Chemistry and Physics of Surfaces and Interfaces
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Lecture - 39
Dynamics of Atoms on Surface

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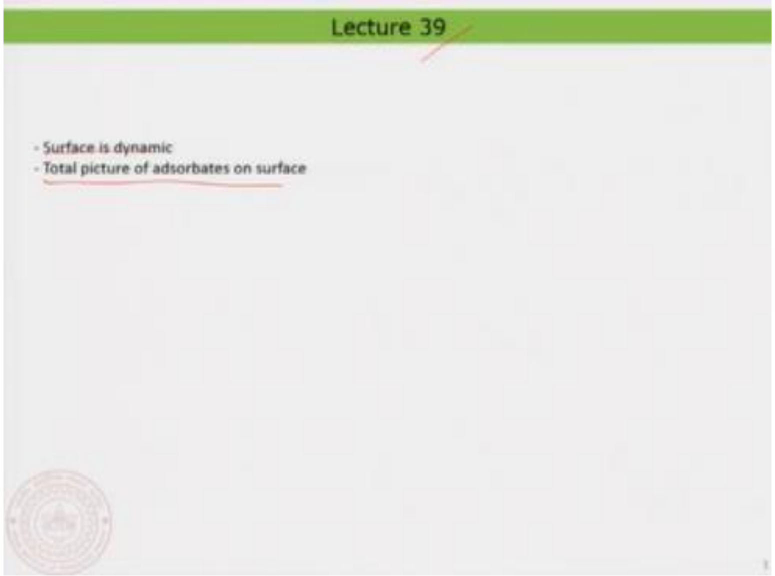

Lecture 39

- Surface is dynamic
- Total picture of adsorbates on surface

Hello everyone, welcome back to lecture number 39. In this lecture, I am going to introduce one more important point to be considered on when you study surface that something we have not so far discussed and that is going to give us a complete picture. This is about surface is dynamic. So, far when we talked about; we said that when you adsorb something on the surface be an atom small molecules or big adsorbates, big molecules or so on.

We always have seen that the molecule or the adsorbate was just at a given position. Well, keep it in mind that all the images that you have looked at are just a snapshot at a given time. Well, if you would have basically just looked at the surface over a longer range of time you would have actually noticed that nothing is basically just stagnant on the surface. Every adatom even the surface atom is basically moving around on the surface. That means surface is dynamic at all the time at all the temperature, only when you go down to very low temperature you can ideally freeze those adsorbates or the surface atoms ideally. Otherwise, they are always dynamic so, that is also something we have to we have to consider we need to take into account when we study the surfaces and interfaces. And that will give us something like the total picture of adsorbates on surface. So, that is what we are going to basically just deal in this lecture and also to quantitatively look how these dynamics actually happens on the surface.

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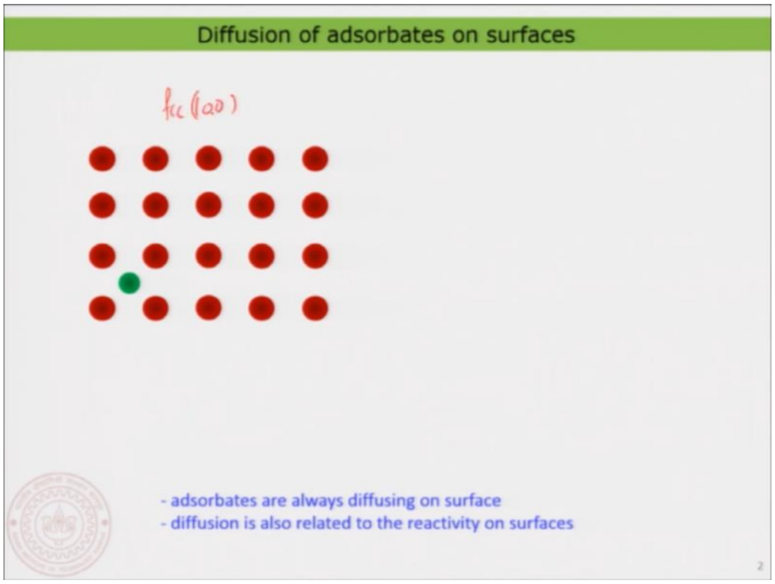

Diffusion of adsorbates on surfaces

- adsorbates are always diffusing on surface
- diffusion is also related to the reactivity on surfaces

Now I just want to demonstrate a very simple schematic exercise of a surface like an fcc 100. So, this would be an fcc 100 surface and the red atoms are nothing but the surface atoms and the green atom is a kind of add atom that you put on the surface. But so far what we have seen is when you put an adatom it will always go and sit at the high co-ordinating site namely here the so called fourfold hollow site. Well, the picture is not the as you see here, this is just a picture at a given time. So, it is just at a given moment but now, if I would look at the surface over a longer range of time over a given time.

