THE RELEVANCE OF THE SCIENCE OF NANOMATERIALS IN CATALYSIS

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1. Introduction

Reduction of the size parameters of a substance to nanometer scale causes appearance of unique properties which can be used in practice for development of novel materials and technologies. This manifestation has not only reflected in physical properties like melting point, optical absorption, electrical and magnetic properties but also in the reactivity of the substance. This has direct consequence in generation of new functional nanomaterials especially in catalysis and adsorbents. Size effects have been explicitly realized in catalysis in the original formulation of the structure-sensitive and structure-insensitive reactions by Prof Boudart.[1] However this concept has been realized and studied for long time in the field of catalysis. The implications of this concept for the field of catalysis is shown schematically in Fig.1
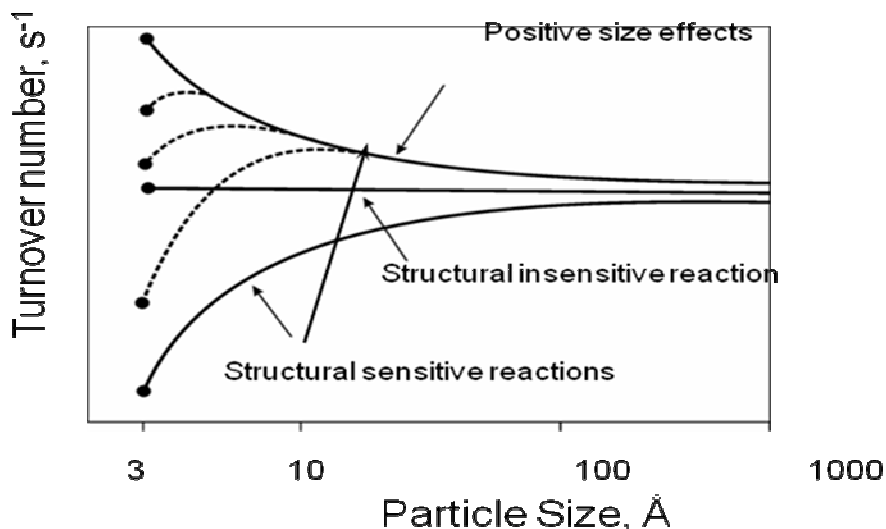

Fig.1. Pictorial representation of structure sensitive and insensitive reactions according to the original classification by Boudart [reproduced from ref.2]

Nanoscience today gives a large contribution to the fundamental understanding and also for designing and fabricating catalytic systems with optimization of the performance. It is a misconception that the prefix 'Nano' implies the dimensionality of the materials, it means the new state of matter which has completely altered behavior as compared to bulk or molecular state materials. The electronic structure of bulk materials (in the frame work of band theory of solids) or molecules (in the frame work of molecular orbital or valence bond theory) has been well studied in the past and has also been exploited for the formulation and design of functional materials. However, the advent of another state, namely nano state, for materials has added another additional dimension to the science of materials. The science of materials itself has to undergo a drastic change with the introduction of nano-state as an additional state to the bulk and molecular states. Even though the advent of this new state has many remarkable and

revolutionary changes in various fields, its introduction as a concept in the field of catalysis has remarkable consequences. This presentation hence therefore is restricted to examining some of the facets of the changes in the field of catalysis. It must be admitted that this presentation is not certainly comprehensive but only leads to some doors in this exciting area.

2. Nano-sized Metallic Particles as Catalysts

It has been the general belief that some of the metals (especially noble metals like Pt, Pd or Rh) are active as catalysts while some other coinage metal metals like gold and silver are not active as catalysts in bulk state. This belief has to be abandoned today since gold has been shown to be active even for exotic reaction like the oxidation of carbon monoxide to carbon dioxide n around room temperature.

Secondly, synthetic strategies have been evolved for generating these metallic systems in the nano state with homogeneous size distribution with the mean particle size which is optimal for catalytic properties. In addition, it is possible today to stabilize these metallic systems on appropriate supports against sintering and thus generate a means for economic viability. The nano state of metals like gold, silver and copper can also find exotic applications in optical sense, health care, drug delivery as well as in biotechnology. It is expected that the application of this state to these areas can have far reaching consequences.

A variety of supported nano-metal systems has been exploited as catalysts for process like energy conversion as well as pollution abatement. Some typical ones are (i) methane oxidation over Pt/Al_2O_3, (ii) low temperature oxidation of CO over gold nano particles, and (iii) noble metal catalysts supported on carbon for fuel cell applications.

Natural gas has today great prospects for different applications like energy conversion, fuels for automobiles and industry and also as a feed stock for chemicals. One of the essential reactions that one has to consider in this respect is the complete oxidation of methane as per the equation at relatively low temperatures

$$CH_4 + O_2 \rightarrow CO_2 + H_2O + Q$$

Pt/Al_2O_3 catalysts can be used for this purpose but optimization of platinum loading should be exercised from economic and viability considerations. It has been shown that metallic nano-particles with sizes around 0.65 nm metals could give a minimum turnover number of 250 while Pt particles of size around 22 nm could only give a maximum turn over number of 230 thus showing that the nanometallic state the Pt on alumina is capable of promoting this reaction effectively and also more economically.

The main applications of low temperature oxidation of carbon monoxide are (i) for indoor air quality control (ii) Automobile exhaust gas treatment (especially under cold start conditions) and (iii) CO removal from reformed hydrogen for fuel cell applications especially from the point of view of poisoning the noble metal electrodes.

