Dehydrogenation of hydrocarbons involves the breaking of two carbon-hydrogen bonds with the simultaneous formation of a hydrogen molecule and a molecule containing a double carbon-carbon bond, which usually represents the desired product. The double bond is a highly reactive point that permits the use of molecules which contain it as intermediates for the production of typical petrochemical products such as polymers.

Dehydrogenation reactions appear very simple; their thermodynamic and kinetic characteristics have, nevertheless, contributed to make the development of technologies that allow for a reliable and efficient industrial application, rather complex.

The dehydrogenation reactions of greatest industrial interest are those paraffins containing 2-5 carbon atoms which are used to produce the corresponding olefins; those linear paraffins with 10-15 carbon atoms, needed for the production of linear-alkyl-benzenes (LAB) and ethyl benzene, dehydrogenated to styrene, the monomer which is the starting point for the production of polystyrene plastics. The dehydrogenation of alcohols to ketones and aldehydes represent other dehydrogenation reactions of industrial interest.

### 11.2.1 Dehydrogenation of light paraffin (2-5 carbon atoms)

Light olefins continue to serve as a fundamental basis for the petrochemical industry and refining. Traditionally, steam cracking and Fluid Catalytic Cracking (FCC) are the major industrial sources of light olefins, such as ethylene and propylene. Both processes, in which various hydrocarbon cuts can be used as the raw material, produce various compounds of interest at the same time. Variations in the operating conditions make it possible to roughly modify the composition of the mixture of products, but this may not be sufficient when an increase in market demand for one particular product is much higher than that for the other co-products. For example, the demand for propylene is growing faster than that for ethylene in many geographical areas. In this case, the ability to synthesize a pure product (such as propylene through the dehydrogenation of propane) can prove far more successful in comparison with the classic “multi-product” approach. In the recent past, the dehydrogenation of isobutane to isobutene, an intermediate stage in the production of such high octane oxygenates as methyl-tert-butyl ether (MTBE), had an extremely important role. However, the decision to change the composition of gasolines in the United States has led to a decreased interest in this particular dehydrogenation product (Sanfilippo et al., 2003); nevertheless, existing facilities are continuing their large scale production, and the technology used in the dehydrogenation of isobutane constitutes the basis for the development of similar techniques for the dehydrogenation of propane.

**Kinetic and thermodynamic aspects**

Dehydrogenation removes a molecule of hydrogen from paraffin forming an olefinic double bond that will be the preferred point of attack for successive reactions:

\[
R_2\text{CH} \rightarrow \text{CHR}_2 \rightleftharpoons R_2\text{C} = \text{CR}_2 + \text{H}_2
\]

Notwithstanding its apparent simplicity, the dehydrogenation of paraffin is one of the most complex chemical processes to realize industrially, since the thermodynamic equilibrium limits the conversion possible per pass and the reaction is highly endothermic, that is to say, a large amount of heat must be supplied to the reactant system. In Fig. 1, the
conversion equilibrium is shown versus the temperature, for paraffins with 2 to 15 atoms of carbon. It is clear that, in order to make the industrial process more economic, it is advisable to increase the conversion per pass as much as possible, so that the cost of recycling the unconverted reagent and that of separating the reagent and the product is reduced. As shown in Fig. 1, it is evident that temperatures between 500 and above 700°C are needed to reach a conversion rate of 50%. However, high temperatures also enhance an undesired parallel process, i.e., thermal cracking reactions that reduce the selectivity to the desired product and make purification operations downstream the reaction zone necessary. A typical scheme that includes the most important types of secondary reactions, such as cracking, oligomerization, isomerization, aromatization and alkylation, is shown in Fig. 2. Oxidative dehydrogenation has been widely studied, as one route to circumvent the thermodynamic limitations. This involves supplying oxygen to the reagent mixture so that it combines with the hydrogen produced by dehydrogenation and forms water. The removal of the hydrogen allows the dehydrogenation reaction to proceed with a higher conversion than would be suggested by the equilibrium. However, the practical application of this approach ran into the problem of making the oxygen react only with the hydrogen, without causing direct combustion of the hydrocarbons and a resulting loss of selectivity. An additional advantage of this approach results from the exothermic nature of the reaction producing water, which contributes heat for the dehydrogenation reaction, reducing the need for an external source.

In non-oxidative dehydrogenation, in order to reach high reaction rates and minimize the effect of its complex secondary reactions, a suitable heterogeneous catalyst is needed.

The energy required to remove two atoms of hydrogen from the alkane molecule is almost independent of the molecular weight of the paraffin and in the range of 113-134 kJ/mol.

The highly endothermic nature of the main reaction (and of the greater part of the secondary reactions) leads to a strong temperature decrease, if the reaction is carried out in an adiabatic manner. For example, in the case of the dehydrogenation of propane with a 25%
conversion, there is an adiabatic temperature decrease of 200°C. Since no catalyst is able to operate in such a wide temperature range, it is clear that a single adiabatic reactor cannot be used, and a heat source must also be supplied in the course of the reaction. We will discuss later how different ways of supplying heat for the reaction characterize the different technologies available.

