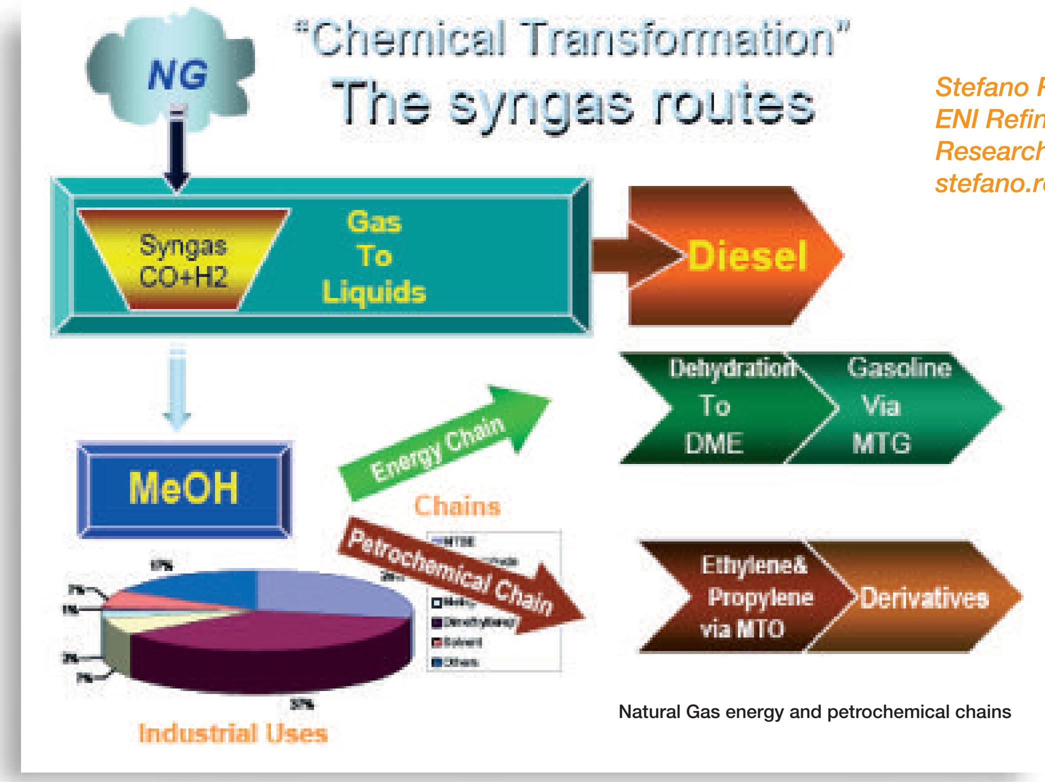

Natural Gas energy and petrochemical chains

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GTL TECHNOLOGY
FROM COMPANY STRATEGY TO CATALYST DEVELOPMENT

A company, like a human being, needs to extend its life into the future. All the actions finalized to this target are reported in company's key documents, one of the most relevant of these, in which the Technology Plan is also included, is the Strategic Plan, that is a document used to plan budget structure, organizational priorities, missions, and objectives.

The Strategic Plan is somehow the master plan and typically includes a mission statement, a description of the long-term goals and objectives, and strategies or means planned to achieve these goals and objectives. The strategic plan may also identify external factors that could affect the achievement of long-term goals. Nested in the strategic plan, other plans are defined to head the company path toward the goals: Financial, Personnel, Technology, etc.; we will focus our attention on the Technology Plan.

The Technology Plan can be viewed as a as comprehensive/integrated roadmap to reach or maintain a competitive advantage. The market of reference or those the company wants to enter should be evaluated based on the actual position, the assets owned and the tools requested. A technology should preferably viewed as a "tool to compete" because either a premium product can be offered or production costs can be lowered or a more environmental friendly manufacturing route can be put on line (less waste, less noxious emissions, etc.). So the Technology Plan is made of statements rationalizing the company requests to have available a certain number of selected technologies. The availability can be reached through the classical statement MAKE or BUY. The MAKE option - the internal development through an R&D department - is pursued whenever the technology is evaluated "key" and it is distinctive in obtaining a better economic performance. The BUY option - acquisition in the technology market from a licensor - is pursued if the technology or a piece of technology package is standard, not distinctive and widely available. A less defined approach is the so called "technology maintenance" where a technology, typically through incremental improvements, is step by step ameliorated, allowing the company to stay on the market reacting to the competitors and/or to upgrade a standard process into a key one because it is used in a novel environment.

Basically the Technology Plan defines the so called technology needs and its motivations. To reach such a detailed viewed and operative guidelines it requires the prediction of markets evolution coupled with the evaluation of own assets and resources identifying points of strength and weakness. Techniques of markets predictions includes making scenarios, taking into account the societal modification, the (macro)economic trends, the external constrains (legislation, environment), and, least but not last, the personal preferences. This is a simplification and many more factors might be included. However it is important to be able to identify the drivers of changement to have the company strategy consistent with them.

