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REVIEW

Laser chemical synthesis of clusters and ultrafine particles using organometallics

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Gas-phase synthesis of clusters and ultrafine particles using lasers and organometallics is reviewed. The general field of laser chemistry is introduced in the context of using organometallics as reactants. Examples of particle and cluster synthesis in flowing gases and in bulk gases, and during laser chemical vapor deposition, are given. A brief introduction to the general field of random irreversible fractal coagulation provides a basis for describing how powders, clusters and ultrafine particles are synthesized. References to applications and characterization methods are given.

Keywords: Clusters, particles, lasers, organometallic, vapor deposition, coagulation, fractal

INTRODUCTION

The most recent growth of fundamental interest in clusters began after Kubo[1] and Gor'kov and Eliashberg[2] made specific predictions concerning the electrical and optical properties of pieces of matter which are small enough to experience size quantization effects on their electronic structure but large enough to preclude having only highly localized internal electronic states. Beyond the fundamental interest, predictions[3–5] of enhanced nonlinear optical properties of metal, semiconductor, and composite cluster structures abound. Metal structures on the 10^2 nm scale are thought to be the site of surface plasmons capable of enhancing the operation of tunnel junction diodes (for one example, see Ref. 6). The catalytic properties[7] of high-surface-area materials whose size spans the cluster to ultrafine-particle range are well known. In fact, most of the large-scale laser syntheses utilizing organometallic starting materials involve production of preceramic sinterable powders for potential application[8] in catalysis and structural materials. Thus there are already many applications for cluster and ultrafine particles as either thin films or bulk powders. Issues such as composition, purity, and polydispersity in size and shape distribution are more or less important, depending on the specific application. For purposes of this Review, the word 'cluster' will refer to objects containing approximately 10^3 atoms or less, while 'particle' will span the range of larger objects. The two words will often be used interchangeably, although the reader should be aware that chemical and physical properties may vary across the entire size ranges of clusters and particles.

As an agent of chemical and physical change and as a means for transferring energy, lasers have temporal, spectral and spatial qualities which lead to unique chemistry, i.e. 'laser chemistry'.[9–12] The rich photochemistry of organometallics,[13] in either the multiphoton or single-photon regimes, makes the use of lasers and organometallics a particularly synergistic approach to generating monomers for cluster synthesis. The synergism results from the fact that a single laser can be used to efficiently produce *and heat* coordinatively unsaturated species. The capacity of lasers to selectively heat or electronically excite specific members of a multicomponent mixture at rates far exceeding the prevailing mass[14] and intermolecular energy transfer rates[15] leads to extreme excursions from thermodynamic equilibrium. These extreme excursions make metastable thermodynamic aggregate states accessible. The aggregation process can be discussed on the basis of gas-to-particle conversion[16] as modeled by the Smoluchowski equation of irreversible coagulation. Although there has been some focus on particle production in its own right, laser-induced clustering is also mentioned in the context of laser chemical vapor deposition (LCVD); see for example Ref. 17. In either case, there is considerable evidence that the nature of the species which are present, their number densities, their internal energy content, and the description of this internal energy content in terms of the quantum state of the species deter-