Examining Fig. 2 once again, one can note how all the reaction paths lead to the depositing of carbon (coke) on the surface of the catalyst. Even with a highly selective catalyst, the depositing of coke gradually makes it less active, so that a periodic regeneration of the catalyst is necessary, normally by burning the coke in air streams. The catalysts for dehydrogenation must therefore be able to accept repeated cycles which alternate between reducing and oxidizing atmospheres. The maximum level of coke accumulation and consequent time needed for each phase in the reaction cycle and regeneration depend on the nature of the particular catalyst used.

From the thermodynamic point of view it is necessary to also consider the negative role played by pressure, due to the increase in the gaseous volume produced by the reaction. In addition, using a diluting agent or operating in a vacuum have the advantage of increasing the driving force that acts in the process.

**Catalysts**

The principal catalytic systems that have a dehydrogenation activity reported in scientific and patent literature are:

- Group VIII metals (mainly platinum with tin) supported on alumina and with promoters.
- Chromium oxides on alumina or zirconium, with promoters.
- Iron oxides supported, with promoters.
- Gallium, as a supported oxide or included in zeolitic structures: gallium in/on mordenite (Pogue et al., 1993), on SAPO-11 (Machado et al., 2002), on MCM-41 (Fajula et al., 2003), on TiO₂ (Nakagawa et al., 2001), on Al₂O₃ (Iezzi et al., 1994).
- Copper, for the dehydrogenation of alcohols to aldehydes.

Including the most recent literature, the situation for dehydrogenation catalysts and their applications is outlined in Table 1.

Commercial application has restricted potential catalysts to those indicated below:

- For the dehydrogenation of ethyl benzene to styrene, oxides of Fe as the only choice.
- For long chain paraffins for LAB, Pt/Sn promoted on Al₂O₃.
- For light paraffins and olefins, Pt/Sn promoted on Al₂O₃ and Cr₂O₃ on Al₂O₃.

The two large families of catalysts for the dehydrogenation of paraffins (based on Pt and Cr) were developed at the same time. The two families do not differ substantially in terms of activity and selectivity, but rather in the quality of some by-products and in the treatment needed to complete the regeneration after the combustion of the coke. In addition, the phenomena that lead to the irreversible deactivation (sintering, volatilization of the active components and transformations of the morphology or the state of the support) are typically connected to the chemical types that characterize the various catalysts.

**Platinum catalysts**

Platinum catalysts are less active in the formation of heavy by-products, compared to chromium catalysts, but cause skeletal isomerization in the case of hydrocarbons with 4-5 atoms of carbon, resulting in possible complications in the process stages.

Patent literature shows a very high number of formulations based on the noble metals of Group VIII and elements of Group IV. However, only two formulations are applied at industrial level:

- Pt/Sn with alkaline metals (and possibility of further promoters) on an alumina support, used in the Oleflex (UOP) (Pujado e Vora, 1990).
- Pt/Sn, preferably with alkaline promoters on zinc or magnesium aluminates, used in the STAR technology.

Both of these applications use tin, believed to be a promoter which improves the activity, selectivity and stability of the catalyst. Various hypotheses have been

<table>
<thead>
<tr>
<th>Active component of catalyst</th>
<th>Dehydrogenation of light paraffin</th>
<th>Dehydrogenation of paraffins C&lt;sub&gt;10&lt;/sub&gt; - C&lt;sub&gt;14&lt;/sub&gt;</th>
<th>Dehydrogenation of ethyl benzene to styrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Sn</td>
<td>excellent</td>
<td>excellent</td>
<td>poor</td>
</tr>
<tr>
<td>Cr oxides</td>
<td>excellent</td>
<td>moderate</td>
<td>good</td>
</tr>
<tr>
<td>Fe oxides</td>
<td>absent/poor</td>
<td>not available</td>
<td>excellent</td>
</tr>
<tr>
<td>Ga system</td>
<td>excellent</td>
<td>not available</td>
<td>excellent</td>
</tr>
</tbody>
</table>

Table 1. Performance of dehydrogenation catalysts
formulated to explain the resistance to ageing found in catalysts promoted with tin (Barbier et al., 1980). Such hypotheses can be summarized as models of three types (Fig. 3), involving: uniform dispersion of platinum on a surface constituted by alumina and tin aluminate; formation of a solid solution with atoms or clusters of tin within the platinum lattice; or formation of platinum-tin alloys.

The type of model that best represents the characteristics of the catalyst depends on many factors. For example, it is possible to move from situations best-described by the first model to situations that fall in the second and third category in the following ways:

- Increasing the ratio Sn/Pt.
- Increasing the calcination temperature of the catalyst.
- Changing from acid supports to neutral supports.
- Modifying the preparation procedure, from an impregnation of the platinum compound on oxides of co-precipitated Sn/Al to a preparation where complexes of Sn/Pt are impregnated on alumina.
- Increasing the concentration of the two metals on the support.
- Decreasing the surface area of the alumina.

The mechanism by which tin modifies the catalytic behaviour of platinum can be explained on the basis of theories that are not closely connected to the types of tin present on the surfaces.

