Hydrogenation Using Precious Metal Catalysts

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Typically 5% palladium/platinum/rhodium on activated carbon/alumina and 10% palladium/platinum/rhodium on carbon/alumina catalysts finds application in a variety of reactions like hydrogenation, hydrosilation, dehydrogenation, hydrogenolysis, dehalogenation, reduction, debenzylation, Rosenmund reduction, alkylation, methanation, carbon-oxygen cleavage, carbon-nitrogen cleavage, etc.

Precious (nobel) metal catalysts has many advantages as compared to nickel based catalysts in terms of reaction parameters, selectivity and applications. The filtration rate is also faster and the catalysts can be recycled in many cases. The above chemical reactions lead to manufacture of critical life saving drugs, fine chemicals and intermediates. Some of these include:

- Indinavir (Anti-HIV)
- Antibiotics like azithromycin, clarithromycin.
- Carvedilol (congestive heart failure and hypertension).
- Ephedrine (hypertensive).
- Isoxsuprine (vascular diseases such as arteriosclerosis, Buerger’s disease, Raynaud’s disease and menstrual pains).
- Cisplatin (metastatic testicular, ovarian, tumors, advanced bladder cancer).
- Pentazocine (interstitial cystitis).
- Theobromine (energizer and weight loss).
- Theophylline and salbutamol (anti-asthma).
- Lisinopril (high blood pressure and heart failure).
- Cyanocobalamine (neurological disorders).
- Rosiglitazone (antidiabetic).
- Benzathene penicillin (diphtheria).
- Enalapril (cardiovascular)
- Succinic anhydride (food additive)
- Pantoprazole (anti ulcer)
- Diminazine (veterinary drugs).

Also, India depends totally on the international market for the purchase of palladium. This makes things more difficult for the consumer. So what can to be done to keep things under control? The best method is to minimize the consumption and maximise the output of the catalyst. Some of the techniques that can be followed to ensure optimization of catalyst use are:

1. Carry out strict analysis of the fresh catalyst supplied. It would be better if proper sampling and homogenizing is done before the analysis. The sampling procedure should include preconditioning, drying, grinding, sieving, homogenization, bulk homogeneity testing and bottling.
2. The reactants should de-aerated by purging with an inert gas for 5 to 15 minutes. This is best suited for a majority of reactions.
3. Minimise palladium leaching (re-deposition) during and at the end of the reaction. Palladium leaching generally correlates significantly with the progress of the reaction, the properties of reactants, the solvent, the base and the atmosphere.
4. In cases of leaching, palladium re-deposition can be achieved by: Further treatment at a slightly increased temperature; addition of reducing agents; and/or addition of distilled water.
5. Efforts should be made to study: the activity/selectivity of the catalyst under ambient conditions; and the complete separation (filtration) from the product mixture.
6. The atmospheric conditions should be preferably inert (e.g. argon, helium, etc.). In some cases, compressed inert gases have been found to increase catalyst activity.
7. The spent catalyst, many a times, may not be spent. A detailed analysis should be done of the spent catalyst before sending the same for reprocessing.

ROLE OF A SOLVENT IN CATALYTIC REACTIONS

Solvents play a vital role in some hydrogenation reactions involving a catalyst, but not necessarily in all reactions.
Among the important reactions carried out by manufacturers of dyes and intermediates are reduction of nitro-aromatics to amines. The reactions should be carried in the molten state, in the absence of solvent, in a stirred tank reactor. In case solvents are desired, then isopropanol or ethyl acetate is recommended. The catalyst loadings depend on the reactant purity with respect to the catalyst poisons and the desired reaction time. The catalyst exhibits high selectivity and activity. Hence, it is not necessary to add bases to neutralize the liberated hydrochloric acid, which can reduce the catalyst activity. The amount of catalyst recommended is 0.5 weight % of the nitro compound. In general, increase in catalyst loading, pressure and/or reaction temperature will increase the rate and decrease the selectivity. The gas-liquid-solid mixing also has an impact on the reaction rate and catalyst selectivity. Optimization of the agitation rate will ensure a maximum yield of the desired product.