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Then what you are going to see is something like this. That the atom on the surface is basically just diffusing over the surface.

(Video Ends: 02:55)

This is again another snapshot after given time. This is what we basically just see. So, the point what I want to make is so far, we have not considered this particular effect which looks like surface is dynamic in nature.

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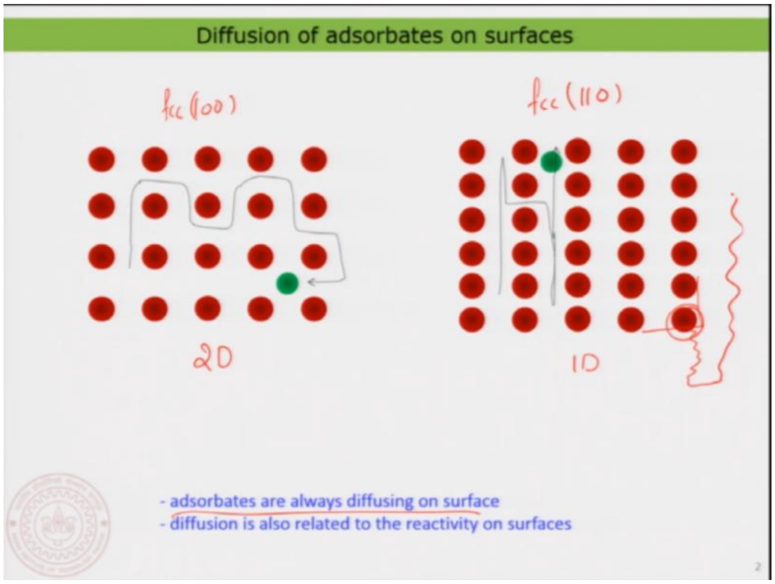

Diffusion of adsorbates on surfaces

- adsorbates are always diffusing on surface
- diffusion is also related to the reactivity on surfaces

Now let me also just show you one. So, this is basically just to track the surface the adatom movement and you see like it actually just started from one given position and end up in a completely random position elsewhere. Well, this process keep on continue so that is the interesting thing. Now I take another surface which is here and fcc 110 surface, now you see that again this surface structure is slightly different. And if I look at the time lapse of this given surface.

(Video Starts: 03:40)

So, what you are going to see is that the atom is again moving on the surface and you can see basically that the atom is all the time moving just along this given track path.

(Video Ends: 03:52)

But in the case of fcc 100 surface you see the atom was actually moving over a larger range of distance. And at the same time the atom was also just moving in all the 2 dimensions. So, basically the adatom was going over the entire two dimension of the surface. But in the case of fcc 110 there is something interesting you have noticed that the atom was most of the time moving along a given path and not really randomly as you have seen in the case of 100. Of course, the final destination is a random position compared to the original one but you see there is some kind of a preference in the way the atom is basically diffusing on the surface. So, the point in any case what we want to make here that any adsorbate it does not matter whether it is an atom or a small molecule a big molecule whatsoever. It is always the adsorbates on the surface are actually just diffusing.

And you will also see the same scenario if you go to for example a step edge. So, assume that this is basically a step edge

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Then what you will also see that these atoms at the stepped edges would also start to go on a random walk around the surface.

(Video Ends: 05:13)

So, that is also something interesting that you have to keep in mind that surface atoms itself and also the adatoms that you put on the surface are always dynamic. That means if you want to basically just use these surfaces in understanding, let us say like the reactivity of the surface or if you want to just look how a reaction would happen on a catalytic surface or on a given surface like this. It is quite important that we also have an understanding about the diffusion of the atom. Because if I want to take two atoms and let them react, I also need to know how these atoms would diffuse on the surface. Otherwise, the reaction would not even happen so that is the interesting effect of it.

