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Growing small metal particle as redox catalyst

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It is now well established that the redox property of small metal particles differs from their bulk value and depends on the size of the particle. This size dependent-redox property has a strong influence on the chemical reactivity of the metal. Our experiment shows that the catalytic property of commonly-used transition metals such as Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au and Hg is also influenced by this size-dependent redox property. We have studied the redox catalytic property of growing small particles which are formed as transient intermediates during the reduction of the corresponding metal salts in water. The growing small particles act as electron relay systems between the oxidant and reductant and thus catalyse the redox reactions which are kinetically inert. In many cases the corresponding larger and stable metal sols behave either as a weaker catalyst or catalytic activity becomes redundant. Catalytic activity of small particles originates from their lower reduction potential compared to the bulk value.

THERE is considerable interest in ultradivided particles as a distinct state of matter, with particular attention being paid to their structure and reactivity[1]. For ultra-small nuclearities, their unique properties originate in the size-dependent distribution of electron energy levels and in quantum size effects. The study of these quantum size effects is a challenge for chemists, physicists and material scientists. The aim of such investigation is to develop advanced nanostructured material for catalysts production, photographic suspensions, supermagnets, various ultramodern molecular devices, etc. Physical and chemical properties of nanoscale metal particles (< 6 nm) differ from the bulk metal due to size effect[2–5]. As the number of atoms in a cluster decrease, the quasi-continuous energy levels become more and more discrete and ultimately the energy levels of very small clusters begin to resemble molecular orbitals. Consequences are the size-dependent optical and redox properties of oligomeric metal clusters.

Experimental verification of this size effect was initially investigated in the laboratory of Belloni[6]. The observation was that the redox potential of M^{+x}/M^0 couple became much more negative compared to the corresponding M^{+x}/M_{metal} couple. Latter experiments indicate that oligomeric metal clusters have redox potentials in between the M^{+x}/M^0 and M^{+x}/M_{metal} systems[2–5]. Henglein et al.[2,3,7] observed that the adsorption of nucleophiles (e.g. PH_3, I^-, S^{-2}, PhS^-, etc.) onto the surface of a metal nanoparticle significantly increases its Fermi potential and thus lowers its reduction potential. This is similar to the ligand effect on the redox potential of M^{+x}/M_{metal} system. The ligands which form complexes with metal ions, can decrease the reduction potential of M^{+x}/M_{metal} system[8]. A similar effect is also observed recently for M^{+x}/M^0 system[9]. Shift of reduction potential of metal nanoparticles by the adsorbed foreign ions was proved to be due to the donation of their electron density to the particle.

The metal clusters are formed as transient intermediates during the formation of metal colloid by the reduction of metal ions in solution. At the initial stage of colloid formation, the metal atoms are produced, which subsequently agglomerate. The agglomeration steps can be written according to the following general equation:

$$M_{n-1} + M^{+x} + xe = M_n,$$
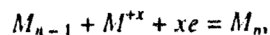
where n is the agglomeration number. The redox potential of a cluster depends on the value of n. With the increase in n, the cluster potential approaches the

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conventional electrode potential value, starting from the potential of the free metal atom which is much lower in value. Henglein et al.[2,10] considered these agglomerating particles as growing microelectrodes (GMEs). These GMEs can take part in reactions where electrons are transferred across the particle solution interface, similar to electrode reactions in electrochemistry.

We are working on the size-dependent reactivity and catalytic property of metal nanoparticles in various organized media[11–14]. These small particles are highly reactive and undergo agglomeration which limits their wider application in the field of catalysis. However, they can be stabilized in suitable solid matrix[15–19] (e.g. zeolites, silica, charcoal, alumina, etc.) or in solution by suitable organized assemblies[12,14,20,21] (e.g. micelle, polymers[11,22–24], ligands[25], etc.) for their subsequent use in heterogeneous catalysis. Catalytic property of small particles differs widely depending upon the particle size which is commonly known as size effect in catalysis[26–29]. As the size of the metal particle decreases, overall surface area of the catalyst increases which increases the active sites of the catalyst surface and in fact active sites obey scaling law[30] with respect to particle size. Again the electronic property of the catalyst particle also plays a significant role in catalysis[31–34]. As the metal particle has a size-dependent redox property, the electronic interaction between the metal particle and the substrate, in other words the role of metal particle as electron transfer catalyst, is expected to vary with the size of the particle. Thus it is worthwhile to study the catalytic property of small metal particles starting from atomic one to the corresponding metal sol where most properties reach the bulk value. This will improve our present understanding of the origin of catalytic property, catalyst selectivity, size effect in catalysis and many other important aspects of heterogeneous catalysis. The subject of the present communication is the redox catalytic property of growing small particles of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au and Hg.

