Chemistry and Physics of Surfaces and Interfaces
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Lecture - 02
Historic Perspective to Surface Science

Hello everyone, welcome back to lecture 2. So, in this lecture as I have already mentioned in the previous lecture.

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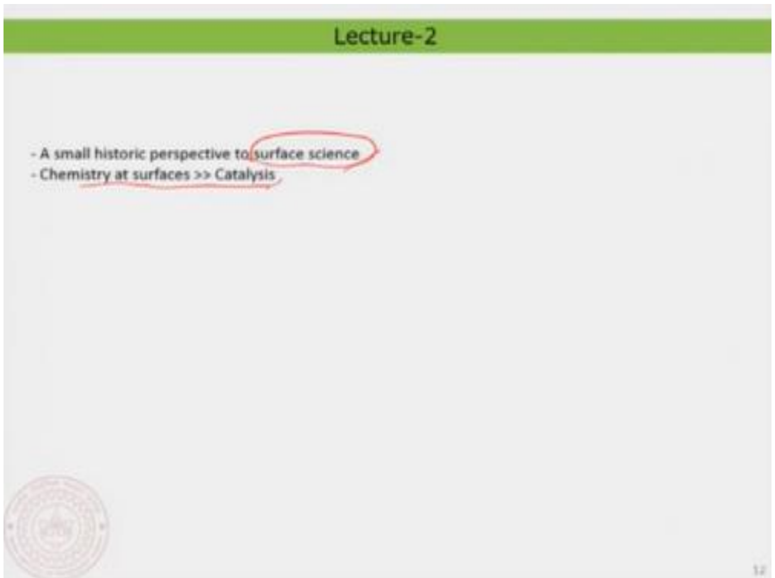

We will be looking at a small historic perspective to surface science. So, in which I would not mention every aspect of every historic aspect. But I will just mention some of the highlighting important aspect that happened actually in the development of surface science or in general to put it in perspective that what you would call actually is the surface science so the development of the surface science. Then, you will also see that while we discuss this, we will also come across an important aspect of surface science or surface chemistry indeed which is actually known as chemistry at surface or majorly known as catalysis. So, we will also have a look at the introduction or to the important beginning part of the catalysis during this historic perspective basically.

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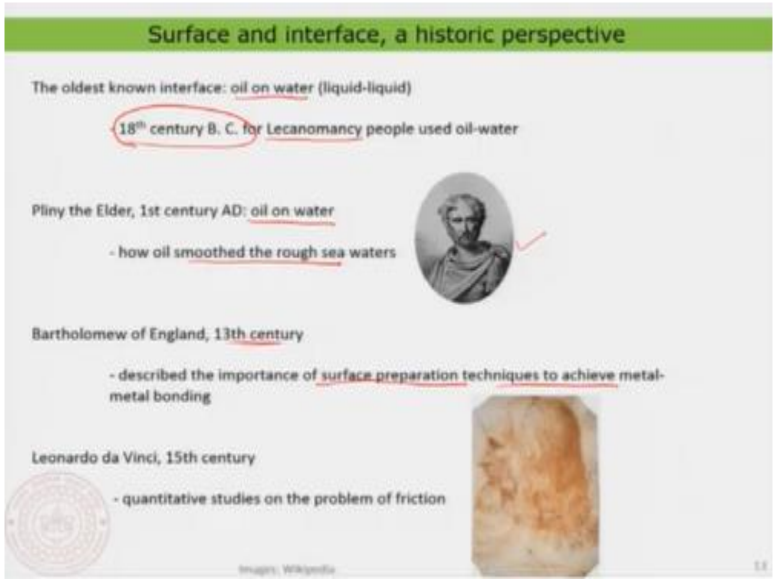

Well, the surface and interface the history actually starts from any centuries or like it is as historic as human being for example or even as historic actually as the universe itself. Because I told you we cannot avoid interfaces while we do anything or even when I stand doing nothing the interfaces are always present. So, that is not what we are going to inspect we would basically just look at some of the important historical events that marks the development of surface science itself. So, like even in the B.C, the 18th century for example people were using always an interesting liquid-liquid interface known as oil water interface. So, people use this oil water interface for predicting the future of people. So, that was actually known as Lecanomancy which is actually by putting a droplet of oil into water. Depending on the shape that the oil is actually forming on top of water people started predicting things.

