Chemistry and Physics of Surfaces and Interfaces
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Lecture - 09
Thermal Desorption Spectroscopy

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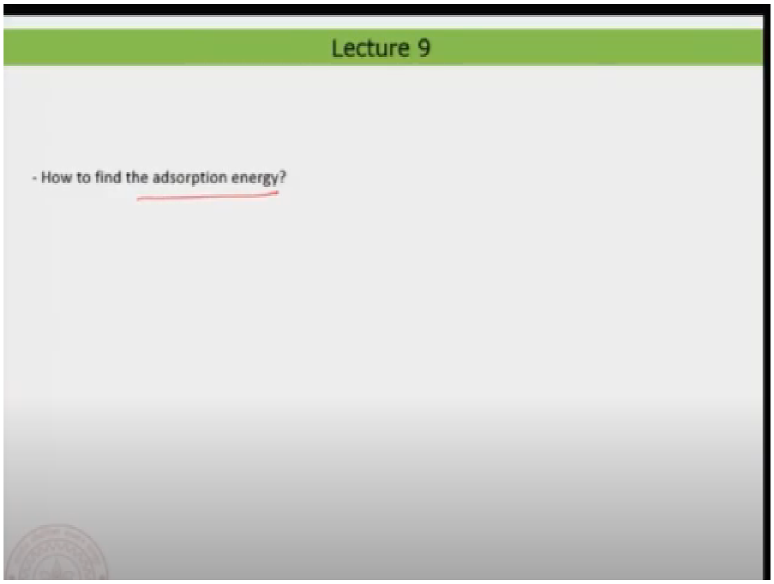

Lecture 9

- How to find the adsorption energy?

Hello again. Welcome back to lecture 9. So, in this lecture as I have already told you in the previous lecture, we are going to determine the adsorption energy experimentally. So far what we have been doing is to basically look at the possibility of adsorption energy and what is the range of adsorption energy that you are going to get. And we have already seen that it is depending on the adsorption sites and depending on the pattern or depending on the adlayer structure that is forming you can have basically different types of adsorption energy.

So, now we will technically determine the adsorption energy so that we have an understanding about the magnitude of the adsorption energy of different atoms on different surfaces.

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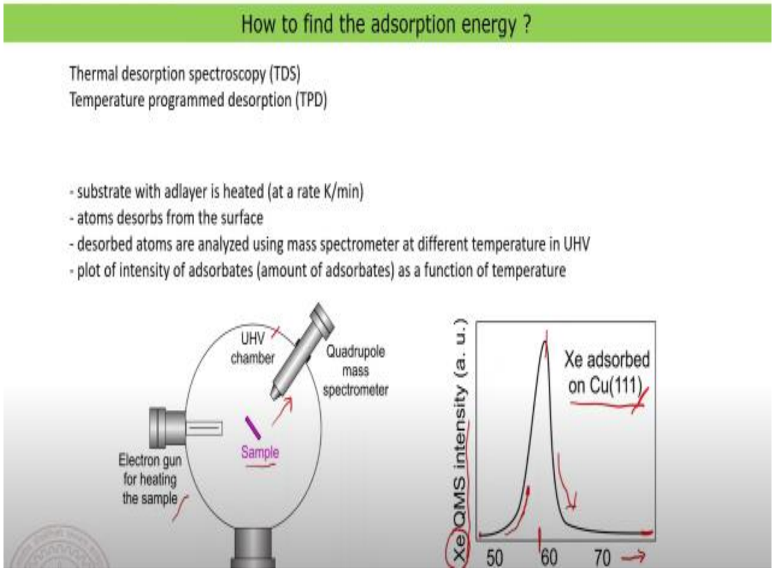

How to find the adsorption energy ?

Thermal desorption spectroscopy (TDS)
Temperature programmed desorption (TPD)

- substrate with adlayer is heated (at a rate K/min)
- atoms desorbs from the surface
- desorbed atoms are analyzed using mass spectrometer at different temperature in UHV
- plot of intensity of adsorbates (amount of adsorbates) as a function of temperature

