Industrial Inorganic Chemistry
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Lecture – 08
Nitrogen Compounds

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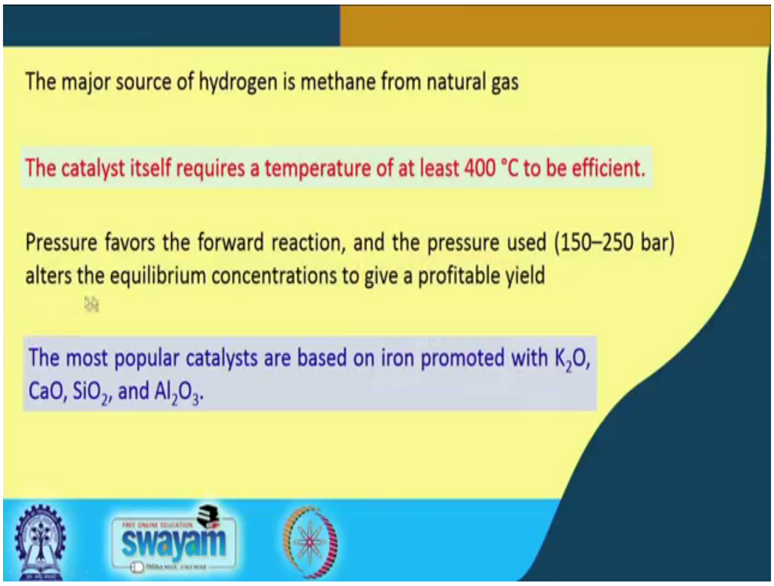

The major source of hydrogen is methane from natural gas

The catalyst itself requires a temperature of at least 400 °C to be efficient.

Pressure favors the forward reaction, and the pressure used (150–250 bar) alters the equilibrium concentrations to give a profitable yield

The most popular catalysts are based on iron promoted with K_2O, CaO, SiO_2, and Al_2O_3.

So, welcome back to this class where we were talking about the production of ammonia in an industrial scale, taking the help of some catalyst which is iron based catalyst.

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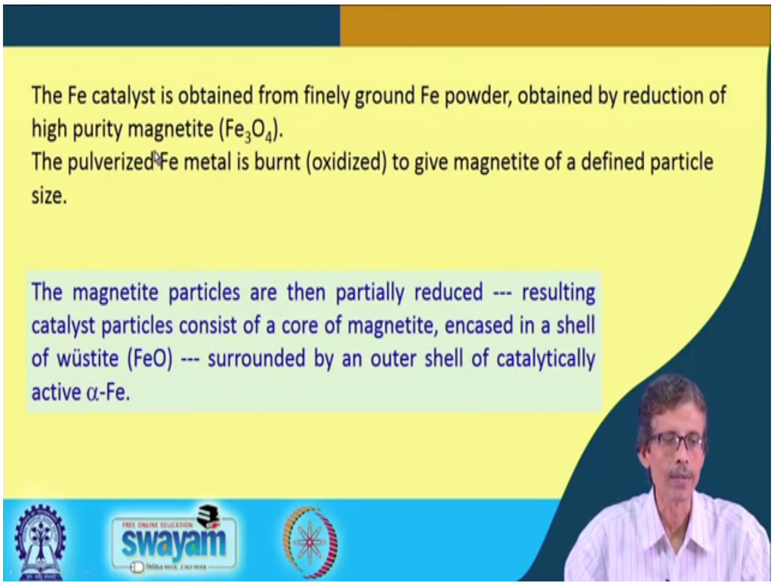

The Fe catalyst is obtained from finely ground Fe powder, obtained by reduction of high purity magnetite (Fe_3O_4).
The pulverized Fe metal is burnt (oxidized) to give magnetite of a defined particle size.

The magnetite particles are then partially reduced --- resulting catalyst particles consist of a core of magnetite, encased in a shell of wüstite (FeO) --- surrounded by an outer shell of catalytically active α-Fe.

So, these particular catalyst which is the iron catalyst which can be obtained from iron powder also. So, if we can have some very good quality of iron powder and that iron powder can be obtained from the high purity magnetite. Magnetite we all know that this is the typical ore of iron, where hematite is one of the ore which is Fe 2 O 3 and magnetite is also Fe 3 O 4.

So, these are spinel type of oxides. So, these spinel type of oxides of iron can be useful for the production of iron powder. So, what we get? The reduction of this particular magnetite will give you the iron powder and very fine particles of those iron metals; that means, the pulverized iron metal; if we can have a very not very good quality of iron metal in our hand, initially we can burnt it; we can burnt it to give you the magnetite of a definite particle size because all these particle sizes are important.