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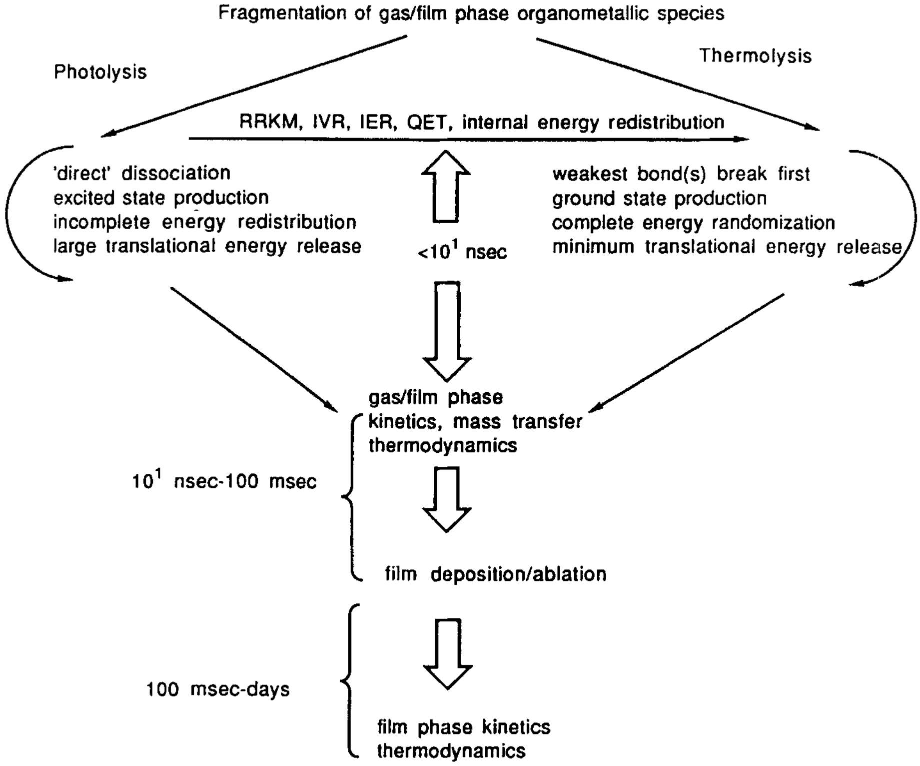

Figure 1 Organometallic laser chemistry flowchart

mine the course of the gas-to-particle conversion process.

This Review will be organized as follows. First, laser chemistry will be introduced in the context of producing specific reactants to initiate the gas-to-particle conversion process. The literature of laser-induced particle formation is then reviewed in the context of this section. A following section will discuss the cluster and particle formation process in terms of random irreversible aggregation, i.e. the Smoluchowski equation. Given the importance of the homogeneity of the rate constants used in the Smoluchowski equation, the identity and quantities of the species formed by the initiation step take on an enhanced importance. In both these sections, mention will be made of the analytical techniques used to characterize the particle properties as well as the conceptual approaches used to extrapolate the properties of a given distribution of particles/clusters to the properties of a macroscopic structure, i.e. a film, composed of those particles/clusters. The purpose of this Review will be primarily to bring the fragmented literature of laser-induced cluster and particle formation starting from organometallic precursors into a heuristic and comprehensive focus.

LASER CHEMISTRY

Figure 1 summarizes the concept of laser chemistry with respect to cluster and powder synthesis. The net process can be crudely broken down into three stages. The first stage of the net process is initiated by irradiating a gas-phase mixture of an organometallic, a buffer gas and potentially other reactants. The laser may provide excitation directly to the organometallic, the buffer gas or other reactants, or to bulk phases which are in contact with the gas-phase mixture. Directly or indirectly, by virtue of this excitation, the organometallics are dissociated and possibly ionized to form products which then participate in bimolecular chemistry.

Rice, Ramsperger, Kassel, Marcus (RRKM) theory deals with the general case of a molecule being energized and dissociating via a unimolecular pathway. In this theory, energy is presumed to circulate rapidly throughout the internal degrees of freedom of the molecule via processes such as internal energy redistribution (IER) or intramolecular vibrational relaxation (IVR), depending on whether the energy involves electronic degrees of freedom or occurs on a single Born–Oppenheimer electronic surface. A version of the basic RRKM idea specifically designed to model fragmentation due to electron-impact processes is quasiequilibrium theory (QET). All of these theories predict that the dominant dissociation process will involve breakage of the weakest bond(s) first and production of fragments with a minimum of translational energy.

Translational energy release is important because it determines the kinematics for subsequent collisions. When free metal atoms are being produced, as in UV–visible multiphopton dissociation of organometallics, these theories are consistent with the observation that ground-state metal atom production is often observed. We mention these theoretical treatments, but it must be remembered that the possibility of exceptions exists. This would involve so-called 'direct dissociations' that would have the characteristics suggested by the flowchart in Fig. 1. One possible example of such a dissociation will be given later. Quantum-dynamical descriptions of unimolecular dissociation and generic internal energy redistribution have predictive utility in determining the reactants for subsequent stages of particle formation.