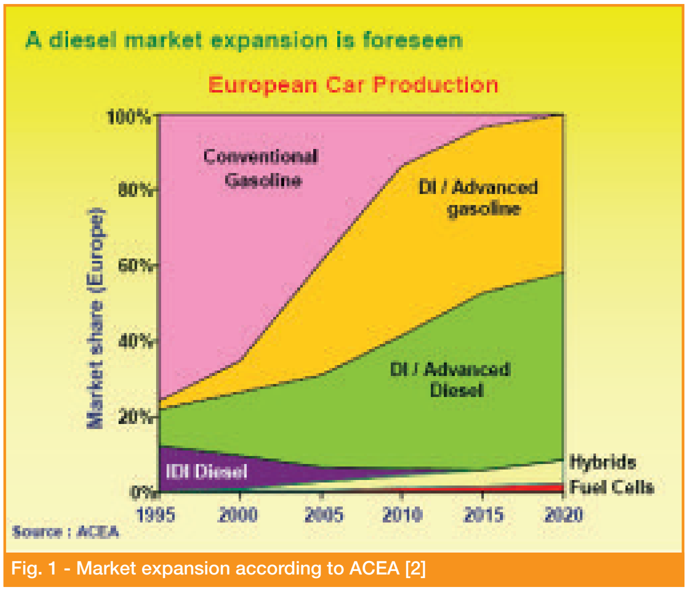


Fig. 1 - Market expansion according to ACEA [2]

In our society two main drivers can be identified: i) the minimization of environmental impact with a more responsible management and conservation of the primary resources and ii) the global economy where distances and markets barriers tend to vanish. The valorization of proprietary assets requires a careful review of own resources, tangible and intangible, to find technological application/transformations that allows either to increase the market appeal of a raw material because of an higher added value or to increase the market share because of a lower price respect to the competitors or to add a "premium" to a certain product. The extreme case is the creation of a market or a market niche as the blossom of MP3 systems could teach us. The aim of the paper is to frame the Gas-To-Liquids (GTL) technology and, more specifically, the Fischer-Tropsch catalyst development into the approach discussed.

The strategy leading to GTL development

The developed countries, closely followed by the great economies experiencing a explosive growth like the Chindia [1] galaxy, are marching towards an augmenting request of self and long-range mobility and the car will be the tool of election. The constrains are the optimal use of fossil fuels and the reduction of the environment impact both on local and planet scale.

The carmarket evolution by ACEA [2] (Fig. 1) predicts a significant increases of advanced diesel engine automobiles which in turn will required higher amount of high quality diesel (low sulphur, low aromatics) allowing the installation of end-of-pipe abatement system for particulate and noxious pollutants. In fact the advantage of the diesel engine over the sparkling ignited one is an overall high efficiency of the fuel energy usage (about 44-45% for diesel versus 25-27% of the sparkling ignited) which turns into a lower CO_2

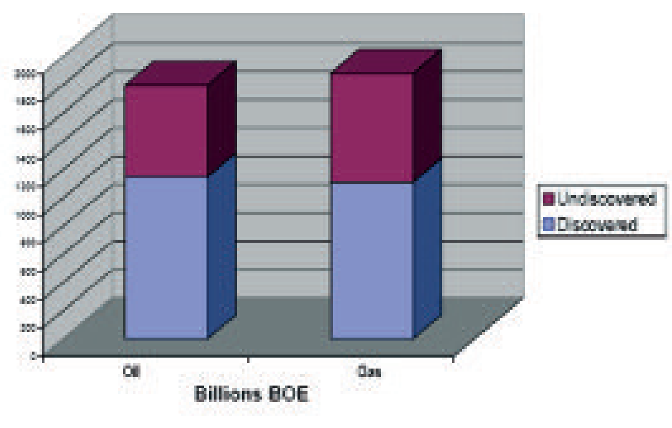


Fig. 2 - World Oil and Gas Reserves [4]

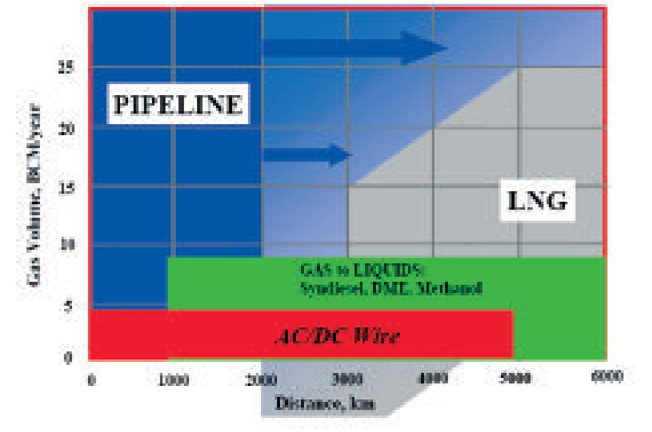


Fig. 3 - Preferred options to bring the natural gas to the final market as function of distance (well-to-end use) and reservoir volume

emission per kilometer driven (environmental benefit). The cost of the fuel is still a little lower than gasoline (economical advantage) and the performances of the diesel fuelled cars are today similar to the gasoline fuelled ones (personal preferences). But the particulate emission PM_{10} [3], and right now the finer $PM_{2.5}$, are suspected to be carcinogenic (health penalty) and need to be continuously minimized. A high quality of diesel fuel can significantly and immediately contribute to such a reduction.

The natural gas - a mixture of C1-C5, carbon oxides, sometimes hydrogen sulphides and nitrogen - is becoming in this years as relevant as the oil as primary energy source because of its cleanness and its relevant availability. The proven resources [4] are matching those of oil (Fig. 2) with about 1,100 billion Barrel Oil Equivalent (BOE) proven. The gas reservoirs are classified accordingly to the exploitability; typically reserves are classified as Remote Gas, when it is too far from a market, making the construction of pipelines prohibitively expensive; Stranded Gas, a natural gas field that has been discovered, but remains unusable for either physical or economic reasons; Associated Gas, when it is found within oil wells, often regarded as stranded, and it has been historically flared. It is also now sometimes reinjected into oil wells in order to maintain the extraction pressure. The dimension of the reserve and the distance from the end users conditions the way of usage, either as primary energy vector transported via pipelines or liquefaction (Liquefied Natural Gas (LNG)) or as secondary vector and petrochemical building blocks through chemical transformation (the GTL route belongs to the second group): the main chains of natural gas transformation are passing through the syngas generation. The Fig. 3 summarizes in the criteria of reservoir dimension and the distance from the market in a quantitative way (as "preferred options"), putting on the same plot the direct and indirect natural gas more rewarding options. Indeed in a project definition phase all the different options should be compared including not only technical indicators but also further business opportunities, overall economics, company strategy.