Well, it is quite unimportant for our perspective in any case but this so called oil water interface was actually interesting even in the 18th century. So, if you now look at some of the major important aspect was actually that oil on water interface which is of course one of the major liquid-liquid interfaces was actually even used in some important applications basically to smoothen the rough sea water. For example, so to actually just decrease the waves on the shores and things like that. So, this was actually one major thing. And Pliny the Elder in the beginning of the first century AD has actually just looked a little bit more into the details of these kind of oil and water interface formation. And how it actually influences the calming down of rough sea water and things like that has been actually systematically investigated.

So, this you could call it actually one of the beginning of the real surface science itself. Then in the 13th century so this is actually some important event what I want to mention in the history of interface. Because people were basically just trying to make or allowing different type of materials or forming even metal-metal bonding. So, it was very important for people to know what is actually the surface microscopic or surface roughness for example or the nature of the surface in order that you can actually stick two metals together.

So, well look this is actually the first interface formation technically speaking where people were really trying to understand actually the importance of the surface preparation ideally in making actually the different type of metal-metal interfaces. This was quite important at that point of time in making tools and devices and things like that. Well, this we could call it actually as an important point in surface science because people started to doing it and then you know for example friction is actually also a property of the interface itself. So, there two materials are coming in contact and depending on the microscopic structure of the surface, you would say well if the surface is more rough then the friction is more and if the surface is smooth then you would say the friction is actually less. So, that means the microscopic structure or even the macroscopic structure of the surface itself is very important in understanding the friction itself.

So, in 15th century Leonardo Da Vinci for example has actually done quantitative studies in friction where actually his main tool was looking at the interfaces for example.

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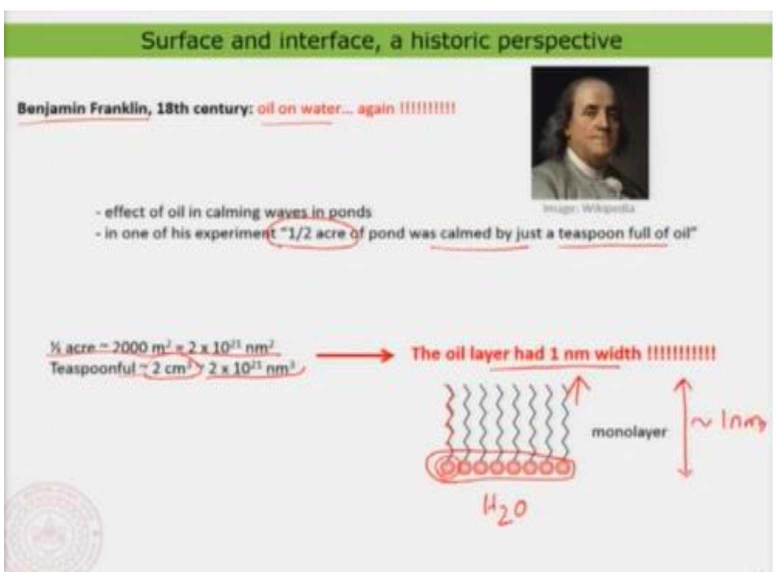

Then in 18th century, something very important has actually happened in the time of Benjamin Franklin where he actually invested much more time in this interface again oil on water. This is actually one of the most famous interface which is even currently we use almost every day. When you cook something, you put basically oil and water. So, this is actually kind of an interface that you cannot avoid and he has for example has done a very systematic study because they also have used oil on water to in fact calm down actually the water in pond or like you know waves and things like that. So, what they have actually just done? They have done a systematic study in which Benjamin Franklin basically just calmed down a pond which is actually half acre in size. That means an extremely large pond was actually come down by just a teaspoon full of oil. So, the interesting question that time he asked was actually how can we do this basically. It is a large pond but just with a small amount of oil you could basically just calm down the waves in this pond. Well, there is an interesting answer to it if you look into the math or if you look into something like a simple geometrical equation you can basically convert the half acre into something like a nanometer square area. So, just calculate the area in nanometer square you would find that is actually 2 into 10 raise to 21 nanometer square and the spoonful can actually be just approximated as something like 2 centimeter cube, it is a small amount. And that actually can also be just converted into nanometer cube volume, and if you now take the ratio of it, you can easily calculate what is the amount that would be spreading on half acre pond and that turns out to be just one nanometer thick. That means the thickness of the oil that you spread on this pond was just one nanometer thick. And what is one nanometer thick? That is very interesting because if you look at the structure of your fatty acid or oil in general. So, you have basically this kind of a hydrophilic end and a hydrophobic alkyl chain basically. So, when you put this kind of molecule on water they always align in this fashion where all the hydrophilic part actually point towards the water interface and this is actually away from the water interface. So, that is actually forming something like a very nice well-ordered mono layer and the thickness of this monolayer is actually turns to be in the order of one nanometer. So, what indeed would happen basically is just that Benjamin Franklin's experiment that he could just come down a complete pond which is half an acre with one teaspoon full of oil and basically, he used a monolayer of oil to indeed calm down.

