Materials Chemistry
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Module - 1
Lecture - 4
Preparative Routes Un conventional Sonochemistry Technique – II

We are in module 1, and one of the lectures that I really decide to give you is on the use of ultrasound in materials synthesis, which is popularly called as sonochemistry. And we can always say sonochemistry is a way to realize unusual form of energy in synthesis. As you know interaction of energy with matter brings about chemical reactions, but sonochemistry or interaction of ultrasound with matter is not a direct reaction. In other words just interaction with any material or matter will not bring forth any useful chemical reaction, but the secondary effect of ultrasound brings about chemical reactions, and that is what exactly I want to teach in this lecture.

So, this is a unusual form or we traditional chemists will also called this as a unconventional wet chemistry route. There are many wet chemistry routes which can be used for chemical reactions, specially material synthesis, whereas sonochemistry is a very peculiar trade off. So, in this talk before I highlight on how the ultrasound can be used for material synthesis; let me at the outset, pullout two important persons, who pioneered in the field of material synthesis, employing exclusively sound waves.

They brought about several perceptions on which many themes have been built in material synthesis, including our own laboratory we have used extensively ultrasound for variety of materials including alloys, oxides and nano particles. The first person is professor Kenneth Suslick from the university in USA, and we also have professor Ahron Gedanken from Israel, who have really pioneered in the area of inorganic solids.

Now, when you talk about ultrasound or sonochemical waves, immediately that comes to your mind or to everyone is a sonication bath, because sonication bath is there almost in every laboratory, for some set of a cleaning purpose. It is almost there in many of the research labs, in the medical laboratories and in the chemical laboratories. And if you can see there are several versions of sonication bath that has come, and this should be there in one corner of the lab almost in every institute.

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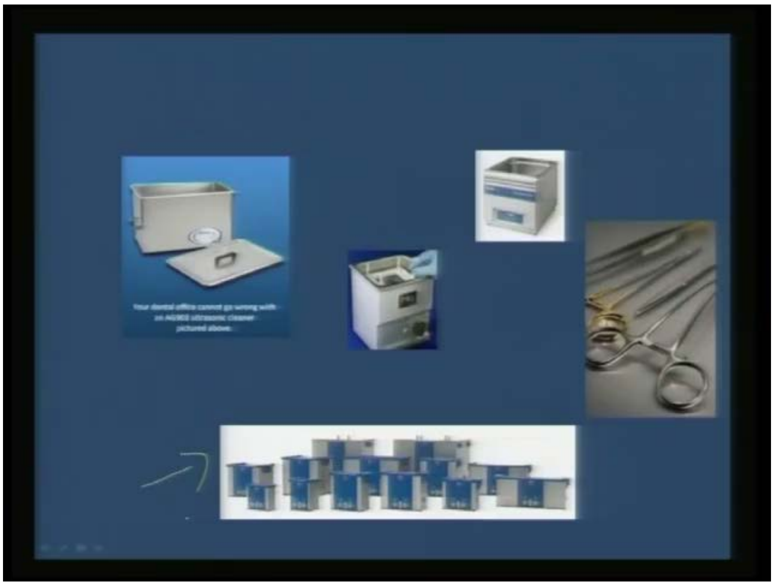

Mainly medical people have used this for sterilization, because you can just get all the mucky or dirty stuff which is sticking, which is not apparent to your naked eyes. So, it is very easy people who are working on thin films, they use this for cleaning all their starting material or the surface of the layer the substrate in which they are trying to deposit it is all clean. So, several versions of it is there, and these are all easily affordable it is start from range of 5000 to 100000 rupees, you can just have any sort of versions of this sonication bath.

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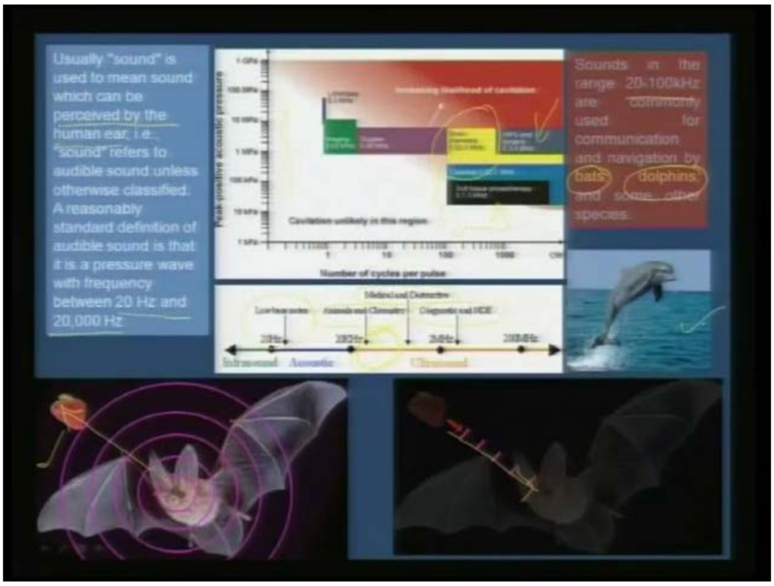

Usually "sound" is used to mean sound which can be perceived by the human ear, i.e., "sound" refers to audible sound unless otherwise classified. A reasonably standard definition of audible sound is that it is a pressure wave with frequency between 20 Hz and 20,000 Hz

Sounds in the range 20-100kHz are commonly used for communication and navigation by bats, dolphins and some other species.

But, precisely I am showing this, because this is not what I am talking about, this is not the ultrasound application that I am going to talk about. In fact, I am going a one step higher taking to another real, where we can play, a costly chemical activity to realize high temperature compounds.

When we talk about sound, we should know that ultrasound is not friendly to ears, and it is not always good. Therefore, first we should understand what can be perceived by the human ear, human ear can take from 20 Hertz to 20000 Hertz that is 20 kilo Hertz; more than this it is not possible. Therefore, when we talk about low bass notes, we are talking about 20 Hertz and categorize as infra sound, mainly this is something that is responded by elephants, we will see that later.

And then animals and chemistry we surpass to kilo Hertz region, and when you talk about medical and destructive purposes, we are talking somewhere close to mega Hertz. And for real diagnostic purposes you are going still for higher ultrasound range, beyond 2 mega Hertz precisely we do it in 3 Megahertz. So, we can achieve several things, namely sonochemistry even for that matter as we saw in the previous slide, cleaning purposes all these come around the same range of frequency, but the pressure that is associated with this sort of applications vary by orders.

For example, you cannot go for anything for material synthesis below, say 100 kilo Pascal, so you need to generate very high pressure. So, we are exclusively categorizing sonochemistry in this frequency range, and in this pressure range. Then you have also the medical diagnostics Island which is forming here, and you can see physiotherapy or soft tissue based physiotherapies in the low pressure ranges. So, this is precisely the place where we stand as far as sonochemistry is concerned, and we are talking somewhere in this region, where we can think about it is usefulness for material synthesis.

So, sounds in the range of 20 to 100 kilo Hertz, as they are very much used even by animals for example, noticeably bats and dolphins, dolphins use sound waves to communicate. Whereas, bats send sound waves to eat, it cannot find its prey unless or until its sends the sound waves, and the feedback it gets clearly tells whether there is any eatable which is in the near proximity.

For example, this cartoon says that sound waves have produced goes and hits a strawberry for that matter, and then it reflects back, so even in the night you can actually get the sound waves, then you know at what proximity you have the, your eatable at hand. So, that is do rely heavily on sound waves to feed themselves whereas, dolphins send sound waves to communicate with each other. So, these are different forms, but let us go one step more, to see where we stands?

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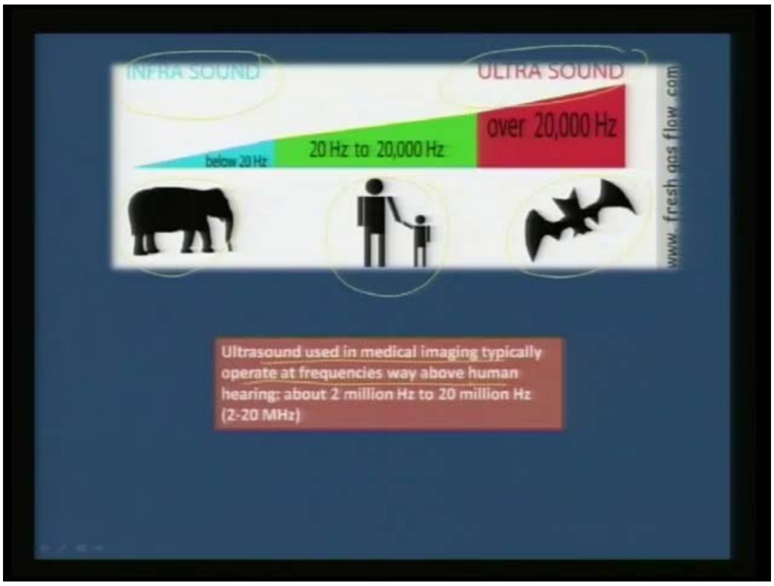

Ultrasound used in medical imaging typically operate at frequencies way above human hearing: about 2 million Hz to 20 million Hz (2-20 MHz)

And this is another cartoon which tells what we characterize as infrasound, and what we characterize as ultra sound, so we are somewhere is the safe region where we are where our human ears can hold. Whereas, when we have bats they go into ultrasound domain, bigger animal like elephant stay in the infrasound domain. Ultrasounds used in medical imaging typically operate at frequencies way above human hearing, about 2 million Hertz to 20 million Hertz that is the region where we do the medical imaging, and even diagnostic and distractive things.

Suppose you want to break some stones using ultrasound waves or so you can rely on using very high frequency ultrasound waves.

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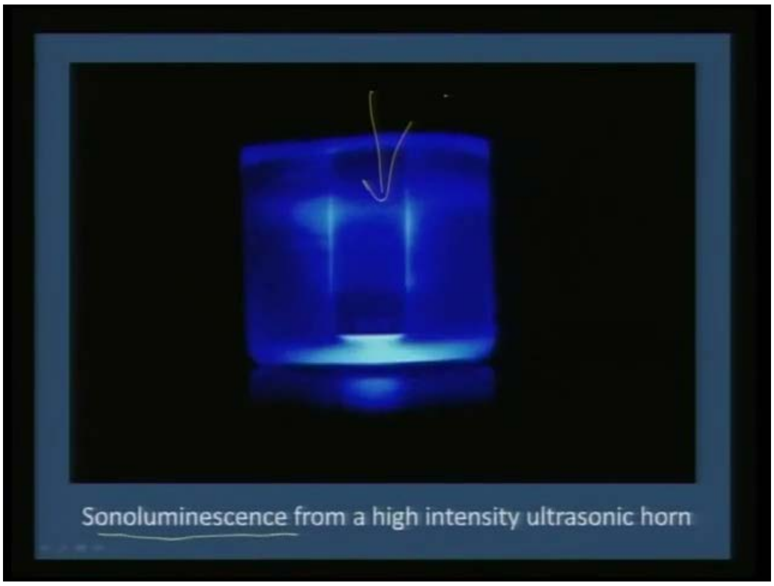
Sonoluminescence from a high intensity ultrasonic horn

But, one of the very important manifestation of ultrasound which really brought the material synthesis to focus is sonoluminescence. Suppose you are going to bubble a sound waves in a solution, actually if you can stabilize a single bubble or a single domain bubble, then you can actually see this bubble luminescing, which is called as sonoluminescence. And when this is a typical cartoon of a sonoluminescence, this is the titanium rod and around this you see a bubble, which is stabilized which is showing luminescence.

So, this actually brought about a series of engineering principles around the issue of cavitations. So, if you can stabilize a cavity what is the dynamic of this cavity, and what exactly happens within the cavity and outside the cavity, and all the chemical reactions that can happen inside is the basis for sonochemistry. So, we will see this in stages as we go through.

