PARTIAL CATALYTIC HYDROGENATION OF ACETYLENE IN ETHYLENE PRODUCTION

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ABSTRACT

Acetylene is a byproduct of modern ethylene production processes, and it acts as a poison to the catalysts used for making polyethylene out of the ethylene product. Due to the above reasons, polymer-grade ethylene product should contain not more than 5 ppm of acetylene. The trace acetylene removal is a great challenge to ethylene producer and catalyst manufacturer due to low acetylene concentration in the reactor feed and nearly 100% conversion of acetylene required in the acetylene converter. In this paper, we will first review the available technologies currently apply in most of the ethylene cracker worldwide, the challenges faced, and the new developments in the catalyst and reactor design.

Keywords: Acetylene, hydrogenation, catalyst, deactivation, regeneration

1   INTRODUCTION

Ethylene is one of the most widely produced petrochemicals in the world, with a production history reaching back to the early 20th century. It has been recovered since 1930 as a product of coke-oven gas and in the 1940's became an important industrial intermediate when American companies began producing it by separation from waste gas. This era also saw deliberate ethylene production from ethane and natural gas. More recently, ethylene has taken the place of acetylene in virtually all large-scale chemical syntheses. However, acetylene itself is a byproduct of modern ethylene production processes, and the removal of this contaminant will be considered.

To begin, the formation of acetylene in ethylene product streams will be examined. More than 97% of ethylene around the world is produced by pyrolysis of hydrocarbons, which is the thermal cracking of petrochemicals in the presence of steam. This process can be described as the heating of a mixture of steam and hydrocarbon to the necessary cracking temperature, which can range from 260 °C to 340 °C depending on the hydrocarbon used. This mixture is then fed to a fired reactor or furnace and heated to between 400 °C and 470 °C. As a result, the original saturated hydrocarbon "cracks" into smaller unsaturated molecules. This process is extremely endothermic, and the product must be cooled back to the original feed temperature upon leaving the reactor in order to minimize secondary reactions. Possible alkane feedstocks for pyrolysis include ethane, propane, n-butane, isobutane, naphthas, kerosene, and various gas oils. In the U.S., ethane and natural gas liquids (often a mixture of ethane and propane) are most commonly used in ethylene production. Incidentally, using an ethane feedstock produces the smallest amount of acetylene byproduct, which averages about 0.26 % by weight of the product stream. For other feeds, this quantity can become as large as 0.95 % by weight. Ethylene to be used for polymerisation processes has to be 99.90% pure. This is known as polymer-grade ethylene and the maximum allowable limit of acetylene should not be higher than 5 ppm.

The reason that acetylene removal from the ethylene stream is so vital is that acetylene acts as a poison to the catalysts used for making polyethylene out of the ethylene product. In addition, acetylene can form metal acetylides, which are explosive contaminants. It is thus imperative that acetylene in the ethylene product be reduced to an acceptable level. In fact, this paper will focus more on the catalytic hydrogenation rather than other technology available such as solvent extraction.

2 ACETYLENE REMOVAL TECHNOLOGY

Treatment of the C_2-stream can take various routes, depending on the acetylene content and whether or not high-purity acetylene is to be recovered. There are basically two main paths, to extract the acetylene from the C_2-stream and recover it as a product, or to convert the acetylene into useful product which is ethylene. Each paths involved different unit operations and it affects the overall process sequences.

2.1 Acetylene Recovery through Solvent Extraction

Acetylene recovery facilities can be located between the deethanizer and the ethylene-ethane fractionator or downstream of the latter (Figure 1 location 3). The typical acetylene recovery process makes use of three towers, the first to absorb acetylene in a suitable solvent, the second to reject and return co-absorbed ethylene and ethane from the solution, and the third to desorb acetylene (Kniel, 1980). Acetone, dimethylformamide (DMF), methanol and n-methyl pyrolidone are the preferred solvents (Miller, 1965). Certain C_3-hydrocarbons in the deethanizer overhead have solubilities in these solvents comparable to the solubility of acetylene and therefore have to be completely removed from the feed. Location of acetylene recovery facilities downstream of the main ethylene-ethane fractionators eliminates this problem but involves high concentrations of acetylene in this tower, resulting in partial pressure that, however, remain well below established safety limits. Acetylene recovery systems in both locations are presently in operation with a better overall safety record than acetylene hydrogenation systems have had.

