THE SCIENCE OF NANOMATERIALS IN CATALYSIS

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Introduction: SIZE EFFECTS

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. However this concept has been realized and studied for long time in the field of catalysis.

Nano science contributes to the fundamental understanding of catalysis and assists in designing and fabricating catalytic systems with performance optimization. It is a misconception that the prefix 'nano' implies the dimensionality of the materials, but it means a new state of matter with completely altered behaviour as compared to bulk or molecular state materials. The electronic structure of the bulk materials (band theory of solids) or molecules (Molecular orbital or Valence bond theory) has been exploited for the formulation and design of functional materials. However, the advent of nanostate for the materials has added another dimension to material science.

The role of size effect in catalysis is pictorially shown in Fig.1.

It has been a general belief that some metals (especially noble metals like Pt, Pd or Rh) are active as catalysts while some other coinage metals like gold and silver are not in the bulk state. However gold has been shown to be active for exotic reactions like oxidation of carbon monoxide to carbon dioxide around room temperature. Secondly, synthetic strategies have been devised for generating these metallic systems in the nanostate with homogeneous size distribution with mean particle size 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 nanostate of metals like gold, silver, copper can also find exotic applications in optical sensors, health care, drug delivery as well as in biotechnology. A variety of supported nano-metal systems have been exploited as catalysts for processes 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 nanoparticles and (iii) noble metal catalysts supported on carbon for fuel cell applications.

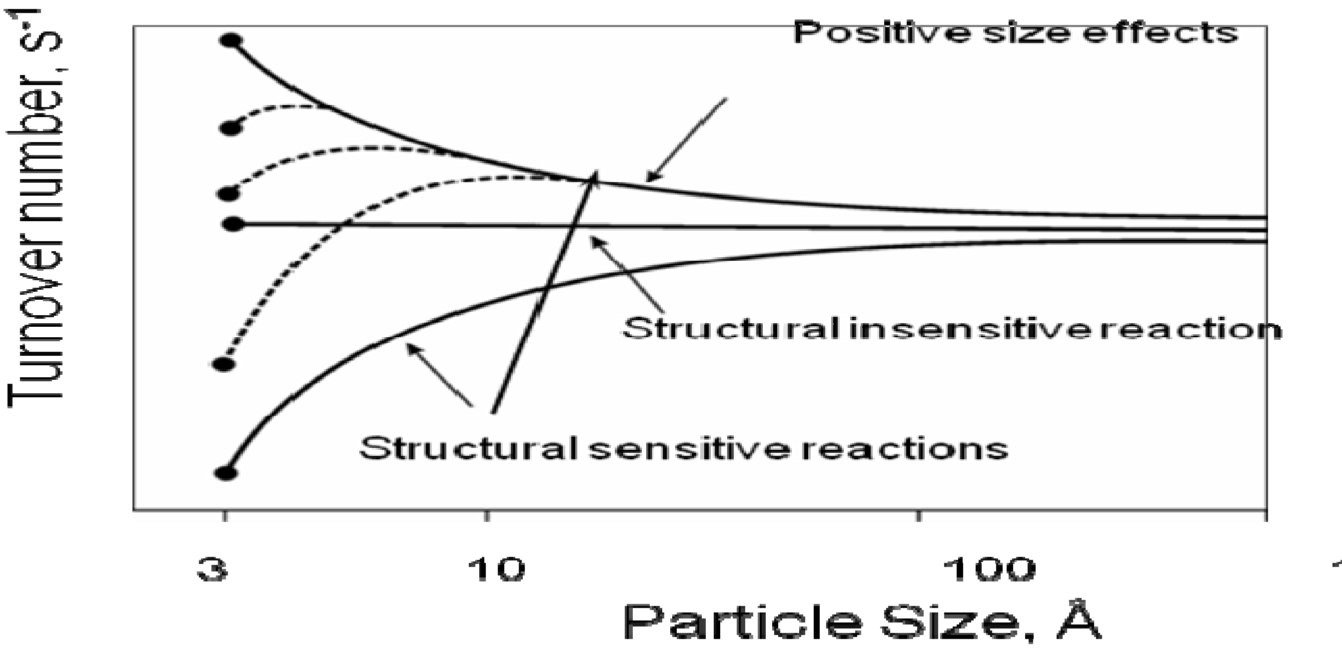


Fig.1. Pictorial representation of structure sensitive and insensitive reactions according to the original classification by Boudart

