

Effects of high intensity ultrasound on inorganic solids*

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Ultrasonic irradiation dramatically affects the reactivity of a variety of inorganic solids. We have found, for example, large increases in the rates of intercalation of a wide range of compounds into various layered inorganic solids (such as ZrS_2 , V_2O_5 , TaS_2 and MoO_3). High intensity ultrasound also enhances the heterogeneous catalysis of alkene hydrogenation by Ni powders. Scanning electron microscopy reveals that ultrasound has multiple effects on the morphology and surface characteristics of inorganic solids, creating substantial surface damage, increasing surface areas significantly and causing increased particle aggregation.

Keywords: sonochemistry; high intensity ultrasound; inorganic solids; electron microscopy

The use of ultrasound to enhance chemical reactivity is becoming a common and widely applicable laboratory technique^{1,2}. The physical origins of the chemical effects of ultrasound lie principally in acoustic cavitation and other non-linear phenomena³⁻⁵. The creation, expansion and implosive collapse of bubbles in ultrasonically irradiated liquids generates localized hot spots from acoustic cavitation which are responsible for most homogeneous sonochemistry. In heterogeneous, solid-liquids systems, acoustic cavitation and microstreaming at the surface are both significant. The former produces high speed microjets of liquid which impinge upon the surface and cause surface erosion and localized heating. The latter creates turbulent flow and can significantly improve mass transport between solution and surface.

We have explored the chemical effects of ultrasound on both homogeneous and heterogeneous systems, including some of the first studies of organometallic sonochemistry⁶⁻⁸, sonocatalysis^{6,7}, the sonochemistry of non-aqueous solutions⁹⁻¹¹ and the sonochemistry of transition metals¹². Recently we have been able to determine the nature of the sonochemical reaction site generated during acoustic cavitation and to measure its effective temperature¹³⁻¹⁶.

The synthesis of new materials with unusual and controllable optical, electronic and catalytic properties continues to attract considerable interest. To this end, we have recently begun to examine the chemical effects of ultrasound on inorganic solids. The two reactions which initiated the present studies are the extraordinary improvements which ultrasonic irradiation causes in the intercalation of various guest molecules into layered inorganic solids¹⁷ and the heterogeneous catalysis of hydrogenation by transition metal powders¹⁸. The kinetics

of intercalation are generally slow and syntheses usually require high temperature and very long time periods¹⁹⁻²². We have found that high intensity ultrasound *dramatically* increases the rates of intercalation into such solids by solutions of guest compounds¹⁷. Along different lines, the hydrogenation of unsaturated hydrocarbons usually requires noble metals (Pt, Pd, etc.) or specially activated metal powders. High intensity ultrasound can generate such activation of Ni powders even at room temperature and pressure¹⁸. Understanding the physical and molecular mechanisms of such heterogeneous sonochemistry is a major goal of our efforts.

Experimental details

In a typical experiment a thermostated glass vessel containing 1g of the inorganic solid and 15 ml of solvent under an Ar or N₂ atmosphere was ultrasonically irradiated for 2 h. The sound field generated from a direct immersion Ti horn (Heat Systems-Ultrasonics W375 Sonicator) is a roughly collimated beam at 20 kHz with an acoustic intensity of $\approx 20 \text{ W cm}^{-2}$, as described in detail elsewhere⁷. Aliquots of the solids were removed at appropriate intervals and electron micrographs taken with a Jeol JSM-35C scanning electron microscope with 25-35 keV accelerating voltage. Surface area measurements were made by N₂ adsorption using the single point BET technique with a Quantachrome Monosorb surface area analyser. TaS_2 and MoO_3 were prepared in the usual fashion²¹ and sieved to give a 60-90 μm particle size distribution. Ni powder (3-5 μm) was used as received from EM Science, Cherry Hill, New Jersey, USA.

Results and discussion

Most of the chemical effects of ultrasound result from acoustic cavitation: in cavitation near surfaces, the implosive collapse is not spherically symmetric and a localized microjet of liquid is driven into the surface at

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extremely high velocities²³. This causes surface damage, removes passivating coatings, creates surface defects and

