therefore earth abundant iron based catalyst is best candidate for ongoing process. Herein, recently we have developed iron supported graphene catalyst for the highly selective RWGS synthesis. Our catalyst is showing good to moderate conversion with more than 95% selectivity for CO, which is best fitted in state of art of catalyst for RWGS. Modern processes for selective synthesis of hydrocarbons via CO₂ hydrogenation have benefitted greatly from advances in fundamental catalytic science and technology. Iron based catalyst.

Conclusion

In the last decade, major developments in surface science, characterization tools and spectroscopic tools provided an impetus to the growth of the heterogeneous catalysis in terms of fundamental understanding. Importantly, the advancements also brought to the fore, some of the major challenges and opportunities in the field. While heterogeneous catalysts are preferred for its robustness and efficiency, it is rather worrying to face situations when, occasionally the efficiency in terms of turn over number and selectivity becomes less reproducible due to heterogeneities of the sites on the catalyst. Despite realizing the strong correlations between processing

conditions and chemical structure of the surface since long ago, the targeted synthesis of catalysts with desired active sites continues to be a major challenge. Many successful catalysts are still being discovered serendipitously or with minimal predictive knowledge to start with. It is an opportunity for researchers working in the synthesis and computational modeling to predict the chemical structure of the active sites and evolve suitable synthetic routes to them.

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