Because the usual particle size depending upon these particle sizes we can have the typical surface area; that means, the amount of area which can be covered by a mono layer of all those particles all those catalyst particles. So, a required amount or required size of these particles will be useful for making this particular catalyst. So, what we do now? We can have our a right size of magnetite particles in your hand, because in laboratory scale we can also synthesize all these useful magnetite particles nowadays. In the era of your nano particle productions in the regime of your nano particle productions from the simple iron salts; that means, the iron as very chloride or iron as some other salt like ferrous sulfate or the iron alum, we can use the typical iron for making our desired sizes or desired quality of nano particles in our hand.

So, if we can have these magnetites as some good particles or the nano particles sometimes of definite size, which will be then reduced. So, the reduction of Fe 2, Fe 3 O 4 will give us the Fe, but what we can have the resulting catalyst particle consist of a core of magnetite, because on the surface if we can have the reduction. So, that in cases is a shell of wustite. So, wustite is Fe O; that means, we can have a partial reduction because Fe 3 O 4 is a corresponding magnetite can have both ferrous state as well as the ferric state in our hand. But, if we can go for the typical reduction of this ferric state to the ferrous state as well as the ferrous state already present in it, we can have a wustite layer of that which can be considered as a shell of that which is surrounded by outer shell of catalytically active alpha iron.

So, the outer self which is there so, the so, code is magnetite, then we have a one particular shell which is of FeO shell and finally, we can have the alpha Fe. So, is basically a 3 layer catalyst system and which is also very much useful, because whatever surface generated alpha iron we generate that will be useful for our conversion of your ammonia production. So, in this way we basically prepare this particular catalyst. So, production of this particular catalyst is also an integral part for the production of ammonia industrially.

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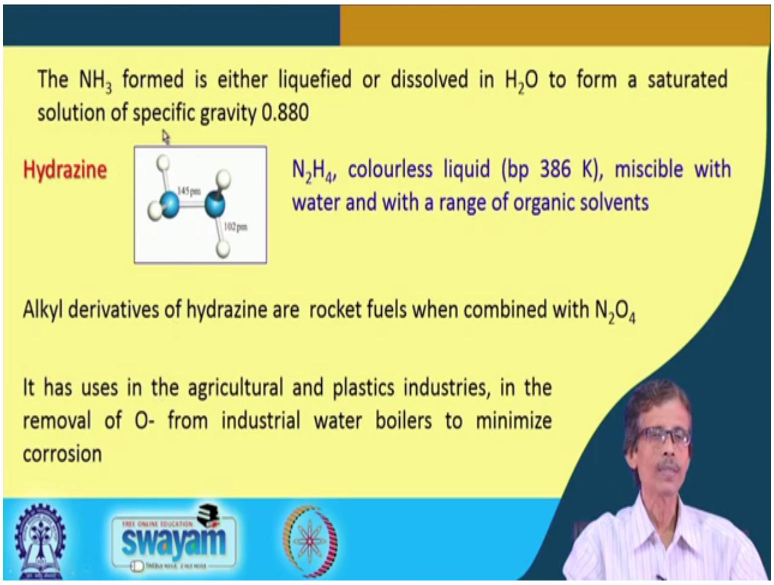
The NH_3 formed is either liquefied or dissolved in H_2O to form a saturated solution of specific gravity 0.880

Hydrazine

N_2H_4, colourless liquid (bp 386 K), miscible with water and with a range of organic solvents

Alkyl derivatives of hydrazine are rocket fuels when combined with N_2O_4

It has uses in the agricultural and plastics industries, in the removal of O- from industrial water boilers to minimize corrosion

Then we can see that once we produce this ammonia that the formed ammonia, which can either be liquefied because it is a gas how we can transfer from one side to the other. Because sometimes ammonia can be utilized as a direct fertilizer to the soil also; so, if we can take it in the gas it will be liquefied first like that of your LPG cylinder or it can be dissolved in water to form a saturated solution of ammonium hydroxide. Because the concentrated ammonia solutions or we call it as a licker ammonia; so, that licker ammonia can be very useful material consumed by all different types of industry, which are dependent on the nitrogen. So, is basically a very useful or a very basic nitrogen based compound which can be utilized for all other purposes.

So, when we dissolve it we should get a very saturated solution very much saturated solution and that saturated solution having a specific gravity because it is not so, easy to achieve a specific gravity high enough like that of your 0.88. So, special conditions are required such that we cannot have the diluted version of it. So, a highest level of specific gravity of 0.880 can be achieved for the production of your ammonium hydroxide.