2.2 Acetylene Hydrogenation System

The acetylene hydrogenation reactor is typically a fixed bed catalytic reactor, normally operated adiabatically (licensed by Stone & Webster). There are also isothermal tubular reactors operated commercially (licensed by Linde AG). There are three major reactor configurations, i.e. the cracked gas train, the back-end and the front-end reactor. Table 1 shows the typical feed compositions as the function of reactor location. (Tiedtke et al.). Basically, acetylenes (inclusive of acetylene and methyl acetylene) in a naphtha cracker is higher than an ethane cracker. We will discuss each configuration in detailed in the following sections.

Table 1: Typical Acetylene Concentration in the Feed Gas and Conversion Rate (Walzl, 2000)

	Feedstock	Concentration (vol %)			Conversion Rate (%)		
		C_2H_2	C_3H_4	C_4H_6	C_2H_2	C_3H_4	C_4H_6
Back-end Hydrogenation	Naphtha	1.3	-	-	100	-	-
Front-end Hydrogenation (deethanizer)	Naphtha	0.61	-	-	100	-	-
Front-end Hydrogenation (depropanizer)	Naphtha	0.53	0.067	-	100	> 60	-
Raw Gas Hydrogenation	Ethane/ propane	0.3	0.13	0.85	100	> 60	> 90

2.2.1 Raw Gas Catalytic Hydrogenation Reactors

In raw gas catalytic hydrogenation, the effluent of the cracked gas compressor, after minimal treatment, enters the acetylene converters for catalytic hydrogenation of the acetylene contained in the feed. Although the use of nickel catalysts has endured in this type of application, a progression to the use of the higher selective palladium technologies is occurring. In raw gas applications where the reactors precede the caustic tower, effective utilization of palladium catalyst is not possible without process modification. The feed in this case contains copious amounts of sulfur, which necessitate the use of supported, nickel-based catalysts. Figure 1 shows a typical flow diagram of the naphtha cracker, the location 1 is the raw gas catalytic reactor. Miller (1969) suggested Cobalt molybdate and Ni-Co-Cr catalysts to be used and steam to be added to improve the selectivity and inhibit the fouling of the catalyst.
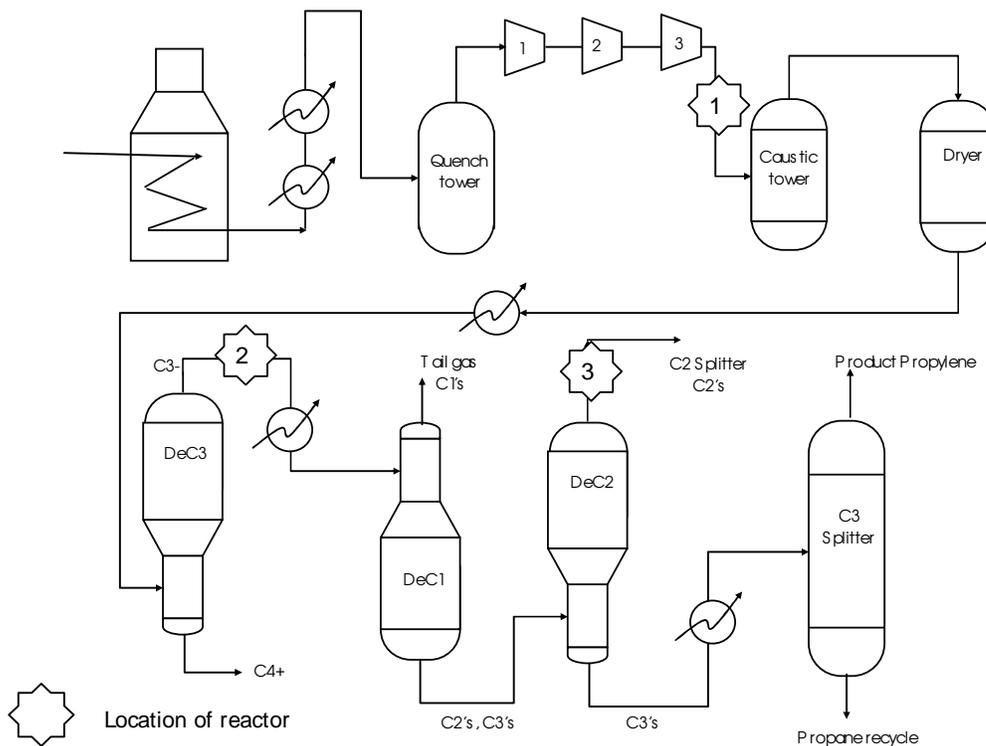
2.2.2 Back-End Catalytic Hydrogenation Reactors

