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Dehydrogenation of paraffins: synergies between catalyst design and reactor engineering

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Abstract

The dehydrogenation of paraffins, especially in the C_3–C_5 range, is a widely exploited way for large-scale production of pure olefins. Its industrial application is however complicated by clashing kinetic and thermodynamic constraints. The nature of these constraints is illustrated and the solutions proposed by different technology providers in terms of catalyst composition/morphology and selection of the type of reactor and means for supplying reaction heat are discussed. The solution to achieve an economically attractive commercial implementation lies in defining the optimal synergy between catalyst design and reactor engineering. Potential new ways to olefins are also examined.

Keywords: Dehydrogenation reactions; Dehydrogenation catalysts; Dehydrogenation technologies; Olefins

1. The World of olefins

We need olefins, since olefins, with their preferential positions of reactivity, have become the building blocks for the production of polymers and consequently for the manufacture of an impressive number of commodities and specialties for daily use. The vigorous development of the human society in the second half of the 20th century has been sustained by the use of Oil and Gas as energy sources, and as raw materials. Unfortunately, natural fossil resources do not contain olefins since they mainly consist of saturated or aromatic hydrocarbons. Olefins production requires sophisticated and costly technologies, highly demanding in terms of investments and energy consumption.

Dehydrogenation reactions are practiced industrially essentially for the dehydrogenation of light alkanes (propane to propylene for polymers and isobutane to iso-butylene for gasoline and polymers) as well as long linear ones (C_{10}–C_{14} to linear-alkyl-benzenes) and the dehydrogenation of ethylbenzene to styrene. The dehydrogenation of alcohols to ketones and aldehydes is another reaction worth mentioning. The light paraffins dehydrogenation sustains a network of technologies allowing an integrated approach to create valuable products from natural gas.

1.1. Light paraffins dehydrogenation: the C_4 scenario

Dehydrogenation has been industrially applied for decades to the production of butenes and butadiene from butane. In the early 1980s, new life to this reaction and push for the development of novel technologies was brought indirectly by the environmental concern on the emissions from transportation: the recognition of the very beneficial environmental effect of oxygenates introduced the oxygenate use in gasoline. MTBE shortly became the "winning" oxygenate because of its environmental benefits, engine performances, economics and fungibility with existing infrastructures.

MTBE is derived from methanol and isobutylene through the etherification reaction:

$$\text{methanol} + \text{isobutylene} \rightarrow \text{MTBE}$$

MTBE appeared in the gasoline pool in 1973 with the first commercial plant (Snamprogetti-Anic in Ravenna). Since then more than 170 plants have been built in the world. The large demand for MTBE "dried up" the available isobutylene supplies from steam crackers C_4, fluid cat cracker (FCC) C_4 and the dehydration of tertiary butyl alcohol (TBA). New processes for producing isobutylene were studied and developed during the 1980s but only the development and implementation of new

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technologies for the catalytic dehydrogenation of isobutane from butanes allowed an increase in the world production by a factor of 15, reaching a MTBE capacity of about 20 MMt/y.

Despite the environmental merits of MTBE on air quality, MTBE was detected in some wells or ground water due to some accidental gasoline leaks in the US. A furious political and environmental campaign against MTBE led to its banning in California and reduced the consumption in some other US states. Basically, no such discussions have taken place in the rest of the world and Europe. There are two alternatives to MTBE as octane source: isooctane from hydrogenation of isooctene, isobutylene dimer, and alkylate [1].

1.2. The C_3 scenario: the imbalance of light olefins

Propylene and ethylene are co-produced in steam cracking units. The propylene demand is increasing faster than the ethylene demand. The expected growth of propylene with respect to ethylene exceeds the ratio obtained from steam crackers. The current tendency for building new ethane crackers in gas-rich countries will aggravate this imbalance. Technologies aimed at a (more) selective production of propylene are expected to become more important (metathesis, overcracking, methanol-to-propylene, etc.). The dehydrogenation of propane offers an option to capture the marginal, additional capacity needed to compensate for the imbalance. Lower cost feed (propane from NG) is advantageous to all ‘‘liquid’’ derivatives in a high oil-price scenario, as shown in Fig. 1.