The bimolecular chemistry leading to particle formation, the second stage in our picture of the net process, can occur either in the same phase in which the organometallic originates, or in some other phase which is initially in contact with that phase, or in a phase which is formed during the course of the particle formation process. Since particle formation is often mentioned in the course of film deposition, the term 'film phase' is used in Fig. 1 to designate the entire range of possibilities. In this stage, kinetics, thermodynamics, and mass/energy transfer best summarize the processes/considerations which determine the course of particle formation. This is a significant distinction because to a large extent the process of fragmentation which creates the reactants is mediated more by quantum dynamics and less by kinetics. While the laser is still being applied to the reaction mixture, the possibility exists that particles at various stages of assembly, as well as films which are partially deposited, can be ablated, thereby producing new reactants for subsequent bimolecular events. This possibility is also indicated in the flowchart.

Of course, any net process must always be *consistent* with thermodynamics, but because of the widely varying timescales of the different processes comprising particle formation, and the existence of metastable thermodynamic states, thermodynamics may not be in itself of predictive value. As we shall see, when the effective temperature of the reaction mixture is high enough and the timescale for reaction(s) is long enough so that a variety of possible products are accessible, thermodynamics can be quite predictive. For example, in the extreme case where all bonds can be broken, reformed and rebroken, etc., thermodynamics predict that the *strongest* bonds will be those that exist when the process is terminated. This is what actually obtains in synthesis of preceramic powders.

To account for the fact that long after particle synthesis has concluded, a variety of chemical and physical processing may be required to meet application design criteria, a third stage was appended to the flowchart in Fig. 1. Pressing, firing and sintering would be examples of post-synthesis processing. Other examples would include post-deposition annealing in air or oxygen to remove carbonaceous impurities from LCVD metal films. Annealing in vacuum to take advantage of known surface and solid-phase reactions is also a viable strategy for accomplishing some synthetic goals.

Examples of indirect processes whereby the organometallic may be dissociated are numerous. If the laser irradiates a surface which is in contact with a gas or adsorbed phase (for a recent overview see Ref. 18), then photoelectrons or even simple induced surface charges or heating can cause dissociation of the organometallic. If there are electrically biased surfaces which can accelerate charges present in a gaseous mixture, then much more organometallic dissociation can be induced by the Townsend discharge[19–21] following a laser pulse than by the laser pulse itself. The properties of the laser give desirable temporal qualities to the discharge, but the energy which is being supplied to the reaction mixture is mostly being extracted from the field. Perhaps the most widely used method of indirect excitation involves the use of an infrared laser to excite one member of a reaction mixture, i.e. a sensitizer, which then transfers the energy to the main reactant to initiate aggregation.

The predictive value of RRKM and other statistical theories of unimolecular dissociation[22-24] chemistry is easily summarized. Energy disposal in that regime[25, 26] is determined by the size of the molecule(s), by the presence of low-frequency vibrations which increase the density of vibrational states and thereby the intramolecular energy redistribution rates, and finally by the presence of structures and symmetries which induce strong intramolecular couplings, e.g. Coriolis coupling. As a general qualitative rule, the greater the density of states having energy over the lowest dissociation threshold, the faster energy is redistributed and the more often the weakest bond(s) break first.

Good reviews of laser chemistry exist[9-12] and a brief patent search reveals reactor designs and other inventions[27-32] for utilizing laser chemistry. Some particular advantages are evident in the context of organometallics. Table 1 shows the temperature to which some bulk metals[33] must be heated to produce 1 Torr of metal vapor. Also shown are the temperatures needed to attain the same vapor pressure of some easily obtained organometallics.[34] Because lasers can be used to strip ligands efficiently off organometallics,[35, 36] the vapor pressure of the organometallic is the upper limit on the pressure of metal atoms which can be produced within the duration of a single standard (approx. 10 ns) laser pulse. This advantage is most acute for refractory metals and represents one of the most interesting advantages of using laser chemistry on organometallics.

