THE EFFECTS OF ULTRASOUND ON NICKEL AND COPPER POWDERS

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The use of high-intensity ultrasound to enhance the reactivity of metal surfaces has become a routine synthetic technique. In spite of this, the origin of rate enhancements in both stoichiometric and catalytic reactions remains unexplored. To this end, we have examined the effects of ultrasound on metal powders in terms of their particle and surface morphology, their atomic composition, and their reactivity. Specifically, we have discovered that ultrasonic irradiation of Ni and Cu powders leads to dramatic changes in morphology: individual surfaces are smoothed and particles are consolidated into extended aggregates. Surface composition was probed by Auger electron spectroscopy depth profiles, which revealed that ultrasonic irradiation removed the surface oxide coating, but also produced (especially for Cu) a deposition of surface carbon. The effects on reactivity can be substantial: ultrasonic irradiation enhances the activity of Ni powder as a hydrogenation catalyst by $> 10^5$ and significantly increases the reactivity of Cu powder as a stoichiometric reagent. We believe that these effects are due to interparticle collisions driven by the turbulent flow created by the ultrasonic field. It is likely that the origin of the enhanced chemical reactivity comes from the removal of the surface oxide passivating layer which these collisions induce.

1. Introduction

The use of high-intensity ultrasound to enhance the reactivity of metal surfaces has become a routine synthetic technique [1–3]. In spite of a large number of recent descriptive reports [4–16], the origin of heterogeneous sonochemical rate enhancements in both stoichiometric and catalytic reactions remains largely unexplored. In comparison, a detailed understanding of the mechanism of *homogeneous* sonochemistry has recently been developed [17–20]. Our knowledge about the reaction conditions created by ultrasonic irradiation of liquid–solid interfaces, however, is much more limited [1,12].

When a liquid–solid interface is subjected to high-intensity ultrasound, acoustic cavitation (i.e. the formation, growth, and implosive collapse of bubbles in a liquid [1–2]) near the surface induces markedly asymmetric bubble collapse, which generates a high-speed jet of liquid directed at the surface [21]. The impingement of this jet and related shock waves can create a localized erosion (which produces highly reactive surfaces) [21,22], improve

mass transport [1], and cause particle fragmentation (which increases the surface area of friable solids [23]).

In order to more fully understand the origins of heterogeneous sonochemistry and sonocatalysis, we have examined the effects of ultrasound on metal powders in terms of (1) their particle and surface morphology, (2) their atomic composition, and (3) their reactivity. In this paper, we report that ultrasonic irradiation of Ni and Cu powders leads to substantial changes in all three areas. The effects on reactivity are especially dramatic: ultrasonic irradiation enhances the activity of Ni powder as a hydrogenation catalyst by $> 10^5$ and significantly increases the reactivity of Cu powders as a stoichiometric reagent. We believe that these effects are due to interparticle collisions driven by the turbulent flow created by the ultrasonic field. The likely origin of the enhanced chemical reactivity comes from the removal of the surface oxide passivating layer which these collisions induce.

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2. Experimental

All sonications were performed with a Heat Systems–Ultrasonics W375 cell disruptor with a titanium immersion horn at acoustic intensities of ≈ 50 W/cm^2 at 20 kHz, as described in detail elsewhere [17,24]. Ultrasonic cleaning baths are often used in synthetic heterogeneous sonochemistry. We find, however, that the low acoustic intensities (< 10 W/cm^2) available with cleaning baths are only marginally useful and that reaction vessel positioning is critical to their reproducible use. Irradiation in a low-intensity ultrasonic cleaning bath does give hydrogenation, for example, but at greatly reduced rates compared to the high-intensity immersion horn [12].

Inert atmosphere work used either standard Schlenk double-manifold techniques or an inert atmosphere glove box. After freeze–vacuum–thaw degassing of solvents it is important to thoroughly saturate with an inert gas by bubbling (preferably with argon, which increases the effectioness of cavitational collapse due to its high C_p/C_v ratio). A Vacuum Atmospheres inert atmosphere glove box was equipped with an O_2 monitor and maintained at less than 1 ppm O_2.