As stated earlier, this is one of the remarkable applications of gold nano-particles in catalysis. There are a number of studies reported in literature on this aspect and the reader is requested to refer to the original literature from the lead references [3] provided.

3. The relevance Gold nano Particles as Oxidation Catalysts

The importance of gold and silver metallic nano-particles stems from the fact that the synthesis strategies adopted for them have given rise to evolution of many other synthetic procedures and also led to the understanding of the formation of nano state materials. Essentially, the synthesis of nano-materials has to follow the conventional route of controlled nucleation and growth. The control strategies have to be adoptable with appropriate size and shape recognition.

At this stage one has to divert a bit and see briefly at least one or more of the synthesis strategies that are adopted for the formulation of nano materials. In fact, metallic nano-materials can be formulated with size and shape control with the use of a variety of agents often termed as capping and reducing agents. Essentially the procedures adopted are to some extent kinetic control of the nucleation and growth of the particles. In fact a variety of methods can be adopted for preparing nano particle catalytic materials. Some of them are (i) by impregnating the precursor material and subsequent manipulation (IMP); (ii) Deposition and precipitation (DP); (iii) chemical liquid phase grafting (CLPG); (iv) Chemical vapour infiltration (CVI); (v) photochemical synthesis routes(PCSR); (vi) Microwave assisted synthesis and also by a variety of degradation/decomposition/formation techniques like laser ablation, electrochemical synthesis, metal vapour deposition, sono-chemical and sputtering methods.

The strategy adopted in one of the methods is outlined briefly. Solid state routes are mostly contamination free and hence ideally suited for catalyst preparation. Microwave heating is suitable since it provides enhanced kinetics of the decomposition, rapid and localized heating are possible and thus the material obtained will be suitable for catalytic applications with appropriate surface area and textural characteristics. A typical synthesis scheme adopted is shown in Fig.2.

$Ag_2C_2O_4$ (50 mg) + Ethylene glycol(40 ml) + Poly vinyl pyrrolidone(PVP)(250 mg)

Medium Ethylene glycol   Stirred purged N_2

Diethylene glycol

Capping agent PVP   Microwave irradiation

(on for 10s off for 5 s)

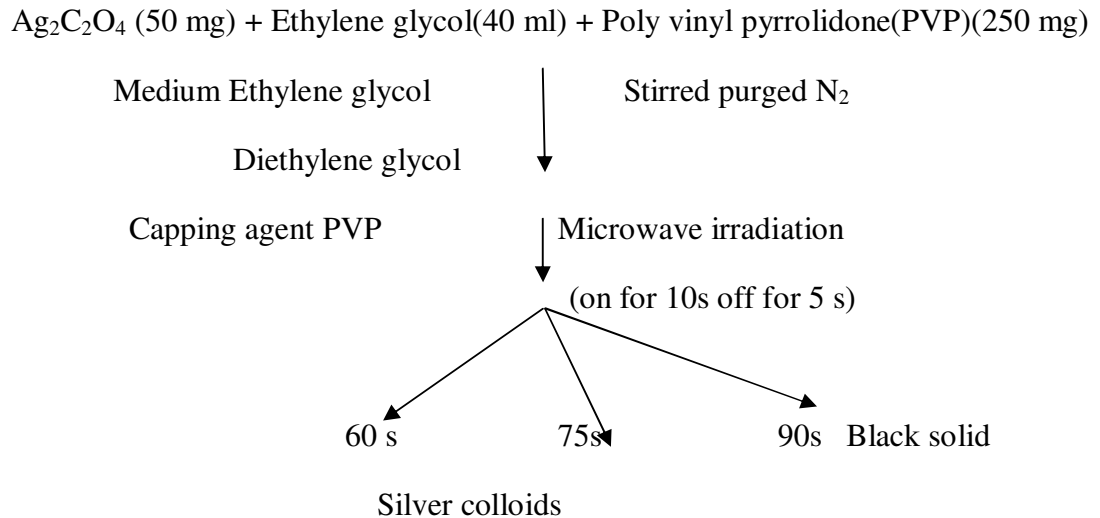60 s   75s   90s   Black solid

Silver colloids

Fig.2. Synthesis of silver nano particles by microwave (MW) irradiation method [4].

It should be noted that only one example of the synthetic strategy adopted for preparation of nanometallic systems for catalytic applications is given. There are a number of other procedures

by which nano state metallic and non metallic systems can be formulated for catalytic applications. Interested readers can access them from the original literature.

As stated above there are a number of synthetic methods that can be adopted for the preparation of metallic nanoparticles. In order to provide a comparative evaluation Au/Al$_2$O$_3$ have been prepared by three different procedures and have been used as catalysts for oxidation of CO at 313. The data generated from these studies are given in Table 1

Table 1 Activity for CO oxidation at 313 K of Au/Al2O3 catalysts prepared by various methods.[5]

Preparation Method	Particle size in nm	Rate (mol CO_2 X $(g.Au)^{-1}$ s^{-1})	Turn over Number $S^{-1}x10^4$
Deposition – Precipitation (DP)	3.7	240	21
Chemical liquid phase grafting (CLPG)	13.3	<1	
Chemical vapour deposition (CVD)	3.8 (T_d = 873 K)	95	6.7
Impregnation	4.1 (H$_2$ reduction after pretreatment)	<1 and 14 (pretreatment with $((CH_3)_4N(OH))$	1.3

Many studies have shown that in the oxidation of carbon monoxide, the nanometallic gold supported on oxides is superior to other nanometallic supported systems [5].