So, we use a technique which is known as thermal desorption spectroscopy or it is generally also known as temperature programmed desorption. So why there is actually the term spectroscopy? So, in this technique what we are going to determine is an energy form that is actually nothing but the adsorption energy or the desorption energy. So, you have seen they are basically connected. That is the reason why some communities call it as thermal desorption spectroscopy or in general it is basically known as temperature programmed desorption. So, what do you do in this technique? You do something very simple. Everything is going to happen in an ultra-high vacuum chamber that is something I have told you. Please keep that in mind always in your background. And within an ultra-high vacuum chamber you have a surface with your adlayer adsorbed on it. Now this particular surface is going to be heated at a rate and the atoms that are actually evaporating into the vacuum will actually be looked at or detected using a mass spectrometer. What you can now measure is as a function of temperature you can basically measure the magnitude or the amount of adsorbed atoms that are coming back from the surface using the mass spectrometer. So that is basically what you do in this technique. Now let me show you the component that you require for doing a thermal desorption spectroscopy. Well, we require an ultra-high vacuum chamber. Because we do not want to have any other component than the dissolving atoms or molecules to be detected. So therefore, the prime requirement is to have a UHV chamber. Then the sample is basically placed at the center of the UHV chamber or ultra-high vacuum chamber and then using an electron gun we basically heat the sample. And when the temperature of the sample increases the adatom or admolecule or that means the molecules that are adsorbed or the atoms that are adsorbed on the surface will start to desorb slowly and depending on the temperature the species that is coming out of the surface will vary and that is something we will see in the next slides. But now assume that you have basically a particular atom coming out of the surface at a given temperature. And then you can basically detect that using the quadrupole mass spectrometer, which is basically placed opposite to the sample. Now, the quadrupole mass spectrometer we can tune to a given mass. And therefore, we can basically detect a particular type of atom or molecule that is actually evaporating from the sample. Now, we can basically measure that particular species as a function of temperature. Well, we can also measure the amount of atoms or molecules that is coming out of the sample as a function of time as well, which will allow us in understanding basically the kinetics and the energetics of the desorption. Now, let me show you first what a typical thermal desorption spectrum looks like. So, on the y axis you have basically nothing but the intensity that you get directly from the quadrupole mass spectrometer. So here it is actually nothing but the intensity of the xenon atom that is coming out of the sample. So, what you are investigating right now in this particular case is the xenon adlayer on copper 111 surface. Now in the beginning you can notice that there is no signal that is corresponding to xenon but as the temperature increases, there is a small increase in the amount of xenon atoms and then of course, it increases and then basically reaching a peak position. And afterwards the amount is basically decreasing and then at a very high temperature you can see basically there is no signal corresponding to xenon. That is meaning that the xenon is basically desorbed from the surface. Of course, xenon is a noble gas and that is a reason why the temperature that you require to basically desorb them from the surface is basically very very low. So, this is around 60 kelvin that is of course low. But depending on the nature and the type of adsorbate atoms or adsorbate molecules on the surface and also the type of surface you will find that the peak temperature basically varies. Now the thermal desorption spectroscopy we can do it in one way in different ways. So, this is the first representation that is basically the signal of a given species as a function of temperature and the peak maximum would give you something like a desorption temperature. So, this is an important quantity that will basically represent the desorption energy of the species from a given surface. But now I can also basically just measure the amount of material that is desorbed as a function of temperature which will also give rise to the understanding of the kinetics of the desorption. So that basically means using the thermal desorption spectroscopy one can basically understand the energetics as well as the kinetics of the desorption. So, to now understand the shape and the nature of this kind of thermal desorption spectroscopy we would need to understand the kinetics of desorption. So first let us look at the kinetics of the desorption itself.

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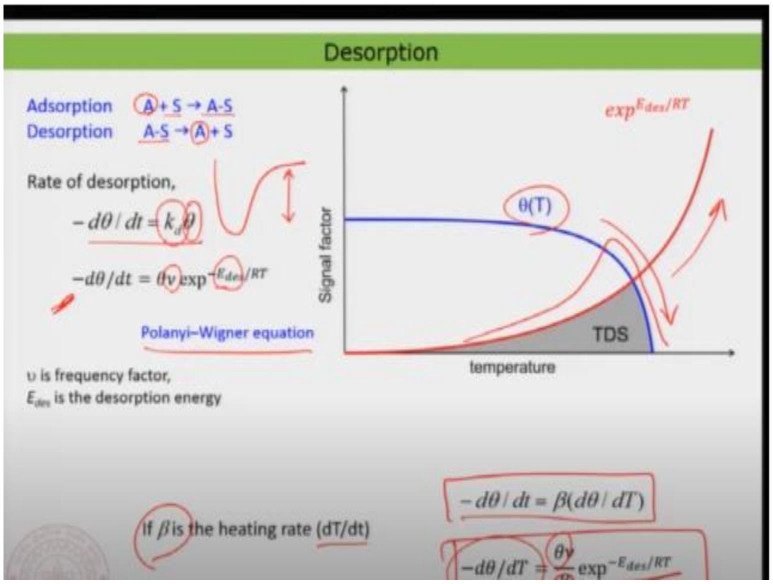

Desorption

Adsorption $A + S \rightarrow A\text{-}S$

Desorption $A\text{-}S \rightarrow A + S$

Rate of desorption,

$-d\theta/dt = k_d\theta$

$-d\theta/dt = \theta\nu \exp^{-E_{des}/RT}$

Polanyi–Wigner equation

ν is frequency factor,

E_{des} is the desorption energy

If β is the heating rate (dT/dt)

