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Dehydrogenations in fluidized bed: Catalysis and reactor engineering

Domenico Sanfilippo*

Via D'Acquisto, 4, 20067 Paullo, Italy

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ABSTRACT

Dehydrogenation is a widely exploited route for large scale production of pure olefins. Its industrial application is however complicated by clashing kinetic and thermodynamic constraints. A commercial bubbling fluidized bed technology for isobutylene production from isobutane has been developed to solve these constraints. An economically attractive implementation was achieved by defining an optimal synergy between chromia alumina catalyst design and reactor engineering. The fluidized bed know-how developed has also led to the development of a revolutionary technology for the production of styrene from ethylbenzene using a riser reactor and a gallium based catalyst.

1. Introduction: remembering David Trimm

David Trimm was always deeply interested in the scientific, technical, and managerial approaches to bringing a technology from the laboratory level up to the commercial implementation. His main attention was addressed to the integration of the diverse backgrounds needed to develop a complex and troublesome route. This contribution, discussing one such situation, is dedicated to his memory.

Here is reported a case history about which he and I talked on several occasions, a pathway that goes from MTBE to styrene, with a continuing chain of new fluidized-bed dehydrogenation technologies.

The origin of this story goes back to the 1970s when the enforcement of the Clean Air Act in the US and of similar legislations worldwide was eliminating lead from gasoline; this was necessary because of its direct toxic effects as well as its poisoning effect for platinum-based catalytic mufflers, mandated for reducing tailpipe emissions. Alkyl–lead compounds were until then used as octane boosters, allowing inexpensive fulfillment of the required specifications of gasoline produced even with relatively unsophisticated refinery assets. The need to achieve the desired lead-free octane numbers required re-configurations of refineries and/or alternative solutions. Snamprogetti selected MTBE (methyl-tert-butyl-ether), from among over 60 products evaluated for engine performance, as a gasoline component since it was an *octane improver*; its use allowed the exploitation of the "useless" *steam cracker C_4s olefins* and also a forerunner GTL with the use of methanol from *Natural Gas* in gasoline.

Snamprogetti developed the technology for MTBE synthesis from methanol and isobutylene

$$CH_3\text{–}OH + (CH_3)_2C{=}CH_2 \leftrightarrow CH_3\text{–}O\text{–}C(CH_3)_3$$

in less than 3 years and the first commercial unit (100,000 MTPY at Ravenna, Italy) was started up in July 1973 [1]. Increasing concerns on the impact of fuels on air quality gave rise worldwide to new more severe regulations and new fuel formulations. With the 1970s oil crisis, MTBE began to be used worldwide because of its gasoline extender properties and the consequent lower dependence on crude. Oxygenates, as combustion improvers, decrease tail gas VOC emissions (CO and hydrocarbons) and, as octane boosters, balanced the octane loss due to the lead phase-out and also to benzene/aromatics reduction. The Clean Air Act Amendments (Nov. 1990) mandated a Reformulated Gasoline containing 2% oxygen. The use of oxygenates in the gasoline pool has since then played an important role, either directly or indirectly, to give an impressive improvement of air quality. Fuel and engine improvements allow today's passenger cars to emit only 3% of the quantity of

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* Tel.: +39 3481504652.
E-mail address: sanfilippo.domenico@gmail.com

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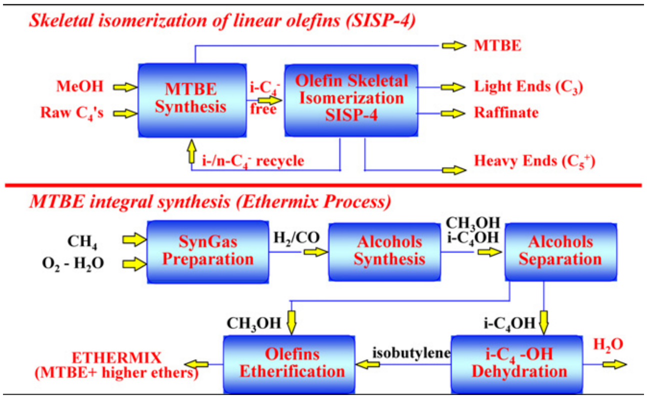

Fig. 1. Alternative routes to isobutylene and MTBE.

pollutants that they emitted in the 1970s. The economics, engine performances and fungibility with the gasoline distribution system made MTBE the most widely used oxygenate in the world for several decades.

As the acceptance of MTBE increased, new competing MTBE technologies were developed and several new plants were built utilizing all the available sources of isobutylene: C_4s from steam crackers or fluid catalytic crackers (FCC) or produced by dehydration of tert-butanol (TBA), a by-product of the propylene oxide synthesis. Soon, we realized that worldwide isobutylene supplies "dry up" in the long term and that new sources would be necessary for de-bottlenecking MTBE from the isobutylene shortage and to sustain the penetration of our MTBE technology. We began to develop new processes for producing isobutylene (Fig. 1) via the "Skeletal isomerization of linear butenes" [2] and for the "Integral synthesis from Natural Gas via syngas" [3].

2. Dehydrogenation of isobutane in fluidized bed

The development of the commercial processes for *Catalytic Dehydrogenation of Isobutane* from field butanes allowed, on the one hand, to overcome the limits of isobutylene availability and, on the other hand, to transform MTBE into a commodity that could be fully obtained from Natural Gas (a GTL route), even outside refineries, in gas-rich countries, allowing it to be traded all over the world. Over 170 plants were built from any C_4 source and the MTBE world capacity reached 20 million ton/y.

Following some contacts in 1980 with the Russian company NIIMSK (now Yarsintez, Yaroslavl), we in Snamprogetti became acquainted with a technology for dehydrogenation of paraffins in a fluidized bed that was then implemented in 34 industrial plants in the Soviet Union and neighboring countries. The technology was strategically utilized in the then USSR for the production of synthetic rubbers: the conversion of *n*-butane to *n*-butenes (further dehydrogenated in a second step to butadiene); isopentane to isoamylene (further dehydrogenated to isoprene); and isobutane to isobutylene. Plant capacity ranged between 20,000 and 80,000 MTPY (metric ton per year). Internal assessment of the technology showed us that there was a huge potential for the conceptual design but that it was unsuitable as implemented for the western market. Innovatively for that time (Cold War and the Iron Curtain), an agreement was signed with Licensintorg (the Soviet organization for technology transfer) for modernizing the process. I had the pleasure of leading, in the early stages, the Snamprogetti team which, in partnership with the Russian scientists, developed the FBD-4 (Fluid Bed Dehydrogenation) technology, an updated fluidized bed version of isobutane catalytic dehydrogenation.