All solvents for the nickel hydrogenation reactions were Gold Label purity from Aldrich Chemical Co. and used as received. All alkenes used in the reactions were obtained from commercial sources and used as received; their purity was determined to be $> 99\%$ by GC. Decane used for the sonolysis of the copper powders was distilled over sodium under nitrogen, then freeze–vacuum–thaw degassed three cycles. Ni powder (200 mesh, EM Science, Cherry Hill, NJ 08034) and Cu powder (10 μm, Alfa Products, Morton Thiokol, Inc.) came packed under argon and were stored under rigorously inert atmosphere conditions.

In a typical sonication, 4 g of metal powder were loaded into a glass sonication cell with ≈ 20 ml of decane in an inert atmosphere glove box. The horn and cell assembly was then sealed, removed from the glove box, sparged with argon for 40 min prior to sonication, and reconnected to the power supply. Sonication of the metal powder was performed at a cell temperature of 15°C for 30 or 60 min. The cell and horn assembly was then returned to the inert atmosphere box. The powder was filtered, washed with pentane, and dried under vacuum at 90°C for 16–20 h. Alternatively, Schlenk air-free techniques were used and transfers made by cannula under a positive pressure of Ar.

Hydrogenation reactions were carried out at 273 K under 1 atm of H_2. In a typical reaction, 1 g of Ni powder was added to a 0.5 M solution of alkene in octane. Products were analyzed by GC-MS and capillary GC on a 30 m DB-1 column (J. & W. Scientific) with heptane as internal standard.

Surface characterizations were obtained at the Center for Microanalysis of Materials, University of Illinois. Auger electron spectra obtained on a Physical Electronics 595 multiprobe spectrometer with Xe$^+$ sputtering at 1 keV and 18 μA/cm^2. Scanning electron micrographs were obtained on both Jeol 35C and Hitachi S-800 electron microscopes. Surface area measurements were done using a single point BET apparatus, with Ar adsorption.

3. Results and discussion

3.1. The effect of ultrasound on particle morphology

The enhancement in rates of heterogeneous reactions upon irradiation with ultrasound is often due to increased surface area of friable solids (either reagents or supported catalysts) caused by shock fragmentation [23]. With large, thin-flaked powders of Cu, similar fracture has been observed [10]. With small diameter (< 20 μm), spherical metal powders, however, such increases in surface area are less likely. This, in fact, proves to be the case: ultrasonic irradiation of ≈ 5 μm Ni or Cu powders does not significantly decrease the particle size, even after several hours of irradiation. BET surface area measurements on Ni powders irradiated for increasing time show only a modest initial increase, followed by a *decrease* in total surface area: 0 min, 0.48 m^2/g; 15 min, 0.69 m^2/g; 120 min, 1.00 m^2/g; 240 min, 0.57 m^2/g with errors of $\pm 5\%$.