$-d\theta/dt = \beta(d\theta/dT)$

$-d\theta/dT = \frac{\theta\nu}{} \exp^{-E_{des}/RT}$

So, to understand that we have to look at the adsorption and desorption itself. So, you know that adsorption is basically you have an adsorbate atom that is going on to the surface. You have the surface an atom is going on to the surface and then you form something called an adsorbate on a surface site. And desorption is just the opposite process. You have the adsorbate on the surface and you basically heat and then you get the adsorbate out of the surface and the surface remains as it is. So, this is basically the adsorption and the desorption. Now you can look at the rate of desorption very simply. So, the rate of desorption is basically dependent on the initial coverage that is the amount of atoms or molecules that is present on the surface or the atoms that are present in the adlayer. And then it is also dependent on Kd that is actually the rate constant of the desorption. Now, we know that the rate constant of the desorption is truly dependent on desorption energy itself. You remember or if you recollect so this was basically our potential energy diagram for the desorption itself where the barrier that the atoms need to cross is basically this double headed arrow. Now and then it is also dependent on the temperature and then also some factor called nu that is actually known as the frequency factor. And this is basically known as the Polanyi-Wigner equation which is actually a popular representation for the rate of desorption.

Now one more important factor we need to consider inside. So here we are only looking at the rate of desorption as a function of temperature or rate of desorption itself meaning the change in the coverage of the adsorbate as a function of temperature. But we need to also consider the heating rate inside which is actually represented by beta that means it is the dT by dt. It is actually related to the d theta by small dt in this way. So that means you can basically rewrite the same equation using beta like this. So finally, now what we are getting is the d theta by dT, that means the change in coverage of the adlayer as a function of temperature because that is something we need for finally determining the energy of the desorption itself. And this is basically the important expression that connects the desorption energy and the coverage. And then, if you plot this expression so you can see there are two variables, one is theta that is the coverage and the other one is basically the temperature. Of course, E des the desorption energy itself we assume that it is a constant during this process or during the range of temperature that we are looking at. And if that is the case then you will have two independent functions that are actually working on the d theta by dT that is nothing but the theta which is a function of temperature. So, in the beginning unless and until you reach a particular temperature the rate of the adsorbate change is a constant. Then as soon as the temperature actually hits closer to the desorption temperature then the coverage basically decreases. So that is the reason why it goes down. Now, you also have an exponentially increasing function because you have this E des or the desorption energy itself has a negative quantity. So, you have basically an increasing exponential function. So, the decreasing and increasing function together finally gives rise to a shape that looks like this and this is the typical shape of the thermal desorption spectroscopy. And that is something you have seen in the previous curve where initially it slowly increases and then it peaks and then it quickly drops down to very low magnitude or a very low signal factor.

Well, now we can actually try to understand a little bit more in detail about the order of desorption whether there is any importance in the order of desorption.

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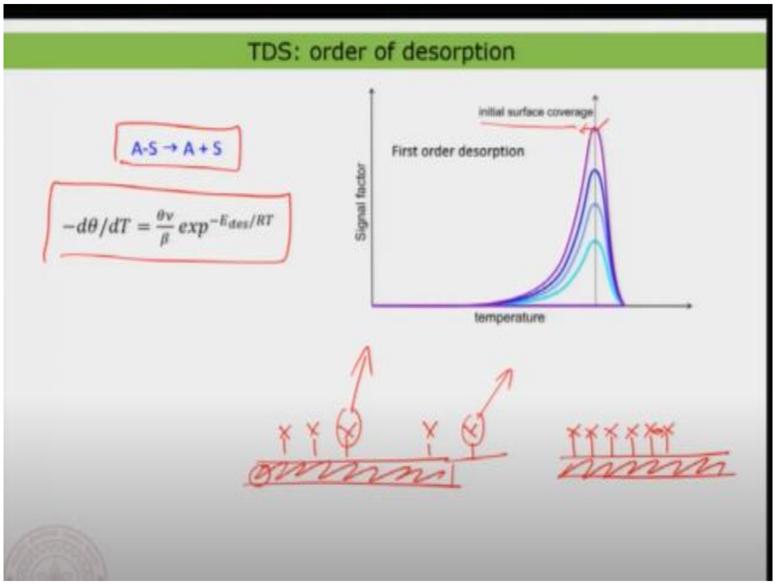