Table 1 Organometallics vs bulk metals as a source of gas-phase metal atoms

Species	Temperature for 1 Torr of vapor pressure (°C)
Pt atoms from bulk metal	2730[a]
Cr atoms from bulk metal	1616[a]
Mo atoms from bulk metal	3102[a]
W atoms from bulk metal	3990[a]
$Cr(CO)_6$	44.36[b]
$Mo(CO)_6$	50.04[b]
$W(CO)_6$	49.06[c]
Benzene $Cr(CO)_3$	141.2[c]
Mesitylene $W(CO)_3$	534.1[c]
$(C_5H_5)(C_3H_3)Pt$	35.2[c]

[a] Clausius–Clapeyron calculation: ΔH and vapor pressures obtained from Ref. 33.

[b] Clausius–Clapeyron calculation: ΔH and vapor pressures obtained from Ref. 84.

[c] Clausius–Clapeyron calculation: ΔH and vapor pressures obtained experimentally.

It is probable that in most cases lamps will not be as effective as lasers for completely stripping off *all* the ligands on a particular molecule before bimolecular processes begin to become manifest. The use of lasers and organometallics allows production of much larger number densities than when lasers are used to vaporize pure metal and alloy rods to produce gas-phase reactants. Scaling up the lasers[10] and the area which is irradiated may actually balance the advantages of these two methods since the metal rods are a source of pure metals as opposed to the organometallics which introduce ligands. Analyses which consider the cost of photons suggest that the final products must have considerable value added, compared with the starting materials, for the overall process to be economically justified.

It is conceivable that in some cases the advantages of one-photon excitation can be combined with the ability to irradiate large volumes using lamps which would allow production of macroscopic amounts of materials. Sonochemical methods[37] also allow large amounts of metal-atom reactants to be produced, and in kinetically useful contexts, but only thermalized reaction pathways are amenable and so no state selectivity is possible. With respect to film deposition and particle formation, the relationship between the timescales of laser excitation, unimolecular dissociation and the prevailing mass-transfer conditions has been explored and reviewed[14] in a number of regimes. Overall, the fact that laser chemistry allows the possibility for extremely high-temperature processing, without the need for the reaction mixture to contact the reaction chamber walls, suggests that the purity of the products can be controlled by the purity of the starting materials. This represents one of the most promising aspects of laser chemistry.

Infrared and ultraviolet lasers provide very different types of excitation. Infrared lasers, while providing excellent selectivity in excitation almost always induce RRKM-like processes. Thus one or more members of a reaction mixture can be selectively *heated* using infrared lasers of the correct wavelength, however, thermalized dissociation products will be formed. The reactants thus formed will be translationally cold, vibrationally warm or even hot, and when metal atoms are formed, the ground electronic state is often formed exclusively. In contrast, it seems likely that ultraviolet and visible lasers can induce either RRKM-like processes or direct nonstatistical processes. Usually both types of processes can be observed to occur in competition with each other. General aspects of multiphoton dissociation of organometallics have been reviewed by Gedarken *et al.*[35] and state selectivity is discussed by Chaiken and co-workers,[34, 38–40] among others. Issues relating to the production of ground-state neutral metal atoms and specific excited states, including Rydberg states,[41] have been discussed.

Based on the data in Table 1 and estimates[35] of the internal energies of the metal atoms and other fragments produced, the laser effectively introduces into the reaction mixture a component having an internal temperature in the 10^2–10^3 K range. Having both the ability to produce metals atoms state-selectively without tight focusing[42] and the capacity to irradiate reasonably high pressures of organometallics allows lasers to induce chemistry involving macroscopic amounts of organometallic reactants. Irradiation volumes exceeding 10^1–10^2 cm^3 are easily attained with commercially available lasers. This is important for many materials-synthesis applications, although, if species are formed which catalyze a process with sufficient efficiency, considerable use can probably be made of small quantities of laser-synthesized catalysts. That is, catalysts are a classic case of extremely high-value-added materials which could justify the cost of the laser photons.