Comparison between catalytic hydrogenation and iron/hydrochloric acid reduction

The disadvantages of Fe/HCl reduction are:
1. Problems are often experienced in sourcing iron powder of desired specifications and quality.
2. It is necessary to steam distil the amine from the iron sludge, which consumes very high energy.
3. Dumping and disposal of the sludge is a problem.
4. If a solvent is used, the iron sludge has to be filtered hot.

The advantages of hydrogenation using palladium/platinum on carbon are:
1. Gives a higher yield of amine.
2. Produces a higher quality amine.
3. Recycling of the catalyst is possible.
4. Optimization of reaction conditions and good house keeping will ensure minimal catalyst consumption.
5. The noble metal can be recovered from the spent catalyst and reprocessed to a fresh catalyst. The subsequent purchases are only small after the initial purchase.

For both the above reactions, palladium catalysts

### TABLE 1

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Temp. (°C)</th>
<th>Pressure (Bars)</th>
<th>Catalyst</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Nitrotoluene</td>
<td>o-Toluidine</td>
<td>5-150</td>
<td>1-10</td>
<td>5%Pd/C</td>
<td>&gt;/=99</td>
</tr>
<tr>
<td>m-Nitrotoluene</td>
<td>m-Toluidine</td>
<td>30-150</td>
<td>1-10</td>
<td>5%Pd/C</td>
<td>&gt;/=99</td>
</tr>
<tr>
<td>p-Nitrotoluene</td>
<td>p-Toluidine</td>
<td>70-150</td>
<td>1-10</td>
<td>5%Pd/C</td>
<td>&gt;/=99</td>
</tr>
<tr>
<td>o-Chloronitrobenzene</td>
<td>o-Chloroaniline</td>
<td>90-150</td>
<td>8-12</td>
<td>1% Pt/C</td>
<td>&gt;/=99</td>
</tr>
<tr>
<td>m-Chloronitrobenzene</td>
<td>m-Chloroaniline</td>
<td>90-150</td>
<td>8-12</td>
<td>1% Pt/C</td>
<td>&gt;/=99</td>
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<tr>
<td>p-Chloronitrobenzene</td>
<td>p-Chloroaniline</td>
<td>90-150</td>
<td>8-12</td>
<td>1% Pt/C</td>
<td>&gt;/=99</td>
</tr>
<tr>
<td>o-Nitroanisole</td>
<td>o-Anisidine</td>
<td>20-150</td>
<td>1-10</td>
<td>5%Pd/C</td>
<td>&gt;/=99</td>
</tr>
<tr>
<td>p-Nitroanisole</td>
<td>p-Anisidine</td>
<td>70-150</td>
<td>1-10</td>
<td>5%Pd/C</td>
<td>&gt;/=99</td>
</tr>
<tr>
<td>2,5-Dichloronitrobenzene</td>
<td>2,5-Dichloroaniline</td>
<td>90-150</td>
<td>8-12</td>
<td>1% Pt/C</td>
<td>&gt;/=99</td>
</tr>
</tbody>
</table>

### TABLE 2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>5% Rh/C</th>
<th>5% Ru/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst loading</td>
<td>1-2% by the weight of reactant.</td>
<td>1-2% by the weight of reactant.</td>
</tr>
<tr>
<td>Solvent</td>
<td>Methyl alcohol</td>
<td>Methyl alcohol, ethyl alcohol</td>
</tr>
<tr>
<td>Temperature</td>
<td>25-100°C</td>
<td>100-150°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1-10 bar</td>
<td>15-50 bar</td>
</tr>
<tr>
<td>Additives</td>
<td>Not required</td>
<td>Water traces.</td>
</tr>
</tbody>
</table>
require high temperatures and pressures to achieve good yields of the product. Platinum catalyst gives lesser yields due to the hydrogenolysis of the carbon-oxygen bond. Rhodium and ruthenium based catalysts overcome these problems to a good extent. Rhodium can be used under mild conditions also. Ruthenium catalysts are also good, but require slightly higher temperatures and pressures than rhodium.