The theory, based on an electronic effect, hypothesizes that the tin in metallic form (both in solid solution and in small bimetallic clusters or as an alloy with platinum or, finally, as an ion \( Sn^{2+} \) in close contact with the platinum atoms) gives up its electrons to the vacancies of the band 5d of the platinum atoms. In this case, small quantities of tin (below the limit of analytical measurement) should influence the platinum properties. A quantity of tin which corresponds to 15% of the platinum’s atomic weight is sufficient to fill the band 5d. In addition, solid solutions or alloys can lead to the formation of small crystallites of platinum, characterized by different reactivity (Burch, 1981; Burch and Garla, 1981). On the basis of the electronic effect, it is possible to explain the promoting effect of the tin, by assuming that the coke precursors cannot fix themselves to the surfaces of the “promoted” crystals of platinum, but instead migrate towards the support, avoiding the deactivation of the active sites (Lieske et al., 1987).

The smaller amount of coke formation can also be connected to an inhibition of the condensation reactions that lead to the synthesis of polymers. For the same reason, the hydrogenolysis of the \( \text{C} = \text{C} \) bond is also inhibited, because the hydrocarbon cannot adsorb itself strongly on the catalytic surface.

The formation of coke and the hydrogenolysis require large ‘ensembles’ of platinum atoms, while dehydrogenation requires small agglomerates of platinum, or well-dispersed active centres (Barbier et al., 1980). The formation of an alloy leads to a dilution of the platinum atoms, with the formation of smaller agglomerates. However, where the formation of alloys is not observed, small quantities of tin in the crystallites of platinum can produce a dilution effect.

A high level of activity of the platinum in the interaction with surface ions \( Sn^{2+} \) (but not with metallic tin) can be explained by the exchange of electrons between tin ions and metallic platinum (electronic effect) or by the stabilization of small crystallites of platinum, caused by a strong interaction with an aluminate of surface tin.

It has been suggested (Beltramini and Trimm, 1987) that tin added in small quantities tends to segregate on the surface of the crystallites of platinum in sites with low coordination (angles and extremities), inhibiting the reactivity of these sites.

The tin also produces a reduction of the surface acidity of the support, responsible for both the cracking reactions and skeletal isomerization, and for the formation of the coke precursors.

The main properties of the support which determine the characteristics of platinum catalysts are as follows: a) surface acidity; b) intrinsic stability and stability of the dispersion of platinum during reaction and regeneration.
c) chemical interaction with the promoters;

d) distribution of the dimensions of the pores.

Zinc and magnesium aluminates are neutral or slightly basic and therefore do not need alkaline promoters; alumina supports, on the other hand, need alkaline promoters to minimize the acidic properties of the system responsible for a decrease in the selectivity and life of the catalyst. The main role of the support consists in stabilizing the dispersion of the platinum, especially during the regeneration of the catalyst, by means of the combustion of the coke. While platinum deposits on silica sinters following oxidative treatments, the sintering is very limited for platinum on alumina and practically absent for platinum supported on magnesium aluminate, even after many regeneration cycles.

The alumina support is optimal for platinum and is based on transition alumina (δ, ϵ, θ), characterized by a high level of thermal stability and low acidity. The pores should be large in diameter, to avoid rapid plugging by the coke, thus prolonging the life of the catalyst (Bricker et al., 1990).

The addition of alkaline metals or rare earths is necessary to mitigate the acidity of the alumina; cesium, lithium and potassium are considered optimal alkaline promoters, both individually and in combination. This mitigation of the acidity is fundamental to reaching high selectivity towards olefins, in that the acidic centres are responsible for cracking reactions, at the expense of both the reagents and the products, as well as the oligomerization-polymerization reactions of the olefins, which lead to the formation of coke.

Platinum catalysts are subject, through continuous and discontinuous operations, to reactivation treatments in situ, using substances such as oxygen, chlorine, steam, hydrogen or small quantities of sulphur.

The oxygen is supplied to the catalyst during the first stage of regeneration to burn the coke. The elimination of the coke can be conducted at a relatively low temperature (about 720 K) and with a low concentration of oxygen, to minimize overheating of the catalyst and sinterization of the platinum crystallites. It seems to proceed in two stages: first, the coke in contact with the platinum crystallites is burnt; then, by increasing the temperature to about 820 K, combustion of the coke, adsorbed on the support by spill-over from the platinum crystallites activated by the oxygen, takes place (Handy et al., 1990). The treatment with oxygen has other beneficial effects, such as the passivation of platinum, thanks to the formation of a mono-molecular layer of oxide, and the re-dispersion of the platinum itself through the formation of platinum dioxide (PtO₂), which is more mobile than metallic platinum. That happens if the temperature is maintained below 870 K; at higher temperatures, the dioxide becomes unstable and tends to break up, forming metallic platinum which sinterizes easily. The oxidation of metallic tin to Sn²⁺ and successively to Sn⁴⁺ takes place by spill-over of oxygen from the platinum. In the case of alloys Pt/Sn, tin is oxidized preferentially, while platinum remains in the metallic state. Not all the oxidized tin returns to the alloy after reduction, due to interactions with the support.

The treatment with chlorine is aimed at transforming the surface layer of tin and platinum oxides into chlorides and oxychlorides, which can sublime or move on the surface of the catalytic system thus aiding dispersion. However, this treatment also creates acid sites that must be eliminated or minimized to avoid isomerisation of the paraffins.