TDS: order of desorption

$A\text{-}S \rightarrow A + S$

$-d\theta/dT = \frac{\theta\nu}{\beta} exp^{-E_{des}/RT}$

Well, this one as you would find that this is simply a first order reaction. But for the first order reaction, we can use the same expression as we have actually elucidated in the previous case. And in that case what is very interesting is that the initial surface coverage or the initial coverage of the adlayer on the surface is actually independent to the peak position. So, the peak position is not dependent at all on the initial surface coverage of the adsorbate layer. Well, this is true for moderate coverage and an extremely high coverage and depending on some material you might find some changes. But generally, this is the case that you would observe in the coverage dependence. So, this actually tells me that the desorption itself what we are observing is a first order process. Now let us look at the molecular level picture. So here again I have let us say a surface and then I have my atoms that are sticking on the surface like this with let us say like different coverages. You can actually have it in around the surface. Now when they desorb you would find that they will basically just desorb independently. So, the atoms would not communicate with each other in a true ideal case. So, if that is the case then of course the point is they should not basically have any kind of interaction between the atoms and that is the reason why the initial coverage and the peak positions are actually independent of each other. Even if you take actually an extremely high coverage. So now imagine a situation of the surface which is extremely covered that means atoms are actually packed extremely close packed. In that case for example, they can have like repulsions between these atoms and that actually can cause a reduction in the adsorption energy and then the energy of this position can actually be shifted a little bit to the lower temperature. This is actually possible at an extremely high coverage for the first order reaction. But normally in a moderate coverage or even to a relatively high coverage the adsorption peak or the so called desorption peak temperature is independent of the initial surface coverage.

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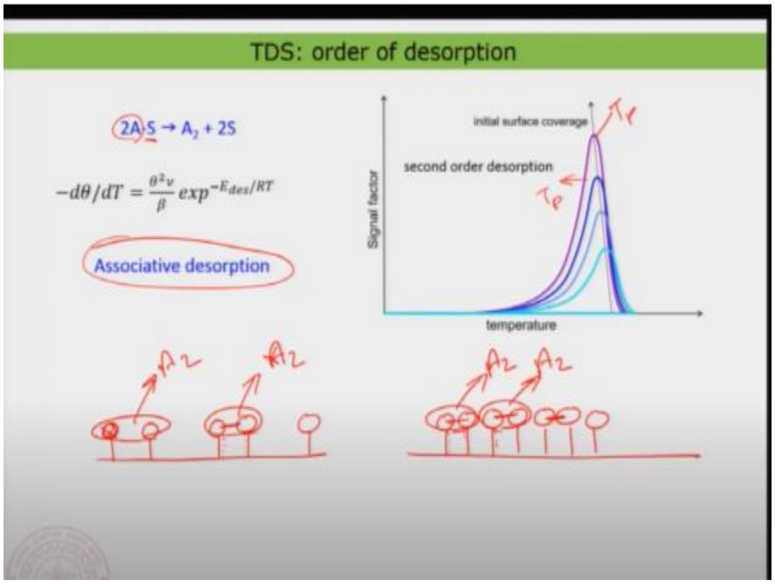

TDS: order of desorption

$2A\text{-}S \rightarrow A_2 + 2S$

$$-d\theta/dT = \frac{\theta^2 v}{\beta} exp^{-E_{des}/RT}$$

Associative desorption

But when it comes to the second order reaction where you basically have something known as an associative desorption. There you have two adsorption atoms and then you have the surface and when they release, they are basically coming as a molecule, a diatomic molecule for example, or a triatomic molecule whatsoever. That means desorption is basically associative. In that case there is something interesting that you would find that the coverage is strongly dependent TO the peak position. So, this is actually the Tp that means the peak position of the desorption curve and you can now see that the initial coverage, if the initial coverage is very high then the desorption peak is basically dependent or the desorption peak is basically going down in the temperature. So that means the temperature you would require is lower temperature to desorb a high density adsorbate surface. So that is something interesting. So why is that happening? So that is something we can try to understand. Imagine the again that you have your surface and at a lower coverage let us say like I am just calling this time circles I have lower coverage the atoms are actually just occupied like this. And I have another situation where atoms are actually occupied very dense like this. Now the point is in this particular case since the desorption is associative in nature when you increase the temperature what happens is actually that the atoms start to pair up and they actually get released as A_2 here. So here atoms start to pair up and when they get released they would basically just released or desorbed as A_2. So now the interesting thing here is since the atoms are actually strongly interacting types of molecules they actually interact with each other and therefore the interaction between the surface is actually getting weaker. And that would particularly happen at a higher coverage because you have a higher density of atoms. So, the chances of forming the A_2 is very high. That means all these molecules are going to be now paired up already in the adsorbed state. That means the interaction between the surface and the adsorbate atoms are actually weaker than in this situation which would mean that you would not require the same amount of adsorption energy as you require in the lower coverage. And as a fact you would find that always the initial coverage is strongly giving you a dependence on the peak temperature. And particularly if the initial coverage is very high the temperature required for the desorption is lower compared to that for a lower initial coverage. So, this is telling you directly that what you are looking at is actually a second order desorption process.