2.1. Main concepts involved in dehydrogenation in fluidized beds

2.1.1. Chemistry of dehydrogenation

Dehydrogenation removes a molecule of hydrogen from an alkane, forming an olefinic double bond that will be the preferred point of attack for further functionalization:

$$R_1{-}CH{-}CHR_2 \leftrightarrow R_1C{=}CR_2 + H_{2,} \qquad \Delta H > 0 \quad (25\text{–}30\,\text{kcal/mol})$$

The dehydrogenation of a paraffinic bond is one of the most complex chemical processes to achieve industrially since the thermodynamic equilibrium limits the maximum conversion per pass and, as the reaction is highly endothermic, a large amount of heat must be supplied to the reactant system. Equilibrium conversion increases at lower pressures or in the presence of a diluent [4,5].

In order to make the industrial process more economically attractive, it is advisable to increase the conversion per pass as much as possible so that recycling any unconverted reagent and purification of the product are cheaper. Temperatures >530 °C are needed to reach an isobutane conversion of 50%. However, these high temperatures also enhance the occurrence of undesired parasite reactions, these being responsible for reducing the selectivity to isobutylene and for making all downstream purification operations more expensive. The products and byproducts of dehydrogenation undergo cracking as well as consecutive reactions such as further dehydrogenation, oligomerization, aromatization. Furthermore, coke is *inevitably* formed and this gradually makes the catalyst less active; hence, periodic regeneration of the catalyst is essential, normally achieved by burning the coke in a stream of air. As a result, each catalyst undergoes a cycle of exposure to alternating atmospheres: reducing during reaction and oxidizing during regeneration.

Many materials have been explored as catalysts for the dehydrogenation of paraffins [6] but, in practice, only promoted chromia/alumina and platinum/alumina have been developed industrially. Since the catalyst works under very severe conditions, it is designed to limit irreversible deactivation due to sintering, volatilization of catalyst components and morphological or phase transformations, usually allowing several years of expected active life. Reaction engineering has to find a way to supply during the reaction significant amounts of heat to the process stream at temperature above 550 °C in such a way that the reactor ΔT operation is reduced within a range of acceptable catalyst activity (<50 °C). The integration of such concepts with the choice of catalyst is the basis for the industrial dehydrogenation technologies that were developed.

2.1.2. Fluidized beds

A fluidized bed is based on the concept that solid particles are kept in suspension by a gas flow passing upwards through them. When the gas velocity is low, the bed behaves like a fixed bed. As the gas velocity is increased, aerodynamic drag forces begin to counteract gravitational forces; the bed then expands in volume as the particles move away from each other. Increasing the gas velocity, fluidization begins (minimum fluidization velocity U_{mf}), the bed behaves like a liquid and bubbles are formed (U_{mb}). When gas velocity is higher than the terminal velocity U_t (i.e. the gas velocity exceeds that of free-fall), the solid particles are blown away and the whole bed of particles is transported upwards by the gas stream. Apart from the gas characteristics, U_{mf} and U_t are both mainly a function of the density and diameter of the solid particles but also depend on the particles shape and size distribution [7–10].

Some features of fluidization can be positively exploited in chemical processes:

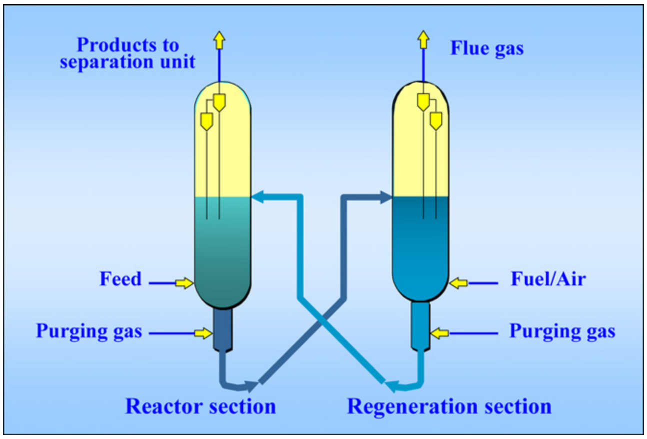

Fig. 2. FBD reactor–regenerator cycle.

- Gas pressure drop through the bed is equal to the weight per unit area of the bed itself and independent of gas velocity.
- A fluidized bed behaves like a liquid
- The upper surfaces of fluidized beds in communicating vessels are positioned at the same height.
- Fluidized solids can be transferred in pipes like liquids.
- The high level of mixing of the solid particles enhances both heat and mass transfer phenomena.

2.1.3. FBD-4 technology

The core concept of FBD-4 technology is the design of the circulating reactor/regenerator system (Fig. 2). Russian scientists derived this technology in the 1960s from the Fluid Catalytic Cracking S.O.D. Model IV technology which had been introduced in the early 1950s by Esso Standard Oil Co. [7].

The dehydrogenation reaction is carried out in a catalytic bubbling fluidized bed operating above 500 °C and slightly above atmospheric pressure. The catalyst circulates (like a liquid) between the reactor and the regenerator. Reaction heat is supplied to the reactor by the heat capacity of the “hot” solid catalyst (hotter than reaction temperature) continuously arriving at the top of the reactor from the bottom of the regenerator. The catalyst is then conveyed back “cold” from the bottom of the reactor to the top of the regenerator through a transfer line system. A countercurrent flow of gas and solid in both the reactor and regenerator is thus obtained.

Pneumatic transfer of the catalyst between the two vessels is obtained by reducing the density of the rising side of the transfer lines by a suitable lift-gas injection. In large scale commercial plants, the rate of catalyst circulation may reach thousands of tons per hour.

In the regenerator, the catalyst is restored to its initial performance by burning the small quantity of coke formed on it during the reaction; the catalytically active sites are also restructured. The main task of the regenerator is to generate all the heat required by the system: reaction heat, enthalpy of reactants and heat losses.