So, this is quite exciting. So, this is basically one of the marking event in surface science where you could say that one has actually come up with a more modern and more systematic study of surface science where people have looked quantitatively interface for example.

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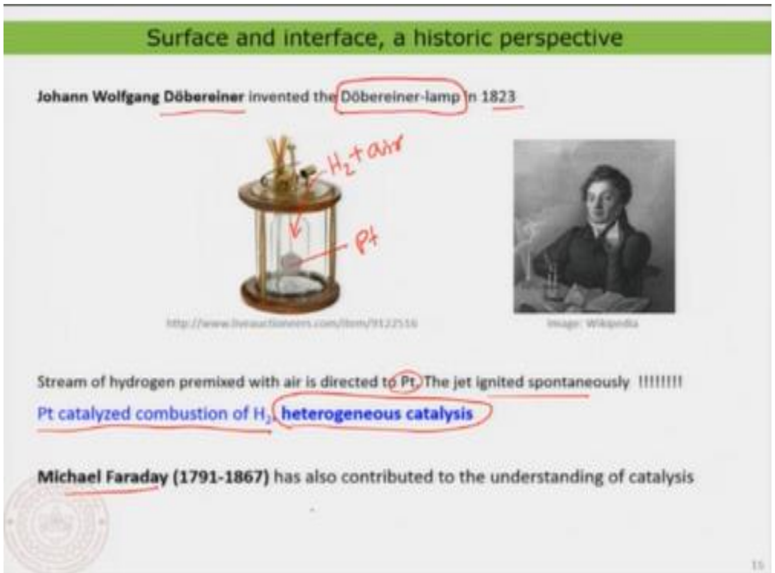

Then there are also interesting example that one can point out which is basically the contribution from surface and interface itself which is actually by Dobereiner. So, he invented a lamp which is generally known as Dobereiner lamp. So, this was also a commercial lamp that was available at this time what the lamp contained is basically just some pieces of platinum. So, you can see here basically it is having platinum flakes and if you now form a jet of hydrogen and air into this. Then what happens? It is actually the lamp ignites spontaneously; this is quite interesting. So, but this was actually turns out to be a commercial lamp. But what is interesting in this particular lamp is actually what happens is nothing but a platinum catalyzed combustion of hydrogen. Hydrogen and platinum is actually known to be a very good catalyst for dissociating hydrogen and the platinum catalyst actually is catalyzing the hydrogen and the combustion is basically giving the fire for example, and this is actually something we can call it as heterogeneous catalysis and that is where one can say that people have even used surface in actually just making the catalyst. So, we will see a few more examples now where you will see basically the surface science, the catalytic aspect of surface science in fact or chemistry at surface can actually be called as the catalysis itself. Then Michael Faraday has also contributed a lot in the understanding of catalysis during this time where he also has actually just worked with different kind of metallic catalyst. And then used it for dissociating molecules for example. So, we will come to that in a minute.