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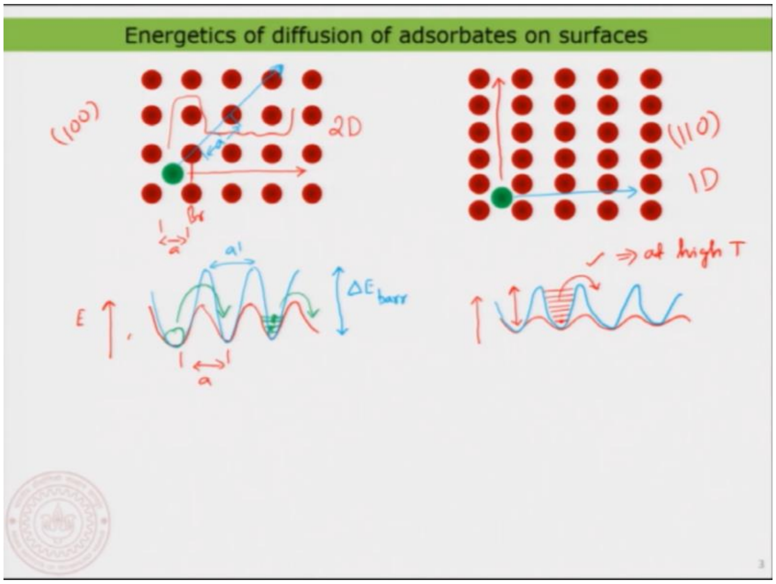

Energetics of diffusion of adsorbates on surfaces

So, like now let us control or let us try to understand what really controls the diffusion of adsorbates on surfaces. Now you see that you know that an atom when you put on the surface or an adsorbate atom when you put on the surface. There is always a so called most preferred adsorption site and if I would take these 100 surfaces you would always find the atom is basically sticking at the so, called fourfold hollow side that is actually because of the highest coordination that you can get there. And therefore, we know that the absorption energy of the adatom is the highest at this particular site interesting. Then we said that if I would just try to take the atom along this path just along this path you would realize that while it goes at the bridge site, at the bridge site. There is basically some kind of an increase or the decrease in the adsorption energy. So, that means if you go along this path like we have discussed previously that there is some kind of a periodic energy profile is something that you are going to get for the movement of the atom. So, that means if I would put plot something like energy over this distance then I am going to basically see that this is the position which is actually having the lowest energy. Then it goes to some high energy low energy and so on. So, you basically going to end up in some kind of a periodic pattern some kind of a periodic pattern and that periodicity is actually controlled by the distance. So, this is basically a and this is basically a. So, that is something we have already talked about. So, the atom always would like to reside at these sites that are the interesting aspect. And that is why you find it but now the point is if the energy at room temperature is sufficient enough then the atom can basically just hop from one side to the other side. Well then, the question is what is the order of energy that you have at room temperature? Let us say like we are looking at the surface at room temperature.

I told you like even at room temperature surface is dynamic. So, the temperature or the thermal energy at room temperature is in the order of 30 milli electron volt roughly. But if you look at the barrier depending on the atom of course can actually be in the order of a few hundreds of milli electron volt. It can be just 400 milli electron volt 500 milli electron volt, it can even be sometime even a few electron volt. So, that depends on how strongly the atom is adsorbing, that means how is it possible that the atom is basically just hopping across. That happens because you have here the so, called vibrational ladders that are present that means every time you have the surface and the atom and the atom is just not stacked in there so this is basically just vibrating like that. So, these vibrational excitations you can see with this vibrational excitation you can take the atom further away. And that would basically means you are just doing this so-called vibrational ladder climbing and then finally the atom can hop to a next site. And the typical energies that you require for the vibrational ladder climbing can actually be in the order of thermal energy. So, therefore at higher at normal temperature or even when you increase of course the temperature you will also find that clearly the diffusion increases.

That is all because you are actually just thermally activating and you are basically just letting the atoms to climb over the vibrational ladder and then it can hop to the next site very well. So, that means we can basically just see that all the time atoms will be diffusing on the surface. Now I want to do one more thing here is that let us imagine that I am just allowing asking the atoms to move along this particular path. You have actually noticed that most of the time that the atom in this particular case 100 was diffusing along this kind of path. So, this was basically the path the atom was following and never this particular part. So, let me just remove this and then, so the atom was all the time diffusing across this path and not basically just along this path, why is that? That is actually because you see that if I have to cross along that particular path you will have to end up in a situation where the atom is actually going to a top site. And we know that the top site is not a most favourable site based on the adsorption energy. That would mean if I have to plot basically the same thing in this kind of diagram, so you would find that the top position will be slightly higher in energy compared to this site. Of course, just keep it in mind that this is actually this distance is a prime because this lattice unit is a prime. So, this is slightly different but I just for the understanding I have actually plotted it together. So, now you see that the barrier for the atom to hop along that particular blue axis is not very favourable. Because the energy barrier, so this is something we can call it now as delta E barrier for the diffusion of atom. So, now this is interesting therefore on the 100 surface generally the atoms are always hopping through the hollow sites and well the surface is symmetric, it is a fourfold symmetric surface of course you would expect basically the atoms would hope in both the two dimensional.