Now, to put in place where this sonochemistry is compared to several other chemical reactions that we are talking about, this is a good slide to talk the interaction of energy with matter. We are talking about photochemistry in this time scale, we are talking about energy, we are talking about time, we are talking about pressure. If you think of pressure induced reactions, then the one which stands foremost is piezo related synthesis, piezoelectric rather.

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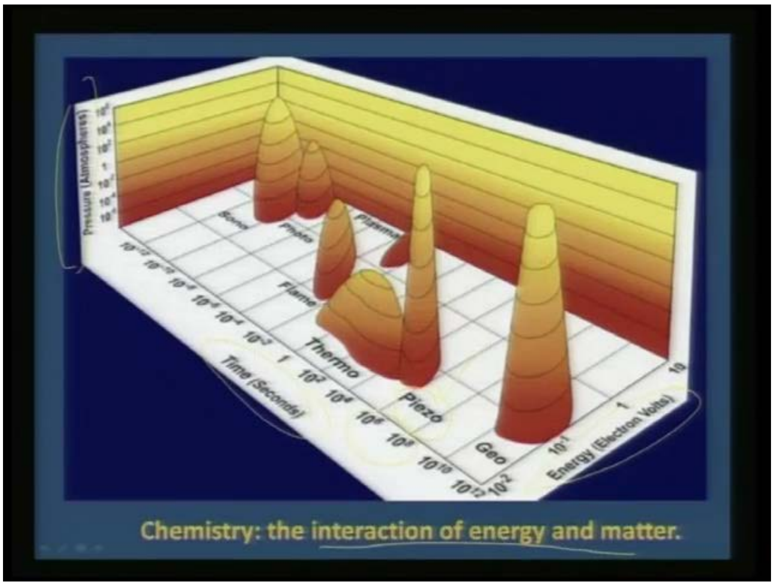

Chemistry: the interaction of energy and matter.

So, in which case you actually achieve very high pressures, but this happens in a time scale of 10 power 6 to 10 power 8, which is very slow process. And then you have this geothermal synthesis, which is also a very slow process of the order of 10 to 10 power 12 seconds, but the energy per se, all this are from falling in the same energy scale, 10 power minus 1 EV and that also includes flame photometry to some extent. But, when you go to plasma which involves a very high energy, we are talking somewhere around this time scale, but energy scale, but those are very fast reactions.

So, to single out between different Islands of chemistry, we can say that photochemistry and sonochemistry fall in one region, where they are happening at 10 power minus 10 to 10 power minus 12 seconds, they are all high pressure and high energy induced reactions. Very fast process, very high energy and very high pressure induced reactions therefore, these are our fundamental importance for us.

So, sonochemistry is a peculiar Island so to say in the material synthesis, now how does it work. Let me start with some crazy examples, because this can tell us what can happen when we start making materials. This is a cartoon of nano crystalline Fe nano particles, and this is a SEM image of cluster of this nano Fe particle of the range of 10 to 20 nano meter which was first published by Kenneth Suslick and group.

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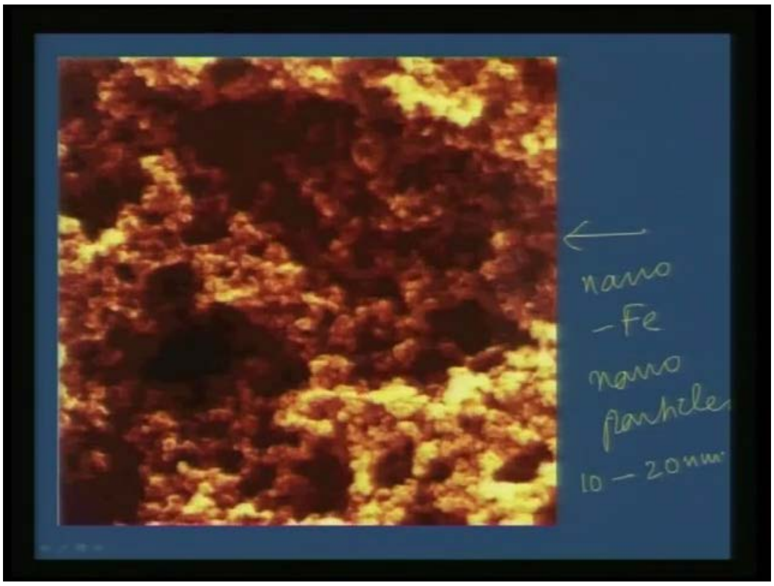

nano
-Fe
nano
particles
10 – 20nm

And you can see they are all mono sized and nearly they are amorphous, one of the main ways to identify that they are really in nano in form is that, they would be mostly X-ray amorphous, if they are truly nano. And at the same time, if they are transition metals which are isolated in nano form, then on exposure immediately they will catch fire. These are quick ways to recognize that they are certainly in the nano regime, so this is a cartoon corresponding to nano Fe particles.

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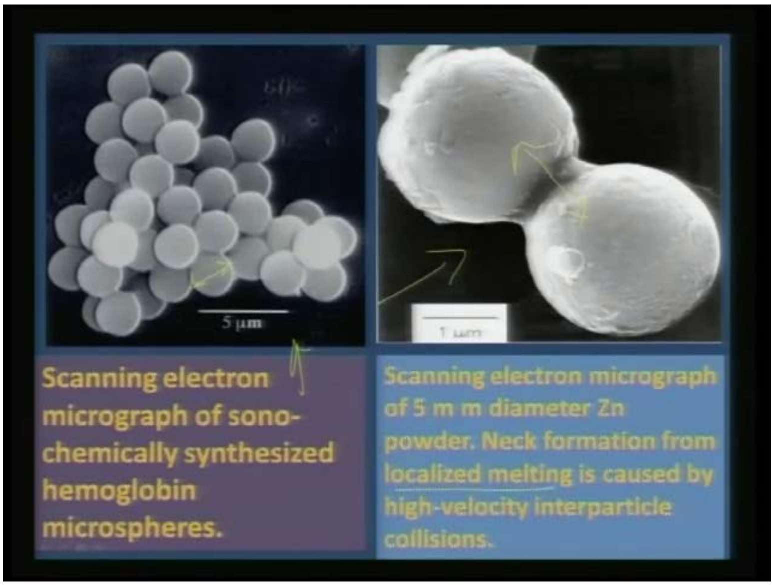

Scanning electron micrograph of sono-chemically synthesized hemoglobin microspheres.

Scanning electron micrograph of 5 m m diameter Zn powder. Neck formation from localized melting is caused by high-velocity interparticle collisions.

But, sonochemistry has gone way beyond simple synthesis, this is a cartoon that shows you can make monosized hemoglobin microspheres by using sonochemistry. And you can see that these are all roughly of the order of 2 micron particles, where you can make such uniform space spears. And here is another cartoon of zinc powders, now if you sonicate zinc powders, then you can see the sort of welding happens between 2 zinc particles. So, essentially there is a localized melting and high velocity interparticle collisions are happening between two particles, that clearly shows what is the sort of energetic that is involved in ultrasound. So, you can study various aspect of the influence of ultrasound, or material synthesis.

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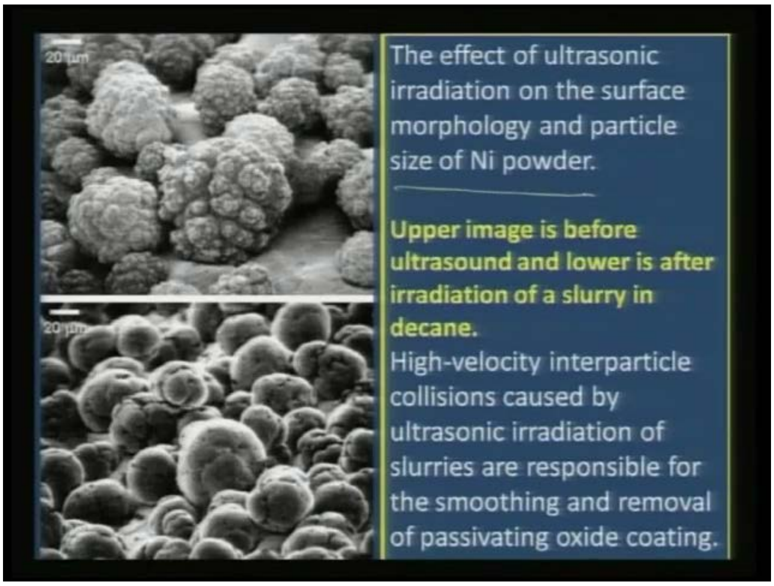

The effect of ultrasonic irradiation on the surface morphology and particle size of Ni powder.

Upper image is before ultrasound and lower is after irradiation of a slurry in decane.

High-velocity interparticle collisions caused by ultrasonic irradiation of slurries are responsible for the smoothing and removal of passivating oxide coating.

Now, this is another very useful cartoon to dry home the point, what exactly the ultrasound can do to surface, this is a cartoon of nickel powder. As you know Raney nickel is a very costly catalyst which is used in organic synthesis, or dehalogenation catalyst or Raney nickel is a very costly powder. At the same time if you take a ordinary nickel metal which is in the shelf, and if you take a look at the surface of nickel powder, it gives this sort of flowery feature and this is a SEM image of that.

Now, you take the same powder and try to sonicate, you can see after sonication or exposing it to slurry of nickel particles. Now, they all look modified in surface, and they seem to have been also broken because both are in the same scale bar, so you see that these cluster seemingly are broken and they are polished. Now, what is the influence, you see that once you try to sonicate this ordinary nickel powders, and take this powder and do your reactions, the reactions are much, much more effective and they are nearly comparable to the Raney nickel.

So, you do not need to go for a very costly Raney nickel, you can just take shelf nickel powder and you can do any sort of catalytic reactions, just by surface treating this with ultrasound. What is essentially does is, it removes all the passivating layers of this nickel, whatever it is it could be carbonates, hydroxide anything or even the particles size can be broken into smaller. And these are all nearly uniform therefore, one can say uniform surface polish nickel particles become highly reactive, comparable to that of Raney nickel. So, you can remove the passivation, you can really bring forth a variety of interesting features with ultrasound.

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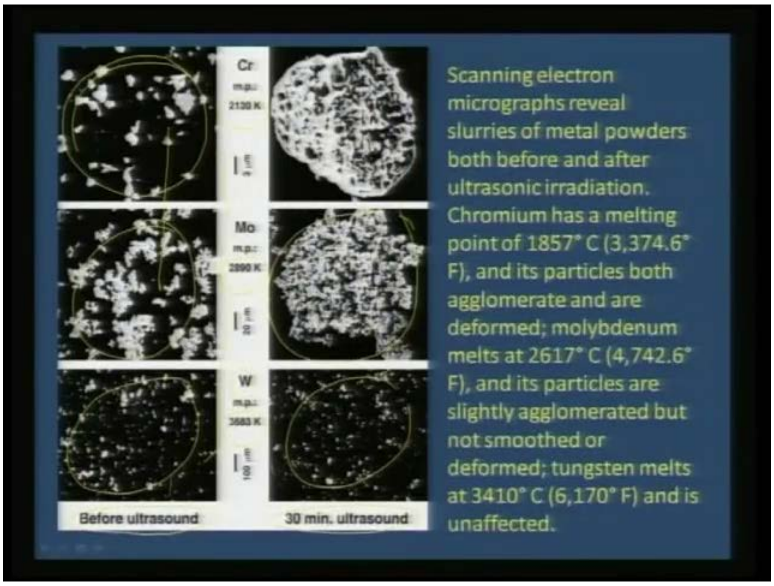

Scanning electron micrographs reveal slurries of metal powders both before and after ultrasonic irradiation. Chromium has a melting point of 1857° C (3,374.6° F), and its particles both agglomerate and are deformed; molybdenum melts at 2617° C (4,742.6° F), and its particles are slightly agglomerated but not smoothed or deformed; tungsten melts at 3410° C (6,170° F) and is unaffected.