Now, we just see that how we can utilize this ammonia. So, from nitrogen we are having in our hand N 2 to NH 3. Now, how we can use directly from your nitrogen or from ammonia the NH 3 another value added molecule which is very much useful for industrials point of view is our hydrogen. Because from academic point of view also the molecule hydrogen is also very much industry, but from industrial point of view how we can make this particular hydrogen, which is a very simple molecule, where we can have a nitrogen-nitrogen single bond. What earlier we know that the dinitrogen molecule; the dinitrogen is the nitrogen gas where we can have 3 nitrogen-nitrogen bonds.

So, nitrogen-nitrogen triple bond making that particular nitrogen molecule is very much inert which is not at all a very reactive species. So, that is why we can use for different types of reactions in the laboratory reactions, the nitrogen as the corresponding reaction blanket, the inert atmosphere what we can maintain through nitrogen. So, once we break all the 3 bonds between these 2 nitrogens, and we add on each nitrogen 3 hydrogen atoms we get the ammonia molecule NH 3. And before that; that means, if we can go for a stepwise reduction; that means, addition of 2 nitrogen each on the nitrogen molecule N 2 molecule because we have seen earlier that is a typical six electron reduction process where six hydrogen atoms or hydrogen ions along with the six electrons are attached to the N 2 molecule.

So, if we just basically lose the triple bond between these 2 nitrogen will be ending off with a double bonded nitrogen, having basically one hydrogen on the each side of these thing. In the next step another 2 electron reduction will give you a nitrogen-nitrogen single bonded species, with two more hydrogens attached to each nitrogen. That means, 2 plus 2 4 hydrogens we are attaching on the dinitrogen molecule giving us this particular molecule which is known as hydrogen.

So, hydrogen is your N 2 H 4 and if we see that earlier we have a triple bonded system; that means, nitrogen hydrogen triple bonded system between 2 nitrogen, now we have the nitrogen-nitrogen single bond. So, it is only 145 picometer. The nitrogen-nitrogen distance and the nitrogen hydrogen distance which is little bit higher than that of your carbon hydrogen distance of 96 picometer, which is 102 picometer. So, what about the corresponding physical characteristics of the hydrogen molecule? The hydrogen is basically a colorless liquid which having a boiling point of 386 K and which is miscible with water.

So, if your hydrogen molecule is not very much stable towards some thermal sock, towards the corresponding sunlight and all these thing, it can break and sometime it can so happen that it can go for some explosive reactions. So, it is always very easy or always to get a very safe solution like that of your dissolution of just now we have seen the dissolution of ammonia to water, giving you a saturated solution of ammonium hydroxide.

So, similarly if you have the hydrogen in your hand so, that hydrogen you can dissolve it or you can pass it into the water molecule and if that is also crystallizable or it can have some other thing which can be considered as a adduct of water molecule; that means, N 2 H 4 dot H 2 O. We can call it as a hydrogen hydrate, which is commercially available to us and for laboratory use or laboratories sake of other reactions or laboratory purpose we use basically instead of this colorless pure liquid of hydrogen, where the concentration is higher, we can use a little bit diluted one which is your hydrogen hydrate and which is also soluble in different organic solvents.

So, if we can use that which is soluble in water giving you a water hydrate, which can also be soluble in your different organic solvents like acetone nitrile or dichloromethane or chloroform. So, that organic solvent can be utilized as a solution for transferring your hydrogen to some reaction. Then we see most important thing for that is that, if we can have some alkyl derivative. How we get that alkyl derivative is a very important question to be asked. That once we can attach 3 hydrogen atoms to the nitrogen center or the nitrogen atom we get NH 3 which is nothing, but your ammonia molecule. But if one of that hydrogen can be replaced by the alkyl group which is typically a organic molecule like methyl ethyl propyl butyl etcetera.

So, what we get that instead of your nitrogen hydrogen bond, we can have one of them as the nitrogen carbon bond and that basically give us the corresponding alkyl derivative of ammonia which can be considered as the alkyl amine. So, if one of the H is replaced by your methyl group we get as the methyl amine, which is CH 3 NH 2. Similarly if one of that is replaced by ethyl we get ethyl amine EtNH 2. So, these are organic liquids unlike your ammonia which is dissolved in water giving you ammonium hydroxide.

So, that corresponding alkyl amines are useful for some other reactions, similarly the hydrogen if that particular hydrogen which are which is having 4 nitrogen hydrogen bonds which is N 2 H 4. So, in place of one NH bond if we go for one alkyl bond; one n ethyl bond or n methyl bond we get the corresponding ethyl hydrazine or methyl hydrazine. So, these alkyl derivatives of hydrogen which are very useful because which can be burnt very quickly or very easily in a very small time of filling, which can be used as rocket fuels when combined with nitrogen dioxide or the dimeric form of nitrogen dioxide NO 2, which is nothing, but your N 2 O 4 which is also a oxidizing agent.