In back-end catalytic hydrogenation reactor, the acetylene is, typically, contained in a C_2-rich stream (Table 1) to which stoichiometric amounts of hydrogen, and in some cases small amounts of carbon monoxide, are added to control the extent of acetylene and ethylene hydrogenation. In this type of application, the reactors are located at the overhead of the deethanizer. Location 3 in Figure 1 shows the configuration of back-end reactor. This configuration is suitable for moderate acetylene contents when the recovery of acetylene is not of interest. The deethanizer gross overhead is heated to a temperature of between 20 and 100°C, hydrogen is added in a molar ratio of approximately 2 referred to acetylene, and the mixture is passed over a fixed bed of palladium catalyst (Kniel, 1980). The heat of reaction is removed in a water cooler and the reactor effluent is further cooled by heat exchange with the feed and partially condensed by heat exchange with propylene refrigerant. The liquid is pumped as reflux to the deethanizer while the vapour flows through the guard dryer to the ethylene-ethane fractionator (ethylene splitter). The reactor effluent typically contains less than 1 ppm of acetylene but is contaminated with traces of hydrogen and methane which represent the major disadvantage of this location of the acetylene hydrogenation system. Yet this location has the advantage over the front-end hydrogenation in that it allows very accurate control of hydrogen concentration and reaction temperature, resulting in a good selectivity of the reaction.

2.2.3 Front-End Catalytic Hydrogenation Reactors

In front-end selective catalytic hydrogenation reactors, the acetylene reactors precede the demethanizer in the process. As a result, these reactor feeds contain a large excess of hydrogen - typically 10 to 35 mol %. There are two types of front-end acetylene reactor configuration, i.e. the front-end depropanizer and the front-end deethanizer system.

In a front-end deethanizer design, the deethanizer is the first distillation column and the reactors are on the overhead stream. Thus, the reactor feed contains a C_2 and lighter stream. Whereas, in a front-end depropanizer unit, the initial distillation column is the depropanizer (Figure 1, location 2). As the acetylene reactors are on the overhead of this column, the feed to the reactors is composed of C_3 and lighter hydrocarbons. The disadvantage is that the hydrogen to acetylene ratio is uncontrollable.