Now, is that all we can see their, we can get lot more clue about what this ultrasound is doing inside the solutions. Now, we take just to understand what is the energy parameter that is involve, take chromium, molybdenum and tungsten powders, make take it in the form of slurry with some sort of a organic solvent. And now try to sonicate it, these are the SEM features of the powders before ultrasound, and this is after ultrasound.

Now, before ultrasound you see that these are the features of the metal particles, but after ultrasound you would see all this chromium particles are getting fused, and they form a cluster sort of thing with the same scale bar. And same is true for the molybdenum particles they cluster together, when you go to tungsten you see there is no change, in fact they remain the same. What does that mean, if you take chromium the melting point is around 2130 Kelvin, molybdenum 2090 Kelvin and tungsten is very high 3683 Kelvin.

So, if you try to sonicate these nano particles, you can clearly see some amount of melting and agglomeration that is happening in the case of chromium, and molybdenum compared to tungsten. So, one can say roughly in this sort of sonication, you can nearly realize very high temperatures to the tune of 3000 Kelvin undoubtedly, otherwise these particles of chromium and molybdenum will not cluster together.

So, this agglomeration essentially says not only we can achieve very high pressures; we can also achieve very high temperatures. But, where is it all happening, and if such high temperatures are happening what is happening to the container or to the chemical reaction, these are open questions. But, we can try to understand all this provided; we know what is really happening in the sonochemistry.

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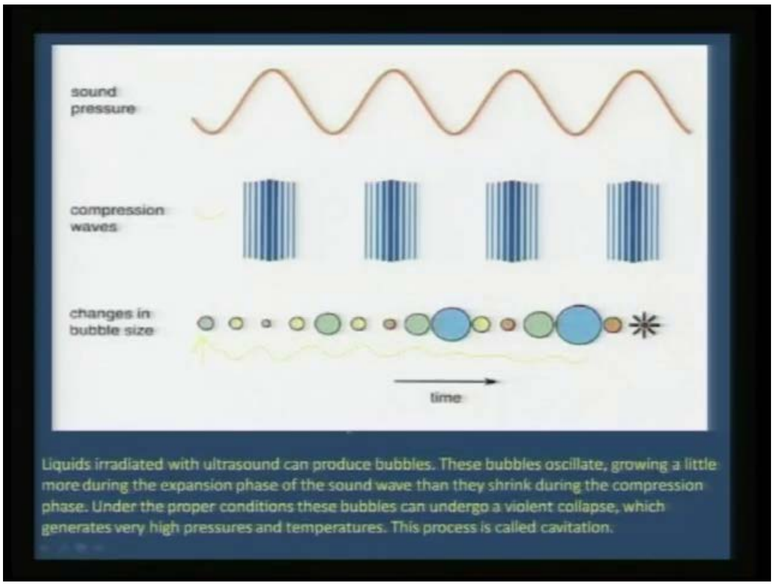

Liquids irradiated with ultrasound can produce bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. This process is called cavitation.

Now, sound pressure, sound waves when they propagate through a liquid lot of things can happen, now as you see here we have compression waves and rarefaction waves, these are the compression waves, and then they relax rarefaction and then compression and then rarefaction. So, when a bubble is trapped or when there is a sufficient frequency of the sound to ripple or to pull apart the solvent molecules, now this sort of cavities are formed.

And once a cavity is formed, you have a continuous propagation of sound through the liquid therefore, this cavity is now going to grow, because of the rarefaction and expansion a compression waves, you are going to have a growth of this particle. And as a result this will grow in size to optimum, and beyond a particular point it is suppose to break, as we know that cavities has to break at some point of time. So, this is a simple cartoon just to tell you that liquids irradiated with ultrasound can form bubbles, these bubbles oscillate growing.

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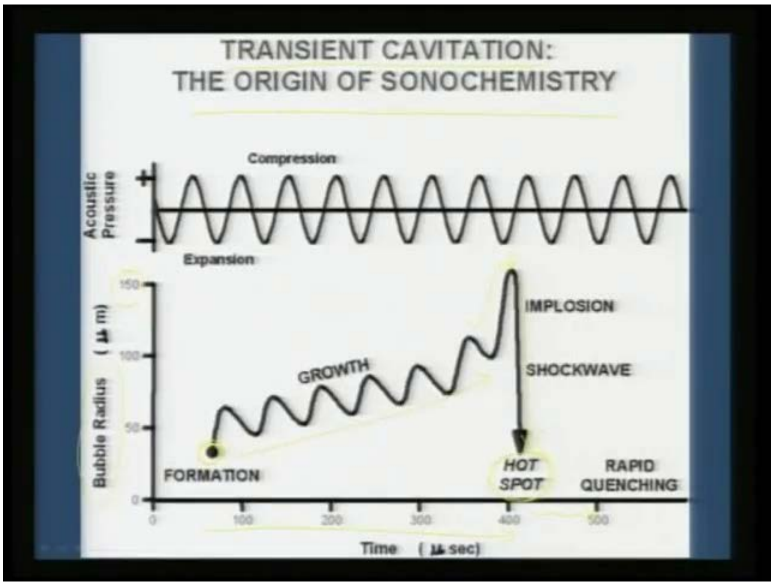

TRANSIENT CAVITATION:
THE ORIGIN OF SONOCHEMISTRY

And in the next slide I will try to show you, how this transient cavitations works, and what is the origin of a sonochemistry here. So, as I told in the previous slide we have the formation of cavity, and this cavity actually grows in size over several cycles, due to the compression and expansion wave. And if you see on the y axis, you see the bubbled radius, so typically from 20 micron range it actually grows up to nearly 150.

Now, when it has gone through several cycles, there is a particular cycle at which in a single step it will grow to this maximum, and this is the optimum bubble size, where the surface tension of this cavity set is maximum. And when there is another compression wave, at this point the compression wave will actually push this cavity to collapse, and how does it collapse, it does not explode whereas, it actually implosively collapses. So, you now that most of the cases the bubbles will rupture, but it is mostly of a explosive nature, but in this case this is a implosive collapse.

So, when there is a implosive collapse, you see there is a shockwave that is triggered which results in a local hot spot. And what is the radius of this hot spot, hot spot is of the radius of 150 micron, so in this what happens all this has happened in the timescale of say 100 to 400 micro seconds. So, it is a fast reaction the bubble growth is dynamic and the implosive collapse is also dynamic, at this point when it implosively collapses very high temperatures and very high pressures are released.

And also it is immediately a rapid quenching technique therefore, whatever pressure is realized whatever temperature is realized, it is all felt only for a micro second. So, whatever reaction that has to happen, chemistry wise has to happen in those micro second times scale. So, these are a fast quenching and high temperature high pressure reactions in the first place; so the principle or the origin of sonochemistry is this transient cavitation that is occurring, and this is actually implosively collapsing.

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Now, to see what sort of a bubble that we are talking about, this is a simulated bubble that shows that this is a implosive collapse, and also because its implosive in nature the whole transformation or the thermodynamics that is involved in this cavitation is adiabatic nature. So, all the temperature that is released is confined within the system and therefore, anything that strapped within the cavity will actually realize the maximum pressure and the temperature of it. So, in this cavity you can try to bring out the fascinating chemistry that you are looking for, so this is the essence of sonochemistry.

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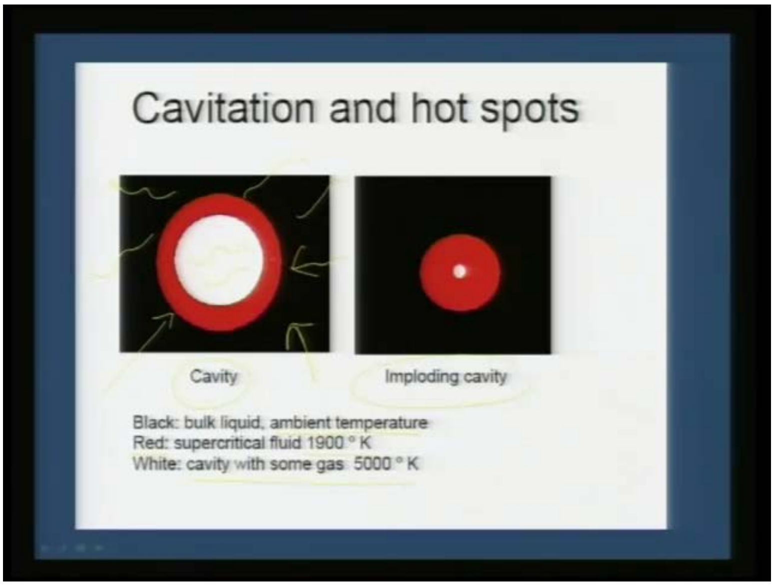

Cavitation and hot spots

Cavity

Imploding cavity

Black: bulk liquid, ambient temperature
Red: supercritical fluid 1900 ° K
White: cavity with some gas 5000 ° K

Now, cavitation and hot spots can bring about lot of issues or data's that are per se very meaningful, you see the cavity here and you see a imploding cavity here and the black region is nothing but your bulk liquid that is at ambient temperature. Now, if you actually proceed towards the bubble that temperature zone, the red one is nothing but your supercritical fluid which can even achieve temperature up to 1900 Kelvin compared to the local areas.

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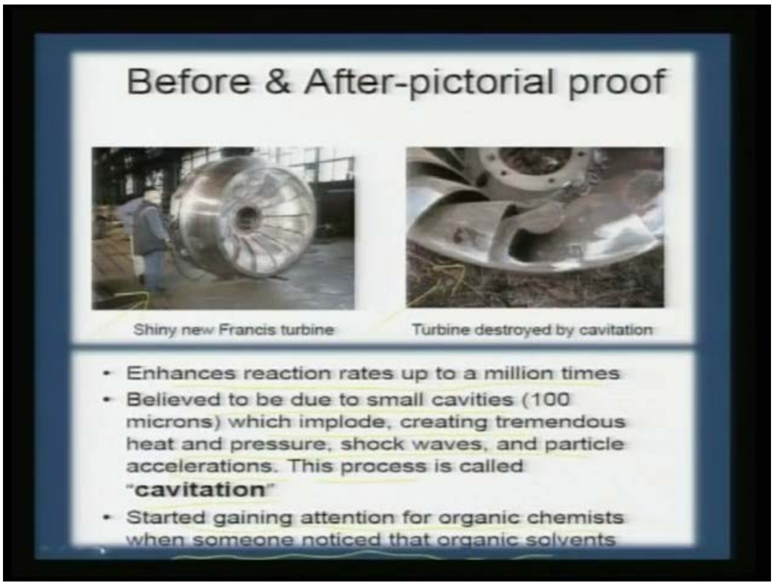

Before & After-pictorial proof

Shiny new Francis turbine

Turbine destroyed by cavitation

- Enhances reaction rates up to a million times
- Believed to be due to small cavities (100 microns) which implode, creating tremendous heat and pressure, shock waves, and particle accelerations. This process is called "**cavitation**"
- Started gaining attention for organic chemists when someone noticed that organic solvents

These are nearly at room temperature, but if you go closer to the cavity then you achieve around 1900 Kelvin. And the white space that you see here ((Refer Time: 23:14)) is nothing but your cavity which is trapped with some gas, and the temperature zone is of the order of 3000 to 5000 Kelvin, and that depends on the nature of the gas that is trapped.

Now, this cavitation became very important, mainly because there was a serious flaw during the British army exercise, they found that the turbines that they have use where fastly getting corroded and collapsing. So, this was one of the main reasons why the issue of cavitation was taken as an engineering problem. Now, here you can see here in this cartoon, a shiny turbine which is being mounted into submarines, and other army applications. But, here you can see that these turbines have catastrophically failed, mainly because of the issue of cavitation.