The other problem in rhodium based catalysts is that Rhodium prices have been fluctuating a lot since recent times, as compared to other platinum group metals. This can hence sometimes increase / decrease the overall cost of the manufacturing process.

THE IMPORTANCE OF SAMPLING

The petrochemical industry also conducts dehydrogenation reactions using platinum based catalysts and chemicals in large quantities. A typical example is chloroplatinic acid. It contains 39-42% platinum and is a red-brown crystalline solid. Some companies use 20% chloroplatinic acid containing 20% platinum. Chloroplatinic acid is also used in electroplating, etching and microscopy.

Spent chloroplatinic acid is in the form of non-uniform crystals and partly in powder form (fines). Hence, care should be taken to perform the sampling procedure for spent chloroplatinic acid before dispatching it to the manufacturer for recovery and regeneration/reprocessing. Discrepancies in sampling may lead to huge financial losses for the consumer. The samples of chloroplatinic acid (CPA) should be drawn as per the following details:

The packing should be done in durable and leak-proof HDPE bottles.

Sampling procedure

The sampling should be carried out in the presence of representatives of the consumer and vendors. The fines of the catalyst also should be mixed for sampling. After the collection is done, the spent has to be weighed, stored, recorded and attested in presence of representatives of the consumer and vendors.

1. Each drum containing the catalyst should be numbered for identification.
2. Gross weight of each drum should be recorded.
3. Each drum should be emptied and its tare weight should be recorded.
4. Contents of each drum should be sieved through a BS mesh to remove fines. Sampling should be done while screening for obtaining composite sample.
5. Weight of material retained on and passing through the mesh should be recorded for each drum separately.
6. Fines collected as at step 5 should be mixed and heaped together for all drums. With the method of coning and quartering, 1 kg samples of fines should be collected in bottles and sealed. The remaining fines should be transferred to separate empty drums (previously weighed and recorded). The number of 1 kg samples will be determined by the number of parties participating in the sampling.
7. The entire quantity of samples collected as per the step 4 should be mixed and heaped for obtaining the composite sample. With the method of coning and quartering 1 kg sample of this catalyst should be

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Net Wt (Grams)</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>10</td>
<td>To be retained by CONS duly sealed by CONS for their analysis.</td>
</tr>
<tr>
<td>2.</td>
<td>30</td>
<td>Bearing CONS code no. and to be sealed by CONS for sending the sample to the third party for analysis.</td>
</tr>
<tr>
<td>3.</td>
<td>10</td>
<td>To be handed over to the vendor i.e. MANU for carrying out analysis in their laboratory.</td>
</tr>
<tr>
<td>4.</td>
<td>10</td>
<td>Jointly to be sealed by MANU and CONS to be retained by the vendor as reference.</td>
</tr>
<tr>
<td>5.</td>
<td>10</td>
<td>Jointly to be sealed by MANU and to be retained by CONS as reference sample carrying CONS code.</td>
</tr>
<tr>
<td>6.</td>
<td>30</td>
<td>Jointly to be sealed by MANU &amp; CONS, and retained by CONS as reference sample.</td>
</tr>
</tbody>
</table>

CONS: Consumer Representative (i.e. user of CPA); MANU: Manufacturers/Vendors (of CPA) representative.
collected separately in bottles and sealed. Out of the balance quantity of the samples, containers for the samples of 1 kg shall be prepared both for fines and coarse catalyst and remaining quantity shall be transferred to drums and weight recorded.