And that is the reason why you have seen in the previous slide. That the diffusion was typically two dimension in nature. But now when it come to the 110 surface there is something interesting here. So, of course the atom is again sitting at the so called twofold hollow site that is the most favourable side this is all clear. But you see that when it actually needs to move along this particular path the barrier that the atom is going to feel is relatively very very less.

So, it is going to be something quite shallow compared to an atom which is actually moving along this path. Because you can see that the atom need to literally climb up. So, that means again the barrier is going to be very very high. This is actually the reason why you are actually just going to get a very preferred direction in the diffusion on the 100 surface. And that is also the reason why you have seen that the diffusion on the 110 surface is more one dimensional than the two dimensional. So, that actually means the symmetry of the surface is going to quite define how the atom diffusing on the surface. Now there are couples of factors to consider here. So, the symmetry of the surface then of course the chemical nature of the adsorbate and the surface and also the so-called adsorption energy or the so-called strength of the interaction of the atom to the surface. These are the three factors which are actually going to define how fast you basically do this. But of course, at a higher temperature any surface you would find the diffusion is possible in any direction because as the temperature increases you would find that this barrier although the barrier is very high when the temperature is very high you can find that it, we can easily climb on these vibrational ladders. Because as the; temperature increases the Boltzmann population of atoms sitting in these vibrational ladders are going to increase. And therefore, the hopping even in this case is becoming easy at high temperature it is becoming easy. So, that is a reason why you would find that at higher temperature every surface is going to be very high reactive. Also, the reason that the atoms on the surface are basically much more diffusive in nature good. So, that is the interesting thing about the diffusion on the surface. So, now you have to keep it in mind that whenever you are now going to work with atoms on surface molecules.

And surface adsorbates and surface you have to also consider now the so-called diffusion of the adsorbates on the surface. So, now the question is can we somehow identify or can we somehow quantify the so-called diffusion barrier or diffusion energy or the type of diffusion on the surface. Well, it is possible because we have learned many experimental techniques with which we should be able to basically address using microscopy or spectroscopy.

If you do something called a time dependent measurement all the spectroscopy that I have showed you XPS or UPS or what so ever you need to find a resonance that is indicating the diffusion or the adsorbate atoms moving on the surface. And if you all the thing that what we have seen was basically a measurement taken at a given time or for example the microscopy that we have looked at all was basically just taken at a given time. That means we have to do a time dependent measurement if you do a time dependent measurement it is no problem that we can basically even understand quantitatively these diffusion on the surfaces.

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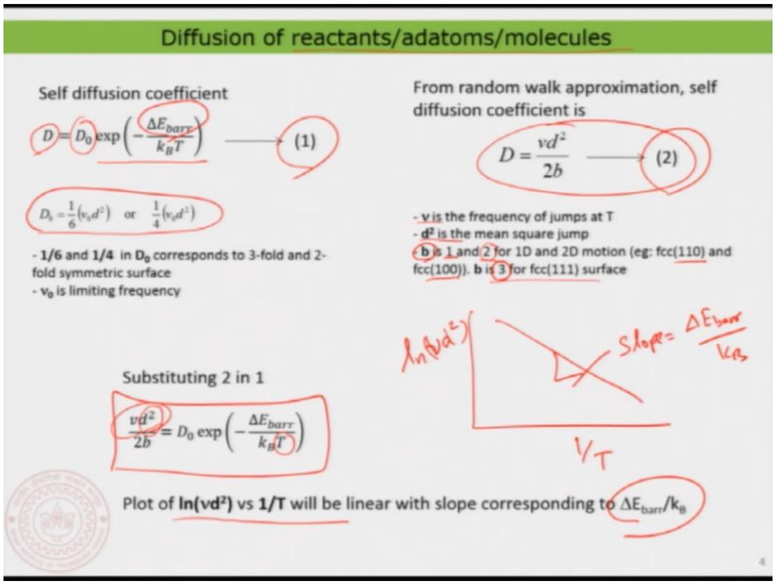