An important difference relative to an FCC reactor is that the small quantity of coke formed by the highly selective catalyst is not enough to supply on combustion the energy needed to heat the catalyst and to satisfy the overall thermal balance [11]. Hence, some additional fuel is burned directly on the catalyst in the regenerator; the regenerator therefore also works as a catalytic combustor.

In a simplified form, the heat balance and catalyst circulation rate are given by:

$$\Delta H_{Glob} = \Delta H_{enth} + \Delta H_{reac} + \Delta H_{loss} = \Delta H_{fuel} + \Delta H_{Coke} \quad [\text{kcal/h}]$$

where ΔH_{Glob} is the global heat flux balance in kcal/h and the other terms indicate the enthalpy change of the products minus reactants, the reaction heat and the heats of fuel and coke combustion. The value of ΔH_{Glob} is given by:

$$m_{cat} \times c_p \times \Delta T_{cat} = \Delta H_{Glob} \quad [\text{kcal/h}]$$

where m_{cat} is the catalyst circulation rate (kg/h), c_p is the catalyst heat capacity (for many catalyst, this is in the range 0.24–0.28 kcal/kg/K), ΔT_{cat} is the temperature difference of the catalyst entering and leaving the reactor. The heat requirements and the chosen regenerator temperature (and not the deactivation) dictate the catalyst circulation rate.

Before being conveyed to the other vessel, absorbed products (oxygenates in the regenerator and hydrocarbons in the reactor) are stripped from the catalyst.

A typical fluidized bed exhibits a top-to-bottom mixing which makes the bed almost instantaneously homogeneous, approaching an ideal CSTR (Continuous Stirred Tank Reactor). To achieve optimal yields and reactor volumes, it is desirable to minimize axial back-mixing of both the phases (the gas rich “dilute” phase and the solid rich “dense” or “emulsion” phase), establishing in this way an axial gradient of concentration and temperature. A sharp distribution of the residence times of the catalyst particles in the reactor/regenerator sections is also essential to preserve catalyst life and performances. (In principle, particles with residence times in the vessels that are either too long or too short could be less active or not be regenerated.) A practical solution, as in the FBD process, is to stage the bed by inserting baffles [12,13] in order to reduce gas back-mixing and hence the reactor works as a series of well-mixed CSTRs. Staging makes a fluidized bed similar to a tray distillation column. A decrease of the open area of these “trays” makes the flow behavior closer to that of true plug-flow in the gas phase. For instance, an open area of 50% halves the degree of gas back-mixing, while an open area of 20% decreases gas back-mixing by a factor of 20. On the other hand, restrictions of the flows of free solid and gas determines the approach to flooding. The final choice of baffle number and fractional open area must therefore be a compromise and requires a particular know-how to be developed. Such internal structures are usually (e.g. FCC or fluid–coke strippers) chevron, inclined slabs; other shapes such as perforated trays are also used. For reactors where the heat has to supplied or removed horizontally, oriented tube bundles can be more convenient. Proprietary design is utilized in any application. Radial mixing is preserved, homogenizing at each level both concentrations and temperatures and allowing operation in nearly a countercurrent plug flow.

The mechanical design of internals is fundamental for achieving full mechanical reliability and good performance. A bubble of 20 cm displaces over 4 kg of catalyst and rising at 1 m/s exerts enormous forces on the structure. Gas distributors must ensure an even gas flow in all cross sectional areas and a correct initial bubble size at all design capacities. The circulating solid entering each vessel also has to be well distributed and quickly homogenized. Optimal design of the cyclones minimizes the losses of catalyst from the streams leaving the vessels. Transfer lines must permit flexibility in the catalyst circulation rate. In general, all the details of the fluidized bed are hydrodynamically optimized taking into account all the potential chemical reactions and equipment erosion.

2.2. Development pathway

The description of the resulting technology has been given above before discussing the R&D work because the same approach has been applied during the FBD process development. At first, let us imagine the appearance of the full scale plant, then downsize these ideas to the smallest scale at which it would be possible to model experimentally and then optimize the process steps (chemistry and hydrodynamics, *initially* not necessarily at the same time and in the same equipment!); then, scale up, and again optimize the integrated chosen solutions. FBD development took advantage of the pre-existing Russian experience and so a closer preview of the target was available.

The main points of attention in the original Soviet technology that required particular optimization efforts were:

- ○ The catalyst: reduce the unacceptably high rate of catalyst consumption due to aging and attrition and increase the performance (selectivity/activity);
- ○ Environmental impact: appropriate principles for the design of internals and emission control;
- ○ Optimal plant capacity: significant scale up factors of reactor/regenerator diameter and related equipment in order to achieve a sound economy of scale in large commercial units.
- ○ The materials of construction, and lining.

Laboratory catalyst performances tests were mainly carried out by downsizing the industrial reactor to a 1″ I.D. reactor which was operated close to U_{mf}. All the thermal and chemical conditions of the complete cycle could be simulated. This phase enabled the achievement of catalyst optimization and the kinetic modeling of the extremely complex network of chemical reactions. Lighter and heavier by-products play a fundamental role in the scale-up to an industrial plant. Hydrodynamic optimization of the technology was performed on large scale "cold" (ambient temperature) equipment ("mock-ups") carried out at room temperature and atmospheric pressure at the facilities of Prof. Zenz in New Jersey. Despite the significant efforts of academic researchers, none of the many hydrodynamic models that have been proposed for fluid beds can be reliably applied "a priori" without experimental verification on a large scale. The scale-up procedure must therefore include experimentation at a scale that can be considered hydrodynamically homologous to the industrial scale. A simplified mathematical model, including reaction chemistry and fluid-dynamics, was developed and this allowing the operation of a pre-existing Russian Process Demonstration Unit (in Yaroslavl, Russia), and subsequently the construction of another PDU in Houston (Texas) designed on purpose and having 1 m I.D. [13,14]. In order to scale up the PDU results to a commercial size, the two-phase model of Davidson [8] was chosen as a basis, since it remains quite simple. A 380,000 MTPY FBD-4 Isobutane Dehydrogenation Plant (reactor I.D. about 10 m) was then designed; this was commissioned in 1997 in Al Jubail (Saudi Arabia) and it is still in operation.

2.2.1. Isobutane dehydrogenation catalyst

A bubbling fluidized bed uses an "aeratable" catalyst having preferably microspheroidal shape and particle size distribution/density such that it can be classified as Class A (Fig. 3) according to Geldart [15].

