HANDBOOK OF HETEROGENEOUS CATALYSIS

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Part A, Chapter 8.6

SONOCATALYSIS

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8.6 Sonocatalysis

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8.6.1 Introduction and the Origins of Sonochemistry

Research on the chemical effects of ultrasound has undergone a renaissance during the past decade and has had a significant impact in a variety of areas [1, 2]. Applications of sonochemistry have been developed in virtually all areas of chemistry and related chemical technologies [3, 4]. We can conceptually divide the effects of ultrasonic irradiation on heterogeneous catalysis into those that alter the formation of heterogeneous catalysts, those that perturb the properties of previously formed catalysts, and those that affect catalyst reactivity during catalysis. In practice, these three classes of effects are often deeply intertwined in reported experimental results.

No direct coupling of the acoustic field with chemical species on a molecular level can account for sonochemistry. Ultrasound spans the frequencies of roughly 20KHz to 10MHz, with associated acoustic wavelengths in liquids of roughly 100 to 0.15 mm: these are not on the scale of molecular dimensions. Instead, the chemical effects of ultrasound derive from several nonlinear acoustic phenomena, of which cavitation is the most important. Acoustic cavitation is the formation, growth, and implosive collapse of bubbles in a liquid irradiated with sound or ultrasound. When sound passes through a liquid, it consists of expansion (negative pressure) waves and compression (positive pressure) waves. These cause bubbles (which are filled with both solvent and solute vapor and with previously dissolved gases) to grow and recompress. Under proper conditions, acoustic cavitation can lead to implosive compression in such cavities. Such implosive bubble collapse produces intense local heating, high pressures, and very short lifetimes. As discussed elsewhere, these hot spots have temperatures of roughly 5300K, pressures of about 1720 bar, and heating and cooling rates above $10^9\ \mathrm{K\,s^{-1}}$ [5-7]. Cavitation is an extraordinary method of concentrating the diffuse energy of sound into a chemically useable form.

When a liquid-solid interface is subjected to ultrasound, cavitation still occurs, but with major changes in the nature of the bubble collapse. If the surface is significantly larger than the cavitating bubble (~ 100 μm at 20 kHz), spherical implosion of the cavity no longer occurs, but instead there is a markedly asymmetric collapse which generates a jet of liquid directed at the surface, as seen directly in high speed microcinematographic sequences shown in Fig. 1 [8]. The tip jet velocities have been measured by Lauterborn to be greater than 100 $m s^{-1}$. The origin of this jet formation is essentially a shaped-charge effect: the rate of collapse is proportional to the local radius of curvature. As collapse of a bubble near a surface begins, it does so with a slight elliptical asymmetry, which is self-reinforcing, and generates the observed jet. The impingement of this jet can create a localized erosion (and even melting), surface pitting, and ultrasonic cleaning. A second contribution to erosion created by cavitation involves the impact of shock waves generated by cavitational collapse. The magnitude of such shock waves is thought to be as high as 10^4 bar, which will easily produce plastic deformation of malleable metals [9]. The relative importance of these two effects depends heavily on the specific system under consideration.

Enhanced chemical reactivity of solid surfaces is associated with these processes. The cavitational erosion generates unpassivated, highly reactive surfaces; it causes short-lived high temperatures and pressures at the surface; it produces surface defects and deformations; it forms fines and increases the surface area of friable solid supports; and it ejects material in unknown form into solution. Finally, the local turbulent flow associated with acoustic streaming improves mass transport between the liquid phase and the surface, thus increasing observed reaction rates. In general, all of these effects are likely to be occurring simultaneously.

In contrast, the effects of ultrasound on slurries of fine particles does not come from microjet formation during cavitation. Distortions of bubble collapse depend on a surface several **times** larger than the resonance. bubble size. Thus, for ultrasonic frequencies of ~2OkHz, damage associated with jet formation cannot occur for solid particles smaller than ~200 μm. In these cases, however, the shockwaves created by homogeneous cavitation can create high-velocity interparticle collisions, with impact speeds of several hundred $m s^{-1}$ and local effective transient impact temperatures of roughly 3OOOK [10]. The turbulent flow and shockwaves produced by intense ultrasound can drive metal particles together at sufficiently high speeds to induce effective melting at the point of collision as shown in Fig. 2. The high-velocity interparticle collisions produced in slurries of malleable materials cause smoothing of individual particles and agglomeration of particles into extended aggregates. Surface composition depth profiles of sonicated powders show that ultrasonic irradiation effectively removes surface oxide coatings. The removal of such passivating coatings dramatically improves reaction rates for a wide variety of reactions. With larger flakes of brittle materials, interparticle collisions causes shock fragmentation instead, which can increase surface areas dramatically and contribute to the increased activity [ll-13].