Successive treatment with hydrogen reduces the oxychlorides of platinum and tin to the metallic state. The reduction of tin is favoured by the spill-over of hydrogen from the platinum. The same phenomenon helps prevent the deactivation of the catalyst, reducing the coke precursors present on the surface of the support. The chlorine is then eliminated by means of a steam treatment, which also contributes to the elimination of coke precursors through the water/gas shift reaction. Moreover, sulfur compounds can be added continuously to inhibit the coking and hydrogenolysis reactions. This last treatment, though, can only be used with supports based on spinels, while, with aluminates, sulphates are formed during the regeneration which contribute to the deactivation of the catalyst and worsen its mechanical properties.

Pt/Sn catalysts are thus subject to two types of deactivation: slow irreversible sinterization, which requires the replacement of the catalyst after a relatively long period of time (years), and the reversible plugging with coke. The catalyst Pt/Sn maintains a good catalytic activity even in the presence of a small percentage of carbon deposits and therefore allows a relatively long period (hours or days) between regenerations.

Daniel E. Resasco (Resasco and Haller, 1994) proposes that the dissociative adsorption of paraffin, which involves two metal atoms, constitutes the slow stage of the reaction with these catalysts. The dissociative adsorption is practically irreversible, while the elimination of the second atom of hydrogen is very fast and almost in equilibrium. In the case of the dehydrogenation of isobutane, the global mechanism can be represented by the following reactions.

\[
i-C_4H_{10} + 2 \text{Pt} \rightarrow \text{Pt} - i-C_4H_8 + \text{PtH} \quad \text{(slow stage)}
\]

\[
\text{Pt} - i-C_4H_8 + \text{Pt} \leftrightarrow \text{PtH} + \text{Pt} - i-C_4H_8
\]

\[
\text{Pt} - i-C_4H_8 \rightarrow i-C_4H_8 + \text{Pt}
\]

\[
2\text{PtH} \rightarrow \text{H}_2 + 2\text{Pt}
\]

**Chromium catalysts**

In scientific and patent literature, two types of chromium catalysts are mentioned for the
The nature of the active sites in supported chromium catalysts has been amply discussed. Cr$_2$O$_3$ is the most stable of the chromium oxides and is formed by heating CrO$_3$ to 770 K, even in oxidizing atmospheres. The difference between the standard free energy of formation in CrO$_3$ and Cr$_2$O$_3$ (Fig. 4) shows that, even at room temperature, Cr$_2$O$_3$ is the more stable form. However, when chromium oxides are supported on alumina, even after calcination at 970 K, a certain percentage of chromium remains in the oxidized state 6+, due to strong interaction with the support (Cavani et al., 1996). Only after reduction with hydrogen or a hydrocarbon, all the Cr$^{6+}$ is transformed into Cr$^{3+}$. The reduction takes place in two stages: a very rapid first stage leads to complete transformation into Cr$^{3+}$ and then a slow stage of transition towards lower oxidation follows. The majority of researchers hold that Cr$^{3+}$ constitutes the active sites for dehydrogenation, but there is no lack of reference in scientific literature to a catalytic activity carried out in addition, or principally, by Cr$^{2+}$ (Grüner et al., 1986; Ashmawy, 1980). There is agreement, though, on the consideration that the formation of solid solutions of chromium and aluminium oxides is responsible for the irreversible deactivation of the catalysts.

In Fig. 5 the different types of Cr$^{3+}$ present on the reduced chromia-alumina system are illustrated (for simplicity the atoms of oxygen between the Cr$^{3+}$ ions are omitted; Puurunen and Wekhuysen, 2002) along with their evolution towards species of α-chromia-alumina ($\alpha$-4Al$_2$O$_3$-Cr$_2$O$_3$) with reduction both of the surface area and catalytic activity.

The entry of Cr$^{3+}$ into the structure of the alumina is helped by localized overheating, caused by combustion of the coke during regeneration of the catalyst. The speed of interaction between Cr and Al can be slowed by an opportune modification of the surfaces (Sanfilippo et al., 2001; Iezzi et al., 2002). Fig. 6 shows how, in the presence of various heteroatoms, such as silica and tin, a reduction in the speed of formation of $\alpha$-4Al$_2$O$_3$-Cr$_2$O$_3$ is observed, both in terms of a smaller concentration of chromia-alumina operating in reaction conditions, and in terms of a reduction in the loss of surface area due to ageing simulated with thermal treatment based on increasing temperatures. It is hypothesized that the heteroatom makes the surface of the alumina less reactive for the Cr$^{3+}$.

The alkali metals have been indicated as promoters of activity and selectivity. Their presence increases the number of active chromium sites and reduces the surface acidity. Not all alkaline metals have been identified as promoters of chromium catalysts, however. Only cesium, potassium and rubidium, due to a stabilizing effect deriving from the large dimensions of their respective cations, have had this characteristic confirmed. All research has, in any case, shown how the activity of dehydrogenation is directly proportional to the amount of chromium present on the surface, independent of any other chemical groups.

Chromium catalysts are reactivated by treatment with air, which has the following effects: partial oxidation of Cr$^{3+}$ to Cr$^{6+}$, which contributes to the dispersion of the crystallites of Cr$_2$O$_3$; and combustion of coke, very probably catalysed by Cr$^{6+}$, which increases the temperature of the catalyst and can be used to supply heat for the endothermic dehydrogenation reaction.