4. One Dimensional Architectures in Catalysis
4.1 Silver Nanomaterials as Catalysts

One dimensional nano materials conventionally termed as nano wires, nanotubes, nanorods and nanocubes have been shown to be excellent catalytic materials. Though it has not yet been explicitly realized in literature the advantages of one dimensional nano architecture, it can at least be formulated that the one dimensional nano material architectures have shown remarkable applications especially in catalysis. The morphologies obtained for the silver nanoparticles prepared by the polyol process were found to be strongly dependent on the experimental conditions such as temperature and the molar ratio between PVP and AgNO3. Reported studies have suggested that the degree of polymerization of PVP plays an important role in determining the morphology of the silver nanoparticle.

X diffraction of the silver nanoparticles synthesised using the polyol process suggested that silver existed purely in the face centered cubic structure. These nano architectures show preferential (111) crystal faces at their surface. The UV-Vis spectrum of the nanowire's solution showed a broad peak at ca. 380 nm that could arise from surface plasmon excitation of the silver nanostructures. TPR profiles, after treatment in O2 for 1 h at 623 K, of the 11% of silver nanowire supported on α-Al2O3 and 15% Ag/α-Al2O3 (prepared by wetness

impregnation)showed two broad peaks for nanowires catalyst at around 633 K (most intense peak) and at around 873 K. However for 15%Ag/α-Al2O3 catalyst these peaks are shifted to higher temperatures (753 and 933K, respectively), with the most intense peak for this catalyst is the second one. The selective oxidation of styrene (Table 1) over Ag catalysts shows phenylacetaldehyde (Phe) and styrene oxide (SO) as main products. [6]
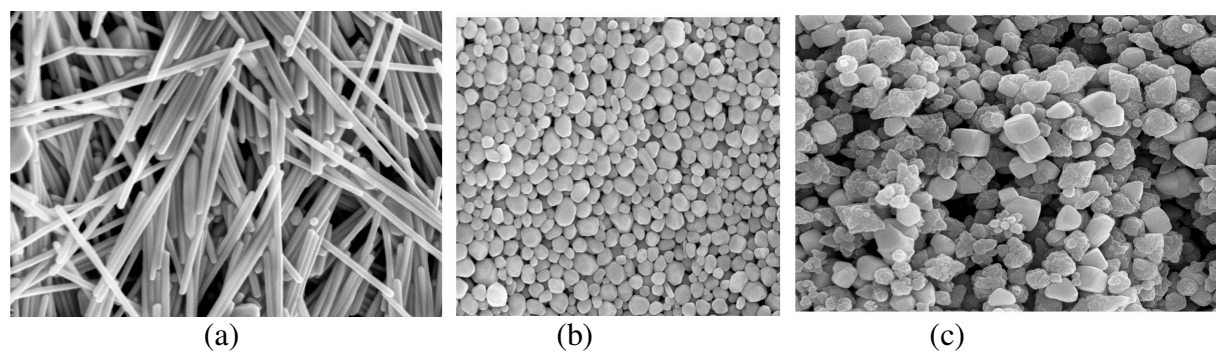

| (a) | (b) | (c) |

Fig.3. SEM images of the different silver nanoparticles catalysts.(a-b) Silver nanowires, (with PVP and Silver nitrate ratio of 1.5) and nanopolyhedra supported on α- Al2O3, respectively (for a ratio of 3 and longer time (11%Ag(NW)-W)/α-Al2O3) and (c) Silver nanocubes supported on CaCO3 (11%Ag(NC)/CaCO3). Scale bar of 500 nm for all the samples.

The direct combustion route of styrene was negligible for silver nanowires nanocubes and nanopolyhedra even at near total conversion condition. This fact was not observed for 15%Ag/α-Al2O3 catalyst which shows combustion products even at lower conversion (around 5%). The pure silver nanowires catalyst (11% Ag(NW)/α-Al2O3) showed a styrene conversion of 57.6% and a selectivity to styrene oxide of 42.5%. Silver nanopolyhedra and nanocubes supported on α-Al2O3 showed similar catalytic performance compared to the silver nanowires. The basic properties of the catalyst, addition of CaCO3 as support, improved the catalytic activity. When CaCO3 was used as support for the silver nanocubes the styrene conversion increased from 42.5 to 93.1% and the selectivity toward phenylacetaldehyde increased (74.4%). It is highly possible that the phenylacetaldehyde obtained in the reaction is formed from the thermolysis of the styrene oxide . Comparing the reaction activity and selectivity with the result of TPR profiles one could suggest that the first peak is the responsible for the different performance and it is probably related with oxygen species that preferentially lead to high activity and selectivity.

Table .2. Results of the catalytic activity tests for the silver nanoparticles in the epoxidation of styrene at 573 K[6]

Catalyst[a]	Catalytic activity		
	$X(\%)^b$	$Phe(\%)^c$	$SO(\%)^d$
11%Ag(NW)/α-Al2O3	57.6	57.5	42.5
11%Ag(NC)/α-Al2O3	56.9	68.6	31.4
11%Ag(NP)/α-Al2O3	57.5	69.2	30.8

[a] catalyst designation, NW nanowire, NC nanocubes, NP nanopolyhedra, [b] Conversion, (X) of styrene; [c] selectivity to phenylacetaldehyde (phe%) [d] selectivity to styrene oxide (SO%) $O_2:C_8H_8$ mole ratio of 50.