Diffusion of reactants/adatoms/molecules

Self diffusion coefficient

$$D = D_0 \exp\left(-\frac{\Delta E_{barr}}{k_B T}\right) \longrightarrow (1)$$

$$D_0 = \frac{1}{6}(v_0 d^2) \quad \text{or} \quad \frac{1}{4}(v_0 d^2)$$

- **1/6 and 1/4** in D_0 corresponds to 3-fold and 2-fold symmetric surface
- v_0 is limiting frequency

From random walk approximation, self diffusion coefficient is

$$D = \frac{vd^2}{2b} \longrightarrow (2)$$

- v is the frequency of jumps at T
- d^2 is the mean square jump
- **b** is 1 and 2 for 1D and 2D motion (eg: fcc(110) and fcc(100)). **b** is 3 for fcc(111) surface

Substituting 2 in 1

$$\frac{vd^2}{2b} = D_0 \exp\left(-\frac{\Delta E_{barr}}{k_B T}\right)$$

Plot of **ln(vd²)** vs **1/T** will be linear with slope corresponding to $\Delta E_{barr}/k_B$

How can we do that? Well, we can do that for any material so this is not a problem. So, we can have like reactants adatoms molecules whatsoever it does not matter we can calculate for anything. Because what we want to know or what we are interested is basically the delta E barrier. And the delta E barrier as you see has actually a direct connection to the adsorption energy of the adsorbed on the surface.

Of course, for molecules we know that it is relatively very very low. So, that is also something we have actually discussed when we looked at the molecular adsorbates particularly the big molecular adsorption energy is not that high. But when it go to adatoms or reactant atoms that means atoms could chemically make bonds. Then of course the delta E barrier is going to be much much much larger that can be in the order of a few electron volts. But in the case of a larger molecule, it will be just a few hundreds of milli electron volt. So, that is the difference so you just keep it in mind. So, now how can we understand that so you clearly see this typical Arrhenius like expression. If D is something like a diffusion coefficient, then it is basically connected directly through the energy barrier and the temperature. So, this is a typical Arrhenius form. And then you have here something called D0 so that is actually kind of a limiting diffusion coefficient. So, how can we basically just calculate that, before that what I want to do is, so this is basically an Arrhenius type. But we can also just look at this problem using a simple random work problem where you look at the as a function of frequency and also the mean square jump. So, like you can see here I have nu that is actually the frequency at which hopping happens. And also, the mean square jump. So, that means the distance that you cover basically in a given time and using that you can basically just also calculate the diffusion. Because that is the two components that directly relate the diffusion. So, that means the diffusion coefficient is directly proportional to the frequency and also the distance that you cover. Now there is also normalization constant. Because the diffusion can actually happen, not just 1 dimensional can happen 2 dimensional, 1 dimensional, 3 dimension what so ever. So, we need to have actually a factor or a normalization factor that actually just controls the symmetry of the diffusion. And that is why you have a parameter here called b which is one for 1 dimensional movement and 2 for the 2 dimensional movements. So, that means if you would have basically taken the 110 surface, we would have basically plugged in one for b and if you would take 100 surface. Then you would have basically taken two because it represents kind of a two-dimensional movement. But interesting thing when you take the fcc 111 surface see it is also not necessary that we need to talk always about fcc but also bcc or diamond structure or whatever but the symmetry of the surface is kind of independent of the type.

Therefore, if you take basically the 111 surface you see that the atoms are going to now move along the compact direction. Where you know; that the void or the so, called high coordination side which is a threefold side and those sides are basically just having kind of a threefold axis. And that means in this case we can basically plug b that would also take care of the correct symmetry for the diffusion coefficient as per the random work problem.

Now I can basically just combine these two and before that let me also just write down the same thing what we have been discussing. So, I can also just write down the limiting diffusion coefficient using the limiting diffusion frequency. Then by combining these two expressions I can basically just arrive at this expression which connects basically the frequency and the mean square jump as well as the barrier. And now if I would basically just plot if I can somehow; calculate the new and the d square. So, that is something I told you what we need to do, the new is basically nothing but the frequency that means if you would basically do a spectroscopy or microscopy. But a time dependent spectroscopy or microscopy I can actually just calculate the frequency because frequency is nothing but the inverse of time. And then d square that represent basically how far these atoms are actually just going. So, that also tells you like how strong is the diffusion and if I know these 2 and then I can basically just check this as a function of temperature and then I can plot the log new d square as a function of 1 by T. And that is going to give me 1 by T so here I have basically log new d square. Then what I am going to get actually is kind of a linear plot and the slope is directly delta E barrier by k B. So, that will the slope will basically just tell me the slope is equal to the delta E barrier by k B. So, then I can basically calculate the energy barrier using this that is nice.