A.G. Zwahlen (Zwahlen and Agnew, 1992), who reports a kinetic study on the dehydrogenation of isobutane, carried out in a complete mixing reactor on a Cr$_2$O$_3$/Al$_2$O$_3$ catalyst, interprets the experimental data by means of a Langmuir-Hinshelwood type of kinetic
equation, assuming that the adsorption of isobutane represents the slow stage of the reaction and that competition with adsorption of hydrogen does not exist.

Reactor design and commercial applications

Propane, n-butane, isobutane and isopentane are presently dehydrogenated to the corresponding monolefin in various industrial facilities around the world. Catofin, Oleflex, STAR and FBD (Fluidized Bed Dehydrogenation) are technologies used industrially, while the PDH (Propane DeHydrogenation) has been used only on a demonstration unit.

An ideal reaction system for the industrial process of dehydrogenation of light paraffins must supply a large amount of reaction heat at a temperature above 770 K, while maintaining strict control of the temperature, to minimize the formation of by-products. In addition, it must permit a periodic regeneration of the catalyst to remove carbon compounds that accumulate on its surface. These conditions, together with the thermodynamic and kinetic limitations described above, have pushed researchers to develop optimal reactor design solutions for the industrial exploitation of dehydrogenation reactions. The available commercial technologies offer different choices as regards the reaction system, tending to simultaneously optimize the reaction conditions and the supply of energy to the reaction.

Catofin Technology

Catofin technology (Arora, 2004), commercialized by ABB Lummus, derives directly from the Catadiene process, originally developed by Eugène Houdry for the dehydrogenation of n-butane to butadiene. The technology uses fixed-bed adiabatic reactors in which there is an alternation between reaction and regeneration cycles. Many reactors are used in parallel in a plant, to permit continuous production. The reaction heat is stored up in the catalyst during regeneration and released during the reaction. The swift passage between an oxidizing environment and a reducing environment, along with a short reaction period, is compatible with the choice of chromium catalysts. The diagram of the Catofin process relative to the reaction zone is shown in Fig. 7 A.

The reaction takes place on catalysts based on chromium and alumina oxides, at sub-atmospheric pressure, and is conducted using a certain number of fixed-bed (at least three) adiabatic reactors, in which the reaction and the regeneration of the catalyst with air (as described above) are cyclically alternated. The catalyst, in the form of cylindrical pellets, consists of between 18-20% in weight of chromium oxide (Cr₂O₃) and 1-2% in weight of alkali metals, supported on alumina with a surface area of about 120 m²/g. During the ageing of the catalyst, which is completely replaced every 1-2 years, the average temperature of reaction is progressively increased in order to maintain a constant production output, causing a gradual loss of selectivity which cannot be overlooked. Typical operating conditions require a temperature ranging from 860 to 920 K, a pressure of between 33 and 50 kPa and a space velocity (based on liquid feed) of between 0.4 to 2 normal-litre/h/litre of the catalyst.

Other interesting characteristics of this technology are:
- Low consumption of reagent, due to the high selectivity ensured by the catalyst.
- Heat of reaction, supplied both by the combustion of...
the coke, and by the surface reduction of the catalyst with natural gas and possibly by co-feed of a fuel during the regeneration phase.

- High yield per pass, made possible by carrying out the reaction below atmospheric pressure.
- Catalyst endowed with high level of thermal stability, resistance to friction and tolerance to potential poisons such as water vapour and heavy metals.

**Oleflex technology**

Oleflex technology, developed and commercialized by UOP, utilizes mobile adiabatic-bed reactors in series. The catalyst flows slowly, pulled by gravity through the reaction system, while the reagents flow radially within the various reactors. The heat for the reaction is supplied directly to the reagents by intermediate heating in fired furnaces, placed between one reactor and another. The catalyst is collected on the bottom of the last reactor, transported pneumatically to the regenerator, and then sent back into the reaction zone. For further details regarding the Oleflex technology, see Section 10.2.1

**STAR technology**

STAR technology (STeam Active Reforming), originally developed by Phillips, is now commercialized by Krupp-Uhde. It uses an idea similar to that normally used in the steam reforming of hydrocarbons to produce synthesis gas. The catalyst is contained in tubes placed inside a fired furnace, in which a fuel is burnt to supply the heat of reaction. In this case, too, the need for periodic regeneration of the catalyst imposes the use of several parallel reactors. An innovative characteristic of this technology is represented by the insertion, downstream of the main reactor, of a secondary reactor (fixed-bed adiabatic) for oxydehydrogenation, a process in which oxygen is fed and reacts with part of the hydrogen formed, permitting further progress of the main reaction. This technology is suitable for the use of platinum catalysts, which allow long reaction times, on the order of hours, before regeneration. The scheme for the STAR process relative to the reaction zone is shown in Fig. 7 B.