The term “sonocatalysis” should be restricted in its use to refer only to the creation of a catalytically competent intermediate by ultrasonic irradiation. One should not refer to a simple sonochemical rate enhancement of a reaction by this term, just as one would use the term photochemistry, and not photocatalysis, to describe a stoichiometric reaction caused by light. In this chapter, the symbol below (eq 1) will be used to indicate ultrasonic irradiation or “sonication” of a solution leading to a sonochemical reaction.

$$\xrightarrow{)))} \tag{1}$$

8.6.2 Effects of Ultrasound on Heterogeneous Catalysts

Ultrasonic irradiation can alter the reactivity observed during the heterogeneous catalysis of a variety of reactions. In addition to the more recent work described in this chapter, there is an extensive (but little recognized) past literature in this area, particularly from Eastern Europe [14].

The effects of ultrasound on catalyst formation can be far reaching; changes in patterns of crystallization, dispersion, and surface properties are all possible. Alteration of properties of preformed catalysts can also have substantial effects. Oxide or other passivating coatings can be removed, and increased dispersion can occur, sometimes from the fracture of friable solid supports (e.g. noble metals on carbon). The effect of irradiating operating catalysts often originates from improved mass transport.

8.6.2.1 Metal Powders

The use of ultrasound for syntheses involving liquid-solid heterogeneous organometallic reactions has been a matter of intense current investigation [15 16]. In general, ultrasonic treatment of these metals promotes reaction pathways favoring single-electron transfers

[17], probably through the removal of thin oxide coatings which are often dominated by acid-base activity. The ultrasonic activation of commercial transition metal powders has also received substantial attention [18-20].

A Hydrogenation and Hydrosilation Catalysts

The most heavily studied sonochemical systems for hydrogenation involve nickel catalysts and has a long history [21-23]. Impressive accelerations have been reported recently. For example, the hydrogenation of alkenes by ordinary Ni powder is enormously enhanced ($>10^5$-fold) by ultrasonic irradiation [18]. The surface area of the catalyst did not change significantly even after lengthy irradiation. Both surface smoothing (shown in Fig. 3) and particle agglomeration occur, probably due to interparticle collisions caused by cavitation-induced shockwaves, as discussed earlier. Auger electron spectroscopy reveals that there is a striking decrease in the thickness of the oxide coat after ultrasonic irradiation. The removal of this passivating layer is probably responsible for the $>10^5$-fold increase observed in catalytic activity.

Hydrogen-deuterium exchange by Raney Ni powder is also improved by ultrasonic irradiation, as first disclosed in a 1986 patent [24] Selective introduction of hydrogen isotopes into aromatic compounds was accomplished by the reaction of haloaromatic compounds with basic deuterated (or tritiated) aqueous solutions over Raney metal catalysts under ultrasound at ≈ 320 K. Others have extended this work to deuterate carbohydrates and glycosphingolipids, with rate increases of roughly threefold upon sonication [25]. These workers concluded that the increased activity originates from fresh Ni surfaces produced daring crack propagation during ultrasonic irradiation [26].

Of special value to the synthetic organic chemist, is that a highly efficient enantioselective catalyst can be sonochemically prepared from tartaric acid treatment of Raney Ni for the hydrogenation of 1,3-diketones to 1,3-diols [27]. Here, the Raney Ni/Al alloy is sonicated in water to remove the Al before exposure to the tartaric acid treatment. Although the mechanism of improvement is obscure, in the best cases, enantiomeric excesses of 90% are observed.