Figure 1: Location of Acetylene Hydrogenation Reactors

3   MECHANISM OF SELECTIVE HYDROGENATION

In the partial catalytic hydrogenation of acetylenic compounds, the triple bond has to be converted into a double bond. In doing so, there arise the following problems of selectivity (Cutmann, 1969):
(a) The double bond which is formed can be further hydrogenated.
(b) The double bond which is formed can be displaced (position isomerism).
(c) The double bond which is formed can have cis or trans configuration (geometric isomerism).
Since acetylene only have two carbon atoms, the problems stated in (c) is not applicable. To achieve high selectivity, the catalyst must not further hydrogenate the partially hydrogenated product. This can be affected by two factors, the kinetics and the thermodynamic factors. Kinetic and thermodynamic effects are frequently combined, and they cannot readily be distinguished. Further, not only the catalyst but also the chemical structure can have an influence on the selectivity.

In case of the subsequent reactions (undesired reaction) proceeding much more slowly than the partial hydrogenation (desired reaction); the selectivity is then based on a mechanistic (kinetic) factor. Besides, the partially hydrogenated product can also be protected from subsequent reactions by being rapidly desorbed from the catalyst surface and then not being re-adsorbed again. This thermodynamically dependent selectivity is based on the triple bond being more strongly adsorbed than the corresponding double bond, because it is more electrophilic character. Even relatively small differences in the adsorption energy are sufficient for the acetylenic compound to immediately displace the primary resulting hydrogenation product from the catalyst surface and accordingly act as a "poison" for the subsequent reactions. The poisoning action is naturally only effective as long as the acetylenic compound is still present.

Acetylene itself is a good example of thermodynamically controlled selectivity. This can be proven from the effluence of a fixed bed palladium catalyst reactor, where the resulting ethylene only contains 1-5% ethane although this catalyst have 10 to 100 times greater activity for the hydrogenation of ethylene than for the hydrogenation of acetylene (Cutmann, 1969).

A general mechanism shown in Table 2 suggested that selectivity is controlled by the equilibrium between the two forms of adsorbed C_2H_3 (step 3 and step 4). The hydropolymerisation (formation of oligomer or "green oil") is consider to be a polymerisation of adsorbed acetylene, $H\overset{*}{C}=\overset{*}{C}H$, in which the free radical $-H\overset{*}{C}-\overset{*}{C}H_2$ is the initiator (Miller, 1969).

Table 2: General Mechanism of Catalytic Acetylene Hydrogenation

| Step 1 : Adsorption	Acetylene is associatively adsorbed on the longer lattice spacing of the transition group metal, and that it reacts with a H_2 molecule (there being no independently adsorbed hydrogen on Ni) or	$H\overset{*}{C}=\overset{*}{C}H + H_2 \rightarrow H\overset{*}{C}=CH_2 + \overset{*}{H}$
	with an adsorbed H atom (on Pd or Pt)	$H\overset{*}{C}=\overset{*}{C}H + \overset{*}{H} \rightarrow H\overset{*}{C}=\overset{*}{C}H_2$
Step 2: Isomerisation	The adsorbed vinyl radical is thought to isomerise in part into a free radical form	$-H\overset{*}{C}-\overset{*}{C}H_2$
Step 3: Hydrogenation to ethylene	The vinyl form hydrogenates to give ethylene which leaves the surface	$H\overset{*}{C}=CH_2 + \overset{*}{H} \rightarrow CH_2=CH_2$
Step 4: Hydrogenation to ethane	The free radical form gives an adsorbed ethylene which can react with more hydrogen	$-H\overset{*}{C}-\overset{*}{C}H_2 + \overset{*}{H} \rightarrow \overset{*}{C}H_2-\overset{*}{C}H_2$ $\overset{*}{C}H_2-\overset{*}{C}H_2 + \overset{*}{H} \rightarrow \overset{*}{C}H_2-CH_3 \rightarrow CH_3-CH_3$

The asterisks indicate adsorption links.