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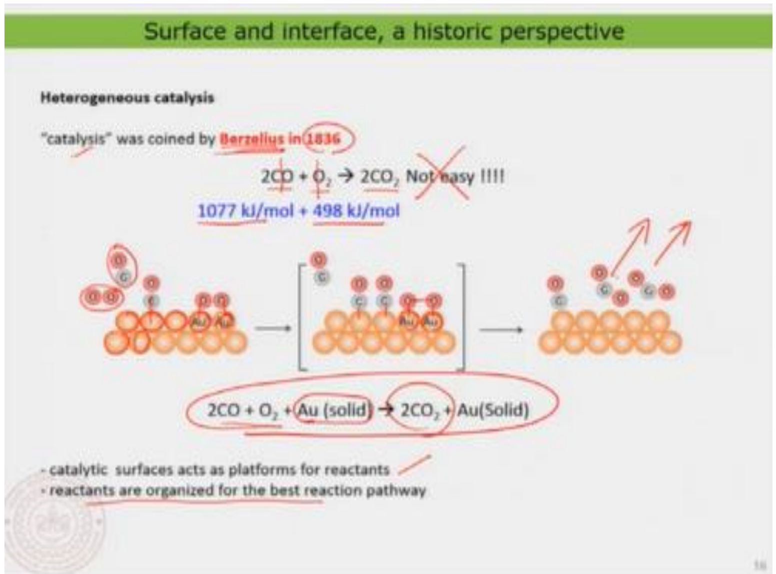

Well, so what we have seen is basically that the heterogeneous catalysis aspect in this particular context and in 1836, Berzelius is actually the one who token the name catalysis itself and from there onwards this particular field is known as heterogeneous catalysis. And now we will see the surface science aspect in catalysis or as I generally call it a chemistry at surface which is actually known as the catalysis itself.

So, let us look at a chemical reaction to understand this. So, you know this chemical reaction which is actually the reaction of carbon monoxide with oxygen giving to carbon dioxide. But the interesting aspect about this chemical reaction is that at normal condition this chemical reaction will not happen. Why is that? The reason is very simple. That you need to break the carbon oxygen bond and the oxygen-oxygen bond during the chemical reaction.

So, what is the problem in doing that? It is very simple. Actually, the energy cost related to the breaking of carbon monoxide and the oxygen bond is very very expensive and therefore at normal conditions we will not be able to do the chemical reactions in an easy way. Therefore, you need something else to do. So, that is actually the time where Berzelius reaction comes into aspect or comes into play where he showed that the carbon dioxide and oxygen reaction can lead to the formation of carbon dioxide. If you would have just used a small amount of gold solid inside the reaction port. Well, gold as you might know that it is an inert material or something known as a noble metal which is supposed to be not doing anything if you add that in the chemical reaction. But surprisingly what you find is that even gold is basically just doing something to the chemistry.

What is really happening? So, right now what I am going to show you is a very molecular or atomic level picture. This picture is not present during the time of Berzelius, please believe me because that time there was no technique to understand basically the chemistry at this molecular level. But we will have a look at the chemistry in a molecular level to understand what actually happened due to the fact that where we have actually just done this chemical reaction in the presence of gold. What is gold doing in this?

Well, gold is actually acting as a catalyst in this case. How does this happens? So, now you have here gold atoms that are present which is basically arranged in a very well-ordered manner because we are using a crystalline gold let us assume. So, now I have gold zero atoms that means actually a neutral gold is present. And now when I adsorb when I do the chemical reaction in the presence of gold, carbon monoxide and oxygen molecules will start to adsorb onto the surface of gold like this. That is the interesting aspect. But now when it adsorbs, you form some kind of an intermediate stage where you can see oxygen-oxygen bond has actually got weakened up. And then the oxygen gold bond has actually just formed. So, that means during the adsorption the oxygen is basically splitting into two and it is being adsorbed onto the gold surface itself. A similar thing also happens to carbon monoxide, it is also adsorbing on the surface. Now the interesting aspect here is you see that now the reactive oxygen atoms are available on the surface. If reactive oxygen are available then the reaction is actually feasible. Because in the next step this carbon monoxide will pick the reactive oxygen and it form a stable carbon dioxide molecule and then it will actually just evaporate or move away from the surface. And now fresh oxygen and carbon monoxide molecules will come on to the surface and then they will again split and then do the reaction. So, now you see the catalyst has not damaged at the end, the catalyst remain as it is. But the catalyst has actually templated the reaction, the catalyst has actually facilitated the reaction to a greater extent by reducing the energy cost because the catalyst itself is splitting the oxygen molecule into two which is then making the reactive at atomic oxygen present on the surface. We will come back to this in a few minutes where we will actually just see who has actually just given this description.