The purpose of this example is to demonstrate the following aspects:

(a) How the nano state of silver is superior for expoxidation reaction as compared to the bulk silver catalysts.

(b) Normally the role of oxygen and the state of oxygen in the active catalyst is not well known and these studies throw some information on this important aspect of the reaction. The selectivity to styrene oxide was enhanced in oxygen rich atmosphere. Furthermore, correlating the epoxidation performance with the XPS results, can be stated that there is a direct relationship between the epoxidation performance of catalyst and O1s signal associated with Oβ specie. The O□ species seems to be critical for the activity of the silver catalysts.

(c) Negligible deactivation of the silver nanowires catalyst promoted with 0.25% of cesium was observed. This indicates the feasibility of shape controlled silver nanoparticles as catalysts for styrene epoxidation and show how the activity and selectivity of the catalyst can be changed by Cs promotion.

5. Metals on carbon - electrode materials
5.1.   Pt on carbon by functionalization method

Noble metals (mainly Pt group metals) loaded on carbon substrates have been used as electrodes for fuel cell applications.   Various strategies have been adopted to obtain effective dispersion of the noble metals (of the order of ≈2 nm Pt particles) on carbon supports especially to optimize the extent of loading of noble metals as well as for their effective utilization.   However, the challenges in the effort of dispersing nanometer metallic particles on carbon supports are the creation, effective dispersion of nanosized metallic particles on the support and the prevention of agglomeration.   Carbon being a surface of equi-potential, the tendency for migration and agglomeration of the metallic species is predominant.

Various strategies have been adopted in this direction.   Recently in the author's laboratory [7] two methods have been adopted for this purpose.   These are

(a) Effect of functionalization of the carbon support by carboxylic, sulfonic acid or by aminopyridine.

(b) Effect of capping agent on the dispersion and activity of Pt nanoparticles on carbon support.

These methodologies are briefly outlined.   The oxidative treatment of carbon support (in this case it is CDX975, a product of Columbian chemicals company USA) with different concentrations of nitric acid has shown to   increase the concentration of carboxylic acid functional groups on the support.   The incorporation of carboxylic aid functional groups on the carbon support was confirmed by the increase in the absorbance due to OH and CO vibrations at 3000-3600 and 1729 cm^{-1} in the IR spectrum.   The data given in Table 3 show that pt is

dispersed on nanometer scale on carbon support as a result of introduction of carboxylic acid functional groups on the carbon support.

Table-3. Cystallite size and electrochemical activity data for the untreated and nitric acid treated carbon support for methanol oxidation (for use as electrode for direct methanol fuel cell applications)[EAS – electrochemical activity surface area; ICP – Inductively coupled plasma emission method][7]

Sample	pH	Crystallite size (nm)	% Pt (ICP)	EAS (m^2/g)	methanol oxidation activity (A/g)
10% Pt/untreated CDX975	6.1	13.5	9.1	18.1	214
10%Pt/1 N HNO$_3$ treated CDX 975 60 min	5.0	21.2	-	24.8	311
10%Pt/concHNO$_3$ treated CDX 975 -60 min	4.5	6.6	-	9.0	406
10%Pt/1 N HNO$_3$ treated CDX 975-95 min	4.1	12.9	9.5	10.2	269
10%Pt/concHNO$_3$ treated CDX 975 -95 min	3.7	13.4	8.1	5.2	265

Even though carboxylic acid functionalization provided a means for nanometer dispersion of Pt metallic particles on the carbon support, the net effect observed in the electrochemical activity for methanol oxidation is not remarkable. Hence, sulfonic acid functionalization was attempted using a variety of reagents like 2-aminoethane sulfonic acid, ammonium sulfate and also sodium sulfide and formaldehyde. The grafting of sulfonic acid groups on the carbon support is possible with these three different sulfonating agents employed. Typical reaction scheme for the grafting of the sulfonic acid groups on carbon support is shown in Fig.3. The data generated for one of the sulfonated systems are given in Table 4 It is generally expected as an example the azo compound formed with the sulfonating agent in presence of mineral acids reacts with the carbon black support and incorporates the alkyl sulfonic acid group on the carbon support. The Pt loading of these carbon materials was carried out using ethylene glycol reduction method. For details see ref.7.

Table 4 Comparison of pH, particle size and methanol oxidation activity for unsulfonated and sulfomethyl modified catalysts [for abbreviations refer to previous table]

Catalyst	pH	Crystallite size (nm)	Weight % Pt (ICP)	EAS (m^2/g)	Peak current density (mA/cm^2)	specific methanol oxidation activity (A/g)
10%Pt/CDX without pretreatment	3.3	13.5	9.1	17.9	61.1	213
Sulfomethyl modified 10% Pt/ CDX975	3.3	4.4	10.0	41.5	138.4	484

Aminopyridine modification of carbon support has shown a better dispersion of Pt nanoparticles with lesser particle size and enhanced activity for methanol electro-oxidation. The data substantiating this aspect are given in Table 5. The presence of aminopyridine on carbon support is ascertained from the IR absorption for C=N vibrations on the modified surface. The specific deductions that have been evolved of these studies include the following:

(a) Functionalization of the carbon support especially with species that are capable of ligating with Pt gives rise to better dispersion of Pt nanoparticles on the carbon support.
(b) The chemical anchoring of Pt crystallites on the modified surfaces is responsible for better dispersion and also for prevention from aggolomaration of pt particles.
(c) These methods not only favoured better dispersion of the Pt nano particles but also accounted for increasing the effective electrochemical active area which accounted for the increased electrochemical activity.

