

## The Enhancement of Intercalation Reactions by Ultrasound

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Ultrasonic irradiation increases the rates of intercalation (by as much as 200-fold) of organic and organometallic compounds into various layered inorganic oxide and sulphide host solids.

The intercalation of organic or inorganic molecules into layered inorganic solid hosts is slow. Syntheses are often lengthy (weeks) and require elevated temperatures.<sup>1</sup> In studying the synthesis and properties of intercalation compounds with organometallic guest molecules, we have found that the use of ultrasound significantly enhances the rates of intercalation reactions, as described herein.

In a typical experiment, a 50 cm<sup>3</sup> thermostatted glass vessel containing 0.5–1.0 g of the host solid and 15 cm<sup>3</sup> of a toluene solution of the guest molecule in a 2 : 1 molar excess under an N<sub>2</sub> atmosphere was ultrasonically irradiated by direct immersion of a Ti horn with an acoustic intensity of *ca.* 20 W/cm<sup>3</sup> (Heat Systems-Ultrasonics W375 Sonicator), as described in detail elsewhere.<sup>2</sup> We have examined the effect of ultrasound

on several representative and chemically varied systems; Table 1 shows a comparison of the rates of intercalation in the presence and absence of ultrasonic irradiation. The reproducibility of the data has been confirmed for each example.

Most of the chemical effects of ultrasound<sup>3</sup> result from acoustic cavitation, which is the creation, expansion, and implosive collapse of bubbles in ultrasonically irradiated liquids.<sup>4</sup> In cavitation near surfaces, the implosive collapse is not spherically symmetric and a localized 'micro-jet' of liquid is driven into the surface at extremely high velocities.<sup>5</sup> This micro-jet can cause surface damage, remove passivating

**Table 1.** Comparison of thermal and sonichemical conditions for the synthesis of (guest)<sub>x</sub>host.

(guest) <sub>x</sub> host	Conditions Time, temp./°C	
	Thermal	Sonichemical
(Cp <sub>2</sub> Co) <sub>0.25</sub> ZrS <sub>2</sub> <sup>a</sup>	50 h, 20	2 h, 20
(RNH <sub>2</sub> ) <sub>x</sub> TaS <sub>2</sub> <sup>b</sup>	50 h, 20	15 min, 20
(pyridine)MoO <sub>3</sub>	30 days, 180	3 days, 80

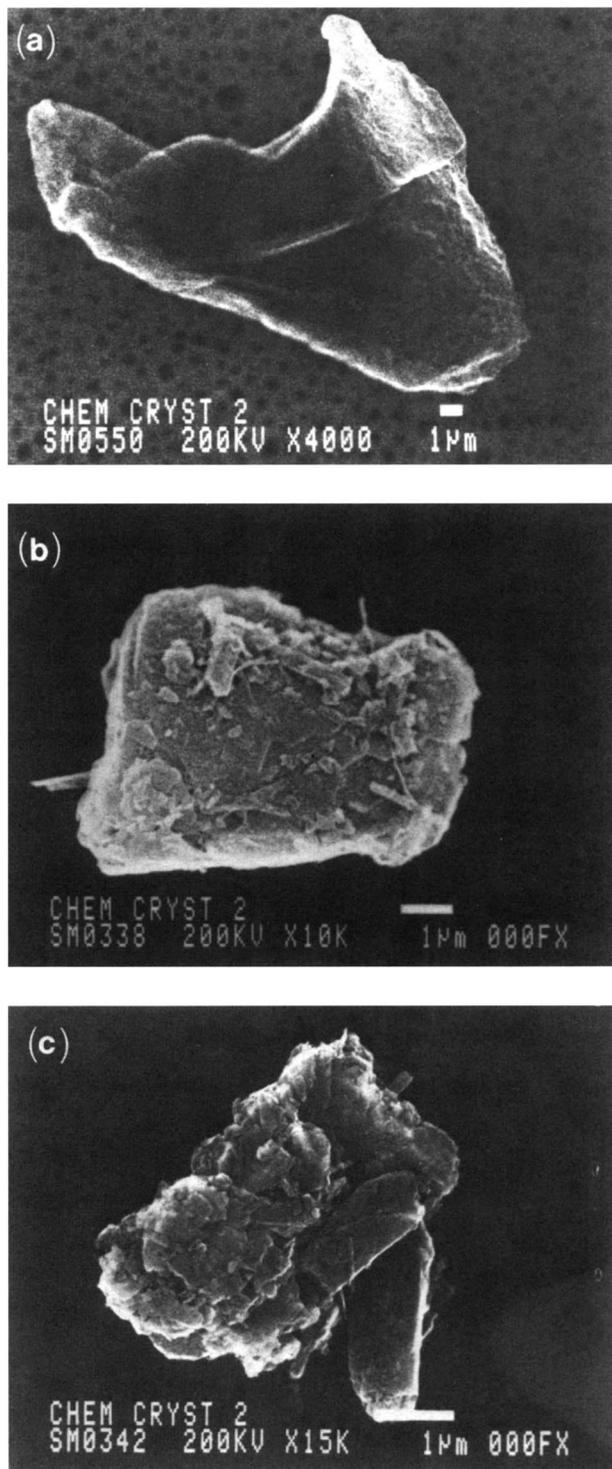
<sup>a</sup> Cp = cyclopentadienyl. <sup>b</sup> R = n-butyl, *x* = 0.46; R = n-hexyl, *x* = 0.4.