To test the size-dependent catalytic property of metals, we consider the reduction of several organic dyes by $NaBH_4/N_2H_4$/ascorbic acid in the presence of a metal salt. The reducing agent can reduce both the dye and the metal ion. However, the dye reduction is not a kinetically favoured one and hence needs a catalyst. In presence of a reducing agent, metal ions are reduced to the metal atoms which subsequently agglomerate to small particles and finally to the corresponding metal sol. The final stable product of GME, i.e. metal sol is termed as FGME. Dye reduction becomes possible if the GME/FGME act as catalyst.

The dyes used as redox probes were methylene blue (MB), phenosafranin (PS), fluorescein (F), 2,7-dichlorofluorescein (DCF), eosin (E) and rose bengal (RB). Spectroscopic and redox properties of these dyes have already been reported[35]. Their $E_{1/2}$ values in ace-

tonitrile are −0.495 V, −0.44 V, −0.50 V, −0.32 V, −0.75 V and −0.70 V respectively. Metal GMEs and FGMEs were prepared by the reduction of metal salts ($CuSO_4$, $AgNO_3$, $HAuCl_4$, $HgCl_2$, $NiSO_4$, $PdCl_2$, H_2PtCl_6, $CoCl_2$, $RuCl_3$, $RhCl_3$, $FeCl_3$) solutions using $NaBH_4/N_2H_4$/ascorbic acid in the presence and absence of surfactant stabilizer. Surfactants used were cetyl-trimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and poly(oxyethylene)isooctylphenyl ether (TX-100). Metal salt solution was mixed with surfactant solution and taken in the spectrophotometer cell. Nitrogen gas was purged through the solution in the cell for 2–3 min to remove the dissolved oxygen. After that a solution of one of the reducing agents was added. For the study of GME-catalysed dye reduction, dye solution was added in aqueous surfactant solution before/after the addition of metal salt solution. Dye concentration was varied from 10^{-5} to 10^{-2} mol dm^{-3}. The stable hydrosol which was produced after the complete reduction of metal ion is considered as the FGME. So, for the study of FGME-catalysed dye reduction, the dye was added after the complete reduction of metal salt. For the catalytic reduction of dye, the reducing agent used was 10–200 fold in excess.

If the dye solution is mixed with reducing agent solution, the colour of the dye remains unaltered for 1–2 h, indicating that the dye reduction if it occurs at all, is insignificant. Presence of surfactant also does not favour the dye reduction except in the case of methylene blue[36]. However, dye reduction occurs very fast in presence of metal salt or metal sol. This signifies that under the experimental condition the metal GME (which is produced from the metal salt by the action of reducing agent) or FGME plays the role of a catalyst. The progress of the catalytic dye reduction can be followed easily by the decrease in absorbance value at the dye spectral band maxima (λ_{max}) with time (Figure 1). The absorption band maxima for all the dyes decreases gradually without showing any change in their shape and position. A very low concentration of metal salt, which is one-tenth to one-fifth of the dye concentration, has been used to see the catalytic activity. When metal ions form particles, the particle concentration becomes very small compared to precursor ions. The plasmon band of the metal sols in the visible region (for Au, Ag) becomes invisible at such low concentration.