In a commercial fluidized bed, the concepts of catalyst life, mean performance and the substitution of catalyst inventory require particular consideration. The catalyst suffers both physical and chemical decay. Due to collision between the particles of the catalyst and the surfaces of internals, even with a smooth engineering design, they undergo to attrition and fragmentation, this resulting in a reduction of the mean diameter and the formation of fines. Attrition is particularly relevant in the regions of the system where high superficial velocities are encountered, e.g. at the gas distributor nozzles, at the position of lift gas injection, in transfer lines and in the cyclones. Fines are necessary up to a certain extent in order to "lubricate" the bed but they cannot be accumulated beyond an optimum level (the mean diameter moves dangerously towards Class C in Fig. 3). In addition, very fine particles are steadily entrained by the ascending gas and in any case carried over from the vessels. Fresh catalyst is added in order to keep the inventory in the reactor/regenerator system constant. In this way there is a continuous dilution of the already chemically aged catalyst with a fresh one. After an initial transition, the catalyst mean age and particle distribution reaches an equilibrium. For the dilution law, with a continuous substitution of the inventory in a period *T*, the fraction X_j having age *t* is expressed by $X_j = e^{-t/T}$.

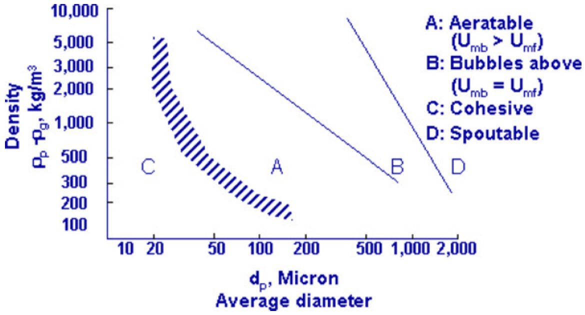

Fig. 3. Geldart's powder classification.

In commercial operation, the addition of fresh catalyst is performed semi-continuously.

Table 1 reports the age% distribution of catalyst bed in which some catalyst is consumed by attrition (fines are blown away from the system) and 10% of fresh catalyst is added at intervals (i) in order to refill the inventory. After the second interval *i*, there is 10% of fresh catalyst and 90% with the age of 2 intervals. After a third tenth, there is still 10% fresh, 9% with 2 tenths, 81% with three tenths, and so on. Continuing with catalyst substitution, there is evidence that a permanent pseudo-equilibrium is soon reached; a relevant fraction of the inventory remains "young" and active. As an example, if the addition of a quantity of fresh catalyst equal to the total inventory happens in two years (equivalent as consumption to a complete catalyst change each two years for a traditional fixed bed reactor) there will be always present in the equilibrium bed some 30–40% of relatively fresh catalyst, aged less than 6 months. Even after several years of operation there will be memory of the catalyst loaded at the plant start-up!

Chemical aging is the second factor determining catalyst consumption. If the equilibrium catalyst is not active enough to achieve the target performance, it is necessary to withdraw catalyst (which then becomes spent catalyst) from the bed and to add more fresh catalyst in an amount greater than that consumed by attrition and removed as fines. The optimization of its mechanical properties together with a control of the activity decay kinetics is crucial for minimizing the catalyst make-up.

In order to overcome one of the major issues of the old Russian technology, the first R&D step was to design the "ideal" catalyst, this having much better attrition resistance, chemical stability and performance.

The original catalyst was an alkali-promoted chromia/alumina/silica material, produced via spray-drying of all the components, and this suffered from poor mechanical properties and rapid aging. In order to preserve the significant Russian know-how on the relationships between the chromia-based catalyst and reaction engineering, it was decided to remain with a chromia based catalyst but with substantial redesign of the formulation and preparation techniques.

The best approach was preparing a strong preformed alumina carrier, followed by the addition of the active components. A gel of pseudoboehmite, a transition mono-hydrate alumina,

Table 1
Percentages of aged catalyst in case of substituting 1/10 of inventory with fresh cat at preset intervals. i = tenths of the period T of inventory's feed.

Age	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$	$i=7$	$i=8$	$i=9$	$i=10$	$i=11$	....
$j=1/10T$	100	10	10	10	10	10	10	10	10	10	10	
$j=2/10T$		90	9	9	9	9	9	9	9	9	9	
$j=3/10T$			81	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1	
$j=4/10T$				72.9	7.3	7.3	7.3	7.3	7.3	7.3	7.3	
$j=5/10T$					65.6	6.6	6.6	6.6	6.6	6.6	6.6	
$j=6/10T$						59	5.9	5.9	5.9	5.9	5.9	
$j=7/10T$							53.1	5.3	5.3	5.3	5.3	
$j=8/10T$								47.8	4.8	4.8	4.8	
$j=9/10T$									43	4.3	4.3	
$j=10/10T$										38.7	3.9	
$j=11/10T$											34.8	
....												

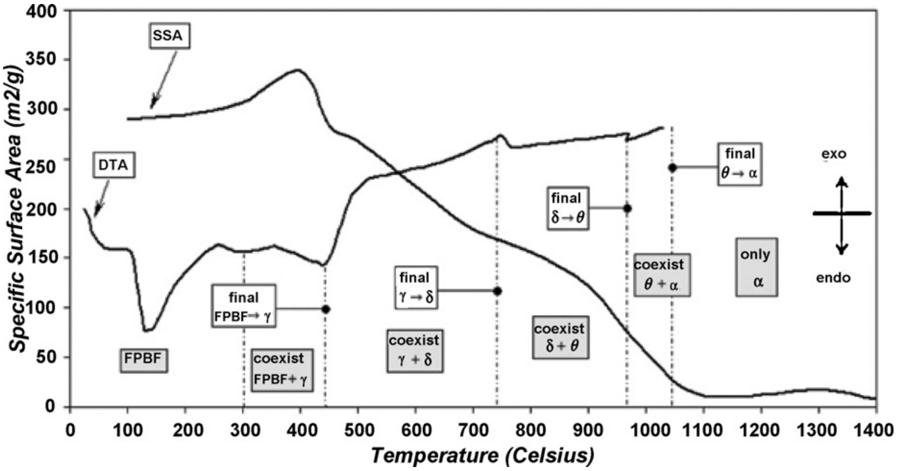

Fig. 4. DTA curve and phase evolution of pseudoboehmite at increasing temperatures.