The allylation of ketones and aldehydes by allylic alcohols (eq 2) has been improved using ultrasonic irradiation of a palladium/tin dichloride catalyst in less polar solvents [28]. Inverted regioselectivity is observed compared to homogeneous carbonyl allylation in polar solvents.

$$H_3CCH{=}CHCH_2OH + H_5C_6CHO \xrightarrow[Pd/SnCl_2]{)))} H_3CCH{=}CHCH_2CH(OH)C_6H_5 \qquad (2)$$

There have been several studies of the effects of ultrasound on hydrosilation reactions, primarily by Boudjouk [29], who extended the use of ultrasound with nickel to the hydrosilation of alkenes [30]. Whereas there are many catalysts for hydrosilation of simple alkenes, relatively few work well for functionalized substrates, such as acrylonitrile. The use of ultrasound to prepare hydrosilation catalysts for the hydrosilation of acrylonitrile with silanes has met with success. Using ultrasound to create a high surface area dispersion of Ni from NiI_2 reduction with Li powder, various alkenes were hydrosilated. Even the reaction of acrylonitrile occurred in yields >95% at 273K. Induction periods of 10–30 min were observed before rapid hydrosilation began. The Ni catalyst can be recycled many times without loss of activity. By comparison, Ni powder from commercial sources is not active even after extensive sonication.

B Fischer–Tropsch (Hydrogenation of CO) Catalysts

There have been four recent reports on the use of ultrasound for catalyst preparation for Fischer-Tropsch synthesis. Liquid-phase hydrogenation of carbon monoxide was accomplished with ultrafine particles (<100 nm) composed of iron, cobalt, and nickel [31]. These were prepared by vapor-phase reduction of their metal chlorides and were passivated by gradual oxidation. The catalysts composed mainly of Fe initially showed high catalytic activity and oxygenate selectivity. During reaction, however, catalyst degradation occurred due to aggregation. Ultrasonic irradiation effectively returned the lost activity and selectivity. In addition, ultrasonically prepared colloidal K was used to modify ultrafine particle catalysts effectively in order to increase the yield of high molecular weight products. In a more recent follow-up, Kikuchi and Itoh [32] examined the liquid phase (in hexadecane slurry) Fischer-Tropsch synthesis from iron ultrafine particle catalysts (40–80 nm). Pretreatment of the catalyst with ultrasound increased activity fivefold, compared to the precipitated powder. The function of the ultrasonic irradiation is simply to create dispersions of the weakly aggregating ultrafine particles. This also appears to be the function of ultrasound in the preparation of zeolite (HZSM-5) sup ported ultrafine iron particle catalysts, where the activity is increased by roughly a factor of 20 compared to catalyst preparations made with rapid stirring [33].

C Amorphous and Nanostructured Metal Catalysts

Very recently, Suslick and co-workers characterized the sonochemically produced iron from the sonolysis of $Fe(CO)_5$ and discovered the surprising result that this material was fully amorphous on the nanometer scale, consisting of a coral-like agglomeration of few nanometer-sized clusters, as seen in the scanning electron micrograph of Fig. 4 [34–36]. Amorphous metallic alloys lack long-range crystalline order and have unique electronic, magnetic, and catalytic properties. The production of amorphous metals (see Section A4.4) is difficult because extremely rapid cooling ($> 10^6$ K s^{-1}) of molten metals is necessary to prevent crystallization. As discussed earlier, acoustic cavitation can induce extraordinary local heating in otherwise cold liquids and can provide enormous cooling rates ($>10^9$ K s^{-1}), which provides a new synthetic route to amorphous metal powders using the sonochemical decomposition of volatile organometallics. From recent work on the sonolysis of volatile Co, Mo, and W precursors [37], it appears that this is a general phenomenon, and extension to the synthesis of amorphous intermetallic alloys is also proving successful.

The sonochemically synthesized amorphous powders may have important catalytic applications, especially given their very high surface areas and nanometer cluster size. For example, sonochemically prepared nanophase iron powder is an active catalyst for the Fischer-Tropsch hydrogenation of CO and for hydrogenolysis and dehydrogenation of alkanes, in large part due to its high surface area ($>120\,m^2\,g^{-1}$). Rates of conversion of CO and H_2 to low molecular weight alkanes were approximately 20 times higher per gram of Fe than for fine particle (5 μm diameter) commercial crystalline iron powder at 523 K, and more than 100 times more active at 473 K. Selectivities were not substantially different. The reactions of cyclohexane prove an interesting case because of its inherent catalyst surface-structure sensitivity. In this manner, the nature of the catalytic process can be useful as a chemical probe of the effect of ultrasound on the catalytically active surface. Catalytic studies were carried out in a continuous flow microreactor on nanophase Fe/Co alloys produced sonochemically. The ratio of cyclohexane dehydrogenation to hydrogenolysis depended on alloy composition. The 1: 1 alloys gave nearly exclusively benzene, in stark contrast to either pure metal [38].