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 relative 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 nanoparticles with sizes around 0.65 nm metals could give a minimum turn-over number of 250 while Pt particles of sizes around 22 nm could only give a maximum turnover number of 230. Thus, it suggests that the nanometallic state of Pt on alumina is capable of promoting this reaction effectively and also more economically. The main applications of the low temperature oxidation of carbon monoxide are (i) 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 [2] provided.

The Relevance of Gold Nanoparticles as Oxidation Catalysts

The importance of gold and silver metallic nanoparticles stems from the fact that the synthesis strategies adopted for them have given rise to man other synthetic procedures and also led to the understanding of the formation of nanostate materials. Essentially, the synthesis of nanomaterials has to follow the conventional route of controlled nucleation and growth. Control strategies should be adapted 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 nanomaterials. In fact, metallic nanoparticles can be formulated with size and shape control with the use of a variety of agents often termed as capping and reducing agents. Essentially, to some extent, the procedures adopted are kinetic control of the nucleation and growth of the particles. In fact a variety of methods can be adopted for preparing nanoparticles catalytic materials. Some of them are (i) by impregnating the precursor material and subsequent manipulation (IMP); (ii) deposition an 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, electro-chemical 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 decomposition and rapid and localized heating is possible. Thus, the material obtained will be suitable for catalytic applications with suitable surface area and textural characteristics. A typical synthesis scheme adopted is illustrated in Fig.2.

There are a number of other procedures by which nano-state metallic and non-metallic systems can be formulated for catalytic applications. To provide a comparative evaluation, Au/Al_2O_3 has been prepared by three different procedures and has been used as catalyst for oxidation of CO at 313 K. The data generated from these studies are given in Table 1.

Table 1 Activity for CO oxidation at 313 K on Au/Al_2O_3 catalysts [4]

Preparation method	Particle size in nm	Rate ($molCO_2$ $X(g.Au)^{-1}s^{-1}$	Turnover 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 process of oxidation of carbon monoxide, monometallic gold supported on oxides has been found to be superior to other nanometallic supported systems [4].

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

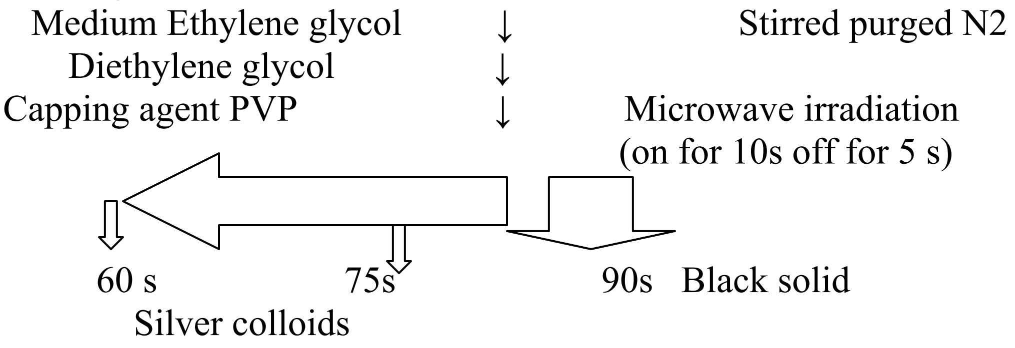


Fig.2. Synthesis of silver nano particles by microwave (MW) irradiation method.