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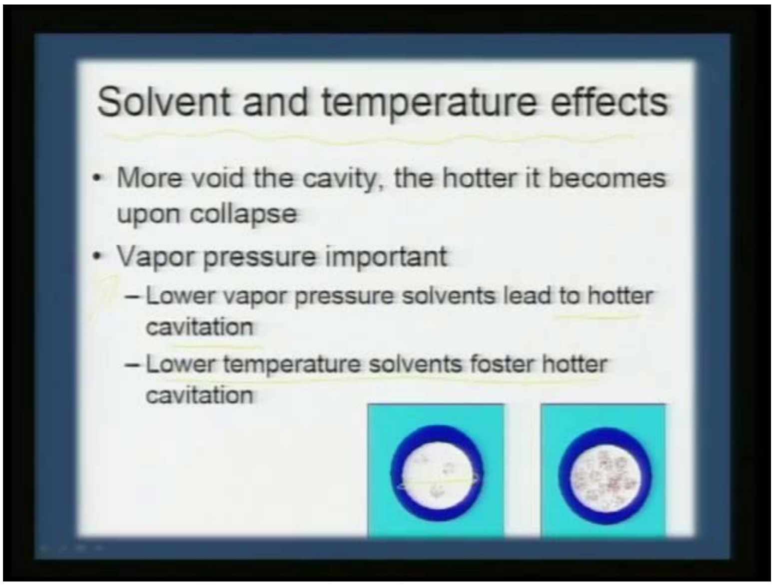

Solvent and temperature effects

- More void the cavity, the hotter it becomes upon collapse
- Vapor pressure important
  - Lower vapor pressure solvents lead to hotter cavitation
  - Lower temperature solvents foster hotter cavitation

So, what really happens in the cavity, cavity enhances any sort of reaction to a rate up to a million times. And it is believed to be due to small cavities of say approximately 100 microns which implode creating tremendous heat and pressure, shock waves and particle acceleration and this process is called as cavitation. So, the key word for sonication is nothing but cavitation and this started gaining attention for organic in the very early years. Because, when someone notice that organic solvents seemingly are responding very much to sonochemical waves or ultrasound waves, it was found that probably this could be extended for chemical reaction, so that was the origin of using sound waves to chemistry.

So, if you look at the solvent and temperature effects more void the cavity the hotter it becomes upon collapse. So, if you can trigger a larger cavity, then you can trigger a hotter region, and it collapses rapidly, then vapor pressure of the solvent also becomes important. Lower vapor pressure solvents lead to hotter cavitation whereas, higher vapor pressure solvents do not lead to such hot cavitation, lower temperature solvents faster hotter cavitations. So, these are some thumb rules or guiding principles to realize very high temperatures, and which are mainly solvent dependent.

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How cavities are formed

- Tensile strengths of liquid important
- When negative pressure exceeds tensile strength of liquid, cavities form
- Nucleated process; without weak points, ultrasound could not form cavities
- Dissolved gasses often help for cavities, as tensile strength is weakened
- Every solvent forms cavities, not just water

Phys. Chem. A 2006 110, 10720

Now, how cavities are formed in solvents, they are mainly dependent on the tensile strengths of the liquid. So, depending on the tensile strength of different solvent cavities are formed, when negative pressure exceeds tensile strength of liquid cavities are formed. So, there should be a negative pressure during this ultrasound waves, you have a compressive and a rarefaction wave, so compression and rarefaction wave when you have a negative pressure, which is exceeding the tensile strength of the liquid, then immediately it results in a cavity.

And nucleated process without weak points ultrasound could form cavities, you do not need a rusted region or some imperfect region in a solid to create a cavity, just based on the tensile strength of the liquid you can create such cavities. Dissolved gases often help for cavities as tensile strength is weakened and every solvent forms cavities not just water, you do not just need water for making cavities, any solvent for that matter depending on its tensile strength can form cavities. And if you are interested you can look at this paper ((Refer Time: 27:12)), which gives you all this useful reactions.

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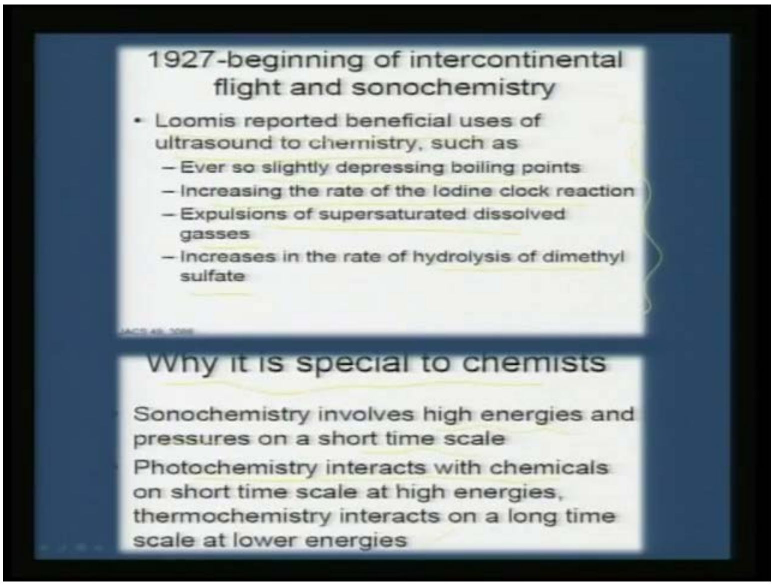

1927-beginning of intercontinental flight and sonochemistry

- Loomis reported beneficial uses of ultrasound to chemistry, such as
  - Ever so slightly depressing boiling points
  - Increasing the rate of the Iodine clock reaction
  - Expulsions of supersaturated dissolved gasses
  - Increases in the rate of hydrolysis of dimethyl sulfate

Why it is special to chemists

- Sonochemistry involves high energies and pressures on a short time scale
- Photochemistry interacts with chemicals on short time scale at high energies, thermochemistry interacts on a long time scale at lower energies

Now, when it is trade back to see when it all happened, two things happened in year 1927, the first intercontinental flight was initiated in other words, transatlantic flight was in year 1927, and it was also the beginning of sonochemistry. And it was Loomis who reported the beneficial use of ultrasound to chemistry such as, ever so slightly depressing boiling points, increasing the rate of iodine, clock reaction, expulsions of supersaturated dissolved gases, and increasing the rate of hydrolysis of dimethyl sulfate.

These were some of the quick results that were coming in those early years, were the use of ultrasound was actually highlighted. But, as you see here this has nothing to do with the material synthesis, but we are talking about some sort of a kinetic reactions, and reactions involving solvents. Why it is so special for chemists, sonochemistry involves very high energies and pressure in short time skills. So, if you are looking for quick synthesis, and issues involving very high pressures you can resort to sonochemistry. And complementary to that is your photochemistry which interacts with chemicals on short time scale at high energies. So, we are actually talking about scaling up of energy in material synthesis, so therefore, this can become useful.

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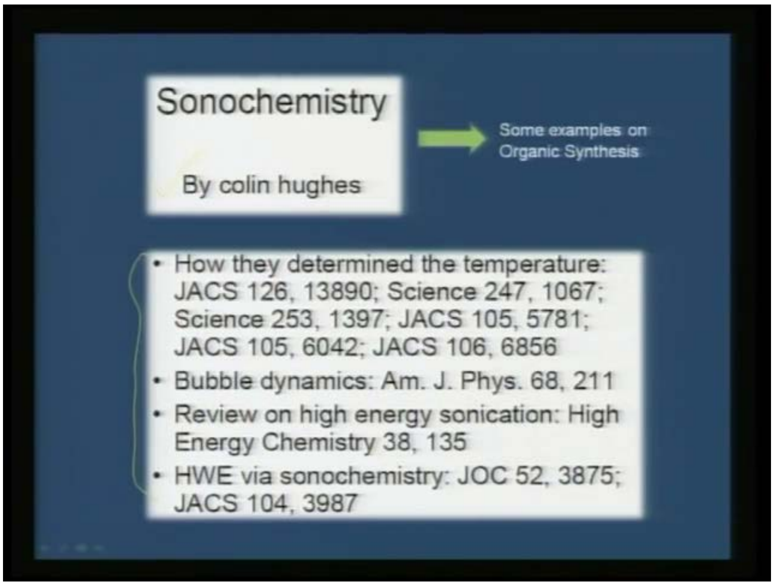

Sonochemistry

By colin hughes

Some examples on Organic Synthesis

- How they determined the temperature: JACS 126, 13890; Science 247, 1067; Science 253, 1397; JACS 105, 5781; JACS 105, 6042; JACS 106, 6856
- Bubble dynamics: Am. J. Phys. 68, 211
- Review on high energy sonication: High Energy Chemistry 38, 135
- HWE via sonochemistry: JOC 52, 3875; JACS 104, 3987

I will take you through few examples of organic synthesis just to give you some background. Because, most of the work has been done in organic synthesis as well apart from material synthesis, just for continuity sake and also to tell that sonochemistry is not exclusively used only for materials. I would like to pin point some of the viewgraphs that were coated by professor Colin Hughes, and he is also summed up some of the literatures that are available to study the basics of sonochemistry, which I thought is useful for our lecture. So, therefore, these are the some of the informations that I have taken from doctor Colin Hughes group.

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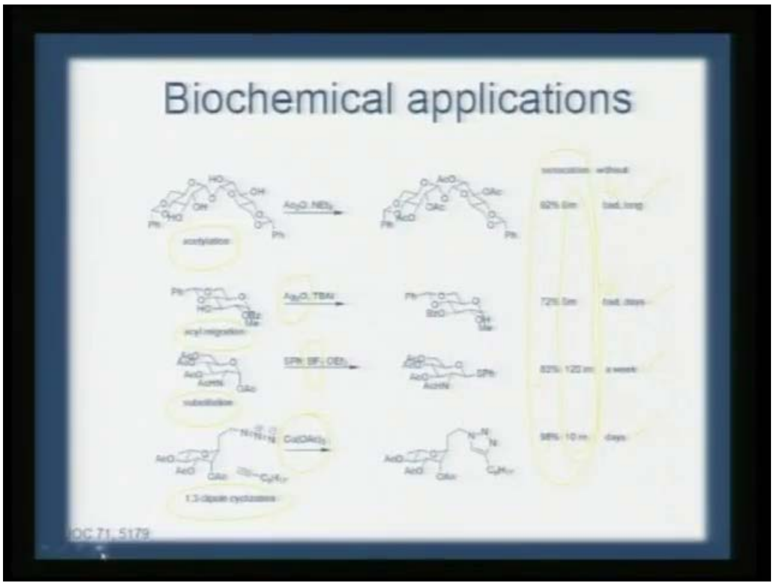
Biochemical applications



OC 71, 5179

And some of the organic synthesis for example, biochemical applications, if you look at acetylation reaction or acyl migration reaction or substitution reaction or 1, 3 dipole cyclisation reaction, several reactions are listed here, and these are for biochemical applications. As you carefully look at this reaction, you could see that most of it are involving metals, metal slats as catalyst; and this metal salt based conversion reactions you can see has phenomenal effect, when you tried to use ultrasound.

Without ultrasound you see the yield is very bad, and it takes long hours, yield is very bad takes many days and this reaction is very slow to the order of a week, and several days of reaction with almost very less conversion. Whereas, if you look at the sonication 92 percent of conversion, 70 to 83, 93 percent and all this are falling in the time scale of few minutes.

So, several reactions whether it is acetylation, acylation reactions, substitution any sort of reactions whichever is mediated by a catalyst or a metal salt catalyst, they have pronounce effect on sonication, so although the complete mechanism of understanding the conversion is not possible. But, there are several clues that we can pick up, as much as we have told about the dependency of the solvent it is tensile strength, and it is influence on the material synthesis, so in this case we see a pronounce effect.