So, in presence of some nitrogen based oxidizing agent, the alkyl derivative of hydrazine because it can be controlled for its burning process. Because, when we can have the controlled burning process, that particular material can be utilized as fuel otherwise if it is uncontrolled we call it as combustion. Hydrogen burning compared to that alkyl hydrogen burning is therefore, a typical combustion reaction immediately decomposes producing your corresponding water molecule based on the hydrogen and the nitrogen oxides from the nitrogen part. And also this particular hydrogen molecule is useful for agricultural and plastic industries. And sometimes it is also used in the removal of oxygen from industrial water boilers to minimize the corrosion is O 2. So, its oxygen is O 2 this is not O dashed is a O 2 form industrial water boilers.

So, water boilers should have less amount of dissolved oxygen; because that dissolved oxygen can be useful at a very high temperature for attacking the material of those boilers. If the material of that boiler is coming from your steel material or any other metallic seeds like iron seeds so, that iron at high temperature can be corroded for making your iron oxides. So, all the time we should have some idea that we should minimize that particular oxygen for the industrial water boiler.

So, hydrogen can be useful for that particular purpose, because that hydrogen can pick up that O 2 to destroy it from the dissolved condition in the industrial water boilers.

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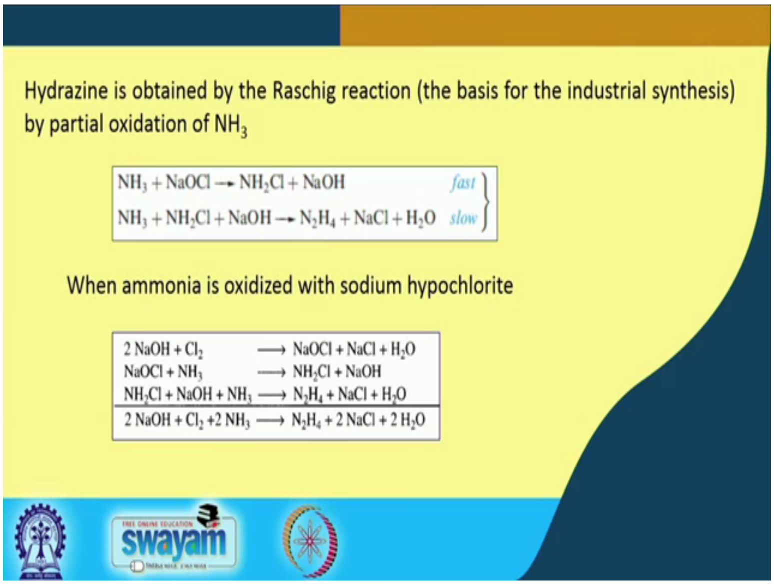

Hydrazine is obtained by the Raschig reaction (the basis for the industrial synthesis) by partial oxidation of NH_3

$$\left.\begin{array}{ll} NH_3 + NaOCl \rightarrow NH_2Cl + NaOH & \textit{fast} \\ NH_3 + NH_2Cl + NaOH \rightarrow N_2H_4 + NaCl + H_2O & \textit{slow} \end{array}\right\}$$

When ammonia is oxidized with sodium hypochlorite

$$\begin{array}{lcl} 2\,NaOH + Cl_2 & \longrightarrow & NaOCl + NaCl + H_2O \\ NaOCl + NH_3 & \longrightarrow & NH_2Cl + NaOH \\ NH_2Cl + NaOH + NH_3 & \longrightarrow & N_2H_4 + NaCl + H_2O \\ \hline 2\,NaOH + Cl_2 + 2\,NH_3 & \longrightarrow & N_2H_4 + 2\,NaCl + 2\,H_2O \end{array}$$

So, making hydrogen industrially is a typical task therefore, how we can think of that, how we can make hydrogen. So, one such is their typical rustic reaction. So, it is well known and a very famous and infinity old one for during the last about 100 years we are using this particular one, but still it is very much useful for making hydrogen to us.

So, this rustic reaction is basically nothing, but the basis of the industrial synthesis of hydrogen, where we can go for a partial oxidation of ammonia. So, partial oxidation means how we can go for a oxidation and that oxidation is not a simple attachment of OH to your NH 3, that we will also see that what other type of thing we can achieve through that. Because the replacement of one NH bond of ammonia by NCl bond now because other sort of oxidation can also be achieved well replacement of one of the NH bond can buy an OH bond, that will also a other type of molecule that we will also see.

So, if we use sodium hypochlorite for the preparation of hydrogen. So, in the first step this is the first process also. So, in the first step the first very first reaction is for the formation of chloramine. It is nothing, but NH 2 Cl is their chloramine formation, ammonia which having less one less NH bond and instead of that you can have one NCl bond and one molecule of NAOH. So, what we can do the in the second step basically the product of these two; that means, the NH 2 Cl and NAOH is further react with other molecule of NH 3.