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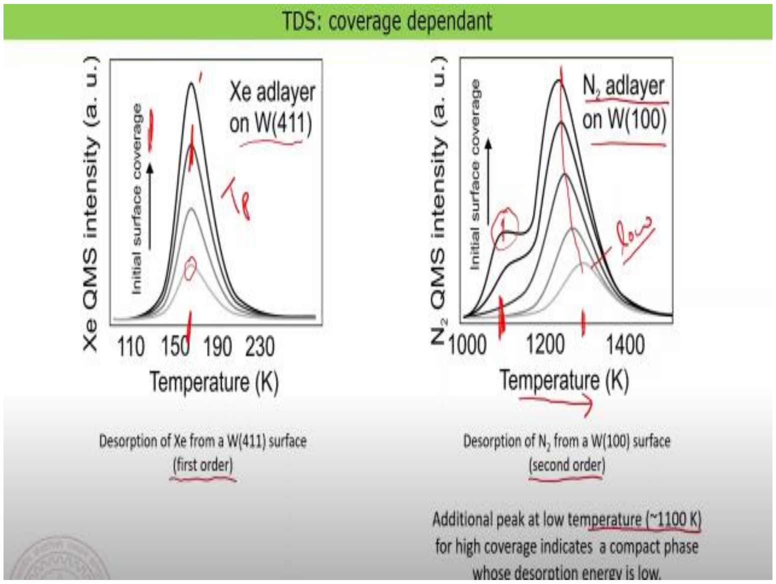

TDS: coverage dependant

Desorption of Xe from a W(411) surface (first order)

Desorption of N_2 from a W(100) surface (second order)

Additional peak at low temperature (~1100 K) for high coverage indicates a compact phase whose desorption energy is low.

Now let us have a look at a few examples of thermal desorption spectrums recorded on different types of adsorption adlayers and also on different types of surfaces. So, this is again the same type of adlayers, xenon but instead on copper 111 we have basically here a tungsten 411 surface. Of course, as we have already seen the high index surface 411 is a more corrugated surface basically. It is basically a surface with more steps and also with more kinks. Now something interesting that you would immediately notice is the desorption temperature which is slightly higher compared to what we have seen for the xenon adlayer on copper 111 surface. Well, the reason is directly imaginable because we have a surface which is more corrugated. Therefore, the reactivity of the surface is larger and even for a noble atom xenon for example, you see the desorption temperature is high which directly means that we have a higher absorption energy or desorption energy. Now something interesting as I have already told you we can do with thermal desorption spectroscopy is also we can look at the dependence and the type of kinetics of this kind of adlayer. And what I have here is basically different thermal desorption spectroscopy recorded at different initial coverages. So that means you have basically a low coverage and then the coverage is basically increasing in the other curve. So here basically I have a thermal desorption spectrum recorded with an initial higher coverage. Now what is interesting is basically that you notice that there is no difference in the peak position. So let us call this as Tp, so that is a peak temperature. So, there is no difference in the peak temperature as the initial surface coverage varies. So, this is a direct indication that the reaction what you are looking is actually or the desorption that what you are looking for is a first order desorption. That is something we have already discussed in the previous slide and now you can see in a real example that we have basically a first order desorption. That means the coverage is independent and the peak temperature is independent of the coverage.

Now let us look at a few more interesting examples then you would basically understand and strikingly that for nitrogen adlayer on tungsten 100 surface and 100 surface is also of course a corrugated surface. Because you have all these four-fold holocytes as we have seen in the previous lecture. You can see basically the nitrogen is dissolving and now we have the temperature dependence and what is striking definitely is the first and foremost important information is the peak temperature of the desorption and particularly at low coverages. So, this is basically the low coverage and for the low coverage you see there is only one peak corresponding to the desorption of the nitrogen from the surface. Now what interesting thing is as the coverage increases you can see basically the peak temperature is also changing and this is particularly going to a lower temperature. And this is something characteristic to the second order reaction because we know that the desorption of nitrogen is associative or the adsorption of nitrogen is basically dissociative, that means as the coverage increases you have more and more molecules packed in a given area which is meaning that there is a competition between the molecule-molecule interaction and the molecule-surface interaction. As we have seen in the previous slides when the coverage is very high there is basically weaker molecule-surface interaction and therefore the peak temperature is basically decreasing and that is exactly what you see here at a higher initial coverage, you basically see that the peak temperature is lower which is directly meaning that our desorption temperature sorry the desorption energy is lower than that at low coverage. Now there is another interesting aspect that you would also see that is actually that you have an additional peak somewhere around 1100 kelvin. So that is a peak here and this is actually showing you that the molecules are actually having a slightly different type of packing. So of course, we have seen the different types of packing you can have like the 1 by 1, 2 by 2, root 2 by root 2 and different types of packing we have already seen. So now what this particular case is indicating is that you have not just one type of adsorption or one type of adlayer packing but you have different types of adlayer packing. And particularly at higher coverages you can actually just notice that there is an additional type of packing and that is a reason why you have this kind of an additional peak. And now interesting thing is that the peak energy or the temperature corresponding to the peak is basically much lower compared to that at the lower coverage. Well, that is something that one can also imagine that at higher coverage you will have basically higher packing density structure or higher packing density adlayers and that is normally corresponding to a lower adsorption energy because their interaction to the surface would be lower compared to that forming at lower temperature. We will see this in greater detail a little later using another technique. So, there we will basically just discuss this even further.