Lasers can be used to induce one-photon absorption or multiphoton absorption. Absorption of a single visible–ultraviolet photon often provides enough energy to labilize at least one ligand from a single organometallic molecule. Absorption of one photon of infrared light can be used to heat one component of a mixture selectively. Although some photoelectrons can certainly be generated, intense infrared lasers *tend* to induce multiphoton processes which produce radicals and other neutral fragments. However, when enough intensities are employed, multiphoton processes most often induced by visible- and ultraviolet-wavelength lasers produce copious quantities of ions and photoelectrons in addition to neutral fragments. With UV–visible excitation, the threshold for inducing multiphoton processes ranges from approx. 10^8 to approx. 10^{12} W m^{-2}. The threshold for multiphoton excitation tends to be higher for infrared excitation although in either case, if the initial photon can be absorbed resonantly, then the overall multiphoton process can have a much lower threshold.

A particular multiphoton or single-photon process involving a *bulk* gas usually has a weak dependence on laser wavelength on a scale of approximately ±10 nm. Whether infrared or UV–visible photons are used, the situation can be much more complicated near any strong resonance. Entirely different products can be obtained at different UV–visible wavelengths whereas, with IR lasers, because the energy tends to be continuously randomized, the product distribution tends to be much more independent of wavelength. In the case of UV–visible excitation, because multiphoton processes tend to produce small-molecule or atomic products which have sparse spectra, there will usually be some strong resonances near allowed one-photon transitions of the atoms which are being generated. Using these wavelengths, it is possible to produce metal ions and atoms state-selectively, although the limits of the quantities which can be produced will vary from element to element.

Much more is known about the fate of the metal atoms involved in multiphoton processes than is known about the ligands. In the case of UV–visible excitation, a conceptual framework exists for correlating the structure of a specific organometallic with the products produced by multiphoton dissociation. All of these processes can be implemented on a timescale much faster than prevailing mass-transfer timescales, so it is possible to produce high local pressures of very-high-temperature reactants which are otherwise extremely refractory. The more refractory the element, the more likely it is that laser chemistry will have advantages over other synthetic methods.

One of the most important potential advantages of one-photon or multiphoton laser chemistry involving organometallics and UV–visible excitation involves the potential for the selective labilization of ligands by electronically selective excitation. If a photon of sufficient energy to break one of a few different metal-ligand bands always causes selective dissociation of the more tightly bound ligand, then the process is non-RRKM. Figure 2[43, 44] shows how either UV or visible excitation can labilize either a carbonyl- or a nitrogen-bearing ligand from the Group VI metal center. The example shown may meet this criterion.

Other examples[45] are known which involve the breaking of either a metal–metal bond or a metal–carbonyl bond. As bond energies become better known it will become easier to determine whether RRKM behavior always occurs under

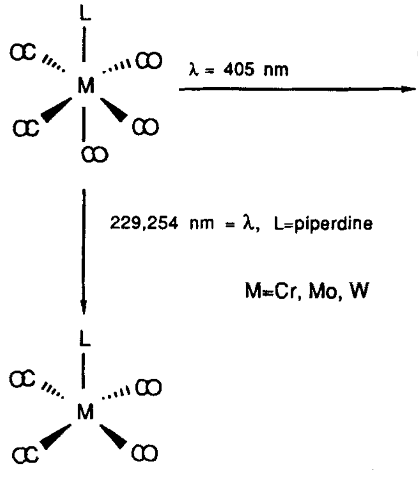

Figure 2 Wavelength selective scheme which may be non-RRKM

single-photon excitation conditions. However, the potential ability to initiate an aggregation process with a species which is accessible only by non-RRKM chemistry would be an extremely unusual aspect of laser chemical cluster formation. Here the monomer for the aggregation process is the coordinatively unsaturated organometallic fragment. Clusters produced from other molecular *fragments* are known, although little is known of their properties. Although the example cited above was taken from matrix isolation results, studies of the one-photon gas-phase substitution chemistry of these types of species using time-resolved infrared absorption spectroscopy reveal the earliest stages of their aggregation chemistry, i.e. dimerization of coordinatively unsaturated molecular species competes with recombination with free ligands.