AlO(OH), was chosen as starting material for spray-drying the microspheroidal carrier, optimizing its shape (rounded full microspheres, not egg-shell) and particle size distribution. Through calcination at increasing temperatures, pseudoboehmite dehydrates and transforms into various transition aluminas, γ-, δ-, θ-, and eventually α-alumina; these transformations correspond to changes in the internal porous texture and decreases in the surface area, from some hundred m^2/g in γ-Al_2O_3 to less than 20 m^2/g in α-Al_2O_3, as shown in Fig. 4 [16].

A long investigation indicated that a δ–θ mixture, minimizing the α-alumina content, had enough mechanical resistance and had the capability of hosting the right amount of chromia and promoters.

According to Fig. 4, the surface area is of the order of 100 m^2/g. In order to strengthen the support, some silica was also added, the concentration of which was optimized in relation to catalyst performances and life. Silica addition gave a slight increase in the alumina transition temperatures.

The dehydrogenation capability of chromia–alumina systems has been well known for a long time. The catalyst design took into consideration other noticeable roles played by the alumina and the promoters. Penetration of the active components within the carrier particles must be homogeneous in order to avoid modification of the composition of the equilibrium catalyst as a result of abrasion.

The nature of active site has been debated and Cr^{3+}, both Cr^{3+} and Cr^{2+}, and coordinatively unsaturated Cr^{2+} have all been suggested as playing a role in the catalytic activity [17–19]. XPS, UV–Vis–NIR diffuse reflectance spectroscopy and XRD studies have shown that several chromium species are present on the catalyst. Their relative concentrations of the various species change with the total chromium loading (see Fig. 5 and the model of Fig. 6):

- At high T °C, Cr_2O_3 is the thermodynamically stable Cr state even in the presence of excess O_2;
- Different chromium species form on the fresh catalyst: alumina-grafted Cr^{6+}, soluble Cr^{6+}, dispersed Cr^{3+} and crystalline Cr_2O_3;
- When the Cr content is increased beyond 4%, it accumulates at the catalyst surface as Cr^{3+};
- Beyond a content of 10%, crystalline α-Cr_2O_3 is observed;

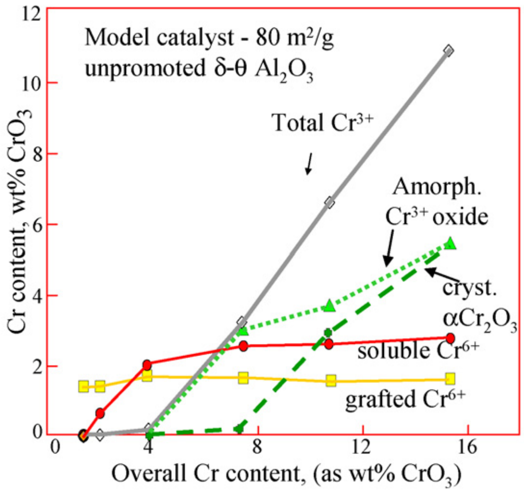

Fig. 5. Different chromium species at increasing loading.

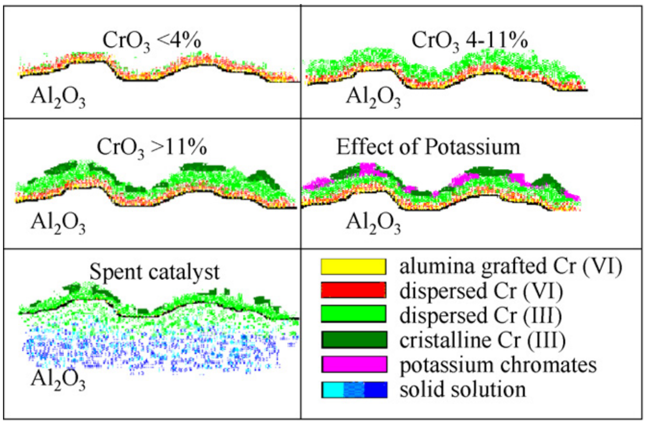

Fig. 6. Model of chromium species with increasing loading.

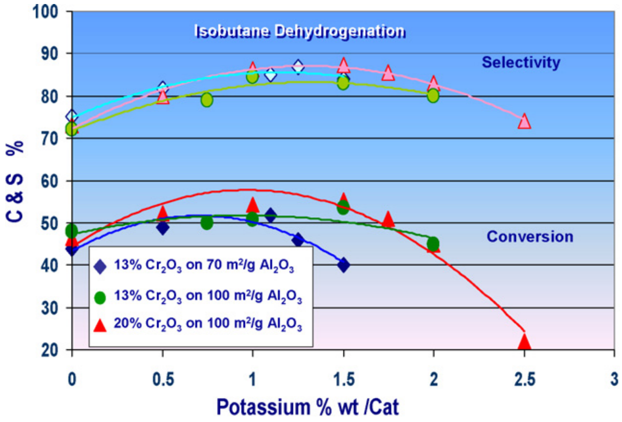

Fig. 7. Effect of potassium concentration on model catalyst performances.

- Alkali stabilize Cr^{6+} as chromates;
- All Cr^{6+} species disappear completely in any reducing atmosphere (H_2, HC).

The catalyst formulation includes promotion with alkali metals, which is fundamental for increasing the chromium active sites and tuning the catalyst surface acidity (of both Cr and Al oxides), inhibiting carbocation induced reactions, cracking, skeletal isomerization, aromatization, and oligomerization. Potassium has shown the best effect, if provided in the right amount. Typically a volcano shape curve of activity and selectivity is obtained by increasing the potassium content. The activating effect of potassium reaches a maximum related to the carrier surface area. With increasing Cr content, the curves are shifted upwards (Fig. 7).

The behavior, activity and stability of chromium catalysts are strongly influenced by the interaction of the active sites with their environment.

The permanent deactivation of chromia–alumina catalysts (chemical death of the catalyst), involves solid-state reaction of the active phase with the support, with chromium entering into the alumina framework, and the formation of very low surface area α-Cr_2O_3·$4Al_2O_3$. Fig. 8 shows a model of the chromia–alumina interaction [20].