Table 5- Comparison of the particle size of Pt, EAS and methanol oxidation activity for unmodificed and aminopyridine modified catalysts[7]

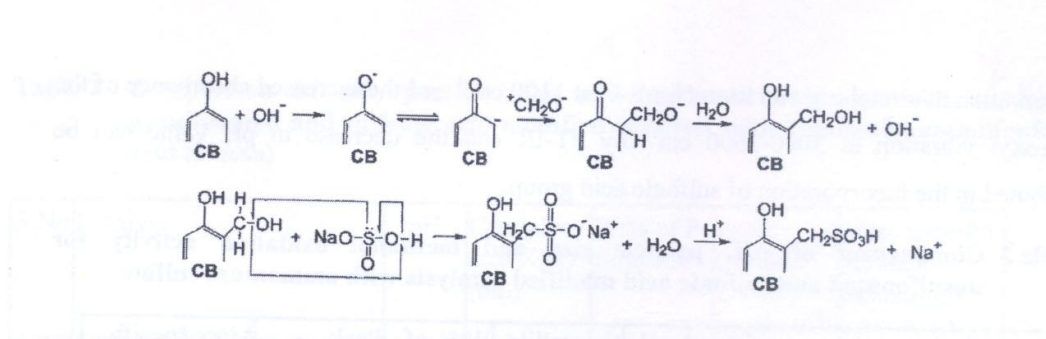| Sample	Crystallite size (nm) (from XRD)	Particle size from TEM	% Pt (ICP)	EAS (m^2/g)	Peak current density for methanol oxidation (mA/cm^2)	Specific methanol oxidation activity (A/g)
10%Pt/untreated CDX	18.5	7.6	9.1	19.3	44.3	155
10%Pt/1%AP/CDX	13.4	-	8.6	38.7	77.1	270
10%Pt/5%AP/CDX	9.4	3.4	8.3	60.0	119	415

Fig.4. Typical reaction scheme for grafting methyl sulfonic acid group on the carbon support

## 5.2.	Pt on Carbon by Capping Method[7]

Another important strategy in the dispersion of nanometallic components on carbon supports is the use of the capping agents.   Normally nanomaterials are kinetically not stable and often lead to aggregation. Hence they have to be stabilized using agents like polymers, surfactants and other molecules which can be tagged on to the nanoparticles.   However, the subsequent removal of these capping agents can impose some restrictions. Various conceptual methodologies have been adopted and one such methodology is the electrostatic stabilization with carboxylic functionalities. One of the common electrostatic stabilizing agents is citrate.   The catalysts with the capping action of citrate were prepared by adding a suspension of citrate in aqueous solution of hexachloro platinic acid and ethylene glycol to carbon support and heat treating at 393 K for 1 h. Independent XPS studies showed the existence of Pt In 0 and +2 oxidation states and the system containing maximum Pt in +2 oxidation state exhibited the maximum activity for the methanol oxidation.   This has provided experimental evidence for the suggestions of the participation of higher oxidation state of Pt in methanol electro-oxidation. In Table 6 typical data generated using this methodology for the preparation of supported Pt on carbon systems are assembled.

Table 6- Typical characteristics of the Pt/Carbon system generated using citrate as capping agent [7].

Mole ratio of citrate/Pt	% Pt(0)	%Pt(II)	Pt crystallite size(nm)(XRD)	Pt crystallite size(nm)(TEM)	EAS (m_2/g)	Methanol oxidation activity (mA/cm^2)
0	73.3	26.7	9.1	7.5	-	148
2.4	83.7	16.3	4.1	3.0	7.3	94
6.0	79.3	20.8	3.7	-	12.4	96
12.0	74.4	24.5	3.3	2.7	17.7	202
24.0	73.3	26.7	3.1	-	11,8	148

6. Hydrogen (Energy) storage in nanomaterials

Activation and storage of Hydrogen are important aspects in catalysis and energy conversion processes.   Various types of studies have been carried out on these aspects.   It has been shown recently that the decoration of magnesium particles with metal nano material leads to promising results for improved hydrogen sorption properties of magnesium in the temperature range of 200-330 ^{o}C under 35kPa. Copper, nickel and palladium nanopartices were deposited on magnesium and samples with copper show a good kinetics for sorption at the higher temperatures . This behavior is probably enhanced by the chemical link between the Cu nanoparticles and the magnesium particles, the interface being constituted of $MgCu_2$.[8] The controlled design of bimetallic Mg@nanoM (M = Cu, Ni and other metals) materials will be developed in future to improve further the hydrogen sorption properties and energy storage

applications. Similarly nanocarbon materials like carbon nanotubes with appropriate substitution especially like heteroatoms like nitrogen and boron have been shown to be viable hydrogen storage materials[9]. It is expected that remarkable progress will be achieved in the future in energy storage applications using nano materials in various formulations.