One-dimensional Architectures in Catalysis - Silver nanomaterials as catalysts

Though one-dimensional nanomaterials conventionally termed as nanowires, nanorods and nanocubes have been shown to be excellent catalytic materials, their advantages have not yet been explicitly realized in the literature. The morphologies obtained for the silver nanoparticles prepared by polyol process were found to be strongly dependent on the experimental conditions such as temperature and molar ratio between PVP and silver nitrate. Reported studies have suggested that the degree of polymerization of PVP plays an important role in determining the morphology of the silver nanopaticle.

X-ray diffraction of the silver nanoparticles synthesized using the polyol process suggested that silver existed purely in the face centered cubic structure. These nanoarchitectures 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 of 11% of silver nanowire supported on $\alpha - Al_2O_3$ and 15% Ag/ $\alpha - Al_2O_3$ (prepared by wetness impregnation) after being treated with oxygen for 1 hour at 623 K showed two broad peaks for nanowires catalyst at around 633 K (intense peak) and around 873 K. However 15%Ag/ $\alpha - Al_2O_3$ catalyst these peaks are shifted to higher temperatures (753 and 933 K respectively) with the most intense peak for this catalyst is the second one. The selective oxidation of styrene over silver catalysts shows phenylacetaldehyde (Phe) and styrene oxide (SO) as main products [5].

The direct combustion route of styrene was negligible for silver nanowires, nanocubes and nanopolyhdra even at near total conversion condition. This fact was not observed for 15%Ag/ $\alpha - Al_2O_3$ catalyst which shows combustion products even at lower conversion (around 5%). The pure silver nanowires catalyst (11%Ag(NW)/ $\alpha - Al_2O_30$) showed a styrene conversion of 57.6% and selectivity to styrene oxide of 42.5%. Silver nanopolyhedra and nanocubes supported on $\alpha - Al_2O_3$ showed similar catalytic performance compared to the silver nanowires. Addition of $CaCo_3$ as support improved the acitivity of the catalyst. When $CaCO_3$ was used as support for the silver nanocubes, the styrene conversion increased from 42.5% to 93.1% and the selectivity to phenyacetaldehyde increased to 74.4%. It is possible that the phenylacetaldehyde obtained in the reaction is formed from the thermolysis of the styrene oxide. By comparing the activity and selectivity with the result of TPR profiles one could suggest that the first peak is responsible for the different performance and it is probably reacted with oxygen species that preferentially lead to the high activity and selectivity.

The purpose of this example is to demonstrate the following aspects (i) how the nanostate of silver is superior for epoxidation reaction as compared to the bulk silver catalysts, (ii) role of oxygen and the state of oxygen in the active catalyst. The selectivity to styrene oxide was enhanced in oxygen rich atmosphere. Furthermore, by correlating the epoxidation performance with the XPS results it can be stated that there is a direct relationship between the epoxidation performance of the catalyst and oxygen 1s signal associated with surface oxygen species. The oxygen species seem to be critical for the activity of the silver catalysts. (iii) 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 shows how the activity and selectivity of the catalyst can be changed by promotion by cesium. The relevant data are summarized in Table 2.

Table 2 Results of the catalytic activity tests for the silver nanoparticle in the epoxidation of styrene at 573 K [5]

Catalyst[a]	Catalytic activity		
	X(%)[b]	Phe(%)[c]	SO(%)[d]
11%Ag(NW)/α-Al_2O_3	57.6	57.5	42.5
11%Ag(NC)/ α-Al_2O_3	56.9	68.6	31.4
11%Ag(NP)/ α-Al_2O_3	57.5	69.2	30.8

Catalyst designation (a); (MW) Nanowire; NC Nanocubes; NP Nanopolyhedra, [b] conversion X of styrene; [c] selectivity to phenylacetaldehde (Phe%); [d] selectivity to styrene oxide (SC%) O_2:C_8H_8 mole ratio of 50.