8.6.2.2 Metal Oxides as Oxidation Catalysts

There are several reports on the effects of ultrasound on metal oxides catalyst preparation, but in no cases have substantial improvements in rates or selectivities been observed. Mixed Cr/Mo and Cr/Fe oxide catalysts have also been prepared with ultrasonic treatment and examined for the oxidation of methanol to formaldehyde [39, 40]. Recent studies by Mokry and coworkers [41] have examined the vapor-phase oxidation of a number of organic compounds after ultrasonic activation of Fe/Te/Mo oxide and Cs/Pb/Mo oxide catalysts. Vapor-phase oxidation of isobutylene, methanol, and ethanol were examined. Although modest increases in specific areas and catalytic activity could be obtained, selectivity toward the desired products decreased.

An entirely separate use of ultrasound for catalyst preparation involves the use of ultrasonic nebulization, followed by secondary gas-phase reaction to prepare TiO_2 photocatalysts [42]. $TiCl_4$ and diisopropoxy-bis-(acetylacetonato)titanium(IV) were employed for the preparation of TiO_2. Products obtained using this method gave photocatalytic activities for the degradation of 1,4-dichlorobenzene, similar to that of the commercially available Degussa P25 titanium(N) oxide.

8.6.2.3 Silica, Alumina, and Zeolites

There have been several recent reports by Zarzycki and co-workers on the "sonocatalytic" production of silica "sonogels" [43–45]. Whereas the term "sonogel" is new and appears to mean either a solve&containing gel or a gas-containing gel (a xerogel) made in the presence of ultrasound, the processes used to make them are similar to those tried 20 years ago, and the term "sonocatalytic" is misused in this context. Silica sonogels have been obtained by the hypercritical drying of gels from the hydrolysis of $(EtO)_4Si/H_2O$ mixture irradiated with ultrasound. In general, the xerogels formed in this manner appear to have a finer porosity and greater reticulation of the network than unsonicated gels. Very recently zirconia sols and gels have also been prepared sonochemically and studied by small-angle X-ray scattering (SAXS) with a synchrotron source [46].

It is well known that alumina itself, acting as a solid acid or base, can be an active catalyst for a variety of organic transformations. Perhaps as a consequence, considerably more work has been done on the effects of ultrasound on catalysis by alumina. Much of the work in this area has been from the group of Ando during the past decade [47]. Ando's initial discovery was the improvement made by ultrasonic irradiation of the liquid-solid two-phase synthesis of aromatic acyl cyanides from acid chlorides and solid KCN in acetonitrile [48]. The extension of this reaction to benzyl bromides led to an unusual observation of reaction pathway switching [49]. With mechanical agitation (i.e. stirring), the reaction of benzyl bromide and KCN in aromatic solvents, catalyzed by alumina, yields diarylmethane products from Friedel-Crafts attack on the solvent (eq 3); whereas with ultrasonic irradiation, one obtains benzyl cyanide (eq 4). Apparently, the ultrasonic irradiation of alumina deactivates the Lewis acid sites normally present that are responsible for the Friedel–Crafts reactivity. It is thought that this poisoning is accomplished by the added solid basic salts (e.g. KCN) with ultrasound, perhaps through solid-solid contacts or through increased access of dissolved bases to the alumina surface.

$$C_6H_5CH_2Br + C_6H_5CH_3 + KCN \xrightarrow[Al_2O_3]{\text{stirred}} C_6H_5CH_2{-}C_6H_4CH_3 \tag{3}$$

$$C_6H_5CH_2Br + C_6H_5CH_3 + KCN \xrightarrow[Al_2O_3]{)))} C_6H_5CH_2CN \tag{4}$$

This is a generalizable class of reactions catalyzed by alumina in the presence of ultrasound. For example, another application is the sonocatalysis of aldol condensations by alumina. Substantial improvements in yields were observed, with greatly diminished reaction times, for several ketones [47]. In the same vein, a useful synthesis of α-aminonitriles, which are important intermediates in amino acid synthesis, has been reported that sonicated carbonyl compounds with salts of amines and potassium cyanide in acetonitrile in the presence of alumina under solid-liquid two-phase conditions [50].