1.3. Characteristics of the dehydrogenation reaction

Dehydrogenation is an endothermic, equilibrium-controlled reaction. These characteristics pose some constraints on developing commercial processes.

Equilibrium conversion is limited by thermodynamics and increases with temperature. In order to achieve reasonable economic conversion per pass (separation costs of unreacted paraffin are high), temperatures exceeding 550 °C are a prerequisite; the lighter the paraffins, the higher the required temperature and the more relevant the engineering difficulties.

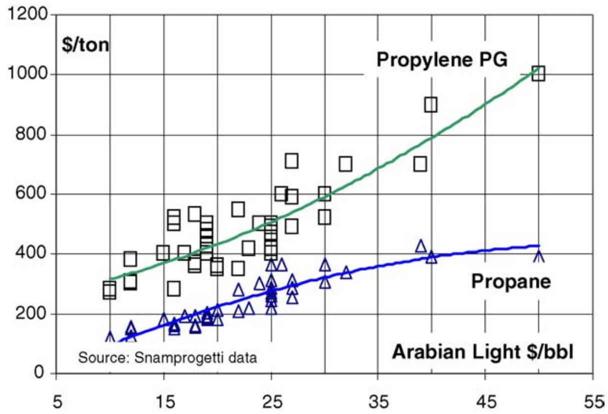

Fig. 1. Propane–propylene historical prices (USGC).

High reaction temperature means magnification of side reactions. The stability of paraffins and olefins becomes critically influenced by the several side reactions. Oligomerization to heavier compounds, cracking to lighter hydrocarbons, skeletal isomerization, aromatization, alkylation of the formed aromatic rings, eventually leading to coke formation, lower the yields. Coke is *fatal* to any catalyst. Periodical catalyst regenerations are necessary to remove coke from catalyst and restore the activity of the catalyst in the light paraffins dehydrogenation.

The equilibrium conversion increases by lowering the pressures. Some technologies operate at paraffin partial pressures lower than one atmosphere (vacuum, H_2 or steam dilution) to get a higher driving force.

Reaction endothermicity (about 125 kJ/mole of extracted hydrogen) results in a higher heat demand on weight basis for producing lighter olefins. *Dehydrogenation requires high heat fluxes* at temperatures higher than 550 °C along the reaction coordinates. The way in which heat is supplied to the gas characterizes the industrial processes.

All the above characteristics mandate a synergetic process design and the integration of the nature of the catalyst and the reactor conceptual design.

2. Dehydrogenation catalysts

The use of a suitable catalyst allows high reaction rates and, above all, high selectivity. The presence of several consecutive reactions is responsible for the typical trade-off between conversion and selectivity to the desired olefin: by increasing conversion, the selectivity drops off. The main types of dehydrogenation catalysts reported in the patent and scientific literature are:

(a) Group VIII metals (basically supported platinum/tin, with promoters),
(b) Chromium oxides on alumina or zirconia, with promoters,
(c) Fe oxides, with promoters,
(d) Ga, supported oxide or included in zeolites,
(e) Cu for alcohols to aldehydes.

This is the scenario of the dehydrogenation catalysts and their applications, including the latest patent literature information:

Active component	Light paraffins	C_{10}–C_{14} paraffins	EB to SM
Pt/Sn	Excellent	Excellent	n.a.
Cr oxides	Excellent	Moderate	Good
Fe oxides	Nil to poor	n.a.	Excellent
Ga based	Excellent	n.a.	Excellent

Commercial implementations have restricted the potential catalysts to:

- Light paraffins to olefins: promoted Pt/Sn on Al_2O_3 and Cr_2O_3 on Al_2O_3.
- Long chain paraffins: promoted Pt/Sn on Al_2O_3.
- Ethylbenzene to styrene monomer: promoted Fe oxides as unique choice [2,3].

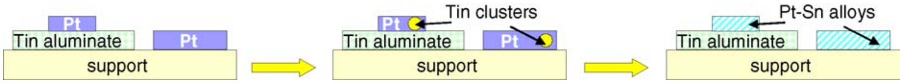

Fig. 2. Models of Pt–tin interaction.