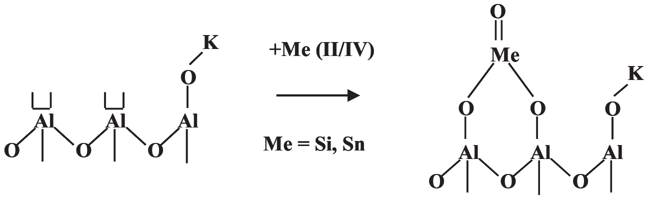

Fig. 9. Lewis acidity control by titration.

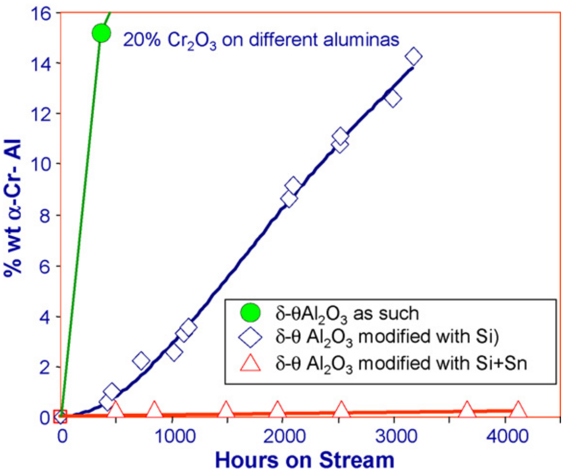

Fig. 10. Stabilization of transition aluminas by Si and Sn.

The kinetics of the reaction of the chromia with alumina can be controlled to a certain extent by proper modification of the carrier surface. Several techniques are available. Fig. 9 refers to a surface "inertization", e.g. by saturation of surface hydroxyls with silica (e.g. via surface titration with tetra-ethyl-ortho-silicate) or by tin deposited at the surface [21,22]. Saturation of Lewis sites helps to reduce the surface acidity and decreases the formation of the relevant by-products.

After long aging on stream or even after calcination at 1000 °C for several hours, both the surface area and the performance of the modified catalyst are both substantially maintained (Fig. 10).

The optimization of the silica content is very important since there is a trade-off between attrition resistance and chemical stability: too much silica for a given surface area hinders a good superficial re-oxidation of the chromia and gives substantial reduction of the long term catalyst activity.

Catalyst attrition resistance of the δ–θ modified alumina and of the final catalyst is very high. Attrition is measured in a relative scale via the Grace Davison proprietary attrition test; Davison Index D.I. gives the percentage of fines (<20 μm) formed by the catalyst subjected to attrition in a standardized equipment and method under highly stressing conditions in turbulent motion. The FBD catalyst

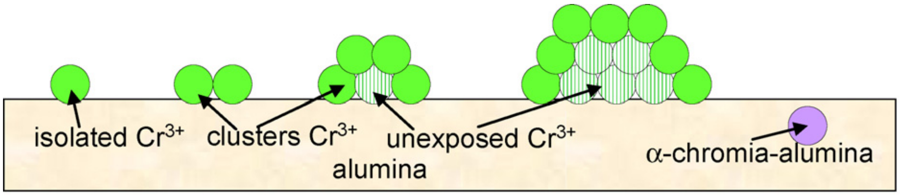

Fig. 8. Model of the chromia–alumina interaction.

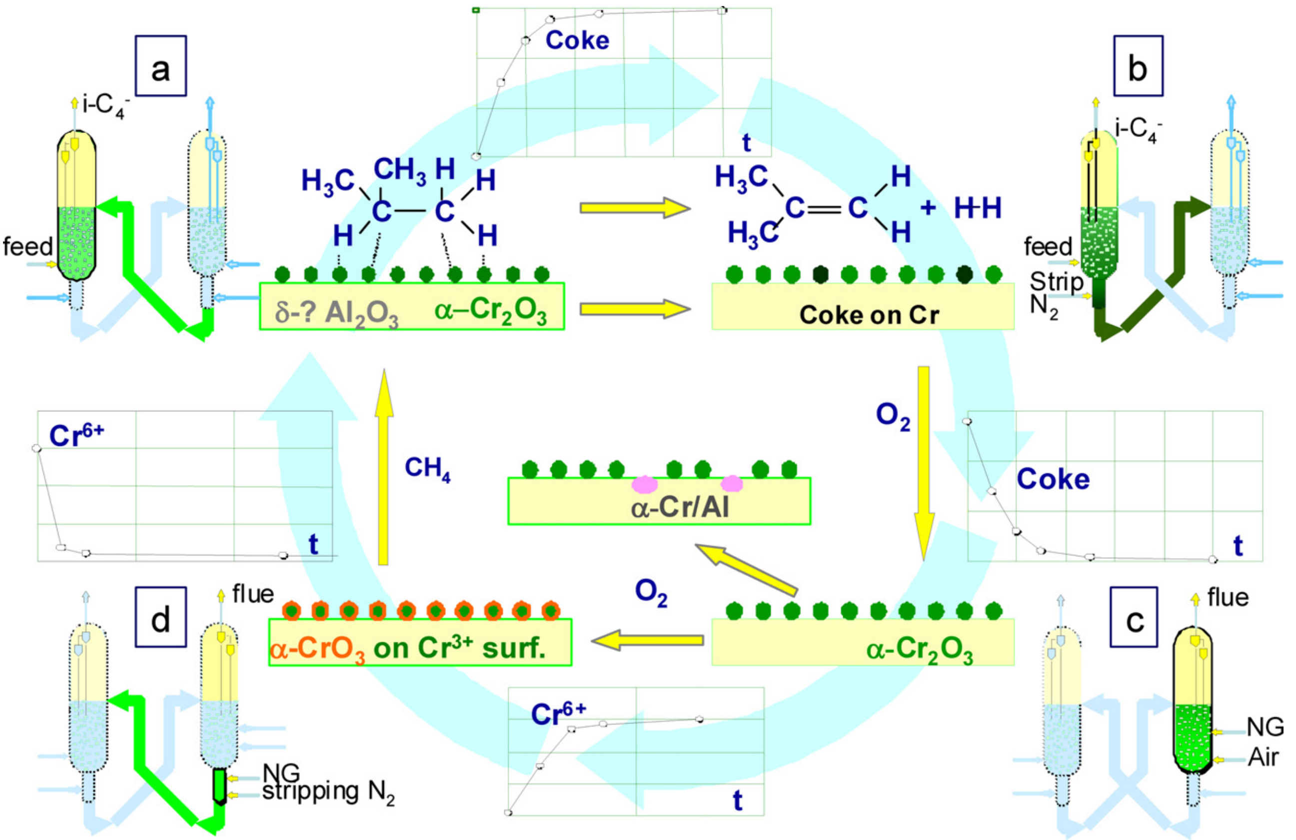

Fig. 11. Catalyst transformations in the reaction–regeneration cycle.

performed better than did the most commonly used fluidized bed catalyst, the fluid catalytic cracking (FCC) catalyst.