Although some investigations on the effects of ultrasound on aluminosilicates and their syntheses have been published, this area remains relatively unexplored. The best characterized study is that of Lindley [51], who examined the sonochemical effects on syntheses of zeolite NaA. Severalfold reductions in nucleation time and rates of formation during hydrothermal synthesis were monitored by X-ray diffraction. Scanning electron micrographs showed significant changes in morphology, as well, with ultrasound producing a more agglomerated product made up of much finer crystallites in the few-micron region.

Finally, the effect of ultrasound on gas-solid heterogeneous catalytic decomposition of cumene to benzene and propylene was examined with a silica/alumina cracking catalyst where the entire reaction bed was subjected to ultrasound [52]. Rate improvements of 160% were observed. Because cavitation cannot occur in such a system, these results must come simply from improved mass transport between the gas and surface.

8.6.2.4 Supported Metal Catalysts

The use of ultrasound on the preparation of supported metal heterogeneous catalysts has been examined primarily for hydrogenation and related catalysts, usually involving the noble metals. For example, ultrasonic irradiation during the deposition of Pt on silica produces an 80% increase in Pt dispersion [53]. Several recent Japanese patents make use of ultrasound to improve the dispersion and reliability of supported noble metal for fuel cells [54, 55]. The general process described involves the reduction of H_2PtCl_6 in the presence of a carbon carrier, often colloidal, in the presence of ultrasonic irradiation.

The use of ultrasound to improve the formation of metal-containing gels has been reported. A patent was issued for a sonochemical process for preparing Zr-containing aluminoxanes [56]. Upon sonication of a toluene solution of $(CH_3)_3Al$ and Cp_2ZrCl_2 with water (Cp = cyclopentadienyl), an aluminoxane gel was formed that was an active catalyst for oligomerization of l-octene. Rhodium catalysts have been dispersed on titania/silica aerogels [57]. Ultrasound was utilized in two different preparations. In the first case, a "sonogel" was obtained by hydrolysis of Ti and Si alkoxides in the absence of alcohol with ultrasonic irradiation, which was then impregnated with a rhodium nitrate solution. In the second, a mixture of the alkoxides and a rhodium nitrate aqueous solution were exposed to ultrasound, thus leading to a ternary Rh/TiO_2SiO_2 sonogel. The behavior of these catalysts was compared with that of a $Rh/TiO_2/SiO_2$ system obtained by conventional impregnation methods, starting from a commercial silica support. The samples prepared by impregnation of preformed aerogels give high levels of Rh dispersion and show an increase in catalytic activity of roughly tenfold for the hydrogenation of benzene.

Another application of ultrasound to supported metal catalysts alters the reactivity of already formed catalysts. Boudjouk and co-workers examined the acceleration of hydrosilation reactions of alkenes and alkynes catalyzed by Pt/C [58, 59]. Various substrates, including l-hexene, styrene, and phenylacetylene, work effectively even at 243 K with various silanes (including $HSiCl_3$, $HSiCl_2Me$, $HSi(OC_2H_5)_3$, and $HSi(C_2H_5)_3$). Catalyst concentrations of 0.01 mol% are sufficient. Because the effect of the ultrasound on the carbon support is the generation of a very fine colloidal suspension, separation of products from catalyst by filtration is not possible, which defeats one of the primary advantages of heterogeneous catalysis.

These researchers extended the use of this system for hydrogenation of alkenes using formic acid as a hydrogen transfer agent [60]. Palladium on carbon was used to catalyze hydrogenations of various alkenes, including terminal and internal alkenes, a diene, a vinyl ether, and an @unsaturated ketone, in very high yields at room temperature and atmospheric pressure. In this case, filtration was still effective for removal of the catalyst. Sonication of the reaction mixtures accelerated the reactions; the effects were not quantified, but seemed no better than the effects of heating to reflux. Han continued this work using hydrazine in place of formic acid as the reductant [61]; again, yields were comparable to those obtained by refluxing the mixture.

Loss of activity during extensive use is a common industrial problem with any catalyst, but especially with supported metal catalysts. The deactivation process will vary depending on the catalyst and conditions of its use, and includes the deposition of carbonaceous contaminants, coking, the oxidation of metal surfaces, neutralization of surface acid sites, etc. There is an extensive patent literature over the past 20 years describing the use of ultrasound to regenerate spent catalysts. Although the mechanism of action has not been examined, it is likely that improved mass transport and increased fine-pore penetration are significant contributors.