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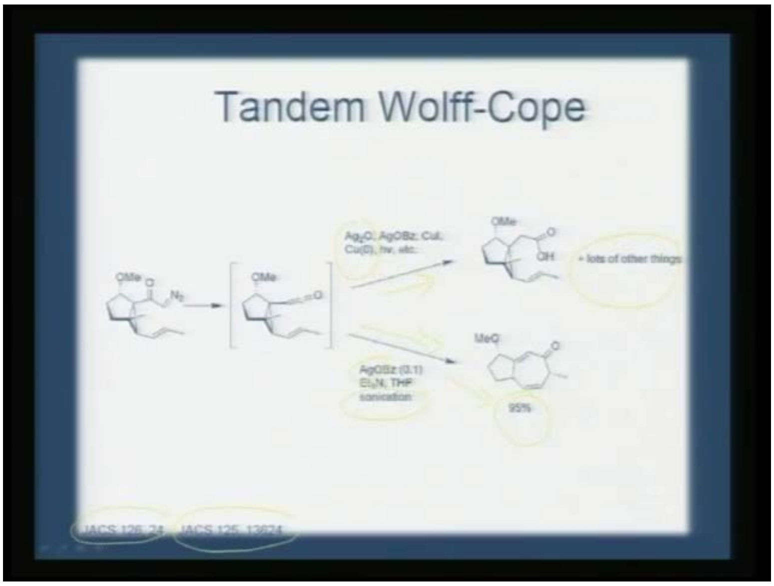

Tandem Wolff-Cope

JACS 126, 24   JACS 125, 13624

And this is another reaction that is quoted it is called Tandem Wolff-Cope reaction, which is both attempted without sonochemistry and without ultrasound. So, if you use sonication, in both cases they have used silver oxide as catalyst, you can see that there is conversion which is highly selective and with the very good yield, if you are using sonication. Whereas, without sonication you seem to have a different product also with a lot of other side products therefore, we can say that you can look for name reactions, which are highly selective, if you are going to use sonication. For more details you are going to look at it, because I am not essentially laying emphasis on the organic reactions, so you can resort to this reference for more clarification.

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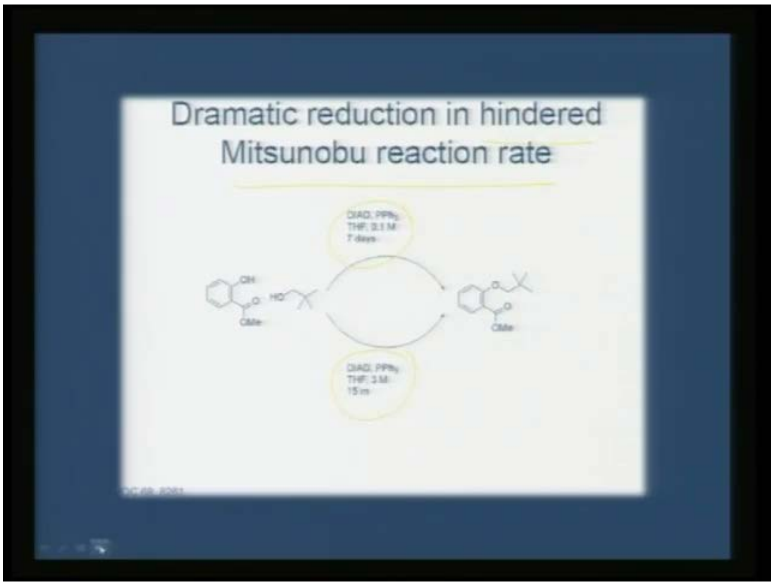

Dramatic reduction in hindered Mitsunobu reaction rate

OC 69, 8261

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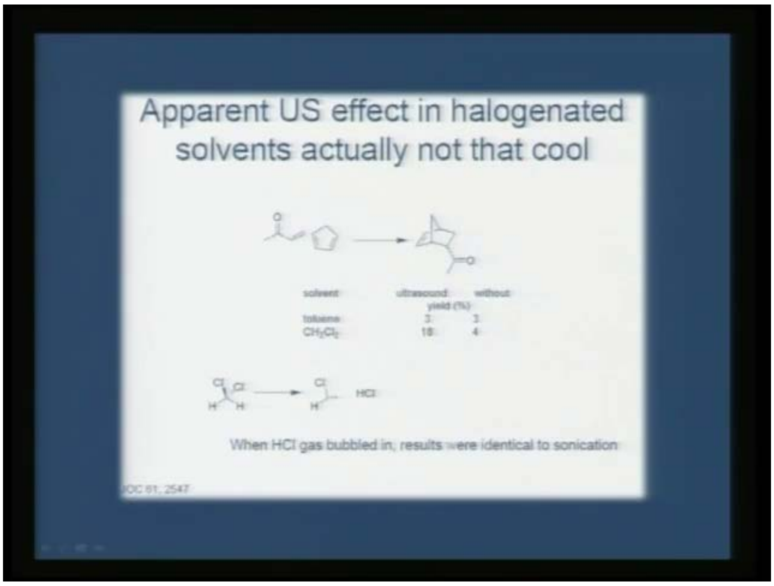

Apparent US effect in halogenated solvents actually not that cool

solvent	ultrasound	without
	yield (%)	
toluene	3	3
CH_2Cl_2	18	4

When HCl gas bubbled in, results were identical to sonication

JOC 61, 2547

And there is an another one, which is called dramatic reduction in hindered Mitsunobu reaction rate. And here again in this case you see a conversion from here to this product involves 7 days whereas, it can be achieved with the lot of selectivity in just 15 minutes time using sonication.

And it was also found out that when you use halogenated solvents, they are actually more influential than using mineral acids. For example, you take the reaction conversion of these two reactants to the product, if you are going to use tolvin whether you use ultrasound or without ultrasound, the yield is nearly 3 percent. When you use dichloromethane for example, you can see when you use ultrasound, it is highly selective whereas, without that it is very poor.

But, at the same time it is not due to chlorine atoms, if you use mineral acid you see that the reaction almost does not happen at all. So, what it what it means is halogenated solvent seemingly have pronounced affect, and it has also been proved in several organic reactions that any reaction, which is undergoing free radical mechanism have a very pronounced effect using ultrasound.

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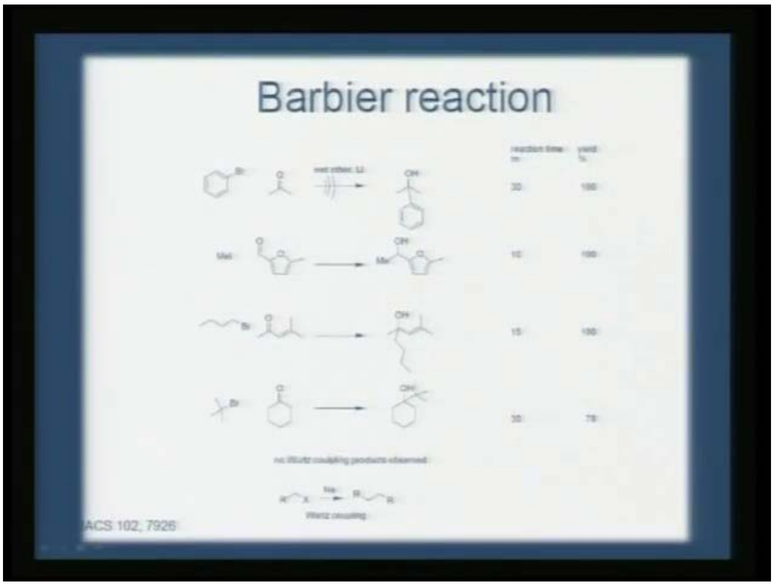

Barbier reaction

JACS 102, 7926

Here again you have a Barbier reaction for a variety of conversions, and one can single out to see, if you are going to use sonochemistry almost 100 percent yield or conversion is affected, when you use sonication. And this is actually reported in JACS, for people who are interested in such named reactions you can refer to this.

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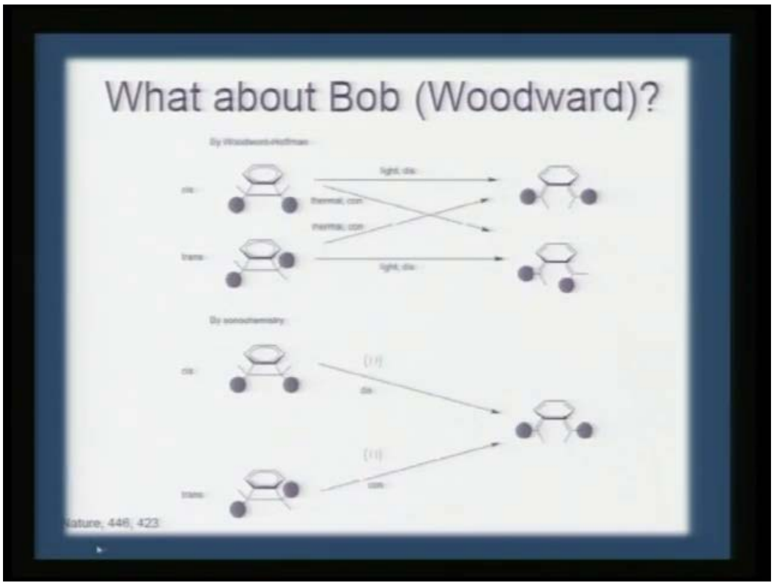

What about Bob (Woodward)?

ature, 446, 423

And what about Woodward Hoffman reaction conversion, say for this is from converting to this product and transform converting to this product, these are stereo specific conversions. And whether you use light or whether you are going to use heat, the conversions are very selective. For example, the conversion of this, cis isomer to this product; it is very selective only if you use thermal reaction whereas, if you use photo induced reaction it converts to this, so it is very selective that way, similarly for the trans one. But, the same thing if you use sonochemistry, the cis or the trans will give only one stereo specific reaction.

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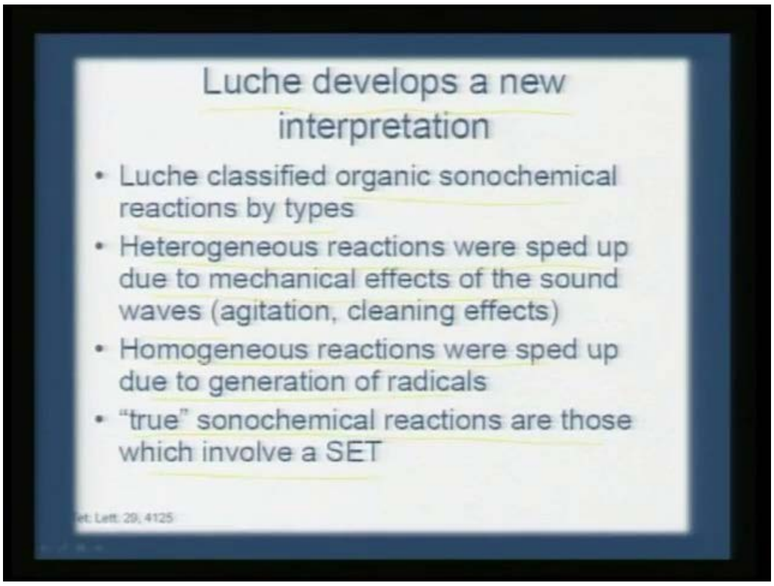

Luche develops a new interpretation

- Luche classified organic sonochemical reactions by types
- Heterogeneous reactions were sped up due to mechanical effects of the sound waves (agitation, cleaning effects)
- Homogeneous reactions were sped up due to generation of radicals
- "true" sonochemical reactions are those which involve a SET

et. Lett. 29, 4125

So, this is not only side selective, this is not only a selective for free radical mechanism, you also see that you can get stereo specific products by using sonochemistry. Actually it was Luche who did several studies using solvents, and he developed a new interpretation, what he said was organic sonochemical reactions by types, the one type is heterogeneous reactions were sped up due to mechanical effects of the ultrasound waves. As I told you if you use metal catalyst, then you have variety of influence and faster conversion, homogeneous reactions were sped up due to generation of radicals. So, you can just single out two issues, one is mechanical effect another one due to radicals, true sonochemical reactions are those which involve a SET type, which is enantiomeric type of activities.