The final catalyst formulation and preparation method achieved the targeted performances of activity, selectivity to isobutylene, and mechanical properties. An industrial plant for the production of several thousands of ton/y has been built and operated by Haldor Topsoe Inc. in the US.

2.2.2. Integration of catalyst and reaction conceptual design

The deep knowledge of the catalyst behavior in oxidizing and reducing atmospheres and of the kinetics of all the physico-chemical transformations allows a synergetic combination of process chemistry and reaction engineering. In the case of the commercial FBD technology, it has been also the basis for scaling up the reactor size and achieving maximum industrial plant capacity.

Fig. 11 illustrates the cycle of the catalyst in the full scale reactor-regenerator system.

In the reactor (a), isobutane is fed uniformly across the full cross-sectional area through a suitable distributor at the bottom of the reactor, and it is selectively (92–95 mol%) dehydrogenated to give isobutylene. The conversion is close to the thermodynamic equilibrium. A small amount of coke is formed on the catalyst. The catalyst remains in the vessel thanks to the freeboard disengaging height (the empty zone above the bed) and to the internal cyclones. Entrained fines are collected by very high efficiency filters. The products are passed to downstream unit operation for condensation and purification.

Due to the sequestration by the baffles and also to the countercurrent up-flow of “cold” ($T < 400\,^\circ C$) gas and down-flow of “hot” ($T \geq 620\,^\circ C$) solid, the reactor temperature profile increases from the bottom (520–540°) to the top (540–570 °C) of the reactor. This arrangement is optimal for achieving the highest conversion.

Reactor sizing takes into consideration several constraints and requires an iterative calculation of the best combination of variables:

- The dehydrogenation activity of the catalyst at a given temperature fixes the space–time range for the gas so that, for each design capacity, the volume of the catalytic bed is determined.
- Gas superficial velocity has to stay between U_{mf} and U_t (generally for Geldart A powders, <1 m/s). This dictates the potential vessel diameter.
- In order to keep a good bubbling regime, the aspect ratio (height/diameter) cannot be cake-like (poor distribution and heat/material exchange) or pipe-like (too high an entrainment).
- Catalyst circulation is dictated by the heat balance but, despite some reversible deactivation, the catalyst must preserve enough activity during its residence time in the vessel.
- If the result is not satisfactory, it is necessary to reconsider all the variables, including modification of the catalyst activity. Optimization is always a joint effort of different disciplines!

Throughout the reactor, the catalyst looses activity due to coke build up (Fig. 11b) and site rearrangement. Before leaving the bottom of the reactor, the catalyst is stripped from hydrocarbons. The sizing of the stripper is based on the space–time required for removing inter-particle and some intra-particle gas which is recovered in the reactor; this would otherwise be burnt in the regenerator.

In the regenerator, the total heat required by the system is generated and the catalyst is restored to a performance corresponding to the beginning of the cycle. At the top of the bed, where it arrives from the reactor, coke is burnt with up-flowing air (Fig. 11c, kinetics dictate the portion of bed required). Moving downwards, the catalyst then meets a mixture of natural gas and air and this promotes the catalytic combustion, the flow rate of the fuel controlling the heat balance. Combustion kinetics determine the portion of the regenerator bed required and the natural gas injection point. The temperature rises to >620 °C. Going further down the reactor, the catalyst meets a more oxidizing atmosphere (more O_2%, less HC%) and a superficial layer of Cr_6^+ is formed. The Cr_6^+ concentration reaches a plateau ($\ll$1%). This phenomenon is fundamental for restructuring the catalyst's active sites: if the amount of re-oxidation is too low, the catalyst deactivates quickly because of the formation of α-$Cr_2O_3 \cdot 4Al_2O_3$ [23]. The size of the oxidation zone of the bed depends on the kinetics of Cr_6^+ formation. However, Cr_6^+ is able to burn all hydrocarbons and, if fed to the reactor, it would destroy some of the isobutane, reducing the overall selectivity. For this reason some fuel is injected in the lowest part of the regenerator (Fig. 11d) and Cr_3^+ is restored. The catalyst is now ready for a new cycle.

In the design of the plant, particular attention has been paid to the dust containment in the flue gas. The technologies applied ensure that they have a chromium content similar to the Arctic atmosphere.

3. Styrene in circulating fluidized bed

Looking to other market sectors where the know-how gained in dehydrogenation reactions and in fluidized bed design, a logical consequence has been the development of the production of styrene via ethylbenzene (EB) dehydrogenation. Synergetic efforts were devoted by the R&D department to the design of a suitable catalyst and by commercial departments to the identification of a potential end user interested in a partnership. An agreement was reached with the Dow Chemical Company, leader in styrenics, and a joint team has worked closely on all aspects of the technology. Ethylbenzene dehydrogenation is extremely delicate due to the high reactivity of the products and to the formation of several byproducts that can make the purification of final styrene difficult or even impossible. Current technologies for the reaction utilize uniquely a promoted iron oxide catalyst, a series of adiabatic reactors and very low hydrocarbon partial pressure (vacuum, with a large dilution with steam) to increase the selectivity and avoid catalyst coking.

The literature indicated that gallium on ZSM-5 is effective in the aromatization of light alkanes (Cyclar process). Believing that such a reaction could proceed via dehydrogenation followed by the formation of aromatic rings on the acidic sites of a zeolite, we tried to stop the reaction chain at the first step by controlling the acidity of the support. Little was known from the scientific or patent literature regarding gallium systems and few examples of non-zeolite catalysts containing Ga had been reported [24]. It was found that a gallium oxide based catalysts had good dehydrogenation activity and a new chemistry and catalysis was developed (Fig. 12).