Metals on Carbon – Electrode Materials

Pt on carbon by functionalization method

Noble metals (mainly Pt group of 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 the noble metals as well as for their effective utilization. However, the challenges in the effort of dispersing nanometer metallic particles on carbon support 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.

Effect of functionalization of the carbon support by carboxylic, sulfonic acid or by aminopyridine and effect of the capping agent on the dispersion and activity of Pt nanoparticles on the carbon support have been studied. The oxidative treatment of the 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 acid functional groups on the carbon support was confirmed by an 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 the Pt dispersed on nanometer scale on the carbon support as a result of introduction of carboxylic acid functional groups on the carbon support.

Table 3 Crystallite size and electrochemical data for the untreated and nitric acid treated carbon supported Pt for methanol oxidation (for use as electrode in direct methanol fuel cell (DMFC) [EAS: electrochemical active area; ICP: inductively coupled plasma emission method] [6]

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
!0%Pt/1N HNO_3 treated CDX 975-60 min	5.0	21.2	-	24.8	311
!0%Pt/con HNO_3 treated CDX 975-60 min	4.5	6.6	-	9.0	406
!0%Pt/1N HNO_3 treated CDX 975-95 min	4.1	12.9	9.5	10.2	269
!0%Pt/con HNO_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 sulpfonic acid functionalization was attempted using a variety of reagents like 2-aminoethane sulfonic acid, ammonium sulphate and also sodium sulphide and formaldehyde. The grafting of sulphuric acid groups on the carbon support is possible with these three different sulphonating agents employed. The data generated for one of sulphonated systems are given in Table 4. It is generally expected as an example that an azo compound formed with the sulphonating agent in presence of mineral acids reacts with the carbon black support and incorporates the alkyl sulphonic acid group on the carbon support. The Pt loading of these carbon materials was carried out using ethylene glycol reduction method [7].

Aminopyridine modification of the carbon support has shown better dispersion and enhanced activity for methanol electro-oxidation. The data substantiating this aspect are given in Table.5. The presence of amino pyridine on the carbon support is ascertained form IR absorption for C=N vibrations on the modified surface. The specific deductions from 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 agglomeration of Pt particles. (c) These methods not only favoured better dispersion of the Pt nanoparticles but also accounted for increasing the effective electrochemical active area which accounted for the increased electrochemical activity.

Pt on carbon by capping method [6]

Another important strategy in the dispersion of nanometallic components on the carbon supports is the use of 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. Catalysts with the capping action of citrate in aqueous solution o hexachloroplatinic acid and ethylene glycol to the carbon support and heat treating at 393 K for 1h. Independent XPS studies showed the existence of Pt in zero and +2 oxidation states and the system containing maximum Pt in +2 oxidation state exhibited the maximum activity for methanol oxidation. This has provided experimental evidence of the participation of higher oxidation state of Pt in the methanol electro-oxidation. In Table 6 typical data generated using this methodology for the preparation of supported Pt on the carbon systems are assembled.

Table 4 Comparison of Ph Particle size and methanol oxidation activity for unsulphonated and sulphomethyl modified catalysts (for abbreviations see the 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

Perception of metallic nanomaterials as catalysts

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

Table 5 Comparison of the particle size of Pt, AS and methanol oxidation activity for unmodified and amino pyridine modified catalysts [6]

Sample	Crystallite size (nm) (XRD)	Particle size (TEM)	%Pt (ICP)	EAS (m^2/g)	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	119	415

Carbon nanomaterials – Electro-catalytic Applications

Novel carbon materials include carbon fibres, porous carbons and pyrolite graphite. Of these, graphitic carbons have shown promise for usage in energy storage and conversion processes. As synthesized carbon nanotubes (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 the graphitic carbons. The most popular method is the introduction of the as-prepare carbon into an atmosphere of ammonia and hydrogen cyanide at high temperatures. The resulting carbon was found to be enriched with nitrogen and had a significantly higher activity for electro-chemical reduction of oxygen. While it has been of general consensus that nitrogen doping increases the activity of these carbons, there has been an ambiguity as to what physico-chemical factor or factors effect this difference in activity.