STAR technology is used for the dehydrogenation of light paraffins and the dehydrocyclation of paraffins C₆-C₇ in tubular, fixed-bed reactors, placed inside a fired furnace, as described above. The process uses a catalytic system which is very stable in the presence of water vapour as a diluting agent. The active phase of the catalyst is made of platinum (0.01-5% in weight), promoted with tin (0.1-5% in weight), supported on zinc or magnesium aluminate and bound with calcium aluminate. The use of alkaline metals with the function of promoting the selectivity is optional. The steam added to the reagent mixture plays an important role, since it increases the driving force of the reaction, while...
allowing a relatively high total pressure to be maintained (around 5 bar); that, in turn, allows an optimization of investment and operating costs of the reaction section and compression of the effluent, while at the same time avoiding the possible infiltration of air from the outside. Steam also acts as a thermal moderator, thus preventing an excessive decrease in temperature that could block the progress of the reaction. In addition, steam inhibits the side reactions that lead to the deposition of coke on the catalyst. All this enables maintaining a cycle of about seven hours of reaction, followed by one hour of regeneration. In the successive adiabatic oxydehydrogenation reactor, the oxygen (about 90% pure) is fed in, which, reacting with part of the hydrogen formed in the dehydrogenation reaction, allows a further advancement of the dehydrogenation reaction itself, because of both the elimination of the hydrogen and the increase in temperature. In the oxydehydrogenation reactor, oxygen is supplied in a molar ratio of between 0.08 and 0.16 with respect to the hydrocarbon supply. Steam, on the other hand, is fed into the main reactor in a molar ratio between 3.5 and 4.2 with respect to the hydrocarbon supply. The starting temperature to the main reactor is about 880 K, with an exit temperature ranging between 920 and 940 K, while the exit temperature on the oxydehydrogenation reactor is about 950 K. The space velocity, based on the supply in liquid state, is typically equal to 4 normal-litre/h/litre of catalyst in the traditional version and increased to 6 normal-litre/h/litre of catalyst in the version with oxydehydrogenation, which allows a reduction in the dimensions of the costly main reactor, while adding a secondary reactor of simple construction.

**PDH technology**

A similar technology but without the oxidative dehydrogenation stage and using a chromium catalyst, was developed originally by Linde, Borealis and Statoil (Zimmermann and Versluis, 1995).

This technology has elements in common with the STAR technology, in that it uses fixed-bed reactors in which the heat of reaction is supplied by burning a fuel externally ([Fig. 7 C](#)). The process requires three parallel reactors, two of which are normally working in the reaction, while the third is the regeneration phase. The distinctive characteristic of PDH technology is the absence of reagent dilution, which permits a reduction of the reactor dimensions and simplifies the purification of the product. This is made possible thanks to strict control of the reaction temperature, which makes the reactors practically isothermal. The catalyst is based on chromium oxide supported on alumina. Recently, Pt catalysts on various oxides have also been indicated (Schindler *et al*., 2004).

**FBD technology**

FBD technology (Sanfilippo, 2000; Miracca and Piovesan, 1999), commercialized by Snamprogetti, uses a fluidized-bed reactor with a catalyst that circulates continuously from the bottom of the reactor to the top of the regenerator plant and vice versa. The heat needed for the reaction process is supplied by a fuel burned directly in the regenerator and transported to the reactor through the heat capacity of the regenerated catalyst. In the reactor, suitable baffles are fitted internally (for example, horizontal grids or tubes) with the end of limiting the phenomenon of back-mixing, typical of bubbling fluidized-bed systems. The FBD process scheme relative to the reaction zone is shown in [Fig. 8.](#)

FBD technology derives conceptually from FCC technology, widely used in refineries to increase the yield of gasoline from crude, converting heavy cuts of lesser value by means of controlled breaking of the bonds between carbon atoms.

Cracking reactions, even if not limited by equilibrium, have characteristics that are very similar to dehydrogenation reactions. In fact, they are also endothermic and lead to the formation of carbon by-products that inhibit catalytic activity. In fluidized-bed reactors a catalyst in microspheroidal form is used (average diameter of particles less than 0.1mm) with particularly suitable fluid-dynamic characteristics and resistance to attrition. The catalyst contains chromium

![Fig. 8. Fluidized-Bed Dehydrogenation (FBD) process scheme.](#)
oxide (Cr₂O₃) in quantities ranging between 12 and 20% by weight, potassium oxide (1-2% by weight) and silica (1-2% by weight) supported on alumina. Typical operating conditions include a reaction temperature between 820 and 870 K, an operating pressure slightly above atmospheric pressure (1.1-1.5 bar) and a space velocity (calculated on liquid feed) of between 0.4 and 2 normal-litre/h/litre of catalyst. In this technology, the flow rate of the circulating catalyst is dictated by the need to transport heat to the reaction rather than that of regenerating the catalyst itself. It is necessary, in fact, to have from 5 up to 15 kg/h per kg of feed of hot regenerated catalyst circulating, to satisfy the thermal requirements of the reaction. The use of fluidized-bed technology allows continuous operation under stable operating conditions. The catalyst can be replaced or filled-up while the plant is operating, eliminating the need to halt operations. In this case, too, the physical separation between the reaction zone and the regeneration zone, together with an operating pressure which is higher than the atmospheric pressure, ensures the safety of the operation. The thermal profile of the gas is characterized by reaching the highest temperature at the exit of the reactor; therefore, the conversion obtainable per pass is higher, due to the approach to a more favourable equilibrium.