It is not given by of course Berzelius at that time they could only just find that by using different type of catalyst, you could trigger chemical reactions. Well, now which actually means that the catalytic surfaces are actually acting as a platform for doing the chemical reactions. And also, the reactants are basically organized in a special way on the surface which allows actually an interesting pathway for the reaction to happen.

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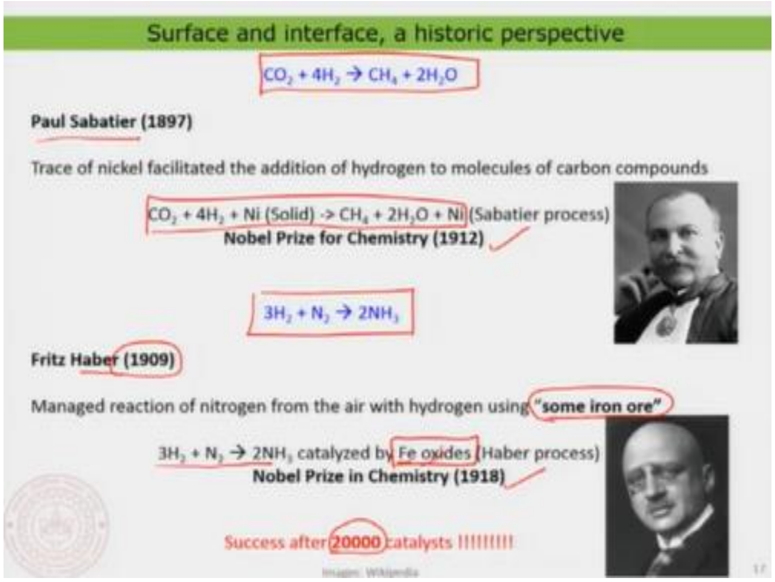

Now let us look at a few more important examples in the history. So, this reaction is also very very important and this is actually a reaction which was then developed for introducing hydrogen atoms to carbon for example. But when you do this chemical reaction again at normal condition, nothing would happen. But then in 1897 Paul Sabatier basically discovered that if you use it little traces of nickel in whatever form. So, it was not very clear at that time.

A small amount of nickel would basically facilitate this chemical reaction and then you can actually make this reaction happen. And this reaction is generally known as the Sabatier process and this is a very well-known chemical reaction used for making this kind of introducing hydrogen atoms to molecules containing carbon. So, he actually was awarded the Nobel prize in chemistry in 1912 and then another important example is basically the reaction of hydrogen and nitrogen and formation of ammonia. So, well again the reaction is of course theoretically feasible but as I told you this reaction will not happen on without having any catalyst. So, this reaction is famously connected to Fritz Haber, he has found out that somewhere around 1909 that by using some iron ore, this is the most important thing to be noted here, some iron ore the chemical reaction would happen. Well at that time when Fritz Haber was doing this chemical reaction; He did not know what is the real form of the iron. But later it was found out that it is basically a form of iron oxide that is actually facilitating the reaction. And then he has actually just made this reaction possible by using iron oxide and this is famously known as a Haber process or Fritz Haber process. And he was awarded the Nobel prize in chemistry in 1918. But the interesting aspect why I want to bring this particular example is that Fritz Haber himself actually tried about 20000 catalyst trial and error methods in order to finally find out that some form of oxide and that is also the reason why it is actually known as some iron ore is actually acting as a real catalyst for this reaction to happen. So, therefore it is important to note that if we would have a clear understanding from the surface science point of view or from a microscopic or molecular level understanding of catalytic process, we would not have actually just spent this much time in looking for different many catalysts instead you would have already predicted what would be the outcome of the reaction by carefully understanding it.

So, therefore the microscopic understanding or the molecular level understanding of chemistry on surfaces are extremely important in actually just selecting the right catalyst and also to trigger the proper chemical reaction.