The importance of surfactant is three-fold. Firstly, surfactant controls the growth of GME[12]. Secondly, it repairs/prevents catalytic activity of GME/FGME from surface deactivation. Thirdly, specific dye–micelle interaction[37,38] leads to a selective catalytic reduction by GME/FGME. The important observations obtained from our experiments are summarized as follows: i) Most of the metal GME/FGME acts as catalyst (Table 1). ii) Catalysis starts after an induction period (Figure 2). iii) The rate of catalytic reduction is faster for GME compared to FGME in many cases (Table 1).
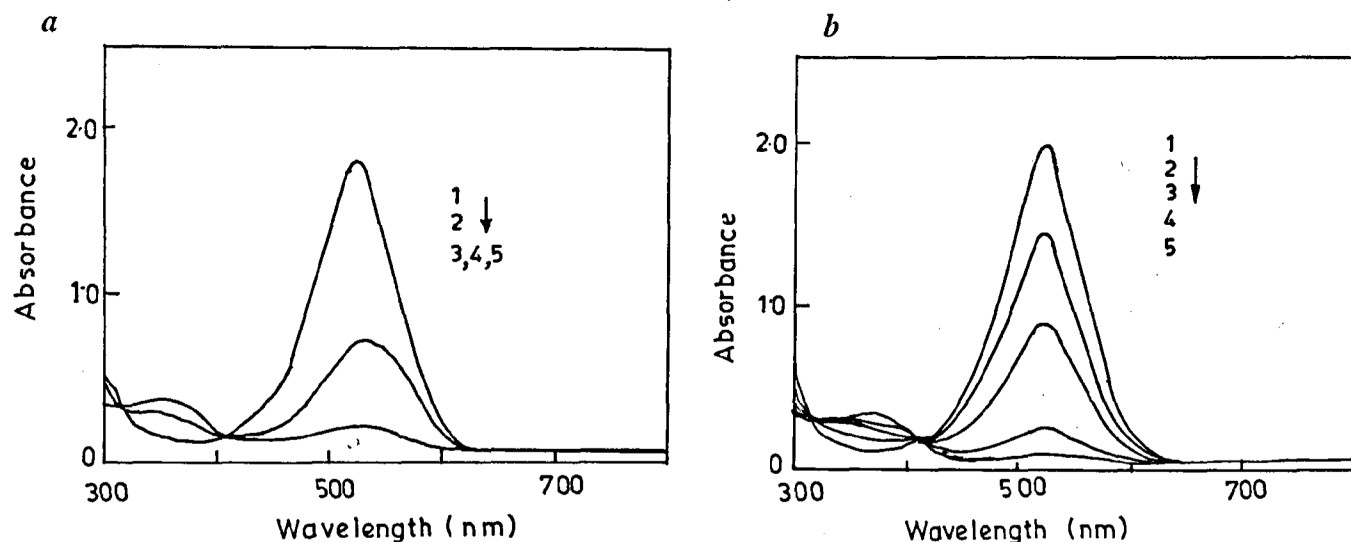
Figure 1. Successive UV-visible spectra of phenosafranin (PS) during its catalytic reduction by Cu-GME (a) and Cu-FGME (b) in aqueous CTAB. Successive spectra are taken at one-minute interval. Conditions: $[CuSO_4] = 10^{-5}$ mol dm^{-3}, $[CTAB] = 0.01$ mol dm^{-3}, $[NaBH_4] = 5 \times 10^{-3}$ mol dm^{-3}, $[PS] = 10^{-4}$ mol dm^{-3}.

Table 1. Catalytic property of metal GME/FGME

Reducing agent	Metal that forms GME/FGME from precursor metal salt	Catalytic property of GME/FGME	Metal–dye system where catalytic rate of GME > FGME*
$NaBH_4$	Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au, Hg	All GME/FGME acts as catalyst	Cu (all dyes), Ag (F, DCF, E, RB), Au (F, E), Pd (F, DCF, E), Ni (E)
N_2H_4	Ru, Pd, Ag, Pt, Au, Hg	Only GME/PGME of Ru, Pd and Pt acts as catalyst	–
Ascorbic acid	Cu, Ag, Au, Pd	No catalysis	–

*For all other cases FGME performance is either greater or comparable to GME.

In most cases of GME/FGME catalysed reductions, the dye reduction stops after some progress or the rate decreases to a considerable extent, when no surfactant is used. This fact is more prominent in GME catalysis compared to FGME. The rate of catalytic reduction increases with the increase in the concentration of the metal ion/metal sol, reducing agent and dye. When dye and surfactant are oppositely charged, then rate decreases with the increasing surfactant concentration, but when dye and surfactant are of the same charge then increase in surfactant concentration generally increases the rate. When all other factors remain the same, the catalytic rate is either greater/comparable/lower for GME in comparison to FGME. However, use of surfactant can alter the trend in some cases.