The combination of the market request for a high quality diesel and the assets valorization of unexploited natural gas reserves claims for the Gas-To-Liquids (GTL) conversion. The GTL includes a syngas generation through a consolidated technology (Steam reforming; Autothermal reforming, Combined reforming); the Fischer-Tropsch reaction where the syngas is converted into a mixture of long chain hydrocarbons, preferably of paraffinic nature with minor amount of oxygenates, mainly alcohols; a hydrotreating finishing step where the hydrocarbons are upgraded to high quality diesel cut with noticeable cold properties and cetane number. A water treatment section should be included to upgrade the large amount produced accordingly to the final use. The step to be developed the most - despite the remarkable age - is the Fischer-Tropsch reaction: exploited in the Twenties' after the pioneristic steps of Sabatier dated at the beginning of the Twentieth century, it allows the production of a mixture of hydrocarbons through a polymerization of $-CH_2-$ like monomer respecting a statistical distribution. This distribution was proposed by Anderson in the Fifties adapting the Schultz-Flory [5] distribution from the polimer science. The Anderson-Schultz-Flory (AFS) distribution (Eq. 1) returns the molar fraction m_n of the n-carbon atoms species as a function of the α-parameter:

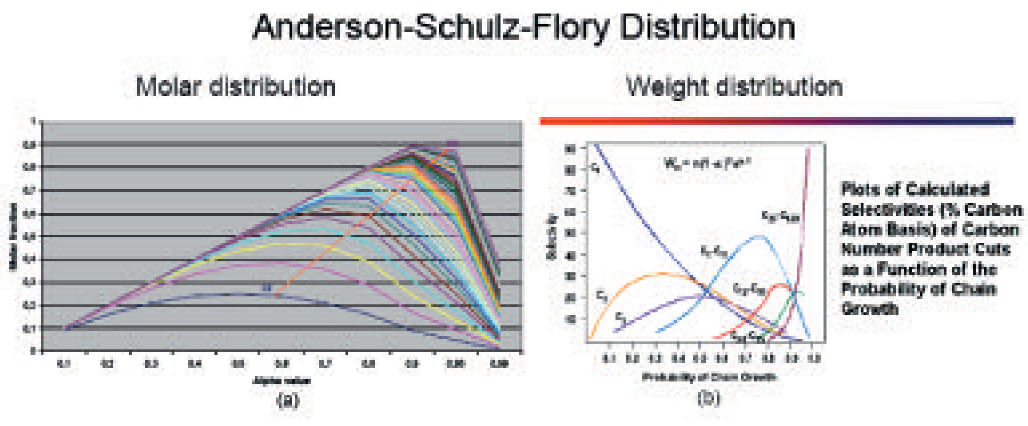


Fig. 4 - Distribution of hydrocarbons from Fischer-Tropsch synthesis versus α values

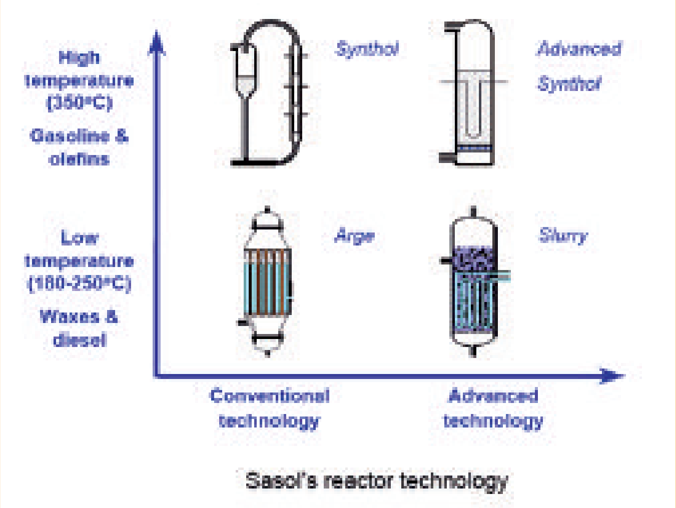


Fig. 5 - Type of Fischer-Tropsch reactor developed by Sasol

$m_n = (1-\alpha) \times \alpha_{n-1}$ (Eq. 1)

$W_n = nx(1-\alpha)_2 \times \alpha_{n-1}$ (Eq. 2)

A simple elaboration gives the weigh fraction (Eq. 2). The plots are reported in Fig. 4 a, b respectively. The α parameter is the ratio ($\alpha = r_p/(r_p + r_t)$) between the rate of chain propagation (r_p) and the sum of rates of propagation and termination (r_t). Values of interest for the α-parameter exceed 0.9.

The reaction is very exothermic (Eq. 3); different reactor configurations were developed to manage the heat of reaction in the two main regime explored, the low temperature (120-250 °C) where waxes and diesel prevail and the high temperature where olefins and gasolines:

$CO + H_2 \rightarrow -(CH_2)- + H_2O \rightarrow -(CH_2)_x-$ $\Delta Hr = -167$ kJ/mol (Eq. 3)

The main type of reactor, fixed bed and slurry for the low temperature regime, and circulating and advanced fluid bed for the high temperature, are shown in Fig. 5. The last developed is the Slurry Bubble Column Reactor (SBCR) which offers ideal heat removal, nearly isothermal conditions for high catalyst efficiency, catalyst make-up and withdrawal, low pressure drops also for large capacities. The technological challenges to be managed are the complex reactor hydrodynamic where the catalyst undergoes a chemical and mechanical stress, the slurry handling and the solid/liquid separation.