In order to explain the initial increase and subsequent decrease in surface area, scanning electron micrographs were obtained on Ni powders of both 5 and 160 μm diameters irradiated for 0, 15, and 120 min, as shown in figs. 1 and 2. As the malleable particles are irradiated, profound changes in particle ag-
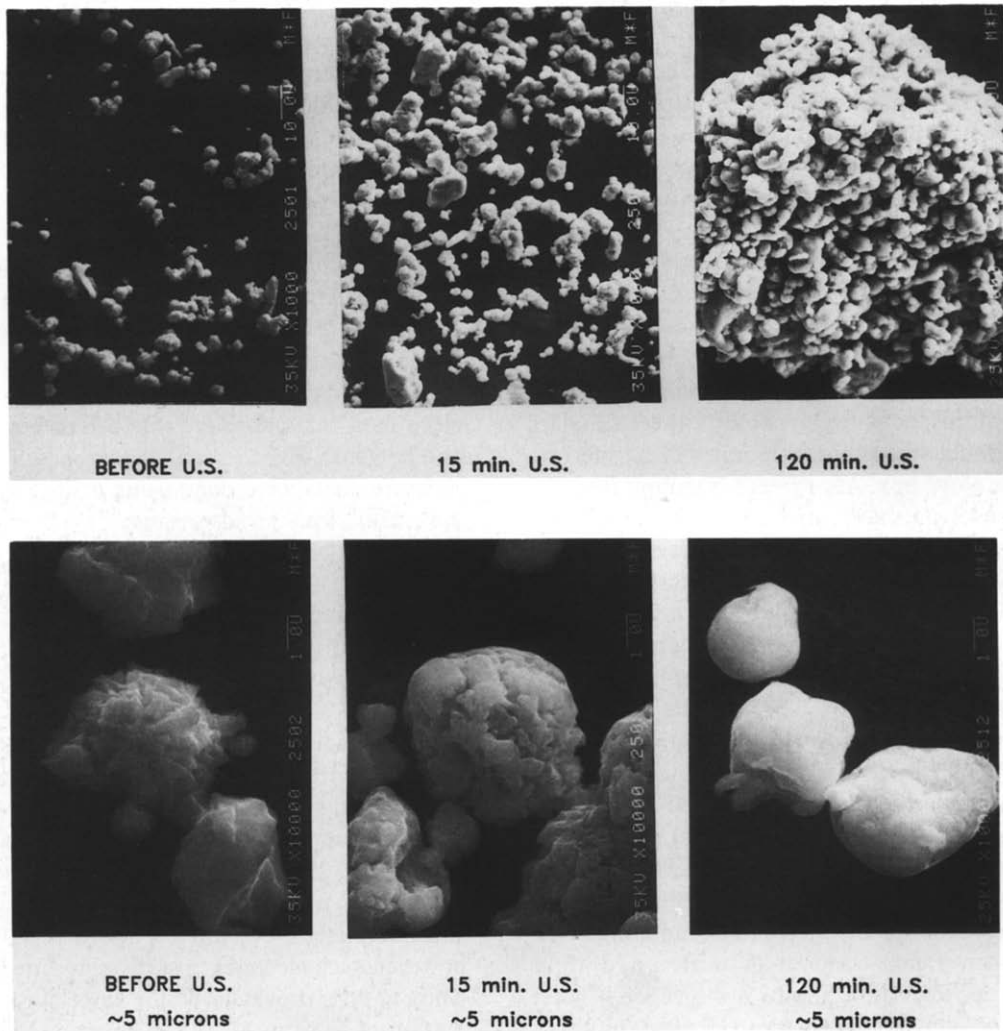
Fig. 1. The effect of ultrasonic irradiation on particle aggregation and surface morphology of fine Ni powder. Note the magnitude of the upper scanning electron micrograph is tenfold less than in the lower.

gregation and morphology are observed. The surface of our Ni powder is initially highly crystalline, but upon sonication the surface is smoothed quite rapidly. For the small particle Ni, the extent of aggregation also increases dramatically.

This same general type of behavior is also seen for the 10 μm copper powder, as shown in fig. 3. In contrast to the Ni sample, the Cu powder initially is not highly crystalline. Nonetheless, the surface texture is noticeably smoothed after 60 min sonication, as can

be seen at the higher magnifications. The Cu powder is initially somewhat aggregated, although individual particles are clearly defined. After ultrasonic irradiation, however, the level of aggregation is much greater, and in fact the full consolidation of small particles into large (> 30 μm), almost featureless, masses is quite dramatic.