To explain the catalysis, we propose that GME/FGME acts as an electron relay system between an electron donor and acceptor and the electron transfer occurs via GME/FGME after the subsequent adsorption of sub-

strates onto the GME/FGME surface (Figure 3). The size-dependent redox property of GME/FGME strongly depends on the foreign ions/molecules adsorbed onto their surface and this governs the chemistry and redox catalytic property of the stabilized metal particles[4,39-41]. It is well known that the adsorption of BH_4^- ion onto a metal particle leads to a large cathodic shift of FGME/GME potentials due to the high electron injection capacity of BH_4^- ion[12,42]. Accordingly a resultant potential is attained. However, this resultant potential of the BH_4^- adsorbed GME system, unlike that for FGME, will gradually increase with increasing size of the particle, because the inherent GME potential itself gradually increases with increasing nuclearity (size). The resultant potential will obviously be anodic to the reductant (BH_4^- ion) and cathodic to the oxidant (dye) and thus an electron transfer via GME/FGME to the dye is possible. N_2H_4 and ascorbic acid being less strong nucleophilic reducing agents could, in principle, reduce the dyes only
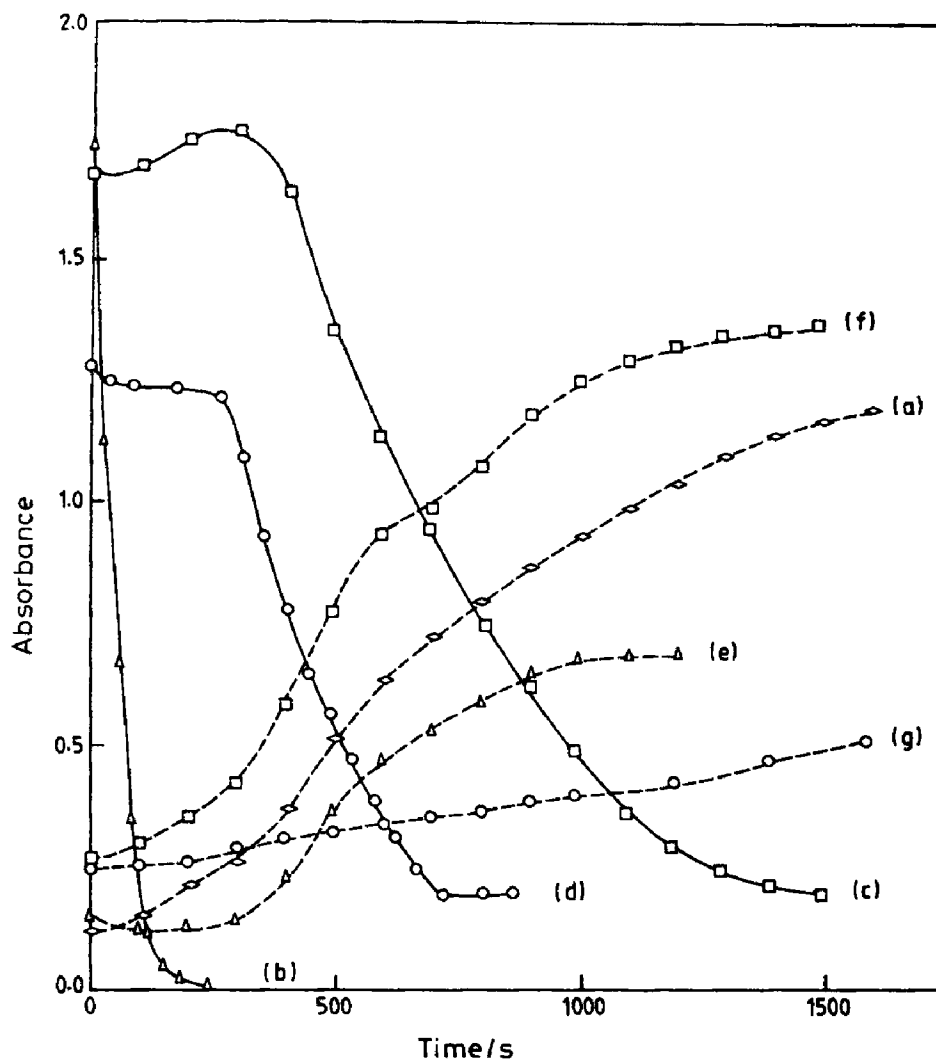
Figure 2. Time evolution of plasmon absorbance of Ag at 410 nm during the formation of Ag-GME in the absence (a) and presence of MB (e), F (f) and PS (g). Curves b, c and d are the change of absorbance of MB, F and PS at their respective spectral band maxima (668 nm, 390 nm and 530 nm) respectively. Here [Ag⁺] is higher so that plasmon band is observable. This figure shows that when all other conditions remain the same, catalysis starts after different induction periods for different dyes. Conditions: $[AgNO_3] = 10^{-4}$ mol dm^{-3} $[CTAB] = 0.01$ mol dm^{-3}, $[NaBH_4] = 5 \times 10^{-3}$ mol dm^{-3}, $[MB] = [F] = [PS] = 5 \times 10^{-5}$ mol dm^{-3}.