In the context of cluster and particle formation, the term 'high local pressures' can be quantified by calculating the degree of supersaturation represented by the laser-produced gas-phase mixture. There are several ways at least to estimate the supersaturation,[46] e.g. the Kelvin equation. Bauer and co-workers[47-50] have discussed the question of supersaturation extensively on the basis of shock-tube results. Given the data in Table 1, it is clear that a room-temperature reaction cell is not in equilibrium with the nascent gas phase produced by the laser. Initiating cluster and particle formation using laser excitation of a gas-phase metal-containing precursor was first reported by Tam *et al.*[51] and then by Yabuzaki *et al.*[52] Both groups reported that electronic excitation of the monomer unit accelerated the growth of the clusters. This is significant because lasers can be combined with organometallics for *state-selective* metal-atom (monomer in the case of metal clusters) or ion production and because nucleation is a chain-reaction-*initiating* event.

Others subsequently used lasers to produce clusters and powders; some examples are collected in Table 2. Draper[53, 54] used an IR laser to excite $Mo(CO)_6$ to produce fine powders for absorbers in solar-energy collectors. Rice and co-workers[55-59] have produced a wide range of carbides, nitrides, oxycarbides, sulfides and other high-surface-area powders using a CO_2 laser, ethylene, ammonia, and metal carbonyls. In some cases the ethylene or ammonia was used as a sensitizer and in others as a reactant. These materials have been evaluated as industrial-scale catalysts with very encouraging results. Although many measured activities were found to be comparable with those of catalysts prepared using standard methods, some striking differences have

Table 2 Types of particles and clusters produced by laser chemistry of organometallics

Starting material	Laser excitation	Product composition	Particle size (nm)	Comments/Ref
Fe, Cr, W, Mo, Mn $M(CO)_6$, ethylene	CO_2	M_xS_y, M_xC_y, M_xN_y $M_xC_yO_z$	10–100	55–59
$((CH_3)_3Si)_2NH$	CO_2	SiC	10–100	57
$Zr(BH_4)_4$, SF_6	YAG, CO_2	ZrB_2	High surface area	58
SiH_4	CO_2	SiC, aSi, Si_3N_4	10^1–10^2	61–65
Cyclopentadienyl(allyl)Pt	Excimer	Pt(C)	10^0–10^2	34
$M(CO)_6$, M = Cr, Mo, W	Excimer	M_x, $M_x(CO)_y$	10^{-1}–10^3	66, 67
$Mo(CO)_6$	CO_2	$M_xC_yO_z$	10^{-1}–10^3	21
NaH	Dye	$(NaH)_x$	10^{-1}–10^3	52
$Mo(CO)_6$	CO_2	$M_xC_yO_z$	10^{-1}–10^3	53, 54
SiH_4/B_2H_6 or PH_3 or $TiCl_4$	CO_2	SiB, SiP, TiSi	Approx. 10^1	60

been observed. At a very early stage, Gupta and Yardley[60] reported similar research also with very encouraging results, with potential application of the products as structural materials. Haggerty and co-workers[61–65] produced an important pioneering series of studies along the same strategic lines. Puretzky and co-workers[66, 67] have produced clusters and ultrafine particles using excimer laser and Group VI metal carbonyls. Using a XeCl excimer laser, Chaiken and co-workers[34, 68, 69] have used cyclopentadienyl(ally)platinum(II) to produce clusters of platinum.

The composition and structures of the clusters and particles is poorly known at best. X-ray diffraction, elemental analysis and electron microscopy have been used on clusters which were collected on filters. A distribution of products is produced in most cases, although Rice reports that it is possible to control the process to a certain extent and thereby to cause one or a few products to predominate. Because they are able to produce sufficient quantities for post-synthetic analysis, Jervis's and Rice's clusters are known to contain substantial proportions of carbon and oxygen. Puretsky's approach produces a polydisperse mixture of pure metal clusters and mixed metal-carbonyl clusters. The platinum clusters produced by Chaiken have been analyzed using transmission electron microscopy (TEM), Auger spectroscopy, electron diffraction and infrared spectroscopy and contain substantial amounts of carbon, mostly in the form of undissociated precursor ligands.