Both the surface smoothing and the increased agglomeration and consolidation are consistent with the effects expected from interparticle collisions dri-
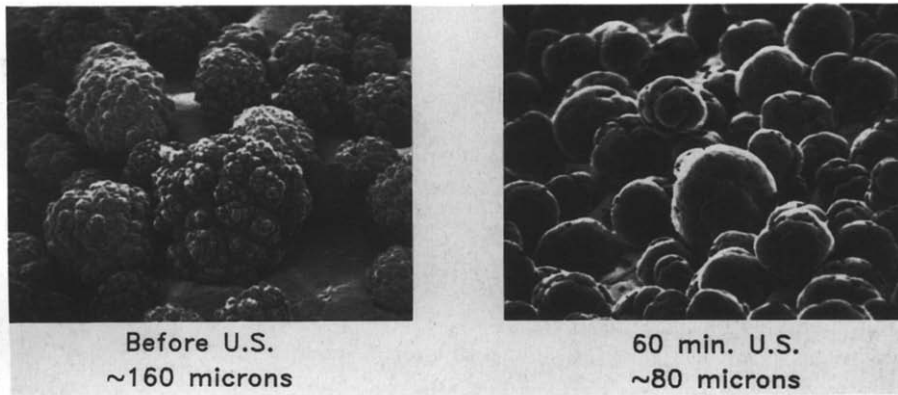
Fig. 2. The effect of ultrasonic irradiation on surface morphology of coarse Ni powder. Before irradiation, the average particle size is ~160 μm; after ~80 μm.
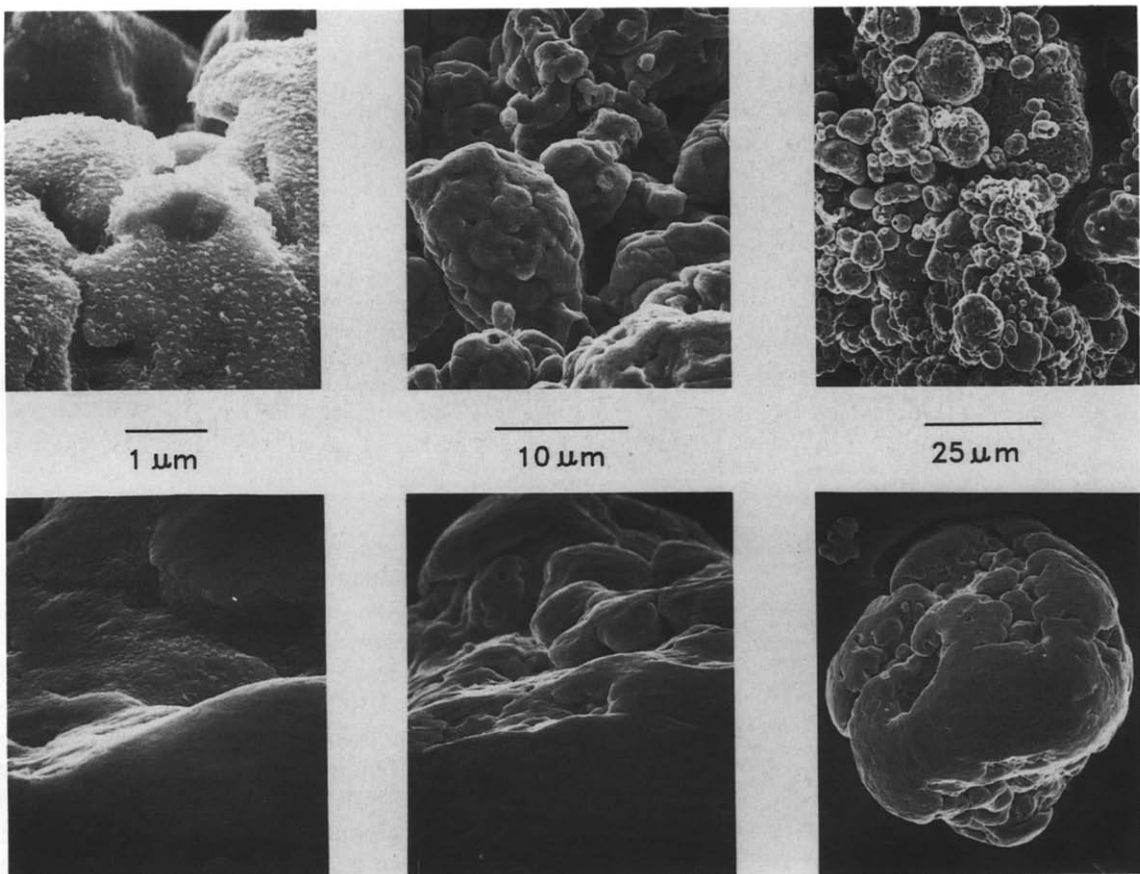