6. Perception of metallic nanomaterials as catalysts

Metal nanoparticles can thus act as best catalyst for industrial application as these have large surface to volume ratio and have unique quantum size effect. Industrial catalysts act on the surface of the metals and therefore metal nanoparticles are promising catalytic materials. Generally industrial catalysts are prepared by heating metal ions at high temperature and sometimes in the presence of hydrogen gas and have complex structures. Supported metallic catalysts have been used in a variety of commercial hydro-treating plants and it can be expected that these plant operations can see remarkable improvements in the economics of the plant operation and the life time of the catalysts may be improved considerably. Secondly the preservation of the active metallic catalysts (normal shelf life or operational life) may become attractive through the use of capping agents.

7. Carbon nano Materials

8.1 For Electro-catalytic Applications

The use of carbon in a chemical process dates back as far as 3750 BC. Early Egyptians and Sumerians were known to have used charcoal to reduce copper, tin and zinc ores for producing bronze. Since then carbon has been evolved for use in a multitude of processes. Traditional carbons or 'classic carbons' such as soot, charcoal and diamond have been mostly replaced with new and novel carbon materials. Since the 1960's a variety of synthetic strategies have been employed to produce carbons that have favorable structure, texture and composition that allow for these new carbons to perform significantly better than classic carbons. Examples of these new carbons include carbon fibers, porous carbons and pyrolitic graphite. Of these new carbons, graphitic carbons have shown promise for usage in energy storage and conversion processes.

While these as-synthesized CNTs perform well in their primary purpose as electron conductors in chemical and electrochemical processes, it would be of tremendous advantage if this class of graphitic carbons were modified to be active in these chemical and electrochemical reactions themselves. Efforts towards this end have involved heteroatom doping – most notably nitrogen doping on graphitic carbons. Oxygen reduction reaction (ORR) is a technologically important reaction that takes place in the cathodic side of a fuel cell. A number of synthetic strategies have been employed in the nitrogenation of graphitic carbons. The most popular method is the introduction of the as prepared carbon into an atmosphere of NH_3 or HCN at high temperatures. The resulting carbon was found to be enriched in nitrogen and had a significantly higher activity for electrochemical reduction of oxygen. While it has been of general consensus that nitrogen doping increases the activity of these carbons, there has been ambiguity as to what physicochemical factor or factors effect this difference in activity. Most of the ambiguity stems from poor reproducibility and stability problems associated with the post-synthetic modification step of these carbons. To this end, efforts have been concentrated on developing facile synthetic

protocols that enable synthesis of systematically doped graphitic nanocarbons in order to elucidate individual physicochemical properties and their contribution to ORR activity.

While a systematic increase in nitrogen doping at graphitic carbons increases the activity for ORR at these nanocarbons, their activities are lower than what is seen with metals known for exhibiting high ORR activity. Efforts undertaken to improve on this particular aspect have involved using these carbons as supports for active metal nanoparticle catalysts to be used in heterogeneous catalysis.

Conventional strategies employed for loading metal catalysts on carbons typically involve inducing surface functionalities such as carbonyl, carboxylate, ester-like oxygen or alcohol on the carbon to facilitate anchoring of catalysts on the support. This is done using aggressive protocols that involve the use of strong acids like HNO_3, H_2SO_4, HCN or strong oxidizing agents like H_2O_2 and $KMnO_4$.
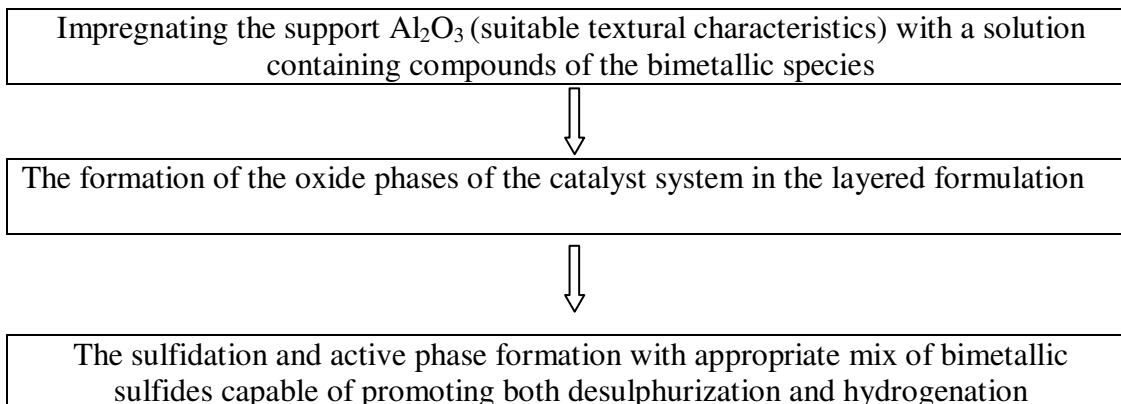
These protocols are often not reproducible and degrade the preferred structural and compositional properties of both the carbon support and active metal catalyst. The ability to manipulate in-situ, the structure, composition, surface area and the density of edge plane sites on NCNTs provides a significant advantage over traditional carbons for use as catalyst supports because there is no further need to modify the surface to facilitate catalyst loading. This offers tremendous advantages in using NCNTs as catalyst supports while circumventing the time consuming and often structurally degrading pre- synthesis steps that are used in catalyst loading protocols like microemulsion, impregnation, coprecipitation, sonochemical and fluidized bed CVD processes. NCNTs as catalyst supports also allow for uniform catalyst dispersion and utilization stemming from control of their surface properties such as the density of edge plane sites and porosity.