Most of the ambiguity stems from poor reproducibility and stability problems with 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 to elucidate individual physico-chemical properties and their contribution to ORR activity. While a systematic increase in the nitrogen doping at the graphitic carbons increases the activity for the 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.

Table 6 Characteristics of the Pt/carbon system generated using citrate as capping agent [6].

Mole ratio of citrate/Pt	% Pt(0)	%P(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

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 the catalysts onto the support. This is done by using aggressive protocols that involve 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 support and active metal catalyst. The ability to manipulate in-situ the structure, composition, surface area and density of edge plane sites on nitrogenated carbon nanotubes (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 micro-emulsion, impregnation, co-precipitation, sono-chemical ad 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 (especially NCNTs) that contribute to oxygen reduction and the advantages in using these properties efficiently and synergistically with active metal catalysts for the ORR have been considered in literature [7]. In addition, heteroatom substituted CNTs have also been proposed as one of the possible for hydrogen storage applications. Extensive literature [7] is available on the various aspects of new carbon materials for catalytic applications.

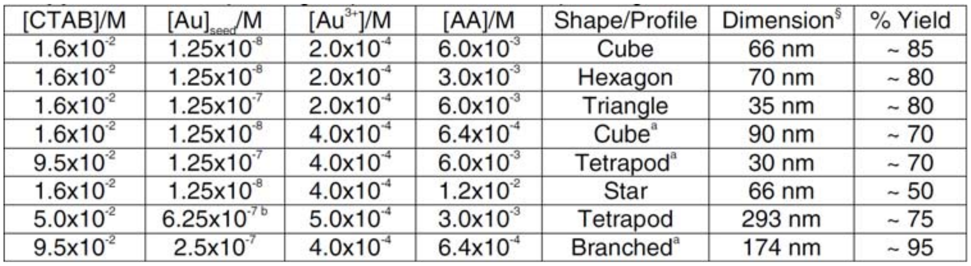
There is yet another aspect of nano metals that has been receiving considerable attention. It is possible to make nano materials with varying shapes and sizes. The shapes can vary from ordered systems like squares and cubes to exotic systems like tripods or other pods and these nano materials have been characterized by the value of the frequency of the plasmon resonance. Though there appears to be no systematic study on this aspect, one can expect sooner some generalizations will emerge in this field. Some typical data collected from literature are given in the following table. The data given in the table are taken from the reference Sau, T. K.; Murphy, C.J. *J. Am. Chem. Soc.* **2004**, 126, 8648-8649.

The essential points that emerge from the results presented in the table below are

- A simple solution based seed-mediated growth method where one could controllably vary the morphology and dimension of the Au nano-crystals by the manipulation of the synthetic parameters has been described.
- Moreover, various shapes of gold nano-particles can be produced in aqueous solution at room temperature and by utilizing surfactant (CTAB) and the methodology can be suitably altered with and without addition of seed solution.
- The shape, size and chemical nature of the nano-particles produced can have considerable influence on the plasmon resonance observed for the various nano-particles synthesized.
- In the case of systems where in more than one plasmon resonance absorption is possible, it may be necessary and desirable to consider the predominant resonance absorption for some correlation between

the size and shape of nano-particles and value of the plasmon resonance frequency.

Table 1. Shapes of gold particles and corresponding reaction conditions.