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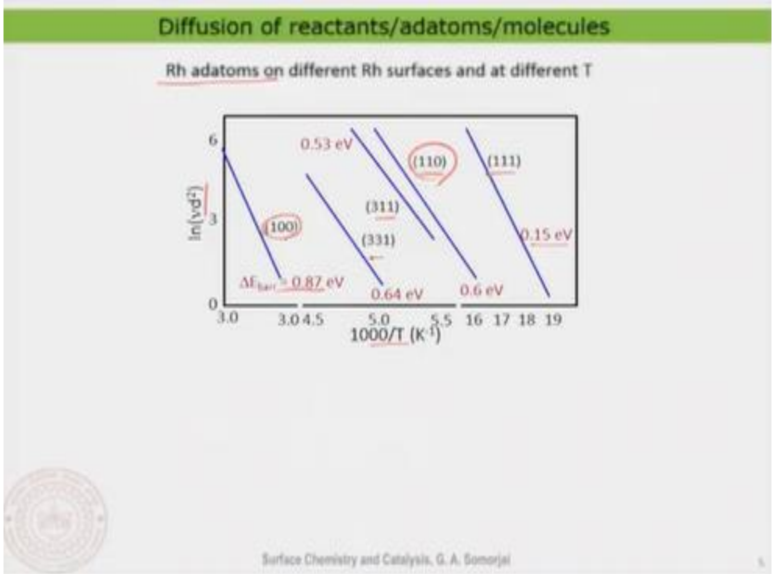

Diffusion of reactants/adatoms/molecules

Rh adatoms on different Rh surfaces and at different T

Surface Chemistry and Catalysis, G. A. Somorjai

But let me just show you a few examples so this is done using a spectroscopic method. So, you already see that in this plot we have basically the diffusion coefficient of a rhodium atom on a rhodium surface on different type of rhodium surfaces the 100 surface 331, 311, 110 and 111. Something striking that you can see the plot already shows you basically the 1 by T versus log new d square here. So, that you can clearly see here. And now the slope is directly giving me the barrier. And you see something quite interesting that for the 110 surface is surprisingly the most reactive surface or the most or the surface where the diffusion barrier is the strongest. What does it mean? If the diffusion barrier is the strongest that basically means the diffusion is actually slow on that surface. But now look at the 111 surface that is quite interesting the diffusion barrier is basically very very small. So, that means at room temperature the 111 surface is going to be looking like all the atoms are moving all the time. But for the 100 surface since it has actually the highest diffusion barrier it is not going to be having as dynamic surface as the 111 surface. Well, the 110 is coming somewhere in between and then you also have these high index surface there you also see that the barriers are basically somewhat high. So, that is quite interesting so that is also generally why we also talked about that always the 111 surface is some kind of a stable and uniform surface.

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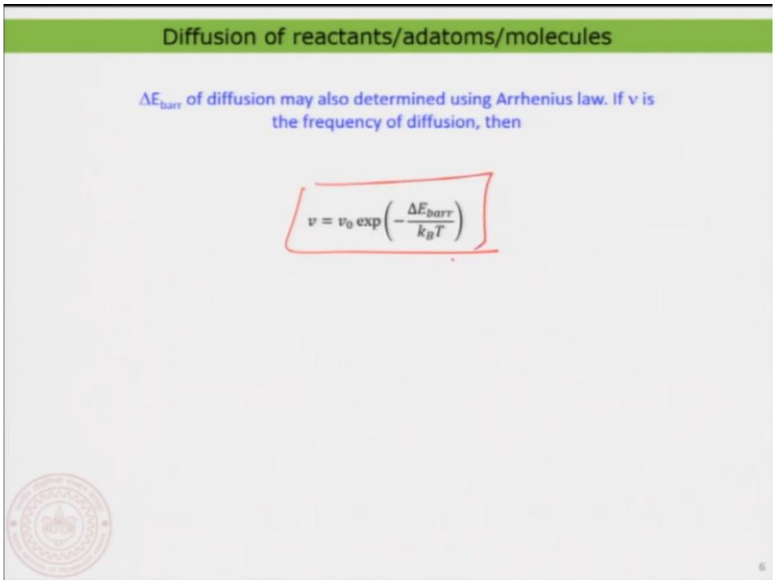

Diffusion of reactants/adatoms/molecules

ΔE_{barr} of diffusion may also determined using Arrhenius law. If v is the frequency of diffusion, then

$$\boxed{v = v_0 \exp\left(-\frac{\Delta E_{barr}}{k_B T}\right)}$$

So, now I can also just write down like I have written previously. So, the delta E barrier can be also directly connected to just the frequency alone. So, that also can be calculated if you know somehow if you can calculate just the frequency.