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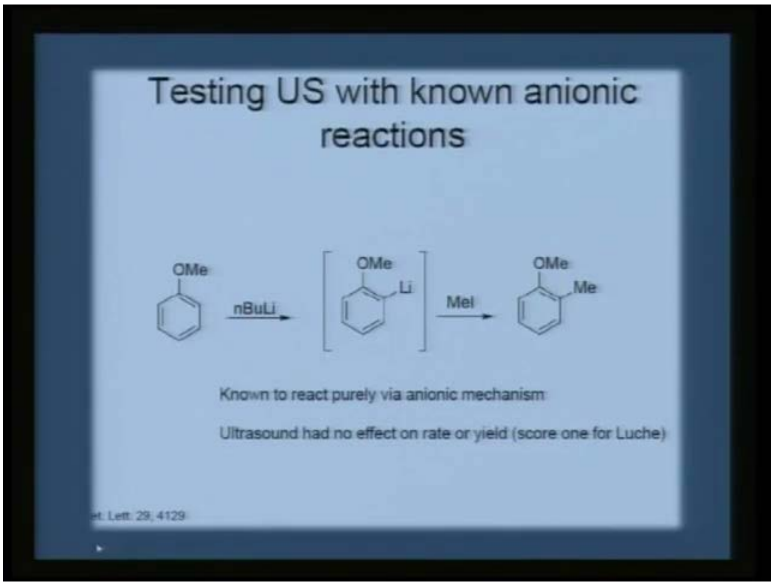

Testing US with known anionic reactions

Known to react purely via anionic mechanism

Ultrasound had no effect on rate or yield (score one for Luche)

et. Lett. 29, 4129

So, we can see one or two examples of that, testing ultrasound with the unknown anionic reactions, one such reaction is this known to react purely via anionic mechanism, ultrasound have no effect on the rate or yield. And if you look at this switching reaction for example, if you tried to conversion of this alcohol using nitric acid with ultrasound, you see complete conversion to this switching form. Whereas, without ultrasound you almost see 0 percent conversion on this, and with ultrasound this is not possible whereas, this is possible.

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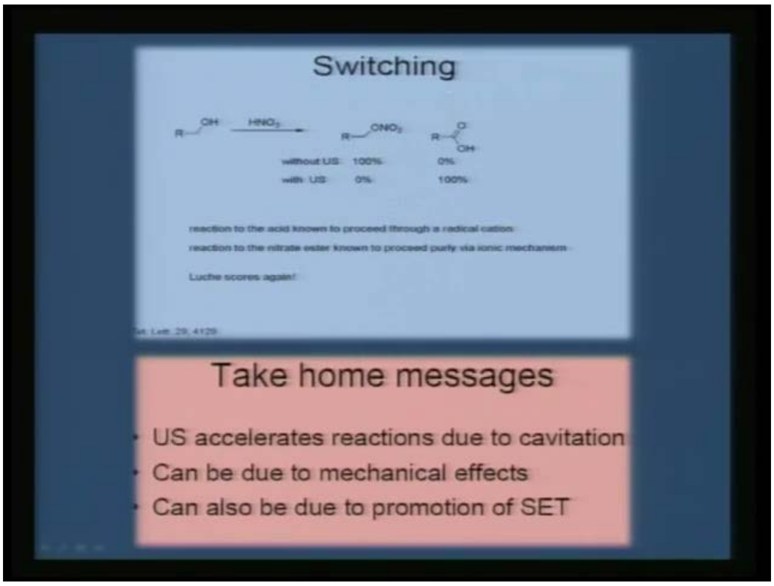

Switching

without US 100% 0%

with US 0% 100%

reaction to the acid known to proceed through a radical cation

reaction to the nitrate ester known to proceed purly via ionic mechanism

Luche scores again!

Tet. Lett. 29, 4129

Take home messages

- US accelerates reactions due to cavitation
- Can be due to mechanical effects
- Can also be due to promotion of SET

Therefore reaction to the acid known to proceed through a radical cation reaction, reaction to the nitrate ester known to proceed purely via anionic mechanism. So, some of the take home messages as Luche has emphasized as far as organic synthesis concern, ultrasound accelerates reactions due to cavitation, this can be due to mechanical effects and due to promotion of cation, anionic based reaction.

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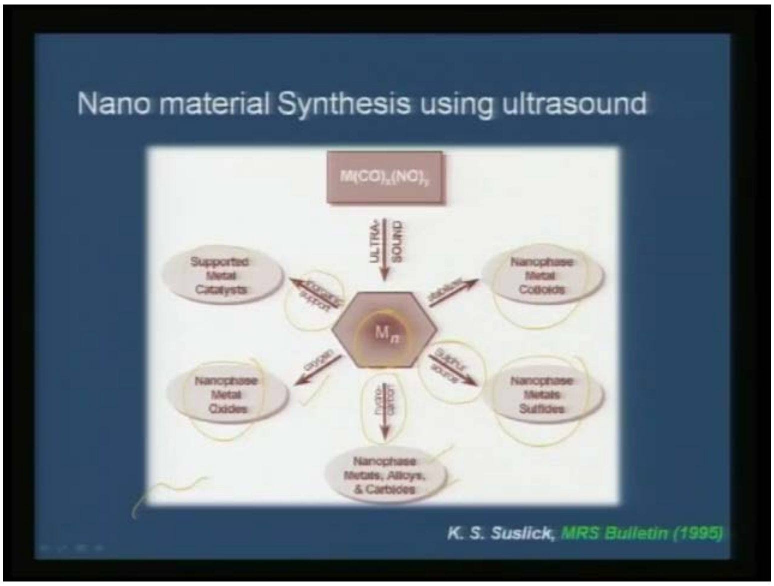

Nano material Synthesis using ultrasound

K. S. Suslick, MRS Bulletin (1995)

Now, when we come to material synthesis the game is different, and the way ultrasound is employed is different which we will see in the next few slides. So, how can we use this ultrasound for making nano materials, this cartoon explains the use of ultrasound, you take any carbonyl nitrosyl ligands or metal carbonyls or metal nitrosyls in this form. And if you can apply ultrasound, the first consequence could be preparing a ending up with a metal nano particle, and this nano particle can be taken to different forms.

Suppose, I am going to use a stabilizer it could be a surfactant or it could be any alkali solvent, you can actually stabilize nano phase metal collides. So, once you get nano particles you can put a stabilizer and convert it into a colloid, where you can essentially stabilize these nano particles in a suspended form, or if you are going to bubble this with some sulphur source, either elemental sulphur of sodium sulphate or some other sulphur source, you can essentially get nano metal sulfides.

For example, if you take cobalt and you bubble it with the sulfur in the presence of ultrasound you will get cobalt sulfide. If you should take any hydrocarbon and try to trap this, then you can get nano phase alloys or carbides, if you are going to use this in ambient condition that is in the absence of any inert atmosphere, like argon or nitrogen. In the presence of oxygen you can directly convert that into any metal oxides, and if you are going to take a inorganic support, then you can get supported metal catalyze.

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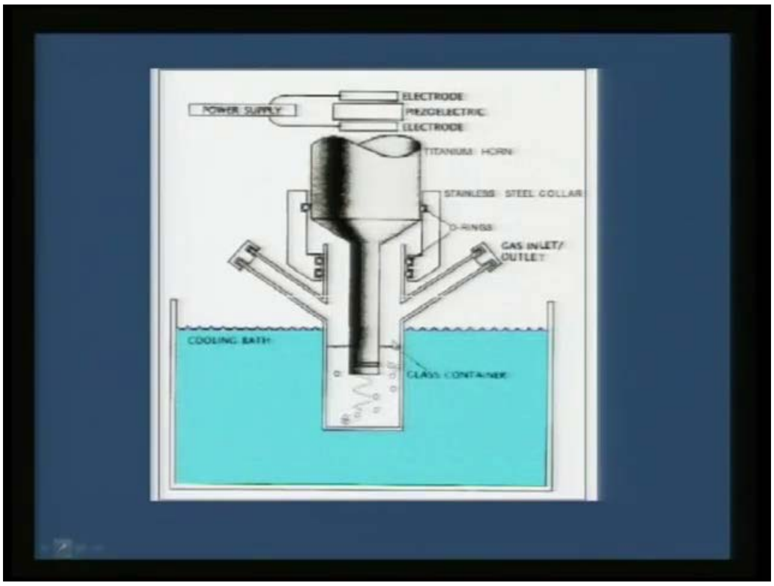

For example, if you want to trap some ion nano particles in alumina support or silica support, then you use such a inorganic support to get this metal catalyst. So, just starting with one particular starting material using ultrasound, you can play around with a variety of compounds, inorganic compounds. And for a good review you can actually look at this which appeared as early as 1995.

Now, this is typically the way you can realize a reaction as you are trying to applies a ultrasound in a sonicator cell, which is a typical cartoon that you can see. There is a power supply which is going through electrode, and there is a horn which is nothing but a piezoelectric horn and this is your titanium rod which is actually mounted or suspended into a solvent. And this is the sonochemical cell that you can have, you can keep sending nitrogen or argon as you desire.

Now, once these sound waves comes in for a long time this will actually be trying to scissor the nitrosyl or carbonyl moiety from the metal. And after a particular time you would see the solution turning black, the moment the solution turns black you can be sure that the metal nano particles are formed. So, typically this conversion would take place of the order of say 1 to 3 hours depending on the nature of starting material that you are employing.

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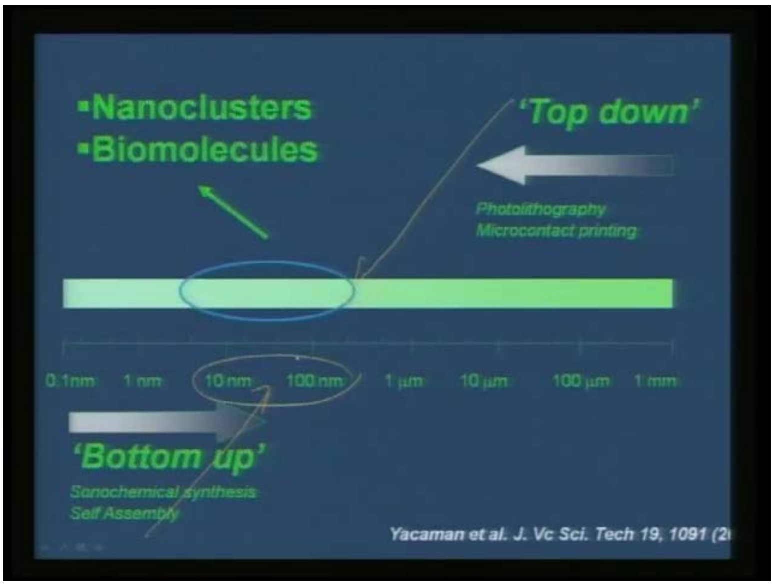

- Nanoclusters
- Biomolecules

'Top down'

Photolithography
Microcontact printing

'Bottom up'

Sonochemical synthesis
Self Assembly

Yacaman et al. J. Vc Sci. Tech 19, 1091 (2

So, once this is formed, then you can try to take the whole vessel into a organ globox, and then you can try to carefully filter, so that this metal nano particles can be preserved in inner conditions. One caution that we need to take during sonochemistry is you need to actually apply ice bath, so that they hotspots which will ultimately keep heating this vessel, will be kept at low temperatures, otherwise your organic solvent can evaporate.

So, most of the reactions we can use decalin as solvent which is preferably used, so this ((Refer Time: 41:52)) is a cartoon which tells typically how a sonochemical synthesis work.

Now, when we talk about the sonochemistry for material synthesis it is two ways, it can either be a top down approach or it can be a bottom up approach, meaning you can actually use a solvent and some metals salts in solutions. And then you can arrive at synthesis of these nano particles or you can start with the heterogeneous reaction, and you can end up with this same regime; so both ways you can end up with nano materials.