Reductant (NaBH₄, N₂H₄, ascorbic acid)

$M^{n+} + xe \longrightarrow M$

$M + M \longrightarrow M_2$

$M_2 + M \longrightarrow M_3$

$M_3 + M \longrightarrow M_4$

$M_{n-1} + M \longrightarrow M_n$

Oxidant (MB, PS, F, DCF, E, RB)

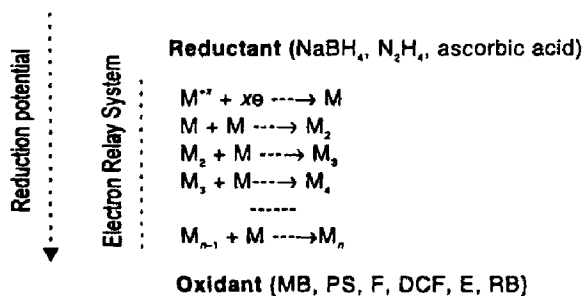Reduction potential ▼   Electron Relay System

Figure 3. Diagram showing the mechanism of GME/FGME as electron relay catalyst.

by their adsorption on the particle at their early stages of formation. At a later stage, the electron injection capacity of these lesser nucleophilic reagents is insufficient to

make the particle potential less negative than the potential of the dye to be reduced. This explains why most of the GME/FGME cannot act as catalyst in the presence of N_2H_4 or ascorbic acid.

The GME catalysed reaction is often associated with an induction period and the induction period depends on the nature of the dye when all other factors remain unaltered. This indicates that a minimum size of GME is needed to initiate the catalysis and the catalysis starts at different stages of growth of GME for different dyes (Figure 2). In many cases GME is found to be a superior catalyst to FGME (see Table 1 and Figure 1). This behaviour of GME may be attributed to the following two properties: firstly, the continuous renewable surface and secondly, its very negative electrochemical potential

which arises owing to the very small size. As usual the rate of catalytic reduction should be determined by the difference in resultant potential (of the BH_4^- adsorbed-GME) and the potential of the oxidant system[43]. The smaller the size of the GME, the more is the potential difference leading to a higher rate of reduction. Strong interaction and adsorption of dyes at the GME surface poison the catalytic sites, and hinder the growth of the particles in the embryo stage before attaining the required minimum size. The question of poisoning in the embryo stage does not arise for FGME, which explains the better performance for FGME over GME in some cases. This also explains why the GME catalysed dye reduction stops after some time in most cases, particularly in the absence of any surfactant. In presence of surfactant, the dye can be adsorbed on the micellar surface[37,38], which restricts its adsorption on the catalyst surface at the embryo stage.

Thus GME emerges as a new generation catalyst with its distinct advantages. The redox property, life time and surface nature of GME changes continuously as all these properties depend on the size of GME. Thus the particle size determines the catalytic property, catalytic rate and catalyst selectivity. However, the nature of stabilizer and the reducing agents too influence the catalytic property of GME. Judicious selection of a surfactant may result in its enhanced or suppressed catalytic efficiency.

A precise explanation of this catalytic effect is a difficult undertaking. It necessitates more experimental as well as theoretical studies. The origin of size effect in heterogeneous catalysis, importance of electronic factor in catalysis, evolution of bulk properties of metals, etc. can be understood by studying the mechanism of GME/FGME-catalysed reaction. Once the property of GME of different metals is understood, it can be used widely in organic synthesis.

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