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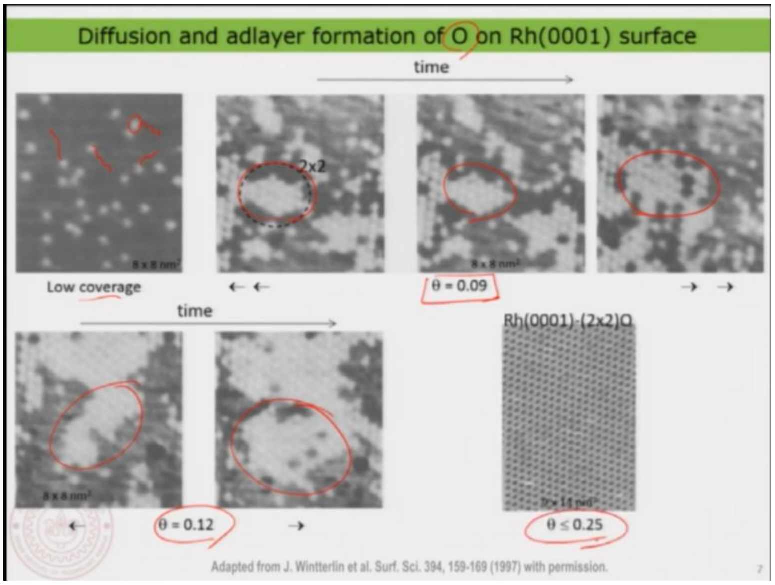
Diffusion and adlayer formation of O on Rh(0001) surface

Adapted from J. Wintterlin et al. Surf. Sci. 394, 159-169 (1997) with permission.

Then let me just show you that a few microscopic images taken as a time lapse. So, this is actually the oxygen adsorbed on rhodium 0001 surface. And what you clearly see, so here are the oxygen atoms and this is of course the picture that I have taken at a given time. So, that is a point. So, now we know that if you take the picture over a long time then what you are going to get is basically that all these atom are going to just move around and then you are going to get something else. So, that the interesting thing. So, now let me just show you really the time lapse images of a slightly higher coverage. So, the coverage is basically a bit higher so this is really really low coverage. So, now the coverage of oxygen molecules or the oxygen atoms on the surface is very high. And this is the same frame taken at three, independent time or something like simultaneous or consecutive images.

You clearly see that this particular island if you inspect you can see that is basically changing and somewhere here it has actually grown really big. So, what has happened? Of course, as expected the oxygen atoms are basically diffusing around and they are basically just coming together. Well, you can also do that at a slightly higher coverage you also see that diffusion is again happening there you can particularly focus on this region you see that the islands are basically forming. And then if you go to a very very high coverage so this is something like particularly for oxygen on rhodium 0001 surface. You see that these are the oxygen atoms so that form some kind of a hexagonal lattice. and once you have a higher coverage then you would find that the diffusion is getting limited So, which is also something you would expect because in that case I need to also basically just use the additional energy that is the molecule-molecule interaction. So, of course when you have a compact layer then definitely it is much more difficult for the atoms to move around. But none the less you would still find in some cases that atoms would suddenly miss or if you increase the temperature, you would definitely find atoms started to get ripped out of the surface and so on.

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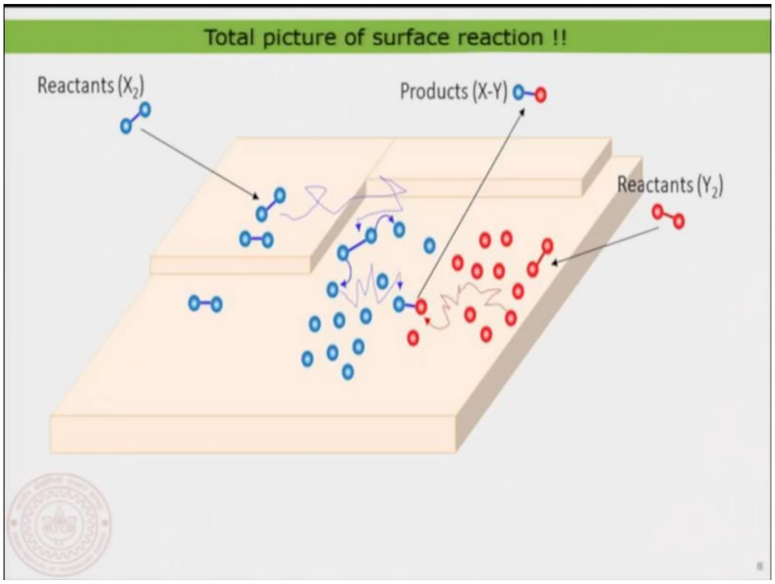

Total picture of surface reaction !!