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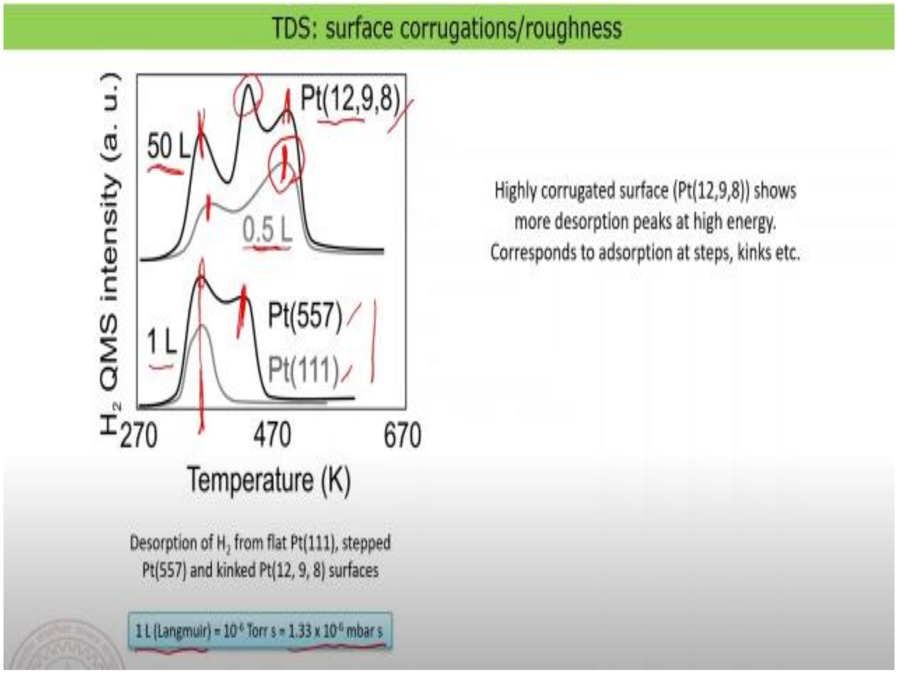

TDS: surface corrugations/roughness

Highly corrugated surface (Pt(12,9,8)) shows more desorption peaks at high energy. Corresponds to adsorption at steps, kinks etc.

Desorption of H_2 from flat Pt(111), stepped Pt(557) and kinked Pt(12, 9, 8) surfaces