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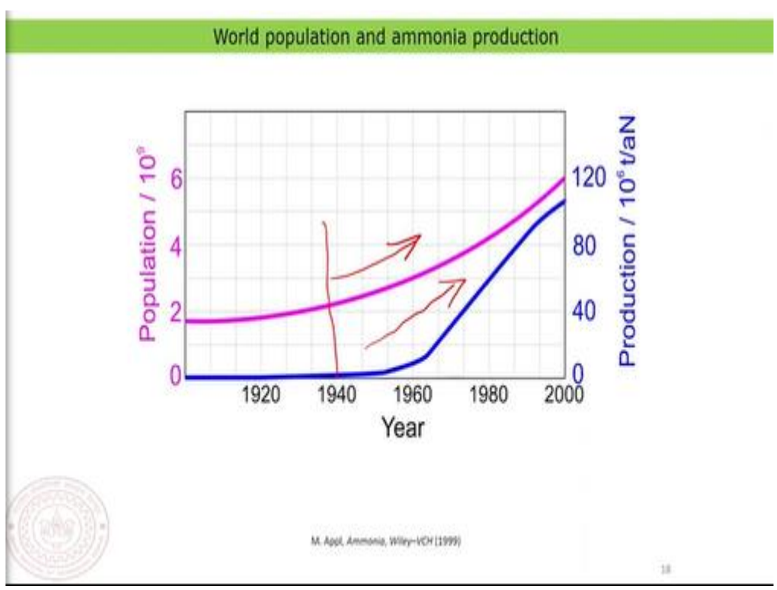

One of the important aspects of Fritz Haber process is actually the increased production of fertilizers or that process itself has helped in easing the production of fertilizers. So, this shows the increment in the production of fertilizers and what you also see is ideally a nice correlation of the onset of the human population increase with the production of the fertilizers. This is quite interesting so that basically means this catalytic process or the production of ammonia itself has helped the human kind in a greater way because that actually has helped the production of different type of fertilizers.

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Now one a few important names that also I would like to bring to your attention in the surface chemistry is the name of Irving Langmuir. So, you might have already studied in your chemistry textbooks. He was awarded a Nobel Prize in chemistry in 1932 and particularly for his contribution in surface chemistry. So, he was actually the one who introduced all the absorption isotherms and understanding how molecules that serve on the surface and the energetics that are basically related to the adsorption process. Then Katherine Blodgett also has contributed greatly to his work to Langmuir's work and she also has actually developed several methodologies in making nice coating on different kinds of surfaces using molecular adsorbate. And this is of course very well known the Langmuir Blodgett films and these films are also commercially used in quoting different type of materials.

So, the surface science has also contributed in that sense which you also have seen in the previous lecture that they have been also used as a squatting material. So, all the contribution basically comes from these well-known chemists.

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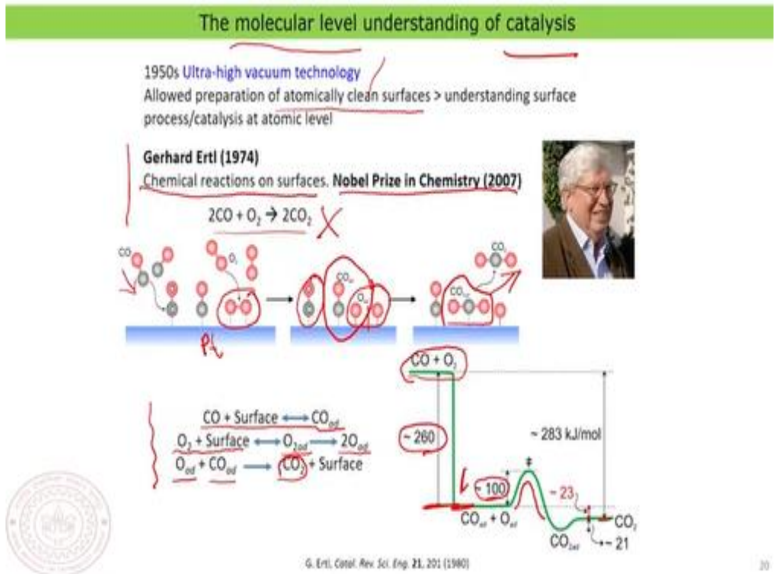

Now in the 1950s there was actually this nice development of ultra-high vacuum technology which is also something that we are going to look in greater detail in the coming lectures. And with the help of ultra-high vacuum technology, one could basically prepare atomically flat clean surfaces. This was quite an important discovery in the surface science. Because that actually has helped the scientists to understand the process of catalysis at molecular level.