Fig. 3. The effect of ultrasonic irradiation on particle aggregation and surface morphology of 10 μm Cu powder. The upper microphotographs are *before* ultrasonic irradiation; the lower ones after 1h irradiation. Note the ratio of magnifications of the scanning electron micrographs in left, middle, and right pairs are 17 to 3 to 1.

ven by the turbulence and shock waves created by the ultrasonic field. When particles collide in a glancing fashion, smoothing of the surface occurs; when particles collide head-on, agglomeration occurs.

3.2. The effect of ultrasound on surface composition

The changes in surface morphology are associated with dramatic changes in surface composition of both Ni and Cu powders. Auger electron spectra (AES) depth profiles were obtained on Ni samples before and after sonication, as shown in fig. 4. Initially, a thick oxide coat is found (with a surface Ni/O ratio of 1.0) extending ≈ 250 Å into the particle. After 1 h ultrasonic irradiation in octane, the oxide is *much* thinner (< 50 Å, with a surface Ni/O ratio of 2.0). In fact, most of the oxide layer in the irradiated sample is due to its air exposure during sample transfer; the oxide coating is fully re-established after ≈ 15 min air exposure. There is, in addition, a small amount of carbon ($< 10\%$) deposited on the Ni surface upon irradiation with ultrasound (which is not present in samples treated identically except for irradiation).

Changes in surface composition of irradiated Cu powders (fig. 5) are similar to those found with Ni.
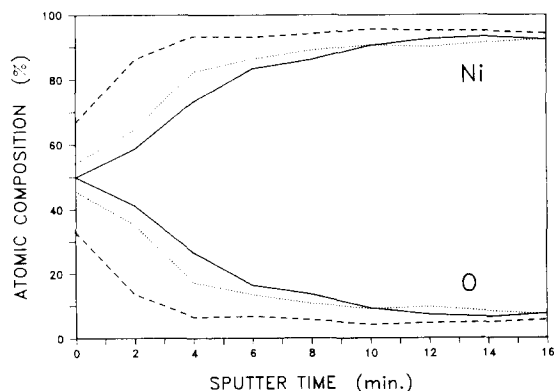
Fig. 4. Surface composition depth profiles of Ni powder, as derived from Auger electron spectra obtained on a Physical Electronics 595 multiprobe spectrometer with Xe$^+$ sputtering at 1 keV and 18 μA/cm^2. Sputtering times correspond to an erosion rate of ≈ 25 Å/min. (————) Ni sample before ultrasound. (---) Ni sample after 1 h ultrasonic irradiation. The sample was exposed to air for 8 min during preparation and loading. Small amounts of surface carbon ($< 10\%$) were also observed after ultrasonic irradiation. ($\cdots$) Ni sample after 1 h ultrasonic irradiation, followed by intentional exposure to air for 13 min.
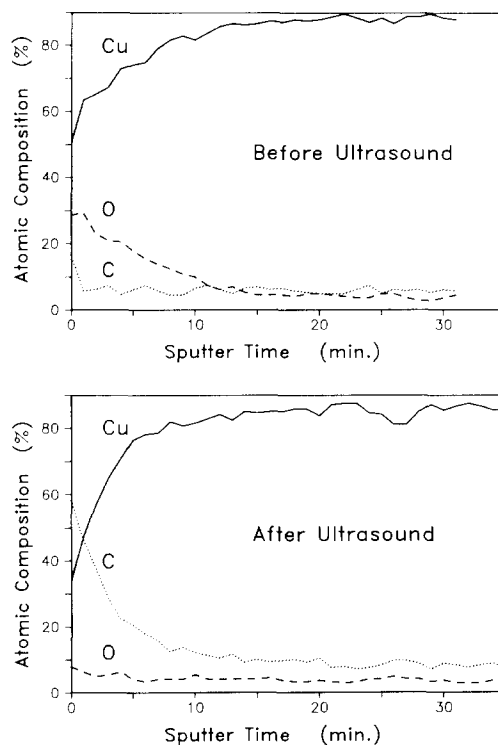
Fig. 5. Surface composition depth profiles of 10 μm Cu powder, as derived from Auger electron spectra obtained on a Physical Electronics 595 multiprobe spectrometer with Xe$^+$ sputtering at 1 keV and 18 μA/cm^2. Sputtering times correspond to an erosion rate of ≈ 25 Å/min. Samples were kept under N$_2$ at all times and were loaded into the spectrometer with the use of an attached glove bag. The upper depth profile is of a Cu sample before ultrasound. The lower depth profile is of a Cu sample after 1 h ultrasonic irradiation.