In Fig. 9, the qualitative thermal profiles inside the catalytic bed are shown for the types of reactor mentioned above, based on the hypothesis of obtaining the same conversion for every reactor. The curve E represents the conversion of equilibrium relative to temperature. In the case of tubular reactors inserted into a fired furnace, the reaction can take place in almost isothermal conditions (curve A). In adiabatic reactors, in which the heat of reaction is supplied to the reagents in a gaseous state before they enter the reactor, the decrease in temperature of the gas caused by the reaction itself is so large, as not to permit the use of a single catalytic bed. The reaction is therefore conducted in a certain number of reactors in series with intermediate heating of the reacting gas in external fired furnaces (curve B). When, instead, the release of heat by the catalyst (that as a result cools) meets the needs of the endothermic reaction, the angular coefficient of the straight line that represents the thermal profile (curve C) can be modified, varying the quantity of catalyst in the reactor and making it possible to carry out the reaction in a single reactor. In this case, it becomes necessary to heat the solid periodically when it has exhausted the stored heat; the reactor works thus in a cyclical mode, and more reactors in parallel are needed to maintain continuous production. In a fluidized-bed reactor (by definition well-mixed and isothermal), the thermal profile can be modified towards a course roughly represented by curve D, if suitable internal baffles are inserted to limit the internal mixing. From a kinetic point of view, a higher average temperature makes possible a reduction in the quantity of catalyst required and diminishes the reaction volume, while a lower average temperature makes it possible to obtain greater selectivity with regard to the desired product, reducing the influence of secondary reactions. To determine the optimal type of reactor, additional considerations are necessary, relating to the efficiency with which the heat of reaction is supplied in the various cases, to the associated cost of investment and to the possibility of distributing the heat in a homogeneous manner, thus avoiding the formation of hot spots that lead inevitably to a reduction in selectivity.

### 11.2.2 Dehydrogenation of heavy paraffins

The catalytic dehydrogenation of heavy paraffins \((C_{10}^\text{C}_{14})\) leads to a family of linear monolefins with the same number of carbon atoms and the double bond in random position along the chain. This family of olefins is used to synthesize alkyl benzenes, used as
intermediates in the production of biodegradable detergents, through reaction with benzene in conditions of acid catalysis. Around 1960, the growing demand for linear monolefins, suitable for the production of detergents, created excellent prospects for the development of dehydrogenation technologies. Since 1969, UOP has commercialized the combined process Pacol-Olex for the dehydrogenation of linear paraffins and the selective extraction of the olefins produced; a process, which even today remains the most successful technology in the field.

From a thermodynamic point of view, the dehydrogenation of heavy paraffins must overcome the constraint resulting from the fact that the energy required to break a bond between two carbon atoms (245 kJ/mol) is less than the energy necessary to break the bond between an atom of carbon and an atom of hydrogen (365 kJ/mol; Griesbaum et al., 1989). Therefore, thermal reaction is not advisable, since it would lead to a predominance of cracking reactions over dehydrogenation reactions. On the other hand, a catalytic process allows the reaction to proceed at a relatively low temperature, minimizing the formation of by-products and obtaining conversion and selectivity such as to make exploitation of the reaction financially attractive.

In Pacol technology, the reaction takes place in a fixed-bed reactor, which works in a wide-range of operating conditions, depending on the type of feed and the conversion per pass desired. The temperature can be between 570 and 820 K and the pressure between 100 and 300 MPa. The conversion per pass is 10-15% in weight, with selectivity towards useful olefins 90-94% in weight. The catalyst is based on platinum supported on alumina, with the addition of promoters (tin, indium, lithium). The low conversion per pass implies that the separation and the purification of the products and the recycling of the non-converted reagents are a fundamental factor in the economics of the process. To this end, UOP developed a process of extraction based on molecular sieves with high capacity to absorb olefins (Broughton and Berg, 1970). Even if the catalyst is very selective, the formation of by-products reduces its activity over time and its useful life is limited to about one year.

### 11.2.3 Dehydrogenation of ethyl benzene

Ethyl benzene is dehydrogenated to styrene and hydrogen on iron-based catalysts in the presence of steam (James and Castor, 1994):

\[ \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CH}_2 + \text{H}_2 \]

Cracking gives rise to unwanted by-products, such as benzene and ethylene (that are in effect the reagents from which we obtain ethyl benzene industrially), toluene and methane; by-products originating from consecutive reactions are phenyl-acetylene and \( \alpha \)-methyl-styrene. Since the industrial technologies do not provide for catalyst regeneration cycles, it is absolutely fundamental to eliminate the formation of coke. Carrying out the dilution with steam and operating under vacuum are essential features; in particular, the dilution with steam reduces the potential for the formation of coke, acts as a diluting agent, maintains the correct state of oxidation of the catalyst and supplies sufficient heat capacity to lessen the adiabatic reduction of temperature associated with the conversion of ethyl benzene.

The temperature of reaction is between 550 and 630°C. At lower temperatures the kinetics are too slow and both ethyl benzene and styrene rapidly undergo cracking above 610-620°C. A rapid quenching is therefore necessary to cool the effluent products from the catalytic bed and minimize the thermal formation of by-products. The conversion per pass is generally 60-70%, with selectivity to styrene over 93-95%.