So, what is basically happening there? That you can have NH 2 Cl so, NCl bond is there available. So, that NCl bond is basically attacking your other NH 3 molecule forming a basically n n bond. So, the n n bond formation. So, we are basically moving from a reverse direction from a reverse side basically, a different pathway is following instead of thinking in terms of your reduction of 3 bonds between 2 nitrogen in a stepwise manner. We cleave it for ammonia production because we are having ammonia in a plenty amount in our hand.

So, from that ammonia basically again we are trying to build the thing; that means, we are trying to attach 2 ammonia molecule giving you one nitrogen-nitrogen single bond. So, this basically gives us that N 2 H 4; that means, the hydrogen molecule itself, and that hydrogen molecule along with NaCl and water is the slow step basically the second step is therefore, a slow step for the production of your hydrogen.

So, when we basically use ammonia. So, ammonia is your starting material or the corresponding bulk material which can be utilized for the production of hydrogen, we use the sodium hypochlorite. So, the stepwise we will see that we can have this. So, in the first step it is the sodium hypochlorite preparation; that means, sodium hydroxide when chlorine is passed through a saturated solution of or a highly concentrated solution of sodium hydroxide, will produce sodium hypochlorite and then the two other steps what we have just now discussed.

So, overall what we are getting basically, if we start only with ammonia and we allow the reaction with the chlorine oxidation. So, that is also another procedure for making hydrogen not that you have to buy sodium hypochlorite because sodium hypochlorite is also available in the market, but instead of using sodium hypochlorite we can use directly the alkaline solution of chlorine gas.

So, chlorine can also be passed over that particular ammonia, in presence of a strongly alkaline solution or alkaline medium with respect to sodium hydroxide not potassium hydroxide or any other hydroxide, because this particular removal of sodium chloride is easier for this particular step giving you N 2 H 4 two molecules of NaCl and 2 molecules of water.

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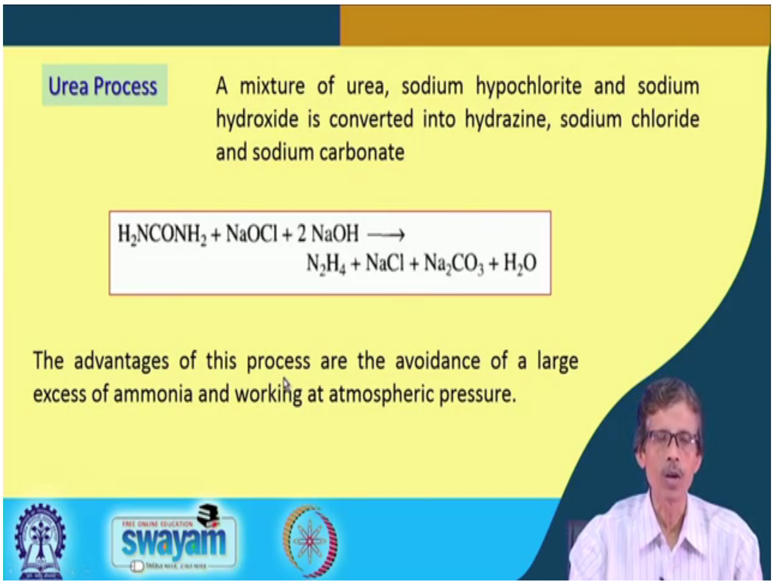

Urea Process

A mixture of urea, sodium hypochlorite and sodium hydroxide is converted into hydrazine, sodium chloride and sodium carbonate

$$H_2NCONH_2 + NaOCl + 2\ NaOH \longrightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O$$

The advantages of this process are the avoidance of a large excess of ammonia and working at atmospheric pressure.

So, that basically gives us a particular process where we utilize this particular production of hydrogen. Then another process the second process when we do not have the source of the starting material for hydrogen preparation, that ammonia. So, instead of ammonia sometimes urea can also be available because we all know that from ammonia we make urea, but people also have tried that whether we can have some amount of urea or urea is also in a plenty amount.

So, urea can also be taken into account because this urea molecule as we all know that urea has NH 2 CONH 2. So, in between 2 NH 2 groups which are being utilized for making that NH 2 NH 2 bond; that means, n n bond for giving you this particular hydrogen molecule in between you have the CO function. So, that CO function can be removed from there as a carbonate.

So, this CO of this urea can be removed as carbonate when we react it with again hypochlorite solution. So, sodium hypochlorite solution again in a strongly alkaline medium can be utilized for the production of your hydrogen in a different route. And definitely why we are trying this urea process compared to the previous one where we are ammonia we are utilizing. The advantage of these processes is that the avoidance of a large excess of ammonia because handling of the ammonia, and utilization of this ammonia and use this ammonia is sometimes is very difficult and the reaction goes at atmospheric pressure.