1 L (Langmuir) = 10^{-6} Torr s = 1.33×10^{-6} mbar s

Now let me introduce to you another type of material that is basically a hydrogen adlayer on a platinum surface. So here what I would like to compare is the variety of surfaces. So, I am going to now compare basically the adsorption of hydrogen on the platinum 111 surface which is supposed to be the least corrugated surface. Because platinum is also an fcc type of packing so you have basically the least corrugated surface. Then you have basically the 557 which is a step surface and then you have a high index surface which is 12, 9, 8 that is actually a step and a kinked surface. So that means you have basically a variety of surfaces of a given adsorbate on the surface. Now something interesting that you definitely notice is that for the platinum 111 surface you only find one particular peak for the desorption of hydrogen, which means that the adsorption sites of all the hydrogen atoms that you have are kind of similar. Now please also notice that here I am also just adding something called the initial coverage at which you have done this experiment, where the L is representing something known as Langmuir, that is a typical unit that people use in surface science to represent the coverage of an adlayer. And one Langmuir basically corresponding to this kind of a pressure and that would give you an idea of how much amount of a gas you would require to form 1 Langmuir. Now of course, these two experiments are done both at 1 Langmuir. Now for the platinum 111 surface as you see there is only one peak but for the platinum 557 you see there are two peaks where one is almost the same as that you have observed for the platinum 111. But the other one is basically a little bit at a higher energy. So, you can now imagine when some kind of a peak which is observing at higher energy would mean that this is directly coming from a species which is adsorbed strongly on the surface. Well, 557 is actually a step surface. So therefore, you would imagine that the molecules that are actually decorated at the steps are corresponding to this high energy peak and the one which is at lower energy which is similar to that of the platinum 111 surface is the one which is actually corresponding to the adsorption of hydrogen molecules at the terrace. Now this is quite interesting. By looking at the variety of surfaces of a given adsorbate you can now understand the possible type of adsorptions on the surface. Now let me also show you one more example of adsorption of hydrogen on a platinum 12,9,8 surface which is definitely a much higher index surface which means that you have not only just steps you also have a lot of kinks. Now when you do this experiment at 0.5 mono layer and at 50 layer there is a strong difference. So, at 0.5 layer Langmuir you would basically find that you have like one peak that is corresponding to the adsorption from the terrace. Because it is similar to that you have also seen for the platinum 111 and platinum 557. But there is something at a much higher energy much higher desorption temperature so that is meaning that much higher absorption energy. And this is actually corresponding to those molecules which are actually adsorbed at the kinks and the step and definitely you find that the amount, so the intensity of the peak is of course the amount of adsorbate which is actually like coming out of a given site. In this case you can see that the higher temperature peak is actually much more intense than that of the lower one which means that there is much more corrugated the surface is of course much more corrugated. And the amount of steps in the kinks are actually much more higher than that of the terraces which means that you have a lot of adsorbed species which are coming from the steps and the kinks. And that is the reason why you have a higher amount at higher temperature. Now something interesting you would also notice that at a very high coverage at 50 layers you have not only just the molecules that are coming from the terrace and so the molecules that are coming from the terrace and also from the step edges. You also have an additional peak which is actually corresponding to a high-density packed structure that is on the surface. Now what I would like to show you using this variety of example is basically that the thermal desorption spectroscopy is a great technique that will allow you to understand the variety of adsorption sites on the surfaces, the variety of packing on the surfaces and also the reactivity of the molecule or atomic adsorbates onto variety of surfaces. So, by doing these kinds of comparative studies one can clearly understand all these characteristics about the type of surfaces, the reactivity of the surfaces, the nature of the desorption. And I also have shown you in the earlier slide that we can also basically look at the time dependent of the signal that is corresponding to a desorbing species. So therefore, thermal desorption spectroscopy is a very powerful technique that is widely used in surface science.

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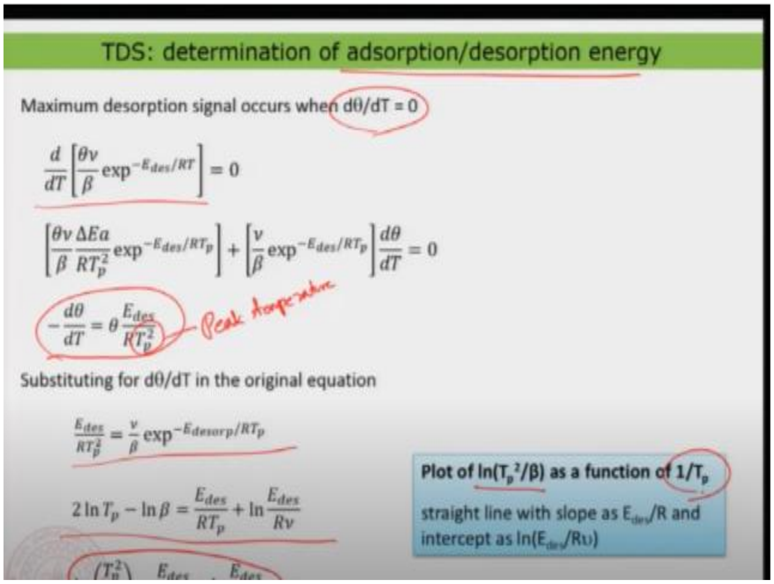

TDS: determination of adsorption/desorption energy

Maximum desorption signal occurs when $d\theta/dT = 0$

$$\frac{d}{dT}\left[\frac{\theta v}{\beta}\exp^{-E_{des}/RT}\right] = 0$$

$$\left[\frac{\theta v}{\beta}\frac{\Delta Ea}{RT_p^2}\exp^{-E_{des}/RT_p}\right] + \left[\frac{v}{\beta}\exp^{-E_{des}/RT_p}\right]\frac{d\theta}{dT} = 0$$