8. From the above steps, the following are obtained:
   - Gross weight of each drum.
   - Tare weight of each drum.
   - Net weight of ‘Off-Spec’ catalyst + the mesh catalyst in each drum.
   - Weight of fines passed through mesh for each drum.
   - Total weight of the ‘Spec Catalyst’ (fines and coarse).
   - 1 kg samples to be given as per Part (1).

It is also important to ensure that the procedures are done by experienced and reliable technical personnel. This is applicable both for the consumer and the vendor.

**CATALYST DEACTIVATION MECHANISMS**

If we could stop or minimize the deactivation process of a noble metal catalyst, it will save us huge revenues. The manufacturing cost of the end product also would be less, with prospects of better markets. This will be the ideal scenario and everyone in the chemical industry would prefer to achieve such goals.

Unfortunately, nothing in this world is indispensable. Everything has a particular life span, a depreciation period and prone to get deactivated. Active precious metals (palladium, platinum, rhodium) are well-known catalysts for gas purification. Among the active metals, rhodium is known to be the most sensitive metal towards sintering at high temperatures. This leads to poor activity, especially in the reduction of nitro group.

The use of a bimetallic catalyst, such as Pd-Rh or Pt-Rh, gives a better catalytic activity at high temperatures. The operating conditions also affect the sintering of active metals; for example, ageing atmosphere and the oscillation between oxidizing and reducing atmospheres can accelerate deactivation.

**Redispersion**

This is an opposite process to sintering. During redispersion, many complex phenomena take place: the particle sizes decrease and surface areas increase. In particular, the interaction between oxygen and precious metals may lead to the formation of species that are mobile on the surface and reverse the process of agglomeration.

Sintering is normally physical, rather than chemical, in nature and, therefore, the magnitudes of thermal activation are quite different. Furthermore, ageing time is important because it correlates both with sintering and redispersion.

The kinetics of catalyst deactivation is a function of temperature, time, pressure and the concentrations of different substances.

**Deactivation by poisoning**

Poisoning is defined as a loss of catalytic activity due to the chemisorption of impurities on the active sites of the catalyst. Usually, a distinction is made between poisons and inhibitors.

Poisons are substances that interact very strongly and irreversibly with the active sites, whereas the adsorption of inhibitors on the catalyst surface is weak and reversible. In the latter case, the catalytic activity can be at least partly restored by regeneration. This irreversible/reversible or permanent/temporary nature of deactivation and the regeneration possibility of a catalyst are the main differences between poisoning and inhibition.

However, the distinction between permanent and temporary poisoning is not always so clear, since strong poisons at low temperatures may be less harmful in high-temperature applications.

Catalyst poisons can also be classified as selective or non-selective. The description of a poison as selective or non-selective is related to the nature of the surface and the degree of interaction of the poison with the surface. A poison can also be selective in one reaction, but not in another.

Poisoning of a catalyst as a result of the accumulation of impurities on the active sites is typically a slow and irreversible phenomenon. The accumulation of poi-
sons on the active sites blocks the access of reactants to these active sites. As a result of poisoning, the catalytic activity may be decreased without affecting the selectivity, but often selectivity is also changed since some of the active sites are deactivated while others are practically unaffected.

In some cases, depending on the adsorbed poison, the poisoned catalyst can be regenerated and its activity can be at least partly restored. Active metal catalysts are preferred in controlling of gas emissions, because they are less liable to sulfur poisoning than metal oxide catalysts. Precious metals have different types of resistance against poisoning. Palladium is more sensitive than platinum and rhodium to chemical deactivation — in particular to poisoning by sulfur and lead.

Climate conditions also affect the catalyst’s chemical deactivation. Especially in countries, where the cold weather and environment keep the catalyst’s temperature low during a long time period. This accelerates the catalyst’s chemical ageing.

The stability against thermal and chemical deactivation can be improved by a proper choice of the catalyst material. In addition, the placement of the active material in separate layers improves the durability.

Other mechanisms of deactivation

There are other essential forms of deactivation of catalysts. For example, pore blockage, encapsulation of metal particles, volatilization of active compounds, fouling, and metal-metal interactions.