For practical purposes, clusters and particles of noble metals which are oxidation-resistant can often be made much more carbon-free by post-synthetic heating in an oxygen-containing atmosphere. Although there is certainly an upper limit to the temperature that can be employed to oxidize the carbon before the clusters are caused to coalesce or to oxidize (which depends on the nature of the metal), temperatures in the 300–500 °C region are usually sufficient to decarbonize safely a platinum cluster film. For comparison, a similar film produced from clusters using Puretzky's method and $W(CO)_6$, which in its nascent state is essentially tungsten and substoichiometric tungsten carbonyl, is nearly completely oxidized to WO_3 by post-deposition heating in air to temperatures in the above range. Singmaster *et al.*[62] and others have shown that well-known surface and solid-state reactions such as the disproportionation of carbon monoxide can be studied with respect to laser-deposited films and the question of decarbonization.

These studies have not been carried out in the context of clusters because it has only recently been better established that many LCVD films can often be thought of as being composed of clusters. The work of Mader[71, 72] on vapor-quenched evaporated films would seem to have definite relevance to the coalescence of clusters to form films. Here a statistical and geometric approach has been applied to understanding so-called 'prenucleated' films produced by standard methods. These 'standard' methods basically involve running an evaporation source at too high a temperature and having the substrate temperature too low. Under such conditions the films are not adequate for electronic device applications. For us, the picture given by this method is useful because it allows one to visualize the LCVD process without considering the effect of the laser on the growing film or the substrate. Of course, other stratgegies[17, 18] for unraveling the effects of these simultaneous processes can also be employed.

IRREVERSIBLE FRACTAL AGGREGATION

The conditions favorable for formation of clusters are easily summarized. Other than obtaining a sufficiently high local pressure of monomers, the only other important condition seems to involve having a high enough pressure of buffer gas present to:

(1) restrict the motion of the monomers, thereby increasing their residence time in the laser irradiation zone and improving their chances of finding other monomers with which to coalesce, and
(2) cool the hot monomers and lessen 'evaporation' of less tightly bound pieces from the growing clusters.

The energy released by the recombination process can be substantial and is the reason that most large-scale syntheses of particles are reported to occur in flames.

Although cluster size distributions are the most direct manifestation of the overall cluster/particle formation process, the only cluster size distribution produced by laser chemistry was published by Chaiken *et al.* using TEM.[34] The analysis of their data strongly suggested that many of the distributions produced by either TEM or mass spectrometry are not rendered meaningless by artifacts such as post-depositon coalescence or fragmentation induced by the ionization process. Puretzky atempted to probe the moments of such a gas-phase distribution using light-scattering techniques with some success. Analysis of *in situ* light-scattering data[73, 74] requires a knowledge of temperature *and* pressure gradients; these have not been available with good precision. Homer[75, 76] and Bauer[47–50] used a similar approach, with much less success, combined with electron microscopy to monitor particle formation in shock-heated mixtures of tetraethyl-lead. Yabuzaki[52] showed that the sizes of particles in the micrometric region can also be studied by estimating their falling velocities under the influence of gravity. Most studies of CO_2 laser-induced particle production report diameters in the range 10–100 nm. It seems probable that special mass spectrometers could be built such as are currently used for analyzing cluster distributions produced using reactive bulk-gas mixtures, oven-produced clusters and expansion-produced clusters.

The only distribution of large metal clusters produced using lasers published so far[29] was obtained using transmission electron microscopy (TEM) to visualize the clusters. This distribution was found to be very closely related to the log normal distribution, although a defect was found which was later discovered to be common to many distributions produced by laser-nozzle expansion distributions. Compared with a perfect log normal distribution,[77, 78] these distributions were all found to have a deficiency in larger clusters. In addition to providing evidence against the possibility of a variety of experimental artifacts skewing the distributions, the most striking aspect of the distributions was that those determined by mass spectrometry only contained a few dozens of atoms whereas the platinum cluster distributions analyzed by laser chemistry involved hundreds of atoms. The similarity of the distributions suggests that the highly nonlinear process of clustering has scaling properties which lead to the same distribution despite the wide range of size scales involved.

The general field of gas-to-particle conversion until 1976 has been reviewed by Friedlander.[16] The aggregation of atoms with each other to form clusters, and then of clusters with clusters to form larger clusters, has been dealt with by many workers on the basis of the Smoluchowski equation.[79] In various regimes[80] of the relevant parameters, the Smoluchowski equation spans aggregation phenomena ranging from colloids to aerosols. There are only three known solutions to the Smoluchowski equation and these have varying relevance to the problem at hand. We introduce only the ballistic and diffusive ranges which seem to have the most relevance in the present case.