$$-\frac{d\theta}{dT} = \theta\frac{E_{des}}{RT_p^2}$$

Peak temperature

Substituting for $d\theta/dT$ in the original equation

$$\frac{E_{des}}{RT_p^2} = \frac{v}{\beta}\exp^{-E_{desorp}/RT_p}$$

$$2\ln T_p - \ln\beta = \frac{E_{des}}{RT_p} + \ln\frac{E_{des}}{Rv}$$

Plot of $\ln(T_p^2/\beta)$ as a function of $1/T_p$

straight line with slope as E_{des}/R and intercept as $\ln(E_{des}/R\upsilon)$

And now what we will try to do is to characterize the adsorption energy or the desorption energy itself. We want to now calculate the energy. How do we do that? So, we have basically a peak. So, at the peak position the change in theta by temperature should be basically 0. So, you can use the maximum of that which is actually equated to 0. So, then you can take our expression for the d theta by dT, and then you can actually equate it to 0 and by solving you can get that d theta by dT is actually equal to theta, E desorption energy by RTp square where Tp is actually the peak temperature. Now you can substitute this d theta by dT in the previous equation in the original equation and then you can actually get this expression. And you can actually put log on to both sides and then you can finally write down the expression in the form of a line-like expression. Now you see if I would plot the log Tp square by beta, beta is actually the heating rate you please recollect. I as a function of 1 by Tp that means what you have to all do is you have to do independent experiments at different coverages and then you have to plot actually the log Tp square by beta as a function of 1 by T and the slope would basically owe you the desorption energy directly. So that is what we want to do.

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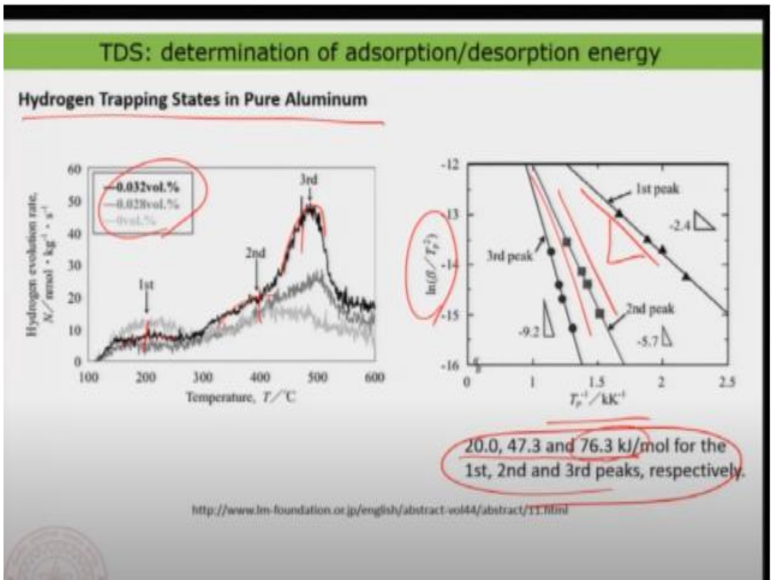

TDS: determination of adsorption/desorption energy

Hydrogen Trapping States in Pure Aluminum

20.0, 47.3 and 76.3 kJ/mol for the 1st, 2nd and 3rd peaks, respectively.

http://www.lm-foundation.or.jp/english/abstract-vol44/abstract/11.html

So, we can now have a look at one example here. So, this is basically done even not on a crystalline surface. This is basically done on even a kind of non-crystalline surface like an alumina, a pure aluminum for example, where what we have done is basically a different surface coverages. They have done experiments and determined basically the different type of hydrogen that is basically coming out of the surface. Now what is interesting is that there are three peaks and the three peaks are basically the three different types of adsorption sites on the surface. And the,n now I can basically plot the log beta Tp square as a function of 1 by T and then you see linear plots I am basically getting. Now, the slope of this would directly give me the desorption energy. Of course, the desorption energy is basically calculated here. The desorption energy for the first peak, the second peak and the third peak you can see the magnitude of energies are increasing. That is exactly what I told you if you have the higher temperature at which things are desorbing which means that the energy of desorption is actually higher and as the temperature goes down the energy of desorption is basically lower. So, this effectively tells me that on the pure aluminum hydrogen can actually get trapped in three independent ways or three different type of sites and the three different type of sites are actually just having different desorption energy like 20 kilojoules and 47 kilojoules and 76 kilojoules per mole and so on. So that is all about it. So, you can basically now using thermal desorption spectroscopy determine the desorption energy or therefore the adsorption energy and you can determine whether the processes are like first order, second order. You can also determine the type of sites that are present, you can also determine basically the different types of adlayer patterns that you form and so on. So, this is a very powerful technique which is commonly used in understanding the energy of the adsorbate layer on the surface.

With this I conclude. Well, I would also like to mention that this technique can also be applied in amorphous cases. It is not just limited only to pure crystalline materials. Well, with this I would like to conclude this lecture and then I see you in the next lecture. Thank you very much for your attention.