4   CATALYSTS

There is not just one universal catalyst suitable for the hydrogenation of acetylene. Different catalyst modifications are applied depending principally upon the gas composition and operating conditions. Laboratory tests are warranted when no exact operating precedent exists to determine which catalyst formulation will give the best results. For satisfactory performance, the catalyst should exhibit these characteristics (Zdonik, 1970):

1. High activity sustained over long operating periods, high space velocity, and consequently a low-catalyst inventory.
2. High selectivity over a relatively wide temperature range to avoid losses of ethylene and to prevent polymer and carbon formation. These latter products result from temperature variations within the catalyst bed due to the exothermic nature of the reactions.
3. Resistance to poisoning by CO and traces of sulfur compounds.
4. Rugged structure to permit periodic regeneration of catalyst pallets.

Nickel, palladium, platinum and several other metals and metallic oxides can act as catalysts in the hydrogenation of acetylene. Usually the same catalyst brings about both hydrogenation and hydro-polymerisation. Although in the absence of acetylene, ethylene often hydrogenates more rapidly than acetylene over the same catalyst, acetylene hydrogenates much faster than ethylene when both are present, because the acetylene occupies the active adsorption sites preferentially. This is the basis of the selective hydrogenation of acetylene to ethylene. Selectivity had been enhanced by disseminating the catalyst over an inert carrier. Adams, et al. (2000) described how advanced technology allows precise control of Pd placement by showing a sample of "eggshell" Pd deposition in thin layer of catalyst surface (Figure 2). This technology is called impregnation. The factors influenced the catalyst performance are Pd penetration depth, Pd surface area coupled with Pd crystal size, choice of promoter, carrier interaction with Pd and promoter, impregnation technique and calcinations temperature.

"eggshell" Pd deposition

porous alumina support
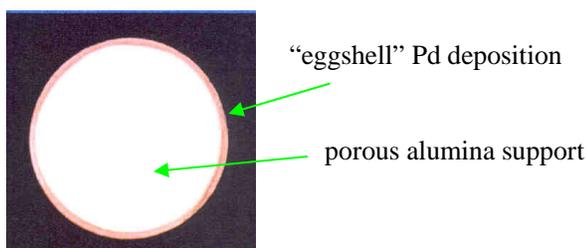
Figure 2: Impregnated Pd Catalyst

4.1   Palladium Based Catalyst (Pd/Al$_2$O$_3$)

The alumina-supported palladium, designated Pd/Al$_2$O$_3$ is commonly used from 1958-1988. A well known product is G-58A, B and G-83 manufactured by Süd-Chemie, Inc. (Adams, 2000). The G-58 A and B have a surface area of approximately 150 m^2/g (Adams, 2000). It requires the presence of carbon monoxide to enhance its selectivity. A catalyst consisting of silica-supported Pd is invented by Flick et al. (1999). It contains between 0.001 and 1 % by weight Pd and between 0.005 and 5 % by weight of a promoter metal, preferably potassium. The catalyst is prepared by impregnating the silica support with a solution containing the promoter metal, and then drying the impregnated support. Then this product is impregnated with a solution containing Pd. Finally, the catalyst is dried and calcined (Flick et al., 1999). It has a BET surface area of 100 to 300 m^2/g, and is usually processed as an extrudate. It can be activated by reduction with hydrogen or hydrogen-containing gas, which produces a thin layer of Pd over the promoter metal oxide. The operating conditions with this catalyst involve a slight excess of hydrogen, pressure of 10 to 30 bars, and a relatively low temperature, usually less than 150 °C. The reactor operates adiabatically and can reduce acetylene content from the typical value of 0.25 % by weight to approximately 1 ppm.