The addition of traces (ppm) of platinum was the key to achieving excellent performances at laboratory level under the typical conditions of a bubbling fluidized bed [25–27]. The promotion effect of Pt has been attributed to a hydrogen spillover effect on the Ga sites. Carrying out tests to determine the reaction kinetics, it was found *unexpectedly* that this catalyst was extremely active even at much higher space velocities than those typically used for a bubbling fluidized bed; a bubbling fluidized bed cannot operate under these conditions since the high superficial gas velocity entrains the catalyst. This led to a technology "revolution" and the reactor design shifted to a "fast riser" configuration, much more convenient as a result of the reduction of the reactor size and of the catalyst inventory. The bases of a new technology (SNOW, *SN*amprogetti - D*OW*) were established [28].

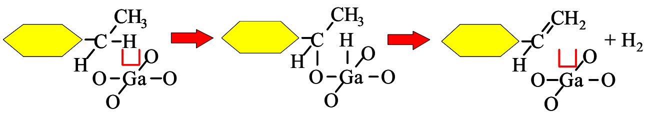

Fig. 12. Ethylbenzene dehydrogenation on Ga catalyst.

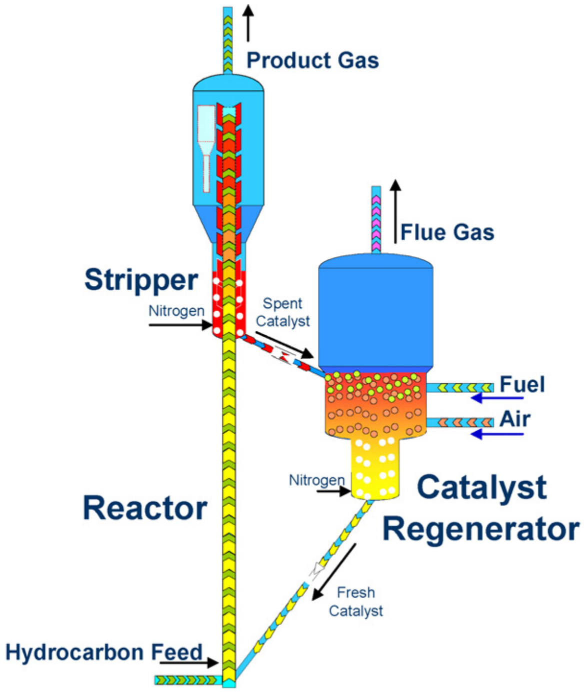

Fig. 13. SNOW reaction section.

The laboratory investigations were performed on very small scale using fixed bed reactors, and confirmed by tests in a circulating-bed rig, typical for FCC catalyst testing. The next step was the design, construction and operation for three years at a Dow site at Freeport (TX, USA) of a large process demonstration unit, having a scale that could allow the safe scale-up to commercial units. The core of the SNOW technology is the circulating catalyst in the riser reactor, similar to the well known and widely applied FCC technology (Fig. 13).

In the riser, the catalyst moves rapidly upwards, it being entrained by the co-current hydrocarbon stream at a gas velocity of 4–20 m/s. The space–time is short (1–5 seconds) and the temperature ranges between 590 and 700 °C, depending on the feed type and riser level.

The total pressure chosen at the top of the riser ensures optimal conversion levels. Proprietary design of the internals ensures suitable fluid-dynamics in each section of the reactor (gas-solid mixing pot, acceleration zone, reaction zone, terminal devices, disengaging vessel, etc.). The products leave the disengaging zone after complete removal of the catalyst using a cyclone system. The reactor effluent is processed using conventional separation technology.

Typical raw materials of conventional styrene complexes are ethylene and benzene, forming first ethyl benzene (EB) in a dedicated unit; the EB is then dehydrogenated to styrene in a separate plant. SNOW can of course work with this configuration (Ethylene Option). However, the extraordinary characteristics of the gallium-based catalyst allow it to be used for the dehydrogenation of ethane; hence, ethane can be used as a raw material together with benzene. In this "Ethane Option", the SNOW complex is fed with benzene and ethane, which is dehydrogenated in the same reaction system used for EB dehydrogenation to produce the stoichiometric amount of

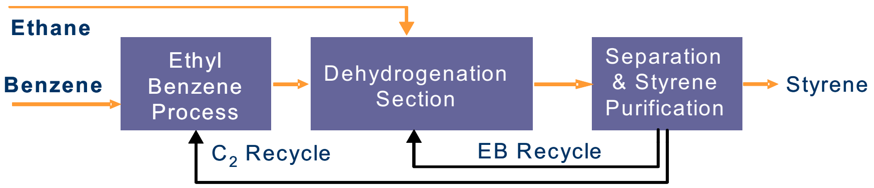

Fig. 14. Conceptual block diagram of SNOW technology, ethane option.

ethylene necessary for benzene alkylation, as illustrated in Fig. 14. The technology is now commercialized as ASM (Advanced Styrene Monomer).

4. Conclusions

The process industry faces challenges requiring innovative efforts. The handling of the complexity of the phenomena involved in the development of catalytic processes involves skills coming from many complementary fields, each developing independently its own progress and advancing towards a very sophisticated level of specialization. Catalysis requires that there is an integration and "bridging of gaps" [29]: gaps between catalyst preparation and performance, between model catalyst and working catalyst, between laboratory and industrial conditions, between reactor engineering and catalyst formulation, between electronic structure calculations at molecular level and experimental results, and, not to be forgotten, between business and science. Integration is achieved when all the team members are able to, and wish to work together synergistically, right from the laboratory level up to the start-up of the industrial unit, with a continuous feedback of information. Such integration requires an intrinsic cultural attitude. Management has the responsibility for the correct involvement of the broad spectrum of specialist skills and for making available a complete view of the total problem under study. A similar form of integration is also required for collaboration between industrial research groups and universities and scientific institutes in order to promote new routes for future developments in technology. These collaborations not only enlarge the cultural basis of the projects but educate synergistically the industrial researchers to apply new scientific concepts in their "real-world" and the academic researchers to introduce "real problems" into their world. Without fundamental science, all technological progress is marginal; in the same way, without technological implementation, cultural and financial efforts aiming at scientific progress become meaningless in relation to social benefits.

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