Challenges in defining physicochemical properties of nitrogenated graphitic carbons (esp. NCNTs) that contribute to oxygen reduction and the advantages in using these properties efficiently and synergistically with active metal catalysts for ORR have been considered in the literature.[10] In addition heteroatom substituted CNTs have also been proposed as one of the possible materials for hydrogen storage applications.   Extensive literature [see ref 10] are available on the various aspects of new carbon materials for catalytic applications.

8. **Catalytic and   Adsorptive Desulfurization – Important Energy Conversion Processes**

Removal of organo-sulphur compounds from diesel is an issue of interest from scientific, social, economic and environmental view points. Production of clean fuel is the goal of petroleum refining industry. The reduction of S below certain levels in diesel fuels becomes difficult due to the presence of sterically hindered S-compounds (such as the 4, 6 - dialkydibenzothiophenes) that are difficult to desulfurize over conventional supported mixed sulfide catalysts. Hence, newer technologies based on novel routes like adsorption, oxidation and chelation are being developed to remove these refractory S-compounds. The desulphurization is usually carried out using a variety of catalysts. One of them is the cobalt-moly (CoO-MoO_3-Al_2O_3) catalyst. Conventionally these systems consist of layered structure with high dispersion of molybdenum sulphide phase over the support phase.   In addition, the active catalyst system is considered to consist of mixed CoMoS phase with layered structure and without any oxygen atom directly

bonded to Mo atoms. The formulation and molecular functioning of this nanocomposite catalyst system   are shown in Scheme 1. [2]

Impregnating the support Al_2O_3 (suitable textural characteristics) with a solution containing compounds of the bimetallic species

⇓

The formation of the oxide phases of the catalyst system in the layered formulation

⇓

The sulfidation and active phase formation with appropriate mix of bimetallic sulfides capable of promoting both desulphurization and hydrogenation

Scheme 1. The flow chart of the formulation of hydro-desulfurization catalyst

The micrographs of the formulated catalyst and also that of the active catalysts are shown in Fig.3.
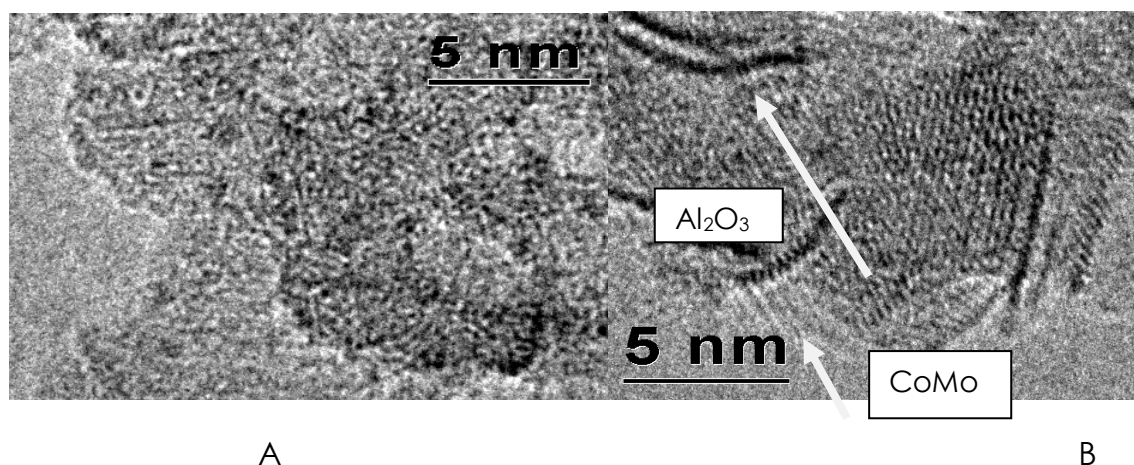

A   B

Fig. HRTEM images of Co-Mo/Al2O3 catalysts – 'A' before reaction Co-Mo clusters (size less than 1nm on alumina surface and B after reaction flat clusters of $CoMoS_2$ on alumina surface.

This type of architectured deep desulphurization catalysts have been developed and commercialized by Boreskov Institute of Catalysis, in Russia from 2007.

Burning of fuel (gasoline or diesel) with S contents beyond permissible limits causes ill effects on human health. Current world demands zero sulfur fuel. Even though the production of clean fuel is the goal of petroleum refining industry, the refinery itself is engulfed now in the vicious circle of a host of problems that include environmental legislation, crude oil variation, product demand, economic imbalances, energy uptake, safety and process efficiency   It should not be

mistaken that conventional HDS can be a panacea to the recurring problem of S specification in the transportation fuels. Newer technologies, if found promising, should be given place and adopted.

The origin of refractory behaviour in compounds such as highly substituted dibenzothiophenes, 4, 6 DMDBT in particular, is related to the steric hindrance encountered for the breaking of the C-S bond. The desulphurization of 2, 6 DMDBT is normally carried out by two routes, namely, the hydrogenation (HYD) and the direct desulphurization (DDS). The partial hydrogenation reaction of 4, 6 DMDBT is a common as well as the primary reaction for either the HYD route or for the DDS route. After the formation of partially hydrogenated products, the C-S bond is cleaved in the DDS route without any further hydrogenation. Unlike the DDS route, in the path through hydrogenation (HYD route), complete hydrogenation of atleast one of the aromatic rings is inevitable for the C-S bond to cleave. The presence of substituents at 4 and 6 positions of DBT hinder the β – elimination step which is necessary for the desulphurization to take place. Presence of refractory sulfur compounds like, 4, 6 dimethyl dibenzothiophene, necessitate the severe operation conditions.