There is no need to go for a higher pressure for this particular reaction. So, the cost effectiveness in terms of maintaining the pressure of the industrial scale is important. So, we just go for one step to the other that means, we can use ammonia and the second point residual we can use urea for the production of your hydrogen.

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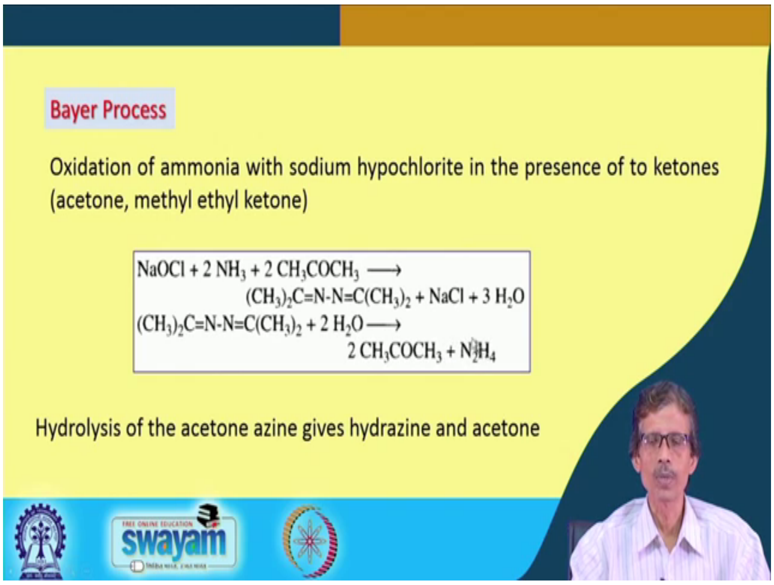

Bayer Process

Oxidation of ammonia with sodium hypochlorite in the presence of to ketones (acetone, methyl ethyl ketone)

$$NaOCl + 2\,NH_3 + 2\,CH_3COCH_3 \longrightarrow (CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + NaCl + 3\,H_2O$$

$$(CH_3)_2C{=}N\text{-}N{=}C(CH_3)_2 + 2\,H_2O \longrightarrow 2\,CH_3COCH_3 + N_2H_4$$

Hydrolysis of the acetone azine gives hydrazine and acetone

Then we see another interesting process, we are just basically talking about the processes for the production of these thing which is Bayer process. Bayer we know that the Bayer ag is the German major the German industry which they can have some their own ideas or sometimes what we can have initially when they produce it, they produce basically through their patented knowledge or patented procedure.

So, neither they are going through ammonia path or they are going nor they are going through the corresponding urea path, they are going in some different way, but utilization of ammonia again, but through some other modification. So, in this particular case, oxidation of ammonia with sodium hypochlorite is achieved in presence of a ketone, which are those ketones we can use acetone or we can use the methyl ethyl ketone.

So, what are the function of this particular ketone basically? Because the reaction what we know already that sodium hypochlorite when react with ammonia giving you the hydrogen. So, in situ an hydrogen is form that hydrogen is being trapped by 2 molecules of acetone from the two ends basically. As we all know that if we have 3 NH 2 function and if the ketone is available. So, that NH 2 and the ketone or the aldehyde can react and that reaction basically give us the formation of the (Refer Time: 23:22) bases or the amine formation or the amine bond formation, which is achieved through the formation of c double bond n.

So, the hydrogen can have 2 double ended NH 2 on the right hand side and NH 2 on the left hand side. So, if 2 acetone molecules approach it hydrogen from the two ends, one from the left and another from the left we get basically 2 amine bond formation. So, basically is a diamide formation; that means, diamine formation rather; diamine formation on the hydrogen backbone. So, basically that is being achieved for this particular reaction. So, acetone on the left and acetone, on the right on the produced hydrogen which is bonded by N N; so, this is basically the corresponding azine we call because basically a C double bond N on the left and basically another C double bond on the right instead of talking in terms of is the azine is the diazine.

So, diazine of acetone is formed along with NaCl and water molecule. So, the second step is the hydrolysis step in that particular step, we go for the hydrolysis of the acetone azine or the acetone diazine giving hydrazine and acetone back. So, it’s basically a typical purification process and the formed hydrogen is being trapped by the acetone, and we can purify it from the contamination of NaCl or any other thing or the any other starting material because this is the intermediate; that means, the diazine is the intermediate which is being hydrolyzed for the formation of hydrazine N 2 H 4 and the acetone back.