Catalyst development

The catalyst needs be in the most suitable form for the SBCR application with the correct particle size distribution (PSD) and resistance to mechanical degradation and chemical decay. The consumption should minimally impact on the production cost per barrel of diesel; this is a complex function of the raw materials prices due to the catalyst formulation, its mechanical and chemical stability and the recoverability of the spent catalyst active ingredients [6]. The typical active phase for the low temperature SBCR application is cobalt, supported on a carrier preferably composed of alumina. This could be a major risk since alumina under the hydrothermal conditions experienced in the FT reactor may evolved back to boehmite which is extremely fragile and once formed it seems to be "autocatalytic" leading to the complete degradation of the carrier with huge amounts of fines blocking the solid/liquid separation devices. Several strategy can be applied to overcome this retro-synthesis obtaining a support suitable to be loaded with the main active phase and eventual promoters. The fines formations becomes minimal as shown in Fig. 6. Once the carrier has been well defined, the optimal recipe is scaled up to produce the catalyst precursor through wet impregnation or slurry dipping or any other methodology loading the active phase on a preformed support.

Once the precursor has been prepared, i.e. the cobalt is present mainly in the tetraoxide Co_3O_4 form, the active catalyst is obtained via reduction to be conducted very carefully since it has been shown that the performances can be influenced by the reduction protocol applied. The tetraoxide is reduced to metallic cobalt through two steps, the first leading to CoO monoxide and the second reducing the intermediate to metallic cobalt. The former is easier and faster while the latter is more complex since it is an equilibrium (Eq. 4):

$CoO + H_2 \rightleftarrows Co + H_2O$ (Eq. 4)

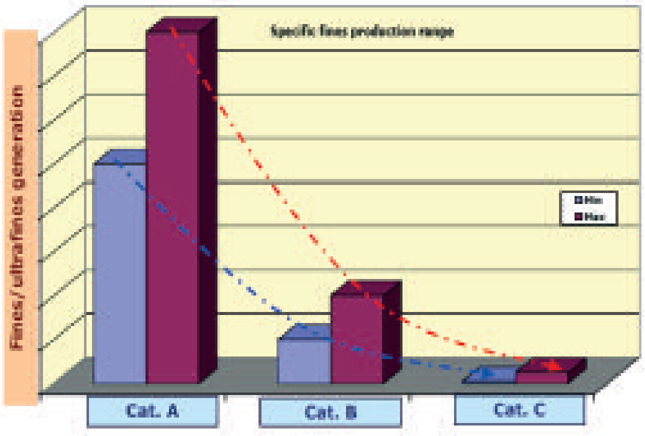
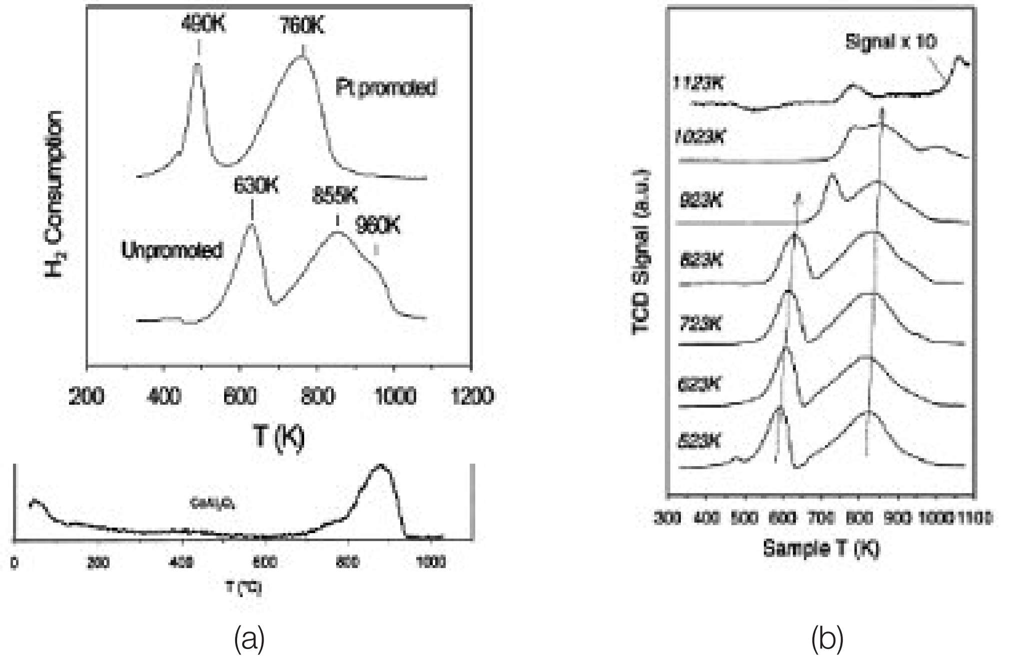


Fig. 6 - Reduction of fine formation in the FT reactor depending on methodologies (B, C) applied to stabilize the support compared to the untreated case (A)



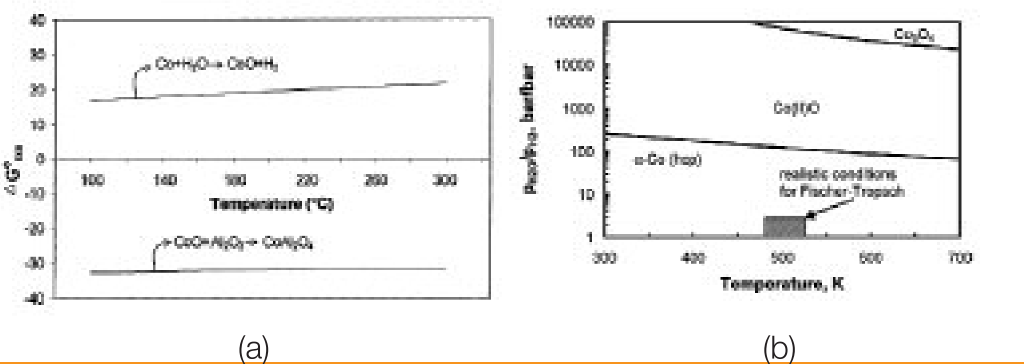
(a) (b)