So, if you asked what is the complete picture. So, the complete picture is this that if you add something on the surface let us say like I am just talking this in terms of a reaction that you have a reactant X 2 and reactant Y 2. And what you are expecting is that a product is formed on the surface. So, we have actually just looked at some of the example like we have seen for the formation of carbon dioxide from carbon monoxide and oxygen. So, what I am having is when you deposit something what actually happens first, they start to diffuse on the surface. And then after certain while they start to get apart so that means they are actually now ripping apart. But now the so-called atoms that formed from the reactant X 2 is now moving around and they are actually coming together and forming some kind of an adlayer. The same thing also would happen to the next reactant they would also just come first move around the surface.

Then get ripped up and then you basically just find they will also start to move around. And finally, somewhere at some point a reaction is happening, it is not just that you put the reactants and then suddenly they react. There are so many processes that goes on at the background or at this surface where everything is basically just controlled by all these factors.

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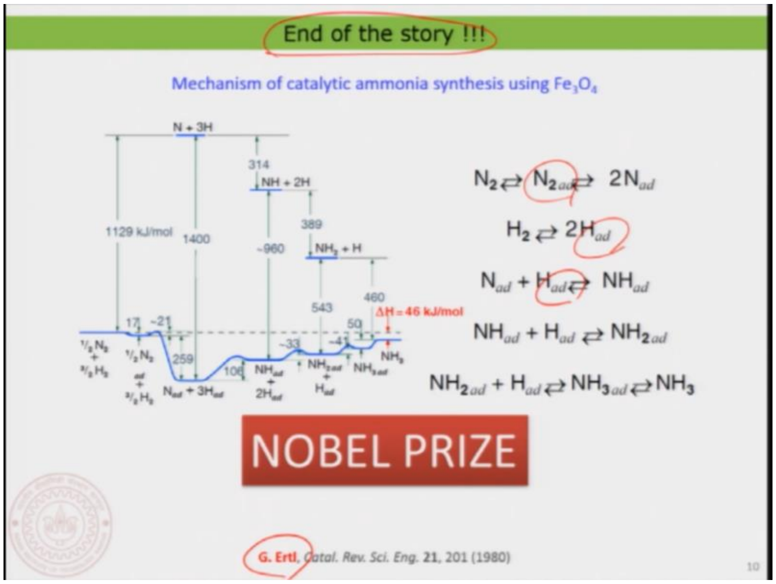

End of the story !!!

Mechanism of catalytic ammonia synthesis using Fe_3O_4

$N_2 \rightleftarrows N_{2ad} \rightleftarrows 2N_{ad}$

$H_2 \rightleftarrows 2H_{ad}$

$N_{ad} + H_{ad} \rightleftarrows NH_{ad}$

$NH_{ad} + H_{ad} \rightleftarrows NH_{2ad}$

$NH_{2ad} + H_{ad} \rightleftarrows NH_{3ad} \rightleftarrows NH_3$

NOBEL PRIZE

G. Ertl, *Catal. Rev. Sci. Eng.* **21**, 201 (1980)

Well, that is what professor Gerard Ertl actually explained during his studies basically. When he was trying to solve basically the chemical reaction on surfaces where he basically just concluded and given basically kind of an end story or a complete picture. Were he looked at reactions of different type of molecules on surfaces where one need to basically consider. You can already see this adsorption adsorption everywhere.

Because it is about a molecule coming on to the surface it is actually moving first then they come together react and so on. So, for explaining this extremely complex process which involves the adsorption, the diffusion and finally the reaction professor Gerard Ertl won the Nobel Prize for the chemistry and particularly in surface science. So, this is the complete picture of the surface and also the adsorption of materials on surface. So, we need to now include also to everything that we have studied we need to also put inside the so-called time dependence. And the time dependence will tell you the picture is actually changing over the time. With this I would like to conclude my lecture thank you very much for your attention.