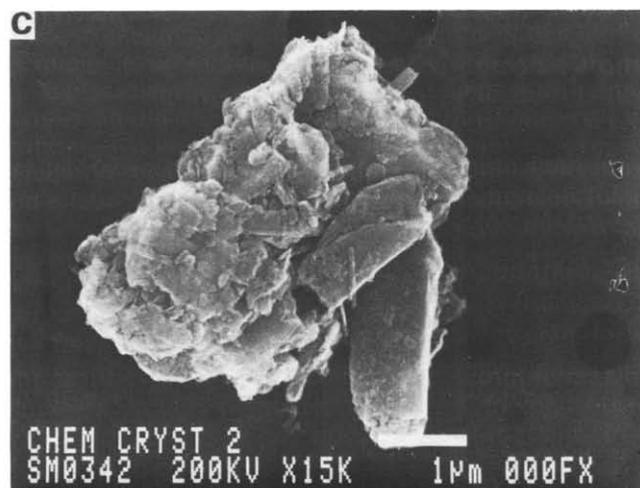
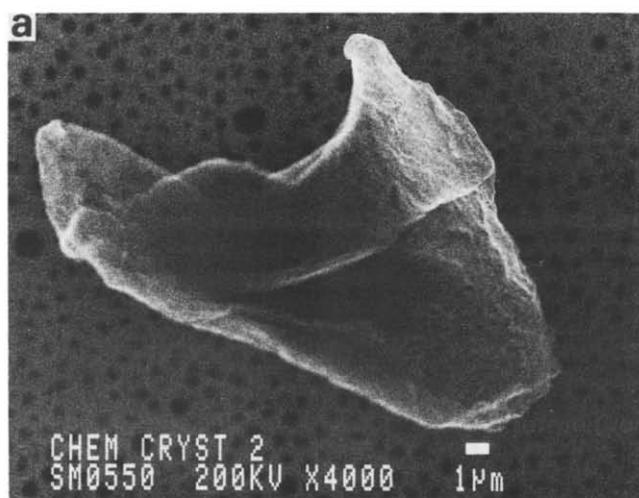


Figure 1 Scanning electron micrographs of TaS₂: (a) before ultrasonic irradiation; (b) after 10 min of irradiation; and (c) after 120 min of irradiation. Note changes in scale

generates local heating. In addition, the shock waves so produced will also cause fracturing of friable solids. Another phenomenon important to such conditions is acoustic streaming, a microscopic turbulence which enhances liquid-surface mass transport.

The effects of cavitation on extended metal surfaces have been extensively investigated for many years²⁴. In fact, the use of ultrasound to produce vibratory cavitation at surfaces is a standard accelerated test for assessing susceptibility to flow erosion²⁵. Crystalline metal faces generally show initial microscopic pitting of the surface and plastic deformation, followed at longer times by grain boundary delineation and, finally, large scale cratering. Secondary corrosive loss of surface material may also occur, depending upon the liquid medium²⁶.

Surprisingly, the effects of ultrasound on surface morphology of powdered inorganic solids has not been examined in detail. In order to help determine the origin of our observed sonochemical rate enhancements, we have applied optical microscopy, scanning electron microscopy and surface area determinations of several inorganic solids subjected to ultrasonic irradiation.

After sonication, we observe a significant decrease in the particle diameters of moderately sized solids. Starting with powders with 60–90 µm diameters, the particle size is reduced to 5–10 µm after a few minutes of ultrasonic irradiation. Upon further sonication, particle diameter does *not* change, for either transition metal powders or layered metal chalcogens. This increases substantially the surface area of large particle samples after longer irradiation. For example, the surface area of TaS₂ with initial particle sizes of 60–90 µm goes from < 1 to 11 m² g⁻¹ after 15 min of sonication, and increases little with further irradiation. In contrast, the surface area of Ni powder with initial particle sizes of 3–5 µm only changes from 0.48 to 0.69 m² g⁻¹ after 15 min of sonication, and even after 2 h only increases to 1.00 m² g⁻¹. This lower limit of particle size diminution is understandable for two reasons. First, the cavities formed upon ultrasonic irradiation are tens to hundreds of microns in diameter and can form jets only at surfaces with at least those dimensions²⁰; thus, small particles will not be subjected to microjet impact. Second, the effect of shockwave accelerations over the whole of the particle decreases with decreasing particle size; thus, small particles will not undergo further fragmentation.

Upon closer examination of the electron micrographs of these samples, as shown in *Figures 1, 2 and 3*, quite unusual changes in the surface morphology continue to occur after the initial ultrasonic fragmentation. For both TaS₂ and MoO₃, extended ultrasonic irradiation creates a badly eroded, pock-marked surface. In contrast, Ni powders show a smoothing, almost a melting, of the initially crystalline surface. We believe this is due to the difference in ductility of these two types of solids: layered inorganic oxides and sulphides are relatively brittle materials, while transition metals are quite malleable.

In addition, we find in both classes of solids a substantial increase in the aggregation of small particles after sonication. The aggregates so formed are quite strong and not fully disrupted even after brief dispersion in an ultrasonic cleaning bath (the usual method of dispersion for electron microscopy). This is not due to increased surface roughening, since the nickel samples show the same tendency. We believe that the interparticle collisions which ultrasonic turbulent flow induces are largely responsible for the effects of ultrasound on powders. Such collisions also probably influence the changes in surface morphology, as well as the observed aggregation.