For Cu powders with small particle sizes (average individual diameter ≈ 10 μm), the sample was received under Ar and was handled under rigorously inert atmosphere conditions. In spite of this, before sonication there is a partial oxide coating with a thickness of ≈ 300 Å, as determined by AES depth profiles. After irradiation, this oxide coating is completely removed. It is replaced by a thin (≈ 100 Å), but heavy ($> 60\%$ atomic composition) surface deposition of carbon. This carbon is *not* an artifact of the reaction workup or transfer: control reactions in which all manipulations are identical, but without the irradiation with ultrasound, do not leave any residual carbon. Ultrasonic irradiation of larger par-

ticle Cu powders (average initial particle diameter ≈ 160 μm) produces a very similar surface deposition of carbon.

The origin of the carbon and its effect on the surface reactivity are not known at this time, but are under active investigation. We have previously demonstrated [20] the sonochemical cracking of alkanes under acoustic cavitation and have also observed [18] sonoluminescence from excited-state C_2 produced during irradiation of alkanes. Regardless of the detailed mechanism by which the carbon surface deposition occurs, it is clear that even low-reactivity liquids are not inert under sonochemical conditions.

3.3. The effect of ultrasound on chemical reactivity

The effects of ultrasound on heterogeneous catalysis has had some exploration [5,6,12–15,25], but the results have generally shown quite modest rate enhancements . There have been some recent reports, however, of large rate enhancements with supported metal catalysts [6,14]; the origin of such effects have not been delineated. We decided to investigate the effects of ultrasound on the catalytic activity of a well-defined metal powder and to correlate that activity with a thorough characterization of the surface before and after ultrasonic irradiation.

Simple Ni powder is an extremely *inactive* catalyst for hydrogenation of alkenes. Even after two weeks, no alkanes are detected with rapid stirring under 1 atm H_2 at 273 K (i.e. the hydrogenation rate is less than 10 nM/min). In comparison, if the nickel is first irradiated with ultrasound under the same conditions, 1-nonene is hydrogenated at rates of 1–2 mM/min, as shown in fig. 6. Ultrasonic pretreatment of Ni powder for ≈ 1 h gives optimal activity, which decreases with longer irradiation. The increased aggregation which is observed after long irradiation, as discussed earlier, probably accounts for the small diminution in activity observed after lengthy sonication. In no case were the irradiated powders found to be pyrophoric upon air exposure.