4.2   Silver/Palladium Based Catalyst (Pd/Ag/Al$_2$O$_3$)

Silver promoted catalyst (Pd/Ag/Al$_2$O$_3$) is a modified version of Pd catalyst. The addition of silver improves the catalyst performance so that only an insignificant amount of ethylene is lost due to over-hydrogenation. This catalyst is activated by wet reduction with an alkali metal borohydride/alkali metal hydroxide solution, and then dried and heated to enable calcining. It can also be oxidatively regenerated. The catalyst has between 0.01 to 0.2 % by weight Pd and 0.02 to 2 % by weight Ag, with the preferred Ag:Pd weight ratio between 5:1 and 8:1 (Cheung, et al., 1996). The particles should be spheres or cylindrical pellets with nominal diameters between 2 – 6 mm with a BET surface area of 1 to 100 m^2/g. The feed should be premixed before entering the reactor, and there should be at least one mole of hydrogen for every moles of acetylene in the hydrocarbon stream. This reactor should operate at between 0 – 150 °C and 100 – 1000 psig. It is possible to regenerate the catalyst by heating it up to about 700 °C in the presence of air. A typical example of such catalyst is G-83C manufactured by Süd-Chemie, Inc.

4.3   Gold/Palladium Based Catalyst (Pd/Au/Al$_2$O$_3$)

In year 2003, a process for the production of Pd catalyst with gold as the moderator had been invented by Blankenship, et al. (2003). The palladium/gold impregnated catalyst has a ratio of the gold to the palladium from 6:1 to about 50:1. It is readily used without in-situ pre-reduction. The catalyst has about 0.001 to 0.028 % by weight palladium metal, and 0.18 to 1.0% by weight gold metal impregnated on inorganic support material; preferable alpha alumina, zinc oxide, nickel spinel and low surface area catalyst support materials with a surface area less than about 100m^2/g; pore volume about 0.2 to 0.7 cc/g. The catalyst particles should have a shape of a sphere, trilobe, monolith, pellet or tablet with about 2-6 mm nominal diameter. The depth of penetration of the palladium metal is present within 250 microns of the catalyst surface. By the process of this invention, enhanced reduction of acetylene to less than 1 ppm is possible with enhanced selectivity. The catalyst is less susceptible to CO concentration swings, as compared to two commercially available catalysts (G-83A and G-83C manufactured by Süd-Chemie Inc.), where the latter experienced thermal run away due to CO reduction. The catalyst exhibits improved selectivity, resistance to temperature run-away, tolerance to CO concentration swing and improved performances at high gas hourly space velocity (GHSV). These improvements are obtainable even if the catalyst is not pre-reduced in-situ by the passage of hydrogen over the catalyst bed, which is critical and mandatory in conventional Ag/Pd catalyst. This catalyst suitable to be used in a front-end acetylene converter, with operating temperature about 35 – 100 °C, pressure about 100 – 1000 psig and GHSV about 1000 to 14000 liters per liters catalyst per hour.

4.4   Others

Other possible catalyst options for gaseous feeds are metal oxides and sulfides, usually ZnO, as well as other supported Group VIII metals (Brophy et al., 1987). Also, if the plant is configured differently it would be possible for the acetylene-bearing hydrocarbon stream to be a liquid. In this case, the proper catalyst would be Pd/Al$_2$O$_3$ with the addition of 0.1 to 1 % by weight of an amine compound, and the reactor should be run at 10 – 50 bars and 20 – 150 °C with excess hydrocarbon (McCue, et al., 1995).

5   CATALYST DEACTIVATION

The causes of deactivation are basically of three kinds: chemical, mechanical, and thermal. The five intrinsic mechanisms of catalyst decay, (*1*) poisoning, (*2*) fouling, (*3*) thermal degradation, (*4*) chemical degradation, and (*5*) mechanical failure, vary in their reversibility and rates of occurrence (Bartholomew, 2003) Poisoning and thermal degradation are generally slow, irreversible processes while fouling with coke and carbon is generally rapid and reversible by regeneration with O$_2$ or H$_2$. Catalyst deactivation is more easily prevented than cured. Poisoning by impurities can be prevented through careful purification of reactants. Carbon deposition and coking can be prevented by minimizing the formation of carbon or coke precursors through gasification, by careful design of catalysts and process conditions and by controlling reaction conditions to minimize effects of carbon and coke formation on activity. Sintering is best avoided by minimizing and controlling the temperature of reaction.