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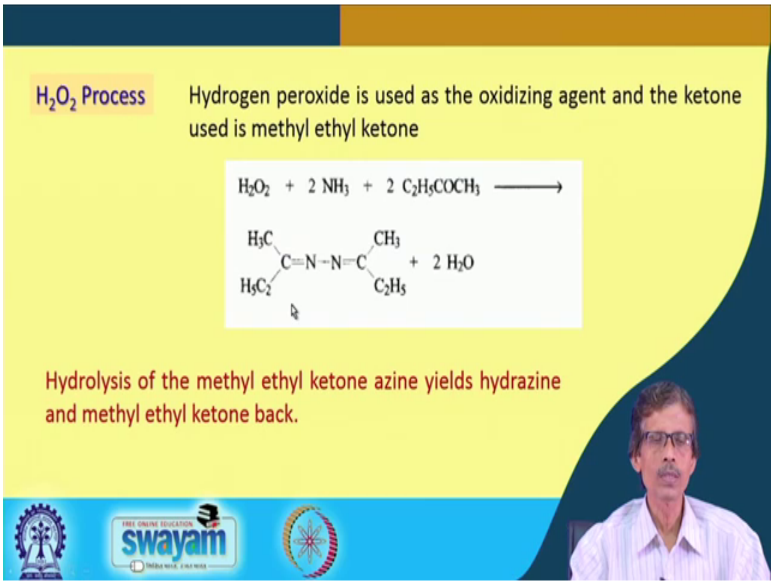

H_2O_2 Process Hydrogen peroxide is used as the oxidizing agent and the ketone used is methyl ethyl ketone

$$H_2O_2 + 2\,NH_3 + 2\,C_2H_5COCH_3 \longrightarrow (H_3C)(H_5C_2)C{=}N{-}N{=}C(CH_3)(C_2H_5) + 2\,H_2O$$

Hydrolysis of the methyl ethyl ketone azine yields hydrazine and methyl ethyl ketone back.

So, this is therefore, the particular process and lastly you will see that whether we can utilize this particular oxidation process; that means, the hypochlorite basically the business of the hypochlorite or direct use of chlorine, whether we can utilize hydrogen peroxide. So, far we are talking so, much about this hydrogen peroxide business; so, whether we can directly use hydrogen peroxide for oxidizing agent and use of ethyl methyl ketone. In the Bayer's process what we have seen that we can use acetone as well as the ethyl methyl ketone because it has a different type of stability because is that asymmetric is not symmetrical or unsymmetric ketone.

So, the same thing is formed, but instead of forming sodium chloride because hypochlorite was there NA OCl was there and OCl minus is your oxidizing part which is oxidizing your NH 3 to hydrogen formation. Here hydrogen peroxide is giving you water molecule and showing this corresponding oxidation reaction for the formation of your diazine of ethyl methyl ketone. Then we can have this particular diazine and like your previous case or the previous process we go for the hydrolysis of the methyl ethyl ketone, diazine yielding hydrogen and the corresponding ketone back.

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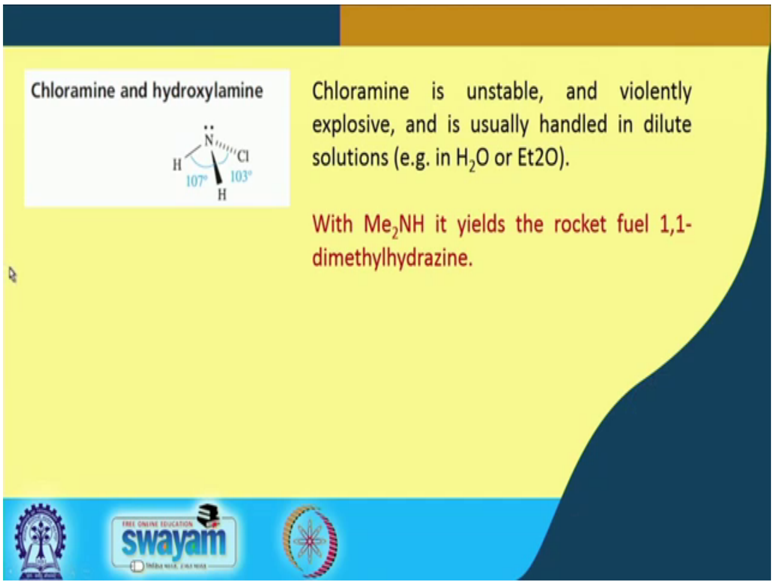

Chloramine and hydroxylamine

Chloramine is unstable, and violently explosive, and is usually handled in dilute solutions (e.g. in H_2O or Et2O).

With Me_2NH it yields the rocket fuel 1,1-dimethylhydrazine.