[CTAB]/M	$[Au]_{seed}$/M	$[Au^{3+}]$/M	[AA]/M	Shape/Profile	Dimension§	% Yield
$1.6x10^{-2}$	$1.25x10^{-8}$	$2.0x10^{-4}$	$6.0x10^{-3}$	Cube	66 nm	~ 85
$1.6x10^{-2}$	$1.25x10^{-8}$	$2.0x10^{-4}$	$3.0x10^{-3}$	Hexagon	70 nm	~ 80
$1.6x10^{-2}$	$1.25x10^{-7}$	$2.0x10^{-4}$	$6.0x10^{-3}$	Triangle	35 nm	~ 80
$1.6x10^{-2}$	$1.25x10^{-8}$	$4.0x10^{-4}$	$6.4x10^{-4}$	Cube[a]	90 nm	~ 70
$9.5x10^{-2}$	$1.25x10^{-7}$	$4.0x10^{-4}$	$6.0x10^{-3}$	Tetrapod[a]	30 nm	~ 70
$1.6x10^{-2}$	$1.25x10^{-8}$	$4.0x10^{-4}$	$1.2x10^{-2}$	Star	66 nm	~ 50
$5.0x10^{-2}$	$6.25x10^{-7}$ [b]	$5.0x10^{-4}$	$3.0x10^{-3}$	Tetrapod	293 nm	~ 75
$9.5x10^{-2}$	$2.5x10^{-7}$	$4.0x10^{-4}$	$6.4x10^{-4}$	Branched[a]	174 nm	~ 95

§ For triangular profile and cubes, this corresponds to edge lengths; for hexagonal profile, this corresponds to the distance between opposite sides; and for tetrapods and branched particles, this corresponds to center-to-tip distances. For cubes, triangles and hexagons, the dimensions are averaged over ~120 particles and are reproducible to within 5% of the given value; for the other shapes, the dimensions are averaged over ~120 particles and are within ~10% of the given value.
a. $6.0x10^{-5}$ M $AgNO_3$ was used.
b. Seed (Citrate) was used here, otherwise results are reported for seed(CTAB).

Metal oxide Nano-materials as Catalysts

Oxide and sulphide nanomaterials have been exploited as catalysts for a variety of catalytic applications. There are various kinds of oxide nano-materials with different shapes and architectures have been reported in literature. Even thought these systems can find a variety of applications, the catalytic role of these materials alone is considered in this write up. Here to we are restricting to only one system for the same of the limitation of the space.

One of the exotic reactions carried out is the conversion of carbon dioxide to methyl alcohol. The relevant data are given in Table 7. It is seen that the nanocrystalline nickel oxide and zinc oxide are better catalysts for this reaction as compared to the conventional materials.

It can be realized from the data given in Table 7 that the nano-state is better than the bulk state.

Table 7 Methanol production from carbon dioxide using metal oxides as catalysts (Comparison of the activity of microcrystalline and Nan crystalline oxide materials [8]

Catalyst	Crystallite size (nm)	Surface area (m^2/g)	Conversion of CO_2 to methanol (%)
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 8 the values of ‘d’ spacing and also crystallite of CdS prepared using various zeolites are given. Another development worth noting is the prediction of activity on the basis of theoretical calculations. Norskov and his coworkers carried out density functional calculations on a variety of catalytic systems. These studies provide a molecular level discussion of the nature of active sites in metal catalysis. The relevance of the fundamental concepts such as Bronsted-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 evolved a concept of degree of structure sensitivity which can be employed for analyzing the structure sensitivity of catalytic reactions. These and similar studies may have relevance for examining the activity of nanoparticles.

Perception:

The possibility of viewing the active sites on the 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 the most efficient manner under milder operating conditions than those demanded by the heterogeneous catalysts and are yielding the most selective product. 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 the biological systems can be replicated in the catalytic systems. This possibility opens up another avenue where the catalyst transformations will be controlled by 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 the frontier wave functions of the nanoscale materials with the normally obtainable 'constraints' on the fragments of bio-molecules which are responsible for the selectivity.

Table 8 'd' spacing and crystallite size of CdS materials prepared using various templates

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 (B)	1.52	1.78	2.93	8.6
CdS(Z)	1.52	1.79	2.97	7.2

Bio-molecules 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 of nano-state of materials and its adoption to catalysis can be expected to turn around a revolution in this field.

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