Poisons reduce the activity of palladium catalysts in two major ways: first, by hindering or blocking the access of the reactants to palladium sites, and second, by changing the electronic properties of the palladium such that the adsorption strength of the reactant on the palladium is greatly reduced. Sulfur compounds represent the first class of poisons. Compounds like hydrogen sulfide (H_2S) or carbonyl sulfide (COS) adsorb strongly on the palladium. In this manner, these poisons block the acetylene from the reaction sites.

Poisons like the sp metals, such as arsenic and mercury, form "alloys" with the palladium. Electron transfer between the sp metals and the palladium drastically reduces the associated adsorption strength of acetylene. Since the reaction rate of acetylene is directly proportional to the rate of adsorption, which in turn depends exponentially on the heat of adsorption, a small reduction in the adsorption strength will translate to a significant drop in catalyst activity. Although to a limited extent, silver behaves like a sp metal, however, its impact on palladium is less drastic in comparison to arsenic or mercury. Palladium catalysts with a silver promoter are not as active as catalysts containing only palladium. The beneficial effect of the silver is its modification of the relative adsorption strength of acetylene and ethylene on the palladium. The result is a catalyst with a small reduction in activity but an improvement in selectivity.

The poisons can be categorized among three types as defined below:
- (a) Inhibitor – those poisons whose effects subside when the concentration of the species diminishes.
- (b) Temporary – those poisons whose effects subside only after the catalyst undergoes proper steam/air regeneration.
- (c) Permanent – those poisons whose effects cannot be alleviated, even after the catalyst undergoes proper steam/air regeneration.

Table 3 contains a list and classification of poisons that are commonly present in feeds to acetylene converters.

Table 3: Classification of Specific Poisons (Tiedtke et al.)

Classification	Type of poison	Examples
Inhibitor	oxides	CO, O_2, H_2O
	MA/PD	$CH_3C \equiv CH$, $H_2C = C = CH_2$
	amines/nitrogen	NH_3, NH_2R
	sulfides	COS, H_2S, MeSH
Temporary	phosphines	PH_3, PH_2R
	carbon oligomers (green oil)	Precursors: BD, acetylene
	chlorides	Cl^-
Permanent	mercury	Hg
	arsenic	AsH_3
	heavy metals	Fe, Mn, Pb, Ti
	main group metals	Na, Ca, Mg

6   REGENERATION TECHNIQUES

Regeneration of deactivated catalysts is possible for many catalytic processes and is widely practiced. The main purpose is to remove the temporary poisons on the catalyst surface and restore the free adsorption sites. Generally regeneration can be categorized into two, i.e. the off-site and the on-site regeneration. In the off-site (ex-situ) regeneration, the catalyst is to be unloaded from the reactor and regeneration is performed in moving-bed belt calciners or conical-shaped rotating drum calciners. (Robinson, 2000).

The on-site (in-situ) regeneration does not require removing the catalyst from reactor. The most common procedure is to burn off, or oxygenate, the temporary poisons, such as green oil, in order to resume the

catalyst activity. Regeneration of the catalyst may be accomplished by heating the catalyst in air at a temperature lower than 500 °C, to burn off any organic material, polymers or char.

Huang, et al. (1994) invented an improved method for regenerating acetylene hydrogenation catalysts which does not require an oxygenation step. The hydrogen stripping involves feeding a mixture of 5 – 10 % hydrogen and the balance nitrogen to the spent catalyst at 350 °C and 50 psig. This is much less time-consuming than oxygenation, since the whole procedure takes between 16 – 24 hours. The only disadvantage to hydrogen stripping is that the catalyst deactivates more quickly so that the procedure must be performed more often.

7   CURRENT AND FUTURE DEVELOPMENTS

Research and development in the partial catalytic acetylene hydrogenation are mainly to improve the acetylene removal efficiency and lower the ethylene losses. Past research is basically focused on optimizing the acetylene reactor operating temperature and pressure, changing reactor configuration and location, optimizing H_2 to acetylene ratio, changing catalyst formulation, etc. In this paper, we will discuss the revamp on the catalyst shape and the research in membrane catalytic reactor.