The hydrogenation activity is quite general and shows relatively little dependence on choice of alkene (i.e. similar rates are observed with 1-nonene, 1-decene, cis-5-decene, trans-5-decene, cyclooctene, and cyclohexene), as shown in fig. 7. *No* reduction of ketones or aldehydes was observed, unlike reduc-
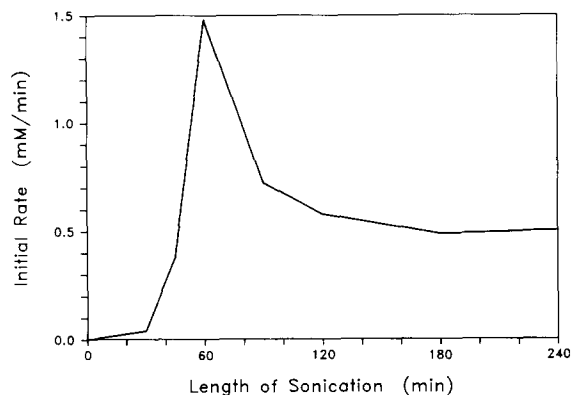

Fig. 6. Initial rate of hydrogenation of 1-nonene versus length of pretreatment of Ni powder by ultrasonic irradiation in octane at 273 K with an acoustic intensity of ≈ 50 W/cm². Reactions run at 273 K and 1 atm H_2 in octane.

tions with Raney Ni [26–28].

Because the intensity of cavitational collapse in homogeneous liquids is strongly dependent on the total vapor pressure [18–20], we examined the effect of this parameter on heterogeneous sonocatalysis. Significant increases in solvent vapor pressure did diminish observed sonocatalytic rates of alkene hydrogenation by Ni. The magnitude of the effect, however, is quite modest, as shown in fig. 8. This result indicates that for heterogeneous sonocatalysis, unlike homogeneous sonochemistry, the intensity of cavitational collapse is *not* rate determining. The factors which are responsible for heterogeneous son-
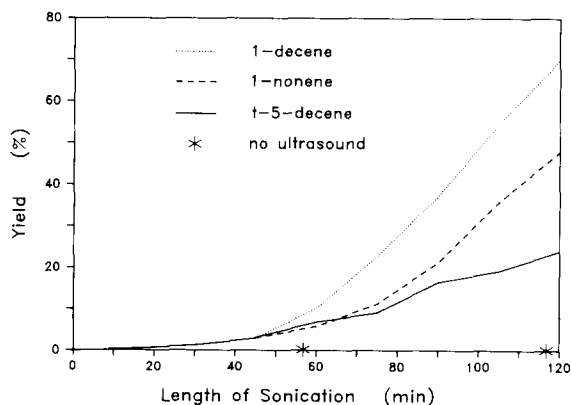

Fig. 7. Hydrogenation of 1-alkenes by Ni powder versus length of ultrasonic irradiation. Reactions run at 273 K, 1 atm H_2 in octane with an acoustic intensity of ≈ 50 W/cm².
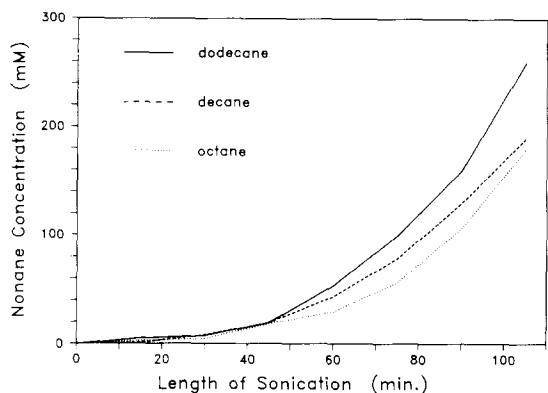
Fig. 8. Hydrogenation of 1-nonene by Ni powder versus length of ultrasonic irradiation as a function of solvent. The vapor pressures for these solvents under these conditions are 0.009 Torr for dodecane. 0.17 Torr for decane and 2.9 Torr for octane [30]. Reactions run at 273 K, 1 atm H_2 in octane with an acoustic intensity of ≈ 50 W/cm^2.

ochemistry (e.g. microjet formation, cavitational shock waves, and interparticle collisions) should not be affected by the content of the collapsing bubble to the same extent as the localized hot-spot which is responsible for homogeneous sonochemistry [18–20].