When the mean free path of the aggregating species is relatively long compared to their own spatial extent, the Smoluchowski equation is said to be in the 'ballistic' regime. Otherwise, gas-phase systems fall into the 'diffusive' regime. In either case, essentially hard-sphere collision frequencies can be calculated between all the interacting species and, together with the assumption that any two particles which collide must stick, it is possible to calculate the rate at which larger clusters are formed and smaller clusters are consumed by the aggregation process. Smooth scaling of the collision frequencies which control the aggregation process occurs because the masses of the clusters determine the relative velocities/diffusion coefficients and because the size of the clusters increases monotonically with cluster size on average. The masses and sizes depend on the number of atoms in the clusters in terms of power laws and this leads to fractal exponents which can be used to characterize the particular regime of the Smoluchowski equation which is active. The smooth scaling, i.e. the homogeneity, of the collision frequencies, which are actually the rate constants for the various agglomeration pathways, was essential for obtaining analytical solutions to the Smoluchowski equation. Chaiken[82] and Goodisman have shown that the homogeneity requirement can be relaxed in a variety of systematic and nearly random ways without disturbing the overall behavior.

Indeed, the Smoluchowski equation is not exactly correct for the process in which we are interested, because it neglects the discontinuous variation in the collision cross-sections which pertain to production of clusters of particular sizes, i.e. 'magic number' clusters. This would seem to be less of a problem for distributions involving hundreds of atoms but may well be very relevant for understanding the variations in mass-spectrometrically characterized distributions involving much smaller clusters. The ballistic regime and the diffusive regime both have been solved exactly but neither published solution[80] takes into consideration even the simplest aspects of the kinematics of the aggregation process. Any two clusters which collide and stick transform some of their linear momentum into angular momentum and so the conglomerate has a lower *translational* energy than the sum of the two separate entities. Larger clusters are disproportionately slower than would be expected on the basis of the translational temperature of the smaller clusters. This was recognized very early by Bauer.[47–50]

Except for the interpretation of the kinematics, the Smoluchowski treatment[16] has been in general use for understanding gas-to-particle conversion. Jullien has provided an analytical form for the distribution function[81] which obtains in the regime of laser chemistry of organometallics. It is not difficult to show that in the limit of long times and large cluster distributions, Jullien's function has as its leading term the log normal distribution.[82] It is clear that the deviation from log normality of most expansion-produced distributions is the direct result of the fact that the aggregation process has not been allowed to go long enough in time. Some distributions which are produced by coalescence growth,[29] e.g. by evaporating wire/bell-jar methods, produce clusters and particles which have much longer to agglomerate and so the size distribution produced shows a smaller deviation from the pure log normal distribution.

Finally, for practical purposes it is useful to know what type of distribution can be produced for a given material. A selection of variants on effective medium theory are available; one good example with particular application to optical properties is Aspnes' treatment,[83] which can be applied to the distribution produced to rationalize the properties of composites produced from the clusters. Properties such as index of refraction, density, and resistivity, and thermodynamic phase are closely related to void volume, which is also given by Mader's treatment on the basis of the size distribution of the particles used to produce a composite.

SUMMARY

Lasers and gas-phase organometallics offer specific advantages for the synthesis of particles and cluster-based materials. Laser chemical production of monomers and initiators for irreversible aggregation chemistry has advantages relating to mass transport and energy transfer, regardless of the pathways of laser-induced dissociation. Laser chemical production of non-RRKM products will produce translationally hot products. This must be taken into account when attempting to estimate the collision frequencies needed to model the aggregation process using the Smoluchowski equation. Similar considerations apply to the internal vibrational energy of monomers produced by thermalized RRKM pathways. This enters into the calculations in the form of the fractal dimension of the clusters as they are formed. Internally hot clusters have more energy to rearrange after the initial coalescence event and thereby find thermodynamically stable structures. This may be related to the reason why some clusters apparently self-assemble from smaller clusters to form extremely stable structures.

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