7.1   CDS (Computer Designed Shape) Catalyst

The catalyst manufacturers are competing in the catalyst design and manufacturing technologies. Besides changing the formulation and the palladium impregnating techniques, the catalyst manufacturer also look into possibilities of improving catalyst performance by varying the size and shape of the catalyst. The Süd-Chemie, Inc or known as Nissan Girdler Catalyst Co. Ltd. had came out a technology called CDS (computer designed shape). Figure 3 shows some of these CDS catalyst.
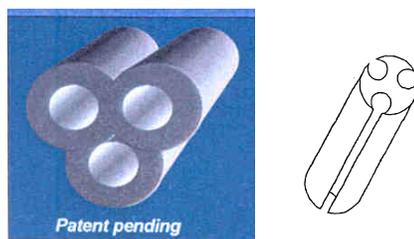
Figure 3: Computer Designed Shape (CDS)

Some features claims by inventor are listed below (Lai: 2000; Süd-Chemie product catalogue):
1. Shape avoids catalyst interlocking, thus maintaining the high geometric surface area and void volume.
2. High void volume results in low pressure drop, thus higher space velocity.
3. Pd is skin impregnated and since there is high geometric surface area, the Pd is better dispersed, resulting in high activity and excellent poison resistance.

Till dates, there isn't been much technical papers discussing the performance of the CDS catalyst. Further warranted from laboratory tests and exact operating precedent are needed to confirm the CDS catalyst performance.

7.2   Catalytic Membrane Reactor

A membrane reactor may be either a supported ceramic layer on a porous support or an ultra-thin solid noble metal. Some metal membrane studies include Pd, Pd/Ni, Pd/Ru and Pd/Ag (Vincent and Gonzalez, 2002). Studies found that the permeate hydrogen was very active and that ethylene was the main product. However, the membrane must be very thin in order to provide the appropriate selectivity. Porous ceramic membranes can support highly dispersed metals on an inorganic oxide to combine the properties of higher permeability with thermal stability, which are absent in the dense metal membranes. A novel approach to the selective hydrogenation of acetylene involves a short contact time reactor is suggested by Vincent and Gonzalez (2002). The experiment by forcing a dilute $C_2H_2/H_2/Ar$ mixture through a thin

Pd/γ–Al$_2$O$_3$ catalytic membrane (about 5μm thick) produced high conversions coupled with high selectivity at high temperatures.

Membrane reactors achieve efficiencies by combining in one unit of reactor that generates a product with a semi-permeable membrane that extracts it. Studies have been done on methanol reforming (Buxbaum, 1997), photocatalytic oxidation of volatile organic carbon (Yeung et al.), Direct synthesis of Hydrogen Peroxide (Svajda, et al., 2002) and others catalytic reactions. Membrane reactors fundamentally change the pressure dependence of conversion in gas phase decomposition reactions so that the reactions are preferentially performed at high pressures rather than low. Higher pressures allow much smaller reactors and more efficient purification. Membrane reactors can be advantageous also for sequential endothermic and exothermic reactions, by using the product extraction to promote heat transfer. The net result is smaller reactors, improved heat transfer, lower capital costs, and often fewer side-reactions.

8   CONCLUSIONS

Trace acetylene removal had been one of the critical paths in ethylene production. The lower acetylene content in the ethylene product nowadays had been a great challenge to ethylene producer. Catalyst which can meet higher conversion and still remain the ethylene selectivity contributed to higher productivity and lower ethylene losses. In other words, better profitability. The research on catalytic membrane reactor if successfully brought over to industrial scale will definitely turn over the traditional means of acetylene removal techniques, which will eventually affected the overall ethylene plant design and operation.

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