Other methods for creating active Ni catalysts exist [26–29], although each has its drawbacks. The thermal hydrogenation rates at 1 atm H_2 and 273 K with high surface area Ni sponge (Raney Ni [26], Aldrich Chemicals, grade W-2) are comparable to those obtained with ultrasonically activated Ni powder. In contrast to Raney Ni, however, our activated Ni powder is more selective (C–O double bonds are untouched), much easier to produce, and much simpler to handle (non-pyrophoric). Activation of Ni powders by H_2 at 150°C and 10 atm will also generate reactive catalysts [27], which rapidly lose activity upon exposure to O_2. Highly dispersed catalysts prepared in a vapor metal reactor are also quite active, but requires a substantial apparatus [29].

It is likely that the origin of our observed sonocatalytic activity comes from the removal (primarily through interparticle collisions) of the surface oxide layer normally found on Ni powders. A clean Ni surface is an active catalyst [26–29]; nickel powder with its usual surface oxide coating is not.

The effects of ultrasound on the reactivity of Cu metal as a stoichiometric reagent have been documented in the literature in two cases: the Ullman

coupling [10] (where $C_6H_4(NO_2)$ is o-nitrophenyl)

$$2IC_6H_4(NO_2) + 2Cu$$
$$\rightarrow (NO_2)H_4C_6-C_6H_4(NO_2) + 2 \; CuI$$

and the reaction of Cu with salicylalaniline to form uncharacterized copper complexes [11]. In the former case, substantial rate enhancements (as large as 64-fold) are reported. This synthetically important rate increase was attributed to multiple possible effects, including particle size reduction and surface cleaning, and required prior irradiation of the Cu in order to achieve optimal reaction conditions. These results are consistent with our present data, which shows a reduction of the passivating copper oxide coating after sonication. Whether or not the surface deposition of carbon is important to the enhanced reactivity remains an open question. Further work is underway to clarify this matter [31].

4. Conclusions

High-intensity ultrasound has found a recent niche in synthetic chemistry as a facile means to increase the reactivity of heterogeneous reagents [1–3]. In order to better understand the origin of such rate enhancements, we have begun a systematic examination of the effects of ultrasound on metal powder surface morphology, atomic composition, and reactivity. We have discovered that ultrasonic irradiation of metal powders leads to dramatic changes in morphology: individual surfaces are smoothed and particles are consolidated into extended aggregates. AES depth profiles revealed that ultrasonic irradiation removes surface oxide coating, but also produces (especially for Cu) a deposition of surface carbon. Ultrasonic irradiation dramatically enhances the activity of unsupported metal catalysts by $> 10^5$ in the case of alkene hydrogenation with Ni and significantly increases the reactivity of Cu powder as a stoichiometric reagent. The enhanced chemical reactivity comes principally from the removal of the surface oxide passivating layer. The surface carbon deposit may also influence the chemical reactivity, but this has not yet been established.

Homogeneous sonochemistry is strongly affected by the localized conditions created during cavitational collapse; heterogeneous sonochemistry ap-

pears to be less susceptible to such influences. Large changes in vapor pressure, for example, do not change rates of sonocatalytic hydrogenation significantly.

The effects of ultrasound on particle morphology, surface composition, and reactivity are all consistent with the importance of interparticle collisions driven by the turbulent flow created by the ultrasonic field. If particles collide at a glancing angle, one would expect the smoothing of surface features and the removal of surface oxide coatings, as observed. If particles collide directly, one expect agglomeration and consolidation, as observed.

Acknowledgement

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