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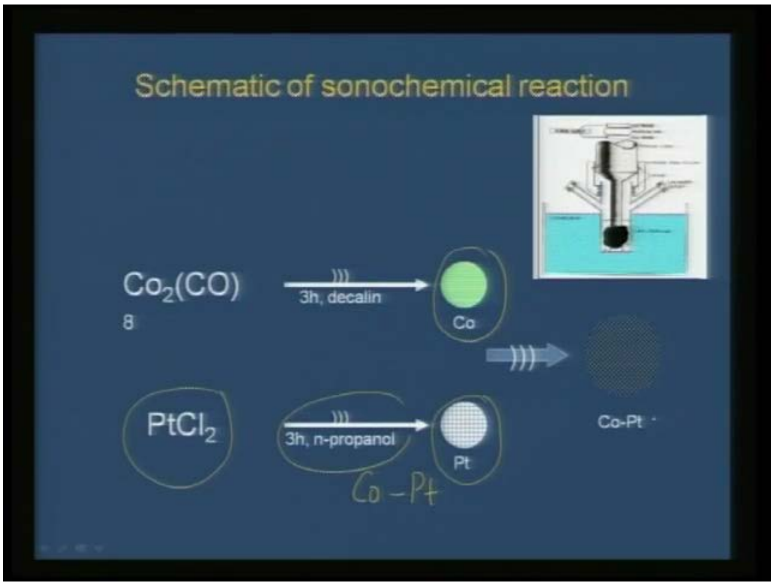

Schematic of sonochemical reaction

$Co_2(CO)_8 \xrightarrow[\text{3h, decalin}]{)))} Co$

$PtCl_2 \xrightarrow[\text{3h, n-propanol}]{)))} Pt$

$\xrightarrow{)))}$ Co-Pt

Co – Pt

Now, I will show some examples of how we can make alloy nano particles for example, one of the most important alloys is cobalt platinum alloys, which is also used in memory storage devices. So, you can take Co2, Co8 which is nothing but cobalt carbonyl and this cobalt carbonyl, if you sonicate for three hours in decalin solution you will get cobalt nano particles. Similarly, if you take platinum chloride, in case of platinum chloride you do not have carbonyl, but you can still use platinum carbonate, and if you can sonicate for 3 hours in n propanol, you get platinum nano particles. So, if you are looking for cobalt, platinum nano particles take these two together and sonicated for 3 hours you can get cobalt platinum nano particle.

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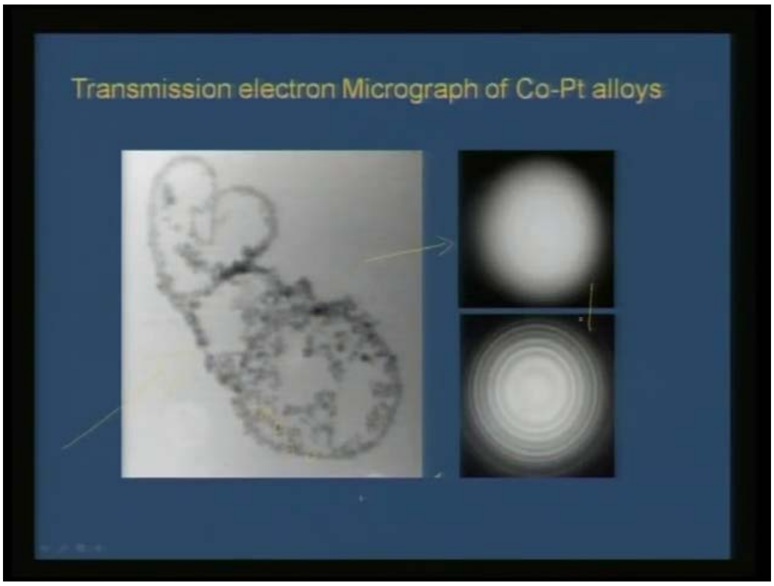

Transmission electron Micrograph of Co-Pt alloys

And some of the view graphs will tell us, what sort of product we can get, this is a typical transmission electron micrograph of cobalt platinum nano particles that have formed, you can see they are making some sort of a heart shaped decorations. And essentially each one of the small dots are cobalt platinum nano particles, roughly of the order of 2 to 3 nanometer in size. How do I know that if you take the selected area diffraction of this particular compound it gives a blurred image, which means it is not even polycrystalline it is really in amorphous form, so you do not get any electron diffraction spots.

But, if you are actually going to focus the same TM, a beam or the electron beam on a particular particle you would see this ((Refer Time: 44:18)), but soon after that you would also find that the same region is getting crystallized to a ring pattern. What does this mean, the electron beam is able to crystallize that nano particle from amorphous to a crystalline form. So, it is that fine at the same time they are very reactive, they can even get crystallized by the interacting electron beam, therefore we need to understand this is the sort of reactive particles that we can end up with sonochemistry. Now, what is so great about these cobalt platinum nano alloys, because cobalt platinum nano alloys show structural disorder, and this can influence the magnetic property or catalytic property to a greater extent.

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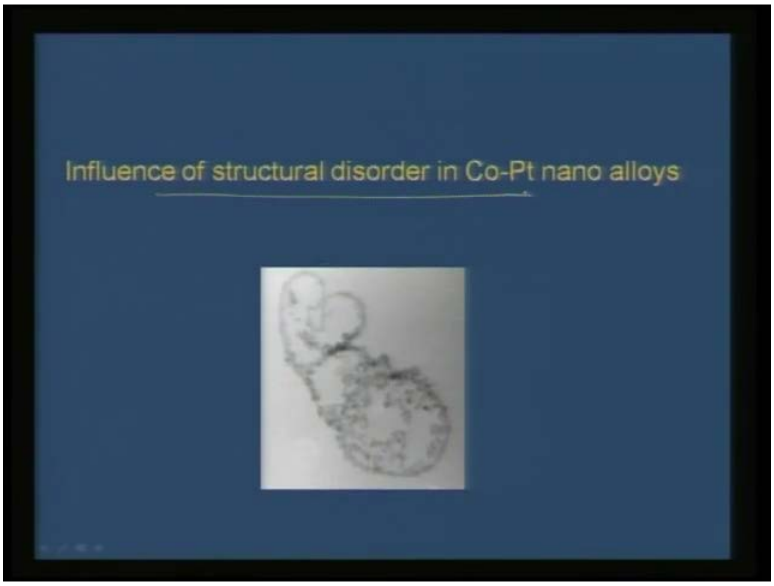

Influence of structural disorder in Co-Pt nano alloys

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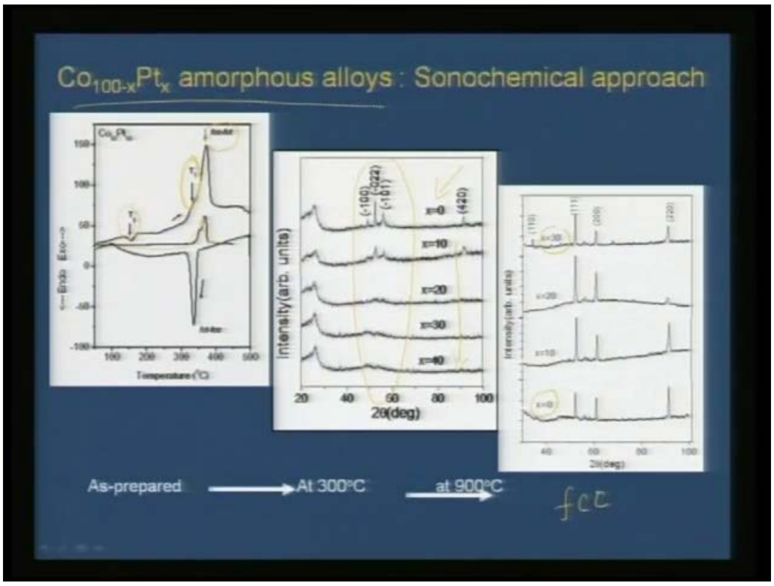

Co$_{100-x}$Pt$_x$ amorphous alloys : Sonochemical approach

As-prepared → At 300°C → at 900°C

fcc

If you take the cobalt platinum amorphous alloys that we have prepared using sonochemical approach, you can see the phase transformation that is occurring. If you do the DSC curve for cobalt platinum, the first peak what you see here is the glass transition temperature; and this amorphous alloy is getting crystallized somewhere around 350 degree C. So, if you want to study this in amorphous form, you should always restrict your temperature for treating these particles well below 300.

Now, one of the beauty of this DSC curve tells us whether this is a reversible transformation. So, first is the glass transition and then is the crystallization, then you see the fcc to fct conversion, and when you reverse it back this fcc to fct, now reverse backs to fct to fcc, so this is a reversible conversion. But, once you have crossed through this crystallization temperature on the second run, you see that this has become smaller this crystallization, and in the reversible you do not see anything.

So, the fcc to fct conversion happens beyond 400 and this is a reversible conversion in the first cycle, but once it is crystallized, then you do not see this reversible conversion. So, this is the essential feature for any sort of usage of this cobalt platinum nano particle therefore, you have a governing principal there you cannot go beyond 300 degree C. So, we can make powder compacts of this cobalt platinum, and you can anneal it at 300 to do electrical resistivity measurements.

And this cartoon tells that the in the XRD for 0 percent platinum you are seeing a small signature of HCP, and as you increase the platinum content you almost see a amorphous pattern, for the as prepared compounds. But, when you heat it at 900 degree C, in case of both the cobalt nano particle as well as 30 percent of platinum nano particle, you do not see the HCP which is supposed to be the case, whereas you see completely a fcc transformation. That is the beauty of sonochemical reaction, because fcc is not possible to be stabilized bellow 1000 degrees for cobalt platinum alloys. So, when you are heating it in 900 degree C you are able to stabilize a fcc pattern at room temperature, which means this is a metastable phase. So, in nano form when you try to prepare compounds, you are essentially able to successfully stabilize metastable phases for a cobalt platinum series.

Not only that you can see that this fcc, fct transformation is occurring as you are going to higher temperature, and this 200 and this 220 incidentally these are the peaks of platinum substrate, this is not the system peak, this is the platinum substrate peak. So, what you should be watching is the crystallization or the fcc to fct transformation which is occurring here, as a function of temperature. So, this is a high temperature X-ray pattern that we have done for cobalt platinum 50, 50 alloy, so you can see how the crystallization and phase transformation occurs.

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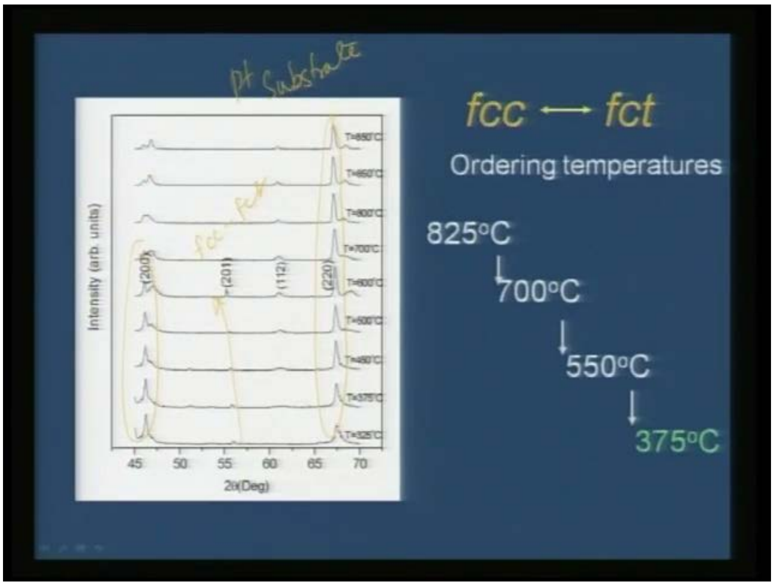

fcc ⟷ fct

Ordering temperatures

825°C

700°C

550°C

375°C

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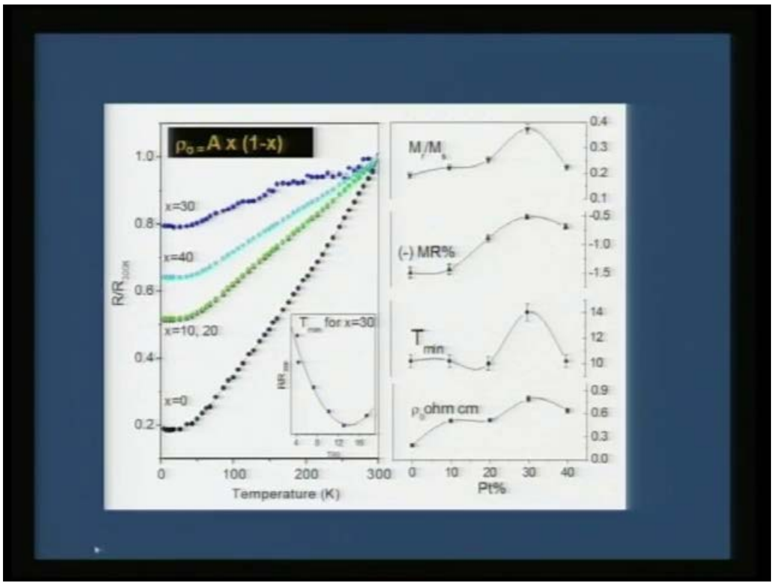

Now, one of the important things that I want to drive home in this viewgraph is, what really happens to the electrical property in this sort of materials, non materials. If you do the normalized resistance versus temperature plot, you can see systematically the resistance is increasing as you increase with platinum. But, what happens in all cases, you have a minima which is important from the physics point of view, this is exactly due to the local disorder or due to the magnon effect, and as a result you have a up curve in the resistivity below this minima.