This is quite important of course one can trial basically any catalyst and then we can basically just find out new catalyst but if one can also understand the molecular level details of a chemical reaction that happens on a catalytic surface then one will have a greater advantage of choosing the right catalysis or the catalyst. And to that Gerhard Ertl in 1974 for his contribution in 2017 he was awarded a Nobel Prize in chemistry and then particularly you notice that he was awarded Nobel Prize in chemistry for all his contribution in chemical reactions on surfaces. So, what he has done? He has basically taught us how the chemical reaction is basically happening on the surface. So, this as we have already discussed this is an impossible reaction in gas phase, nearly impossible reaction in gas phase because of the high energy cost of the breaking of carbon monoxide and oxygen. But we already know that on different surfaces we can basically just do this chemical reaction with greater is or with less energy goes. So, how does it happen? We have already quickly seen it before. So, we take a surface so this could be for example a platinum surface because Gerhard Ertl has focused his search mainly on platinum. So, platinum what you do is you absorb the carbon monoxide and oxygen.

So, this is actually the gas phase molecules and they basically adsorb on the surface. And then once they adsorb you have basically the adsorbed carbon monoxide and also the adsorbed oxygen species. But the interesting thing is that upon adsorption the oxygen molecule is basically breaking into two different reactive oxygen species which we call it as the O ad. And now the oxygen, the adsorbed oxygen is reacting with the adsorbed carbon monoxide and then forming basically the carbon dioxide molecule. In that carbon dioxide at the initial stage is absorbed again on the surface, but the absorption energy of the carbon dioxide on the surface is very low and it eventually evaporate from the surface and we produce basically carbon dioxide. So, with the help of the surface we can basically just do this reaction. Now this is not anymore, the way you should be basically representing. So, this is not anymore, the way you should be representing basically the chemical reaction instead we should include the surface. So, when you include the surface now you see the chemical reaction is basically represented like this where the carbon monoxide first adsorbs on a surface site and form a carbon monoxide subspecies. Similarly, the oxygen adsorbed on the surface and form basically like an adsorbed or two and then it is split into two reactive adsorbed oxygen and then finally, the reactive adsorbed oxygen and the reactive CO adsorbed would form the carbon dioxide molecules and leave the surface intact. Now also using a more modern spectroscopic technique and also using an adsorption energetics analysis technique which is known as the desorption analysis technique which we will also cover in our lecture, he has actually just understood the energetics of the chemical reaction. So, now you see something quite interesting. The moment the carbon monoxide and oxygen adsorb on the surface, it basically just loses a lot of energy about 260 kilojoules per mole of energy. So, that basically means the entire reaction is actually now happening from this particular point which is actually the adsorbed position. So, that means the reaction is basically requiring only a small amount of excitation energy approximately 100 kilojoules per mole and then finally the molecule is formed the carbon dioxide. So, you can basically see that this is actually the reaction path and that reaction path only has a cost of about 100 kilojoules per mole and then finally you form the product. And now the interesting thing is also that if you would have basically done this reaction without the help of a catalyst or without the help of a surface you would have basically never been able to do this reaction at this very low energy cost and that is basically the idea of using a catalytic surface and of course Gerhard Ertl has actually given a very quantitative understanding about these particular reactions at the molecular level.

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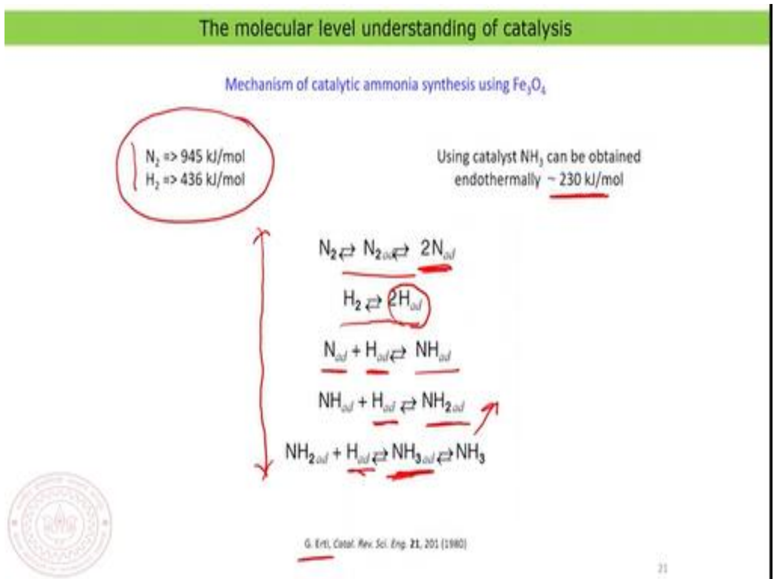