An early disclosure of the use of ultrasound to reactivate a deactivated hydrocarbon conversion catalyst goes back to Exxon Research and Engineering in 1978 [62]. Highly deactivated hydrocracking catalysts, which had resulted from successive use and conventional regeneration, could be reclaimed by oxidizing the catalyst at elevated temperatures followed by ultrasonic irradiation of the catalyst in a nonreactive liquid. In an example, a conventional Ni/Mo hydrocracking catalyst on an amorphous support was treated with air at 783 K, then suspended in low-viscosity white oil and treated with ultrasound.

A variety of similar applications of ultrasound to clean or reactivate various catalysts have also been reported. The most common carrier/cleaning liquid phase has been either aqueous [63] or standard feedstock flow. Commercial noble metal catalysts supported on alumina used either for NO, removal or hydrogenation of hydrocarbons have been regenerated efficiently with ultrasound [64, 65] with nearly complete restoration of specific surface area, porosity, and activity. In the same manner, substantial regeneration has been disclosed for deactivated industrial oxide TiO_2/V_2O_5 catalysts for oxidation of *o*-xylene to phthalic anhydride [66] and for flue gas denitration [67]. Ultrasonic reactivation is also useful for a partially &activated BF_3/graphite intercalate catalyst used in an alkylation process [68].

8.6.2.5 Polymerization Catalysts

There are only a few examples of the use of ultrasound to modify catalysts for polymerization. The first was in a 1961 patent [69], which found a substantial decrease in catalyst particle size and a consequent increase in activity due to diminished aggregation [70]. A further investigation of Ziegler-Natta polymerization under high-intensity ultrasound of styrene using a $TiCl_4/Et_3Al$ catalyst has been recently published [71]. The polymers are produced in better yield and with more control over the molecular weight distribution than in the conventional, unsonicated process. For example, polystyrene produced under the same conditions with stirring yields polydispersities above 10, while with ultrasound they are 2.5, with comparable mean molecular weights of ≈50 000. In part, this may be due to preferential cleavage of the longer chains by the ultrasound [72].

A European patent has recently described another application of ultrasound to polymerization catalyst preparation [73]. By spraying catalyst precursor solutions through an ultrasonic nozzle into an inert gas, small droplets are formed which solidify into catalyst microparticles. Thus, molten $MgCl_2$ $3.5C_2H_5OH$ at 403 K was fed through an ultrasonic atomizer at 5 kg h^{-1} into a cooled N_2 atmosphere, yielding uniform oval or spherical particles with 30–40 μm diameters.

8.6.3 Concluding Remarks

In principal, ultrasound is well suited to industrial applications. Since the reaction liquid itself carries the sound, there is no barrier to its use with large volumes. In fact, ultrasound is already heavily used industrially for the physical processing of liquids, such as emulsification, solvent degassing, solid dispersion, and sol formation. It is also extremely important in solids processing including cutting, welding, cleaning, and precipitation.

ultrasound has already become a common laboratory tool for nearly any case where a liquid and a solid must react. The production of heterogeneous catalysts involves high value-added materials, where processing costs are not always economically limiting. In this context, ultrasound is a viable method for the preparation and treatment of heterogeneous catalysts. The ability of ultrasound to create highly reactive surfaces, to improve mixing even in viscous media, and to increase mass transport makes it a particularly promising technique to explore for catalyst preparation, activation, and regeneration.

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Figure 1. Cavitation near a liquid-solid interface. High-speed microcinematographic sequence of laser-induced cavitation near a solid surface, showing the formation of a microjet impact; 75 000 frames s^{-1}. The sequence is from left to right, top to bottom; the solid boundary is at the bottom of each frame. Photograph courtesy of W. Lauterborn; reproduced with permission [8].

Figure 2. Scanning electron micrograph of 5 μm diameter Zn powder. Neck formation from localized melting is cawed by high-velocity interparticle collisions. Similar micrographs and elemental composition maps (by Auger electron spectroscopy) of mixed metal collisions have also been made. Reproduced with permission [10].

Figure 3. The effect of ultrasonic irradiation on the surface morphology and particle size of Ni powder. Initial particle diameters before ultrasound were $\approx 160\ \mu m$; after ultrasound, $\approx 80\ \mu m$.

High-velocity interparticle collisions caused by ultrasonic irradiation of slurries are responsible for the smoothing and removal of passivating oxide coating. Reproduced with permission [11].

Figure 4. Scanning electron micrograph of amorphous nanostructured iron powder produced from the ultrasonic irradiation of $Fe(CO)_5$. Reproduced with permission [34].