Now, if you look at the T minima that we are talking about, and if you try to plot this T minima as a function of platinum concentration, you would see only for a 30 percent cobalt platinum alloy, using the T minima is more pronounces, and also the residual resistivity seems to be more pronounced only for 30 percent. As a result if you plot the MR by MS from the hysteresis loop, you also see the same trend for the cobalt platinum alloy and as a result the magneto resistance ratio seems to be maximum only for 30 percent platinum doped alloy. So, what do we see from here, we can make correlations between magneto resistance and the local disorder in this cobalt platinum nano alloys, and we can make several interesting observations as a function of platinum doping.

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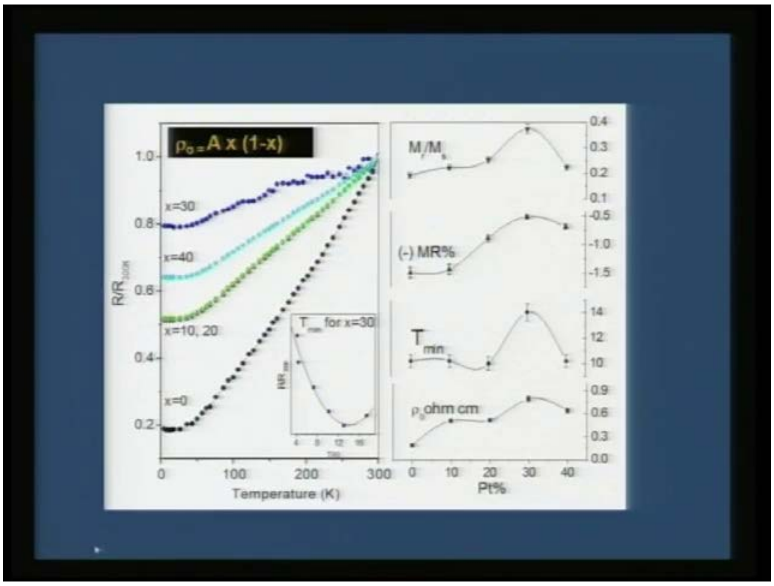

So, one can systematically study what is really the governing factor that controls the properties, as you see here all the amorphous alloys show magneto resistance 0, 10, 20, 30, 40 percent. But, when you do the magneto resistance at 300 percent you see a positive MR only for 30 percent doped once, whereas the other once are showing feeble magneto resistance. And this positive MR is due to the local order and also, because of the resistivity which is higher for the 30 percent case. So, we can bring in interesting conclusions based on the structural property correlations.

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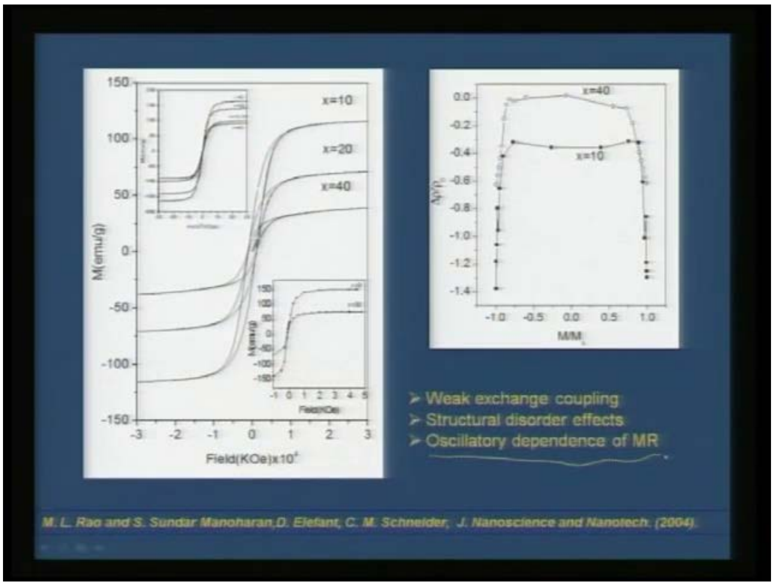

- Weak exchange coupling
- Structural disorder effects
- Oscilatory dependence of MR

M. L. Rao and S. Sundar Manoharan,D. Elefant, C. M. Schneider, J. Nanoscience and Nanotech. (2004).

And we can also see that there is a very strong coupling for 10 and 40 percent platinum doped one, compared to the 30 percent stuff and therefore, there is a oscillatory dependence of MR that we can notice in these compounds.

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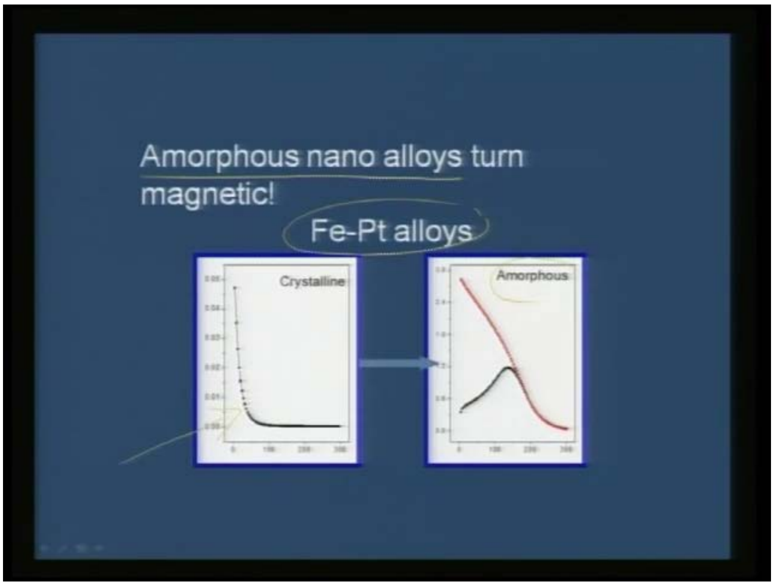

Amorphous nano alloys turn magnetic!

Fe-Pt alloys

Another interesting alloy is ion platinum nano alloy, we can prepare it in amorphous nano form. But, there are interesting features that we see in ion platinum nano alloys, this is the resistivity curve for a typical ion platinum nano alloy prepared by sonochemistry, where you can see a crystalline one shows a resistivity curve like this. And amorphous curve actually shows the magnetic transition in a peculiar form.

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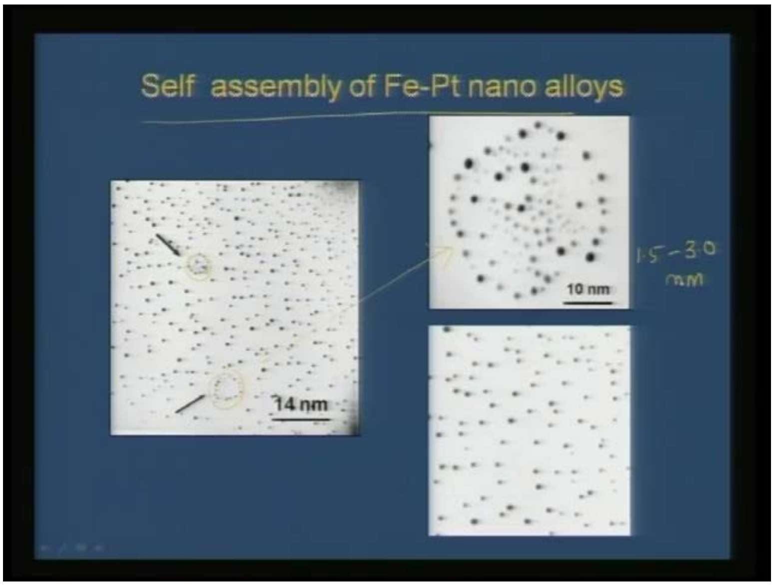

Self assembly of Fe-Pt nano alloys

Let me bring forth some examples of that, before that you can see how the ion platinum nano alloys form a self assembly. As you can see here, there are several regions where this sort of clustering of these nano particles are happening which I have shown in this cartoon. And if you calculate the nano particles, these are typically from 1.5 to 3 nano meter size, so in such particles size we can isolate ion particle nano alloys.

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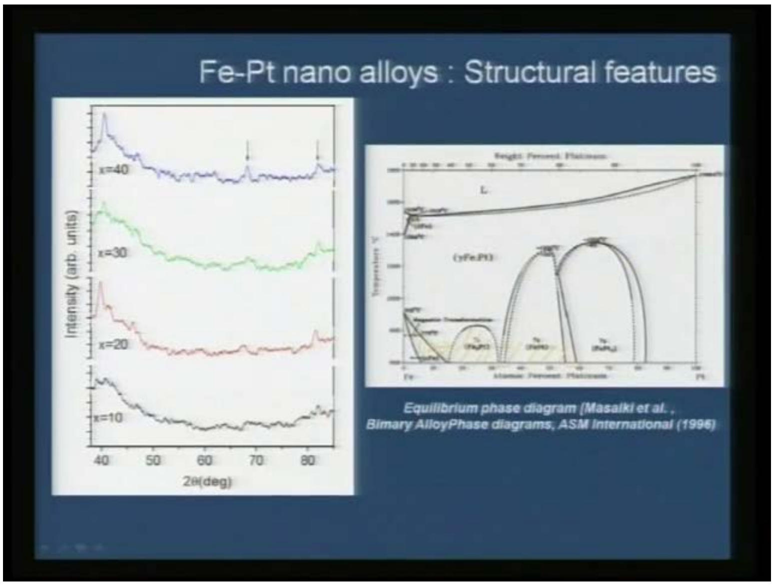

Fe-Pt nano alloys : Structural features

Equilibrium phase diagram [Masalki et al., Bimary AlloyPhase diagrams, ASM International (1996)

And if you can actually look at the phase diagram, there are interesting things that we can understand, one is there are several regions where the equilibrium phase diagram indicates, there are magnetic phases as well as non magnetic phases. For example, in this case you have alpha Fe face and this is the region where the alloy is magnetic, and this is the region where alloy is magnetic. And this is the region where alloy is magnetic and there are regions, where because of order disorder transformation you do not see magnetic phases.

So, if there are no magnetic phases in between in this region, then those regions should not show magneto resistance. So, in the next few graphs I will try to show you, how critically the magnetic phases depend on magneto resistive response. And how sonochemically derived powders can influence the magnetic property, and this we will see in the subsequence slides.