Let me also show you one more example which is basically the catalytic formation of ammonia itself. So, we know that the dissociation energy of the nitrogen and hydrogen are very very high and therefore they cannot be done on without any catalyst. So, that is the reason why you need the catalyst and now when you do the reaction of this catalytic surface what you require is basically the chemical reaction is now going to be written using these different steps. So, what happens? The nitrogen first adsorbed on the surface and formed two reactive nitrogen and then similarly the hydrogen also adsorb up on the surface and it also forms two reactive hydrogens adsorbed on the surface. Now each nitrogen atom would interact with one adsorbed hydrogen and form an NH which is again adsorbed on the surface. And then the NH basically react with one more adsorbed hydrogen and form an NH_2 adsorbed and then the NH_2 adsorbed would again react with one more hydrogen and then finally form the ammonia and then that releases to the out of the catalyst and then basically you have the formation of ammonia. Now something interesting is basically that you can see here without the catalyst you would have basically at least use this much the sum of these two quantities you would have used as the energy required for the reaction. But at the end of the day, you can see using the catalyst you are actually just using the doing the reaction at a very much much smaller energy cost. So, that is the importance of using basically the catalyst. And also, now after the contribution from Gerhard Erlt. You can also read more details in this particular article one can actually now understand the process that are happening at the molecular level.

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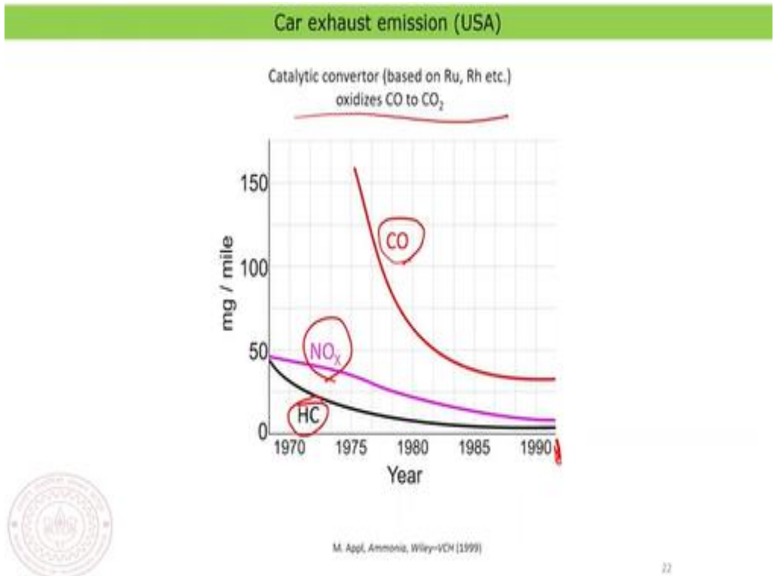

Now I also just wanted to wind up by showing this particular example. This shows basically the reduction in the greenhouse gases like carbon monoxide, nitric oxides and hydrocarbons which are emitted by automobiles. So, this of course shows only up to 1990 of course now the technology is similar and we have a better reduction in any case. And this particular case what it shows is that using this kind of catalytic converters particularly by using Rubidium, Rhodium. One can oxidize carbon monoxide to carbon dioxide and that way you can basically using a catalytic process. You can in fact remove the greenhouse gases from the exhaust of an automobile. So, this is also marking a very important example of the contribution of surface science in general and also catalysis in particular. So, well with this I like to conclude here. This lecture where I could show you a historic perspective and also the formal starting of surface chemistry; and also a branch which is actually then turns out to be like very important in the chemical industry in non-active catalysis which is also a branch of the surface science itself. In the next lecture what we will be looking is we will be starting to create surfaces and then we will be starting to understand the surfaces at the microscopic level. Thank you very much for your attention.