The catalyst is essentially based on iron oxide, with potassium as a promoter. Other metals are used as supplementary promoters, such as chromium oxides, cerium, tin, calcium, molybdenum, magnesium, titanium and others (Muhler et al., 92). The most recent formulations do not use chromium and are able to operate at low ratios of steam/carbon, limiting the formation of phenyl-acetylene to 20-40 ppm. The principal technologies are commercialized by Lummus/UOP and Atofina/Badger.

Typically, fixed-bed and radial flow adiabatic reactors are used to reduce the load losses subdividing the reaction between multiple reactors in series with intermediate heating. Recently, the use of more innovative reactor concepts has been proposed (Sanfilippo et al., 2004), in particular those involving fluidized-bed reactors and catalysts which are not iron based, but use gallium with promoters (Pelati and Gulotty, 2004).

### 11.2.4 Future developments

A high number of R&D initiatives are attempting to develop new production processes for olefins, but only a few have real prospect of eventual success on an industrial level, due to both intrinsic difficulties with the technology itself and the question of their economic viability.

In the last decade, research in the field of dehydrogenation of paraffins has concentrated on oxydehydrogenation, that is to say, the coupling of the
dehydrogenation reaction with a controlled combustion of the hydrogen co-produced through the co-feed of oxygen to the dehydrogenation reactor.

This would make it possible to get around the constraints imposed by thermodynamics and conduct the reaction at low temperature, in conditions which completely inhibit the side reactions of thermal cracking and even eliminate the need for periodic regeneration of the dehydrogenation catalysts.

Although there are encouraging results, the realization of industrial oxydehydrogenation applied to the principal reaction still seems far off. In reality, this application requires the development of a catalyst with very particular characteristics, one that must be extremely selective in the oxidation of hydrogen, avoid combustion of the hydrocarbons, maintain its activity in the presence of steam and be sufficiently active to consume the supplied oxygen completely.

It has been proposed that different catalysts be used for the oxidation process and for that of dehydrogenation, to be installed in different parts of the reactor. The possibility of burning the hydrogen between the two stages of dehydrogenation, to move the thermodynamic equilibrium to the right, has also been suggested in scientific literature (Grasselli et al., 1996). Indeed, it has been proposed in various technologies, for example the STAR technology, limited only to the completion reactor, operating with a very reduced quantity of oxygen with respect to the hydrocarbons present. In the dehydrogenation of ethyl benzene, this technique is also applied: in the Lummers/UOP/SMART technology an intermediate palladium catalyst bed burns the hydrogen that is formed in the preceding dehydrogenation bed with added oxygen, supplying heat for the endothermic dehydrogenation reaction. In this way, by reducing the hydrogen content, the thermodynamic constraint is removed, and a better conversion rate reached.

It would appear more difficult to develop a sole material able to catalyse both reactions simultaneously. Attempts carried out so far have focused on the addition of more promoters to platinum catalysts, to make it possible to direct the combustion preferentially towards hydrogen. Recent studies have concentrated on molybdates of cobalt, manganese or nickel. The possibility is also being evaluated of using both molecular oxygen and structural oxygen, of a catalyst able to accumulate or release oxygen with a redox mechanism (Iglesia et al., 2002). Although there are encouraging results, there is no prospect of an industrial application in the short term.

A certain interest has been sparked in the production of ethylene from ethane by means of oxidising dehydrogenation, using extremely low contact time (milliseconds) reactors on platinum catalysts (Schmidt Bodke et al., 1999; Beretta et al., 2001; Font Frede et al., 1990; Bharadwaj et al., 2000; Donsi et al., 2005).

An alternative method involving the separation of hydrogen as soon as it is formed consists in the utilization of hydrogen permeable membranes placed directly inside the dehydrogenation reactor. In this case, the challenge consists in developing membranes which are able to reliably endure a high temperature environment and potential abrasion from the catalyst. The use of reactors with permselective membranes for H2 that can carry, with supports, the active phase for dehydrogenation, or, be limited to the separation of hydrogen, is being studied. Catalytic combustion of hydrogen is also being studied (Iglesia et al., 2003).

The extension to ethane of traditional catalytic dehydrogenation, does not appear to be suitable as such: in fact, to reach economically attractive levels of conversion, it would be necessary to operate at very high temperatures (greater than 700°C) and in this case thermal reactions are already prevalent, as they take place in classic steam cracking. Nevertheless, catalytic dehydrogenation at lower temperatures (and obviously with lower conversion rates) appears attractive, if it is coupled with a direct use of “diluted” ethylene contained in the effluent flow from the reactor, as, for example, in alkylation benzene, and producing ethyl benzene that is then dehydrogenated to styrene (Pogue et al., 1993; Buonomo et al., 1998) or that of propylene diluted by dehydrogenation of propane, to alkylate benzene and obtain cumene (Paggini et al., 2002).

Obviously, future developments will depend on the possibility of obtaining high selectivity (more efficient use of raw materials), on the energy efficiency of the new process, on its technological reliability and economics with respect to existing technologies.

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Domenico Sanfilippo
Ivano Miracca

Snamprogetti
San Donato Milanese, Milano, Italy

Ferruccio Trifirò
Dipartimento di Chimica Industriale e dei Materiali
Università degli Studi di Bologna
Bologna, Italy