In most of the diesel fuels, 4, 6 DMDBT, the most difficult S containing compound to be desulphurized, is present in > 100 ppm. In view of the increasing process severity of diesel HDS units to meet the upcoming stringent specifications of permissible S content, alternate methods of desulphurization are being examined.

Table 7- Hydro-treating performance of Ni_2P/C nano catalysts and the comparison with commercial $NiMoS/\gamma$- Al_2O_3 and Ni_2P/SiO_2[11].

Reactant type	Type	Conversion(%)		
		Ni_2P/C	$NiMoS/\gamma$- Al_2O_3	Ni_2P/SiO_2
4,6-dimethyldibenzothiophne	HDS	99	76	68
Quinoline	HDN	100	92	94
Tetralin	HYD	10	10	19

Nickel phosphide nano particles on C have been synthesized by temperature programmed reduction and the activity for sulfur removal from the refractory compound 4,6-dimethyl dibenzothiophene with a steady-state conversion of 99%, which is higher than that of a commercial NiMoS/ c-Al_2O_3 catalyst of 68%.

In the author's laboratory, carbon materials have been generated in various nano forms and have been exploited for the adsorptive desulphurization of Nariman (cauvery basin crude) crude. The typical data generated in the laboratory for this process are given in Table 8.

Table 8- S removal capacity of different commercial activated carbon materials[12]

Activated Carbon as Sorbent	*ml-diesel treated/g of adsorbent	S removed (ppm)
IG 18 x 40	4	134
IG 12 x 10	4	81
IG 8 x30	4	76
AC 4 x 8	4	12
AC 6 x 12	4	73
AC 12 x 30	4	92
Calgon carbon as received	4	181
Adsorbent carbon	4	229

* 20 ml initial product collected from the column packed with 5.0 g activated carbon and analyzed for S

9. Metal oxide nano materials as catalysts

Oxide and sulphide nanomaterials have been exploited as catalysts for a variety of catalytic applications.   One of the exotic reactions carried out is the conversion of carbon dioxide to methyl alcohol.   The relevant data are given in Table 9. It is seen that nanocrystalline nickel oxide and zinc oxide are better catalysts for this reaction as compared to the conventional materials.

Table 9 - Methanol production from carbon dioxide using metal oxides as catalysts (Comparison of the activity of microcrystalline and nanocrystalline oxide materials). [13]

Catalyst	Crystallite size (nm)	Surface area (m^2/g)	Conversion of CO_2 to CH_3OH (%)
Nano crystalline Nickel oxide	3	320	64.2
Commercial Nickel oxide	59	1.2	0
Nano crystalline Zinc oxide	4	130	37.1
Commercial Zinc oxide	44	3.9	0

Similarly the photo-catalytic activity of CdS as a function of particle size has been evaluated. In Table 10-the values of 'd' spacing and also crystallite of CdS prepared using various zeolites are given.   In Fig, the corresponding photo-catalytic activity data are presented.

Table 10- d spacing and crystallite size of CdS materials prepared using various templates

d' spacing catalyst	(002)	(101)	(112)	Crystallite size nm
CdS (bulk)	1.52	1.79	2.97	21.7
CdS (bulk)(HF treated)	1.52	1.79	2.93	21.7
CdS-Y	1.53	1.79	2.96	8.8
CdS-β	1.52	1.78	2.93	8.6
CdS-Z	1.52	1.79	2.97	7.2

Another development worth noting is the prediction of activity on the basis of theoretical calculations. Norskov and his coworkers [14] have carried out density functional calculations on a variety of catalytic systems. These studies provide a molecular-level discussion of the nature of the active sites in metal catalysis. The relevance of the fundamental concepts such as "Brønsted–Evans–Polanyi relations" and "volcano curves" are considered.   These correlations have been used to establish a strict partitioning between the so-called "electronic" and "geometrical" effects From these studies they have evolved a concept of degree of structure sensitivity which can be used for analyzing the structure sensitivity of catalytic reactions. These and similar studies may have relevance for examining the activity of nano particles.

10. Perception

The possibility of viewing the active sites of catalysts that has become possible by the advent of the high resolution microscopy has slowly transforming the field of catalysis science.   The biological systems (especially enzymes) have been transforming molecules in most efficient manner under milder operating conditions than what is demanded by heterogeneous catalysts and are yielding most selective products.

The nanostate of catalytic materials can be approximated to these biological systems and hence it is possible that one can expect catalytic efficiencies similar to the biological efficiencies with respect to specificity up to atom economy.

The structural and electronic properties as well as geometric constraints obtainable in biological systems can be replicated in catalytic systems. This possibility opens up another avenue where the catalyst transformations will be controlled by the frontier wave functions of the catalytic systems. Up to now the new catalyst systems are designed from chemical information only while in future the postulates for new generation catalyst systems will be based on the nature of frontier wave functions of the nanoscale materials with the normally obtainable 'constraints' on the fragments of biomolecules which are responsible for the selectivity.

Biomolecules adopt unusual geometrical configurations due to internal hydrogen and other non bonding interactions in the species. These are probably the reasons for the generation of active sites which operate as 'lock and key'. The advent 'nano state' of materials and its adoption to catalysis can be expected to turn around a revolution in this field.

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