Fig. 7 - a) TPR of 15% cobalt on alumina catalyst unpromoted and Pt promoted, b) TPR of a similar material as a function of calcinations temperature

The reduction can be used like a finger print of the catalyst precursor since the reduction profile, measured in a Temperature Programmed Reduction (TPR) apparatus, is strongly influenced by various factors, like support, Co_3O_4 dimensions, temperature of calcination, promoters, etc. A typical TPR profile on alumina supported Co_3O_4 catalyst is shown in Fig. 7 (left side as "unpromoted"). The peak between 500-700 K is assigned to $Co_3O_4 \rightarrow CoO$ and $CoO \rightarrow Co$ reduction, the latter being in the upper part and partly overlapping the former. The 700-950 K peak is ascribed to cobalt species with different degree of interaction with the support: a general formula $xCoO{\cdot}yAl_2O_3$ can be proposed, although in literature references are made also to Co^{3+} and Co^{2+} ions. Indeed, the broadening of the peak is to be attributed to the surface interaction of small cluster of cobalt oxides. The extreme case of interaction is the formation of the spinel $CoAl_2O_4$, whose reduction takes place close to 1,000 K (see left lower pattern). The reduction temperature can be affected by the calcination temperature: the TPF profiles of 15% Co/Al_2O_3 in Fig. 7b show how the peaks move upwards increasing the calcination temperature. At lower temperature (<823 K) the total area of the two main peaks is approximately constant indicating that there is not a significant interaction with the support. The spinel phase start to appear above 823 K but it is significantly present from 1,023 K. A noble metal like Pt shifts the temperature peaks of about 100-150 K.

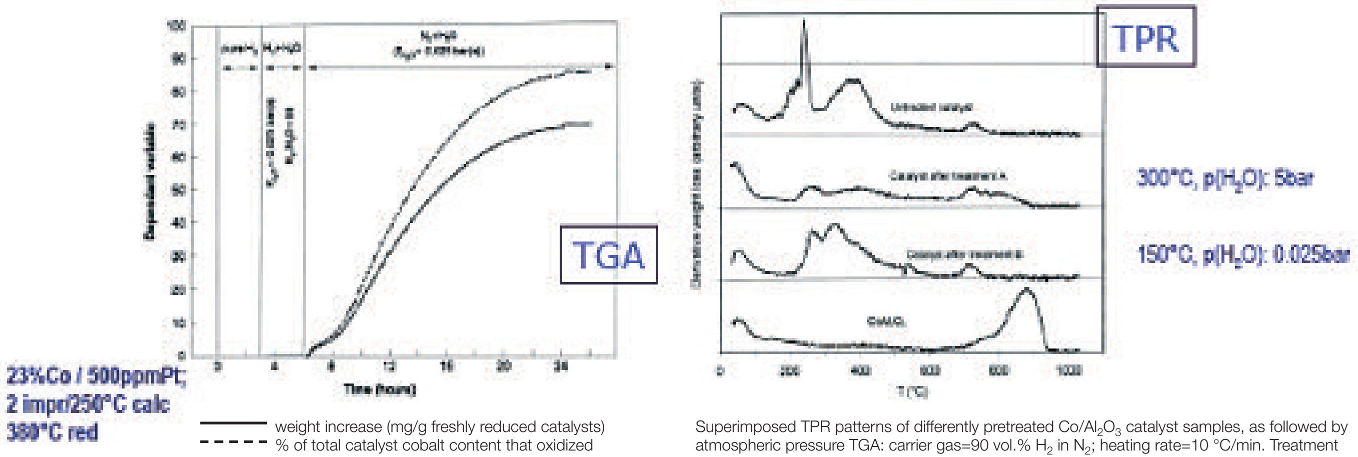
The noble metal is assumed to increase the rate of nucleation of sites on the cobalt species being reduced, presumably by hydrogen spill-over from the Pt metal atoms.

The thermodynamics and the kinetics of (Eq. 4) can teach a lot more about the catalyst evolution under real Fischer-Tropsch conditions. A first statement was that the metallic cobalt could not be oxidised under realistic Fischer-Tropsch conditions. In fact combining the standard Gibbs energy (Fig. 8a) of the two main reactions, oxidation (reverse (Eq. 4)) and spinel formation, it turns out that the first one is not favoured or possible (under realistic Fischer-Tropsch conditions, see Fig. 8b) while the second, once the cobalt monooxide is somehow available, could proceed. It has been shown [7] that indeed water oxidises similar material (see Fig. 9a) and the severity of the oxidising treatment heavily affects the final state of the catalyst: see Fig. 9b where a water softer treatment (B) allows the active phase to retain part of its original structure while a stronger



(a) (b)

Fig. 8 - a) Standard Gibbs energy for the kinetically coupled reaction; b) cobalt phase stability versus temperature [7]



weight increase (mg/g freshly reduced catalysts)
% of total catalyst cobalt content that oxidized

Superimposed TPR patterns of differently pretreated Co/Al_2O_3 catalyst samples, as followed by atmospheric pressure TGA: carrier gas=90 vol.% H_2 in N_2; heating rate=10 °C/min. Treatment A: standard reduction+complete oxidation at 10 bar(a) $Ar+H_2O$, 300 °C, P_{H2O}=5 bar(a). Treatment B: standard reduction+complete oxidation at 1 bar(a) Ar+H2O, 150 °C, P_{H2O}=0.025 bar(a). $CoAl_2O_4$: calcined at 800 °C

(a)

(b)