Conclusions

Ultrasound dramatically increases the rate of intercalation of a variety of organic, organometallic and inorganic compounds into layered inorganic solids; it also enhances the reactivity of a variety of transition

metals both as reagents and as heterogeneous catalysts. High intensity ultrasonic sources are inexpensive, readily available from commercial sources and extremely reliable. Their ease of application on the scale of up to hundreds of grams ensures the continued and eventually routine use of ultrasound as a standard laboratory

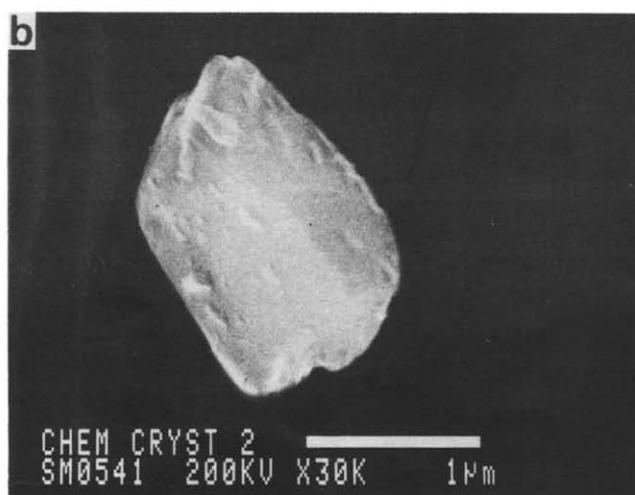
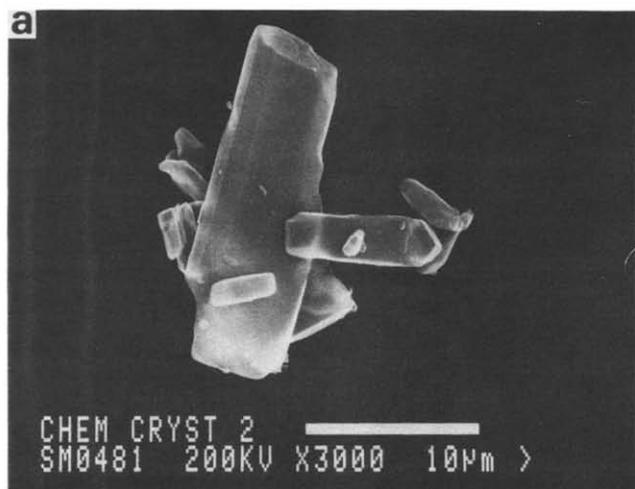


Figure 2 Scanning electron micrographs of MoO_3 : (a) before ultrasonic irradiation; (b) after 30 min of irradiation; and (c) after 120 min of irradiation. Note changes in scale.

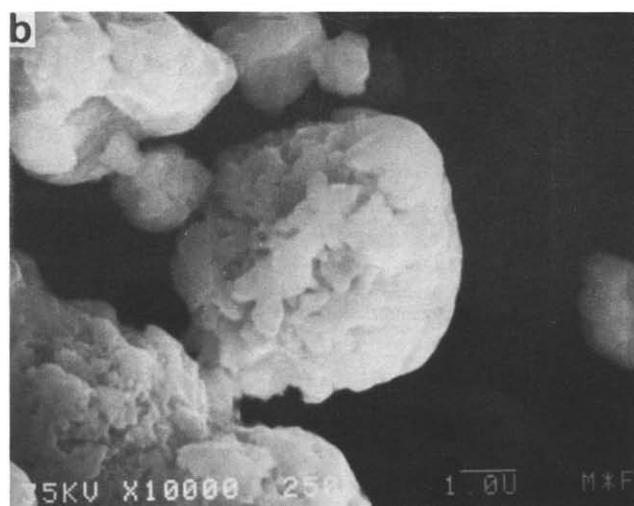
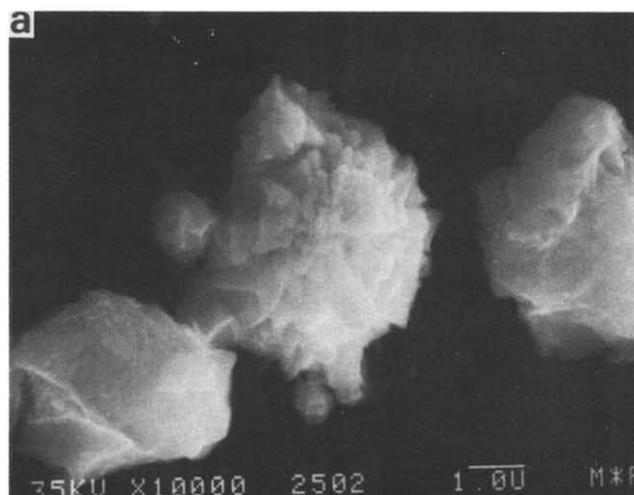


Figure 3 Scanning electron micrographs of Ni: (a) before ultrasonic irradiation; (b) after 15 min of irradiation; and (c) after 120 min of irradiation

technique.

The effects of ultrasound on inorganic solids is strikingly revealed by scanning electron microscopy. In all cases, high intensity ultrasound rapidly reduces particle size to $\approx 5 \mu\text{m}$, with no further reduction even after lengthy irradiation. With brittle solids, such as TaS_2 and MoO_3 , longer irradiation produces substantial surface damage with large scale pitting and erosion. With malleable microcrystalline solids, such as Ni, ultrasonic exposure causes surface smoothing. In both cases, significant aggregation of particles occurs. The effects of interparticle collision, as well as microjet and shockwave impact, are probably important in causing these changes in surface morphology.

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