High temperature ageing may result in deep encapsulation of sintered precious metal particles as the surface area of the catalyst layer decreases. This is a serious type of deactivation because of its permanent nature. The encapsulated metal particles cannot participate in catalysis since they are inaccessible to the molecules. Fouling covers all phenomena where the surface is covered with a deposit, e.g. with reactant residues or with mechanical wear. There are probably as many other mechanisms of fouling as there are reactions where such phenomenon is encountered with precious metal catalysts. During this period carbonaceous residues cover the active surface sites and decrease the active surface area.

First, this blocks out the active compounds from reaching the surface sites, and second, the deposits block the internal pores in the catalyst. In many cases, the reactants and aromatic materials are primarily responsible for such type of scenario. Among these other deactivation mechanisms, pore blocking is probably one of the most important mechanisms. Pore blocking is often connected to fouling and is high on the catalyst’s surface.

At high temperatures, catalysts may suffer from the loss of active phase through volatilization. Metal loss through direct volatilization is generally an insignificant route of catalyst deactivation. By contrast, metal loss through the formation of volatile compounds is important over a wide range of conditions.

Large amounts of catalytic materials can be transported to either substrate where they can react, or into the gas phase where they are lost in the effluent gas stream. High volatility limits the selection of otherwise useful catalytic materials. For example, the oxides of Pt, Pd and Rh formed during the reaction cycles are not as volatile as other noble metal oxides, such as RuO$_2$, OsO$_4$ and Ir$_2$O$_3$.

The thermodynamics of volatilization and thermodynamic equilibrium calculations are useful in the evaluation of the volatility of metals and metal oxides in order to assess which materials are stable over long periods at high temperatures. Thermodynamic equilibrium calculations of the oxidation/reduction behaviour of palladium have shown that phase stability in a Pd/PdO system changes as a function of temperature and oxygen partial pressure. The lower the pressure and the higher the temperature, the more likely is the Pd phase. The vapour pressures of Pt, Pd and Rh as metals and metal oxides increases with temperature, and is also strongly dependent on the composition of the surrounding atmosphere. Pd is volatile at temperatures around 850°C and above, depending on the surrounding environment. The orders of vapour pressures of active metals and their oxides are as follows:

- Pure Metals: Pd $>$ Pt $>$ Rh
- Metal Oxides: Pt $>$ Rh $>$ Pd

Hence the vapour pressure of metallic Pd is clearly several magnitudes higher than the vapour pressures of Pt and Rh, while as oxides, the situation is the reverse.
CONCLUSIONS

The main causes for catalyst deactivation and selectivity are:
• Poisoning.
• Fouling.
• Reduction of active area i.e. sintering or migration.
• Loss of active species.

The main causes for catalyst poisoning:

• Impurities in the feedstocks (reactants, hydrogen gas, etc.).
• If the reaction product is strongly adsorbed, then the catalyst can get self-poisoned or self-inhibited.
• The surrounding climate conditions, level of atmospheric pollution, etc.

Poisoning of the catalyst can lead to alteration in the bond strength of the product through its electronic effects.

Also, the precious metal content in a poisoned precious metal catalyst is found to be lesser by around 8-10% than in a non-poisoned catalyst.

SEMINAR ON ‘OPTIMISING USAGE OF PRECIOUS METAL CATALYSTS’

There are many procedures which can be employed in industry to optimise the usage of precious metal catalysts.

This paper is intended to provide only a brief outline of the applications and the challenges in the use of precious metal catalysts. More information on the subject of catalyst optimisation & recovery and the relevant reactions involving precious metal catalysts will be provided during a Seminar to be organised by Practicals India Enterprises as per the following details:

Date: 21-22 May 2004

Venue: Gujarat Bhavan, Sector 15, Vashi, Navi Mumbai.

Contact: Mr. Ketan Patel at info@practicalsindia.com