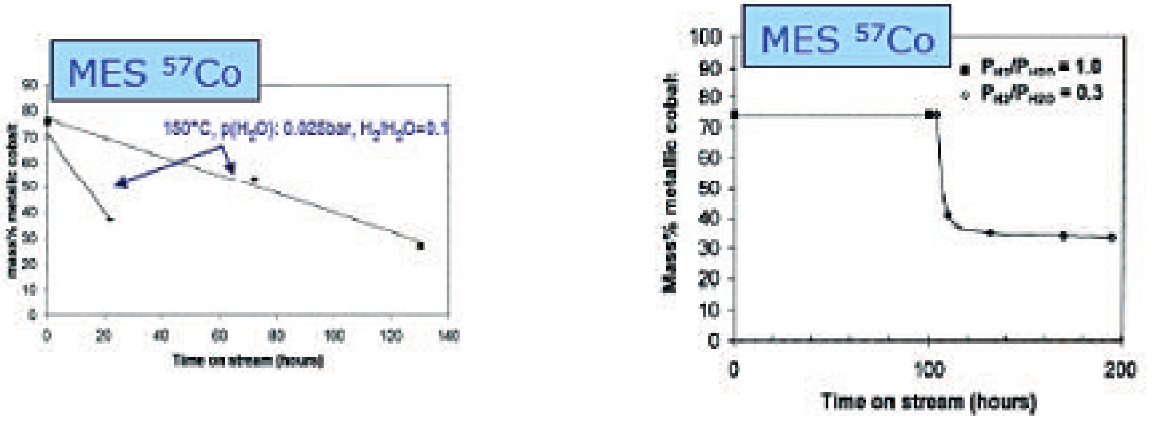
Fig. 9 - Effect of water treatment on cobalt supported on alumina [7]

one almost completely destroy it leading to phase more similar to a spinel. The oxidation can be reversed by hydrogen treatment but then there are evidences that the oxidation is even faster (Fig. 10a). The feasibility of the oxidation is driven by the oxidation potential of the system that can be represented by the H_2 to H_2O ratio: the lower the ratio the higher the amount of cobalt oxide formed (Fig. 10b).

The rational for the thermodynamically impossible oxidation is given by the dimension of the particles of cobalt oxide [8]. The surface energy γ depends upon the diameter of the particles (d_{Co} in nm) and the destabilization (shown in Eq. 5) is different for the metallic cobalt and the oxide, as naively represented in Fig. 11a):

$$\gamma CoO/\gamma_{\beta Co}=0.2167 + 0.011/d_{Co} - 0.063/d_{2Co} \qquad \text{(Eq. 5)}$$

The thermodynamic stability of two phase can be calculated as a function of particle size and the H_2O to H_2 ratio; Fig. 11b shows that the formation of the oxide becomes possible and it is driven,



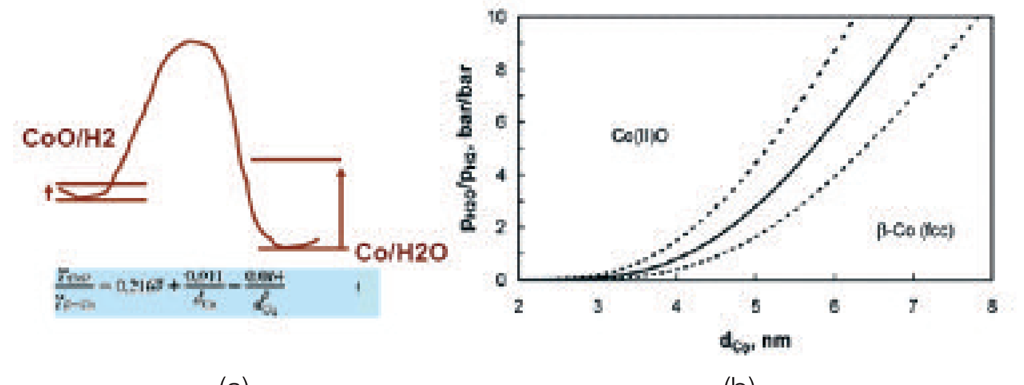
Repeat oxidation profiles of the look-alike catalyst as observed with MES at the conditions: (150 °C; 1 bar(a); $Ar+H_2+H_2O$ environment, P_{H2O}=0.025 bar(a) and H_2/H_2O=0.1): (■) LA2-6, (+) LA2-8

Catalyst oxidation as directly observed with Mössbauer spectroscopy (150 °C; 1 bar(a) $Ar+H_2+H_2O$ environment; P_{H2O}=0.025 bar(a)

(a)

(b)

Fig. 10 - a) Reaction rate and b) effect of H_2 to H_2O ratio in the oxidation of cobalt supported on alumina. The cobalt catalyst has been enriched with ^{57}Co [7]



(a) (b)

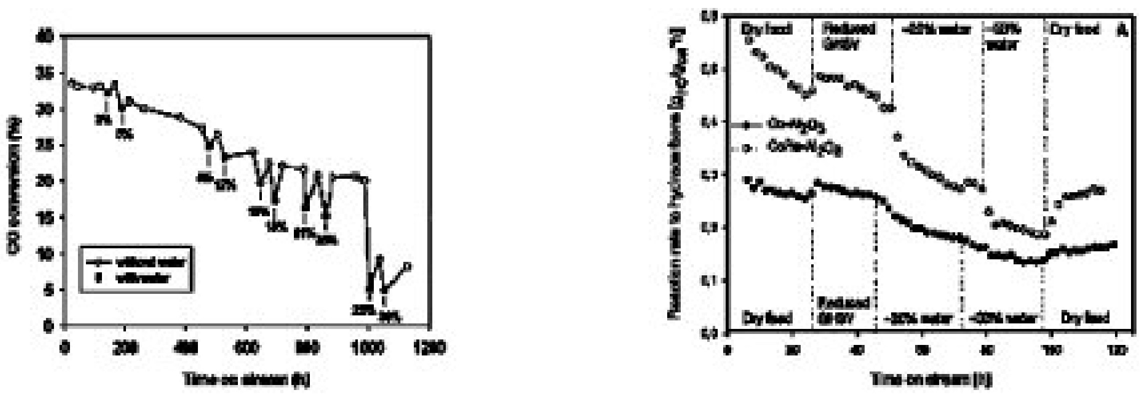
Fig. 11 - a) Modification of the Gibbs free energy (↑) in the cobalt oxide and metallic cobalt due to surface energy γ, different in the two species, and consequent modification of the equilibrium of the two phases represented in b) (d_{Co} diameter of cobalt particle in nm) [8]