Then we just can see and we can continue to our next class that, whatever we are talking in terms of the corresponding formation of our chloramine and hydroxylamine. So, chloramine is nothing, but we have seen just now in our previous class that we can have the ammonia which is a pyramidal molecule. The nitrogen hydrogen, nitrogen hydrogen as well as the corresponding nitrogen chlorine thing. When we have when we have the ammonia molecule all 3 are same type of bond; that means, H NH bond which is 107 degree, but when one is substituted by Cl you can have a different bond angle you see that Cl NH bond is little bit shorter which is 103 degree.

And this particular chloramine formation which is also very much useful for making other thing; that means, one very important molecule for that is that 1, 1 dimethyl hydrazine preparation. So, 1, 1 dimethyl hydrazine preparation is also very much useful; how we can get it because we have seen already that i told you earlier also that if you have one of the NH bond is replaced by methyl function, we get is methyl amine. When the second one is replaced we get dimethyl amine when third one is replaced is get trimethylamine.

So, at the step where we substitute 2 of the NH bond by methyl group, we will get the dimethyl amine. So, dimethyl amine that means, the one part of this in place of use your ammonia we have this dimethyl amine. So, one part will be converted to your dimethyl part and if we take or if we use the other part as your NH 2 function we get the corresponding one as 1, 1 dimethyl hydrazine molecule, which can have some corresponding controlled burning process; that means, which is not a typical combustion or a burning process, but which can give you energy for fuel purpose for propelling your rocket how we can make that particular hydrazine out of this?

So, for that basically we can have the use the corresponding chloramine and that particular chloramine is unstable and violently explosive. So, this cannot be your fuel also. So, chloramine is highly explosive. When it is highly explosive we have to handle it in a very regular manner and very controlled manner and we should pay respect to this particular chemical because it is highly explosive. And therefore, it is easily handled in a very dilute solution because when things are very much concentrated, the corresponding risks for explosion is bigger and bigger or higher and higher that it explodes very fast when the concentration is very high and is a reaching some concentration which is corresponding concentration basically controlled the explosion.

So, dilute solutions where we can dilute it? We can dilute it by use of water as we have seen the in case of hydrazine also for making hydrazine hydrate and by diluting it with ether. So, next day what we can see that the making of this chloramine and its use basically as well as your corresponding hydroxyl amine formation.

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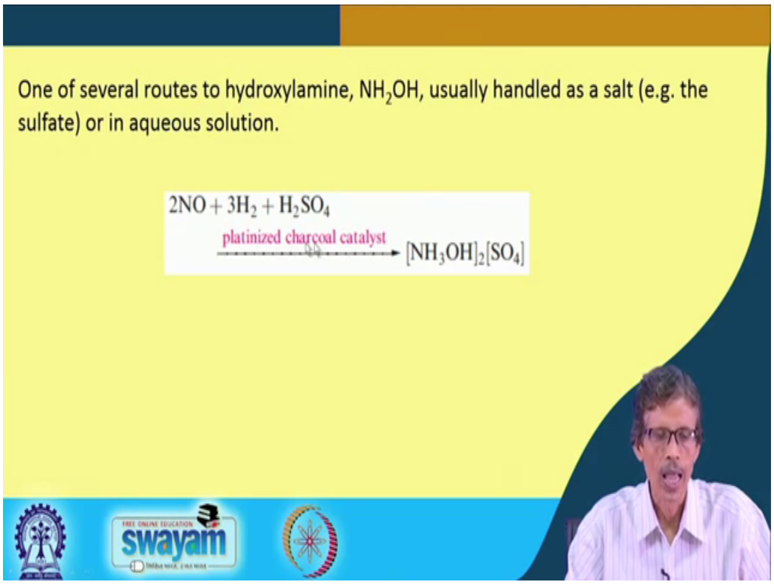

One of several routes to hydroxylamine, NH_2OH, usually handled as a salt (e.g. the sulfate) or in aqueous solution.

$$2NO + 3H_2 + H_2SO_4 \xrightarrow{\text{platinized charcoal catalyst}} [NH_3OH]_2[SO_4]$$

Because one of the routes for hydroxyl amine, which is nothing, but instead of NH 2 Cl we can have NH 2 OH and that we will see in our next class in detail that we can handle it as a salt or as aqua solution through some process where we can oxidize the thing from nitric oxides.

So, we can have some nitrogen oxides now. So, these nitrogen oxides are also very much useful and in some other indirect pathway like that of our making your chloramine. So, this particular one that we can use it directly for the making of this particular chloramine, and this chloramine can be directly used for the production of some other useful molecules and then we will see that how we can change this NCl bond to NH to giving us hydroxyl amine, because those hydroxyl amine molecules are also very much important and also interesting.

Thank you very much.