**Table 2.** Ultrasonic synthesis of (n-hexylamine)<sub>x</sub>TaS<sub>2</sub>.

Entry	Sonication time/min	Solvent <sup>a</sup>	Surface area/ m <sup>2</sup> /g <sup>b</sup>	<i>x</i> <sup>c</sup>
a	0	Toluene	0.3	<0.01
b	15	Toluene	2.4	0.40
c	45	Toluene	7.1	0.41
d	180	Toluene	8.0	0.54
e	180	C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>	—	0.49

<sup>a</sup> Sonication in toluene was followed by stirring for 180 min in neat n-hexylamine. Toluene does not react with TaS<sub>2</sub>. <sup>b</sup> Surface area measured by N<sub>2</sub> absorption using a single point B.E.T. technique.

<sup>c</sup> Determined by thermogravimetric analysis (TGA) measurements with an error of ±0.02; intercalation confirmed by X-ray powder patterns.



**Figure 1.** The effect of ultrasonic irradiation on particle morphology: TaS<sub>2</sub>. (a) Before u.s., ~60 µm; (b) 10 min u.s., ~7 µm; (c) 120 min u.s., ~5 µm.

coatings, create surface defects, and generate local heating.<sup>6</sup> In addition, the shock waves so produced can fracture friable solids until the particle sizes are roughly the same size as the collapsing jet (at 20 kHz this is ca. 10 µm).<sup>7</sup> Another important

phenomenon under these conditions is acoustic streaming, a microscopic turbulence which enhances liquid–surface mass transport.

Our experiments show that ultrasonic irradiation does not increase intercalation rates through improvement of mass transport. If host solid suspensions are irradiated in an inert solvent and subsequently treated with the guest, the rate of intercalation is significantly enhanced without any further sonication (see Table 2, d and e). Thus sonication causes an irreversible change in the host which is responsible for the increased intercalation rates.

We have used electron microscopy to help determine the origin of our observed rate enhancements. We find that sonication causes a significant decrease in the particle size of the host solid, regardless of the presence of a guest compound.<sup>7</sup> 1T TaS<sub>2</sub> of initial particle size 60–90 µm is reduced to 5 µm after 15 minutes of sonication. Upon further sonication the particle size does not significantly change, but the extent of surface damage continues to increase substantially, as shown in Figure 1. Brunauer–Emmett–Teller (B.E.T.) surface area measurements are consistent with the results of electron microscopy. The surface area increases significantly during the first 45 minutes of sonication, but increases only slightly on further irradiation (see Table 2).

The intercalation of n-hexylamine into 1T TaS<sub>2</sub> was studied in detail in order to determine whether it was possible to differentiate between the initial decrease in particle size or the subsequent surface damage as the cause of the rate enhancements of intercalation. In these experiments 0.3 g portions of TaS<sub>2</sub> were ultrasonically irradiated in toluene slurries at 20 °C for varying lengths of time and then stirred in neat n-hexylamine for 3 h at 20 °C. The data are presented in Table 2. It appears that the initial particle size diminution is more important than surface damage, since the intercalation rate is increased the most significantly with only 15 minutes of sonication.

In conclusion, ultrasound substantially enhances the rate of intercalation of a variety of organic and organometallic compounds into layered inorganic solids. The mechanism does not involve mass transport, but rather the ability to generate very small particle sizes by ultrasonic irradiation.

We thank the S.E.R.C. (to M. E. T.) and the National Science Foundation (CHE 8319929) (to K. S. S.) for their support.

Received, 19th January 1987; Com. 062

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