fixed the particle diameter, by the H_2/H_2O ratio as the standard equilibrium of Eq. 4. So it is still the thermodynamics that interprets the observed phenomena but it needs to be properly applied, that it is to say that the thermodynamics of the bulk phase cannot be used in case of supported, highly dispersed phase.

This evidence becomes a key factor in interpreting the most detrimental fact during the catalyst life: the loss of activity. Several causes can be proposed to explain it: oxidation by water; sintering of the metallic phase since the Hutting temperature [9] of cobalt (525 K) is close to the operating temperature (480-500 K); pore blocking due to very heavy hydrocarbons causing diffusional limitations; loss of surface area to the collapse of the carrier structure. Indeed a combination of some of them is also very likely.

Many evidences in literature refer to the role of water as one of the major cause of deactivation. Evidences are given that water co-fed with syngas inhibits the activity up to a certain level of water where the effect becomes permanent [10] (Fig. 12a); this level is somehow quantified in a $p(H_2O)/p(H_2)>0.6$). Indeed other evidences are reported [11] where after similar water addition (30% as in [10]), the catalysts recovers the activity (Fig. 12b). The different behaviour can be speculated to be the different composition or the crystal size; but indeed also other clues can be derived from the evidence [10] that that the decay is faster when lower space velocity are used (Fig. 13). Lower space velocity means higher conversion and therefore higher water partial pressure (and lower hydrogen partial pressure) but also a longer gas residence time. So it not only the oxidation potential of the reaction mixture but also the time water is contacting the metallic species as a kinetic factor.

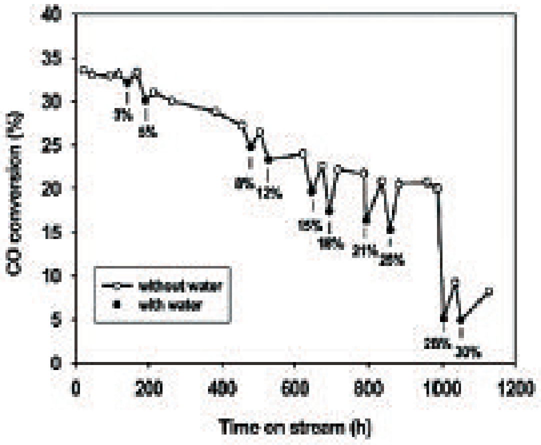
The modelling of the decay proposed by Qin and Ramkrishna [12] includes the oxidation and the sintering. The approach used is shown in Fig. 14a where the particle can be so small that can be considered a 2D particle spread onto the surface and well in contact with it. The h is the distance within which the surface exert its influence, mainly causing deactivation. Bigger crystallites have an semi-spherical shape whose e represents the maximum area of deactivation. "It appears the deactivation of the catalyst with small average



Effect of water on CO conversion for Co-Pt/Al_2O_3 catalyst (*T* = 483 K, *P* = 28.9 atm (2.9 MPa), $P_{H2} + P_{CO}$ = 20.0 atm (2.03 MPa), H_2/CO = 2.0, SV = 8 SL/gcat/h; (%) is vol.% of total)

(a) (b)

Fig. 12 - a) Effect of water addition to the performances of a Pt-Co/Al_2O_3 which become irreversible at percentage greater than 28-30% [10]; b) same as in a) showing a recovery after a 33% water addition in the feed for a Re-Co/Al_2O_3 and Co/Al_2O_3 [11]



Effect of water on CO conversion for Co-Pt/Al_2O_3 catalyst (T = 483 K, P = 28.9 atm (2.9 MPa), P_{H2} + P_{CO} = 20.0 atm (2.03 MPa), H_2/CO = 2.0, SV = 8 SL/gcat/h; (%) is vol.% of total)

Fig. 13 - Different decay rates at different space velocities [10]

particle size (~5 nm) shows only weak size dependence, which is because most of the particles in these catalysts are so small that the whole particles interacts with the support and therefore is susceptible to deactivation; thus only sintering shows size dependence. On the other hand, the deactivation of catalysts containing big particles (>15 nm) also shows little size dependence, as most particles in these catalysts are so big the effect of metal-support interaction becomes very small and the particle behaviour approaches that of bulk cobalt with sintering also not being so significant. For the catalysts in between, which is also the typical size range used, the size effect is significant" [13]. The overall results of the modelling are reported as function of time on stream and particles (Fig. 14b) while Fig. 14c shows how the model fits a set of experimental data quite convincingly.

The combination of all the information brings a major attention on the particle size of the active phase because it can have a severe impact on catalyst behaviour: the focus is on the metallic particles. Rather than the average particle size, the distribution should be considered as relevant but it is not easily measurable after the reduction also because the pirophoric nature of the metallic cobalt. Sasol, a major leader in the field, reported in a patent [14] that the small particle are lost during the very first hours on stream - a sort of pre-initial o start-up phase - where the catalyst is still evolving after the reduction step. This was the basis to claim some rights on the correlation of active phase, dimension of the crystallites (i.e. Co surface area) which characterize the optimum catalysts.

Catalyst and process

To move on from lab to (semi) industrial scale, a fundamental step is the scale-up of catalyst production because the recipe used at lab scale has to be transformed into a series of unit operations suitable to be applied in the production of hundreds of tons.

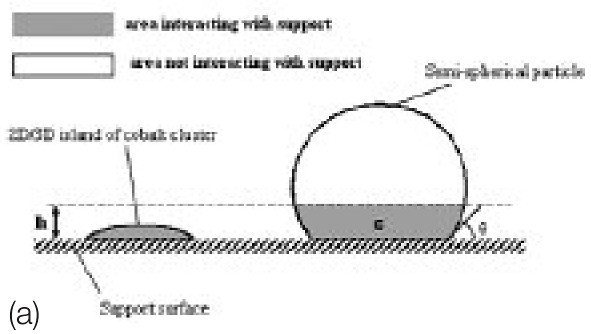
Manufacture repeatability and the economics of production, once assured at industrial scale, allow the material to be taken as the base of the process.

The catalyst properties need to be consistent with the selected reactor configuration - or vice versa the kind of reactor should permit the best usage of the catalyst - because the fluid dynamics imposes constrains. In Eni we designed the reactor - passing through the effect of liquid properties, of solid concentration, of operating conditions (P, T), of scale, of internals - through the use of mock-ups of different diameter (0.15, 0.4, 1.0, 3.0, 5.0 m) corresponding to a capacity up to 1,000 bpd. The literature models were not be able to predict univocally the liquid linear velocity as a function of reactor productivity (i.e. reactor diameter). They were diverging quite substantially at reactor diameter of ten meter which is considered to be the size of the single train maximum capacity. The linear velocity has a considerable relevance since it has a direct impact on the mechanical stress the solid has to resist. These effects have been measured and modelled as part of the necessary scale-up [15] strategy. Similarly the slurry handling and solid-liquid separation devices have been carefully examined and tested in the pilot unit located in San Nazzaro de' Burgundi where several campaigns have been run.

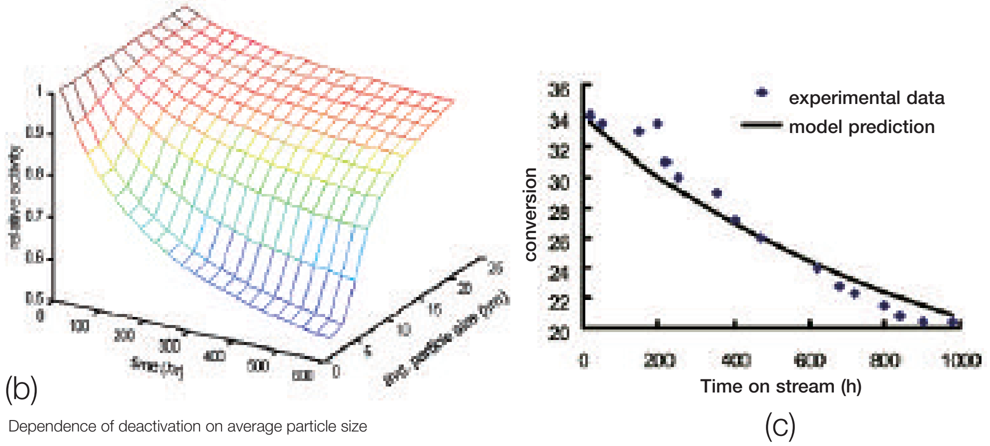
Criteria have collected on specific lines and vessels design to keep corrosion-erosion under control, the critical slurry pumps, the shutdown dedicated procedures to have safe conditions for the catalyst, etc. All this know-how is merged into the catalyst handbook which is a chapter of the technology handbook.

Conclusion

The aim of the paper was to frame a catalyst development into a major scenario starting from the Company Strategy Plan and passing through the Technology Plan. In industrial R&D activities the goal is not the basic knowledge but the availability of technology as a tool offering a competitive advantage to the company on the market of reference. So market evolution, costs vs. potential rewards, time-to-market should be continuously monitored and updated during the project life. The experimental activities should fill the gap from the initial statement "We need to know how to... " to the final "We know how to...". Each technology can be unbundled into a series of technical needs - a sort of work breakdown structure - to which the "We need to know how to... " statement has to be applied and satisfied.



Metal crystallite and its interaction with supporting material. Crystallites bigger than *s'* have a semispherical shape with contact angle q depending on the interaction between metal and support; those smaller than *s'* form 2D/3D islands with irregular shape. *h* is the distance the effect of support can reach. The dark area is the part interacting with the support and therefore the part can be deactivated. e is the maximum extent of deactivation, which is the ratio of the surface area of the dark region over the total surface area



Dependence of deactivation on average particle size

Fig. 14 - a) Model description; b) decay function versus time and particle sizes; c) simulation of experimental data [13]

The Fischer-Tropsch catalyst development - including preparation at industrial scale and understanding the decay rate (which is inherent to all catalysts), a sort of "from cradle-to-grave story" - has been selected because it has been possible to link the relevance of the technology into the today's world energy scenario with the studies of how the particles dimension and the working conditions impact on the economics of the transformation, i.e. its market potential and appeal.

The link is the catalyst consumption, transformed into the operative expenses per barrel of product: the delta valorization between the raw material and the final product should be able to allocate all the operative expenses, the plant deprecation and the return on the investment. This "simple" (!) calculation distinguishes a success from a failure and the market is the final judge.

References and notes

[1] Chindia is a portmanteau (fusion of words) neologism that refers to China and India together in general, and their economies in particular. The credit of coining the now popular term goes to leading Indian economist and politician Jairam Ramesh.

[2] ACEA European Association Automobile Manufacturer at www.acea.be/node

[3] PM10 Particulate Matter with dimension lower than 10 micron.

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