2.1. Platinum–tin based catalysts

Typically, Pt/Sn is supported either on alumina or on either $ZnAl_2O_4$ or $MgAl_2O_4$.

- The catalyst is promoted with alkali metals and further promoters; scientific and patent literature reports and claims an impressive amount of combinations.
- The role of tin is to improve activity, selectivity and stability since it neutralizes acidity of supports, interacts electronically with Pt, and reduces the ''ensemble effect'' that favors coke formation [4,5]. Fig. 2 reports some model of the Pt–Sn interaction [6]. Increasing the loading of Pt + Sn, or increasing the Sn/Pt ratio or increasing the reduction temperature, the system shifts to the right. The system evolves to the left by increasing the carrier surface area [7–9].
- The catalyst preserves some bifunctional, acidic, noble-metal activity resulting in a moderate tendency to skeletal isomerization (e.g., *i*-C_4 *n*-C_4).

Some characteristics of the catalysts have significant impact on the industrial implementation:

- The Pt/Sn catalysts undergo a ''double mechanism'' ageing through coke fouling and sintering.
- The Pt/Sn catalyst can tolerate *several percentage points of coke* build-up, preserving enough catalytic activity, allowing period ''on stream'' of several *hours/days* before mandating a ''regeneration''. Large pore carrier helps coke build-up [4].
- The catalyst activity and its resistance to coke formation are increased by the presence of H_2 and commercial technologies can utilize H_2 recycle, despite a minor reduction of the thermodynamic driving force. Higher H_2 partial pressure reduces the formation of coke precursors (diolefins) presumably via H_2-spillover from Pt to the acidic centers of carrier [10].
- Coke formation is operationally solved by a regeneration cycle with streams of oxygen/steam/chlorine. Pt redistribution by chlorine (through surface mobility of Pt-chlorides) helps reduce the long-range ageing via sintering.
- The choice of optimal carrier supports its surface acidity (reduction of cracking and isomerization tendency), of hydrothermal stresses during regeneration cycles, of coke plugging of small pores etc. Alkali-neutralized and high-transition ($\delta - \theta$) aluminas or M^{2+}-aluminates are used commercially.

2.2. Chromium-based catalysts

Two potential supports are reported in literature: ZrO_2 shows low acidity and high thermal stability, and transition aluminas ($\delta - \theta$) selected as actual support for commercial catalysts.

The catalyst formulation includes promotion with alkali metals, which is fundamental for increasing the chromium active sites and decreasing the surface acidity (of both Cr and Al oxides). *K* has 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 nature of active site is debated: Cr^{3+}, both Cr^{3+} and Cr^{2+}, coordinatively unsaturated Cr^{2+} has been indicated as playing a role in the catalytic activity [6,11,12].

The selection of carrier, the ''design'' of its exposed surface, the optimization of promoters plays a fundamental role in the catalyst performances.

- Cr_2O_3 is the thermodynamically stable Cr state even in the presence of excess O_2.
- Different chromium species form on fresh catalyst on alumina-grafted Cr^{+6}, soluble Cr^{+6}, dispersed Cr^{+3} and crystalline Cr_2O_3.
- All Cr^{6+} species disappear completely in any reducing atmosphere (H_2, HC)

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 involves solid-state reaction of the active phase with the support with formation of α-$Cr_2O_3 \cdot 4Al_2O_3$. Fig. 3 shows a model of the chromia–alumina interaction [13].

The kinetics of the chromia reaction with alumina can be controlled to a certain extent by proper modification of the carrier surface. Several techniques are available. Fig. 4 refers to a surface ''inertization'', e.g., by tin deposited at the surface or by saturation of surface hydroxyls with silica (e.g., via surface titration with tetra-ethyl-ortho-silicate) [14,15].

3. Dehydrogenation in industrial applications

3.1. Catalysts constraints

The two promoted and optimized catalytic systems (Pt–Sn/Al_2O_3 and Cr_2O_3/Al_2O_3) show comparable performances in terms of selectivity to olefins.

A periodical regeneration with air is mandatory for all the catalysts to burn off the coke. The catalyst will therefore

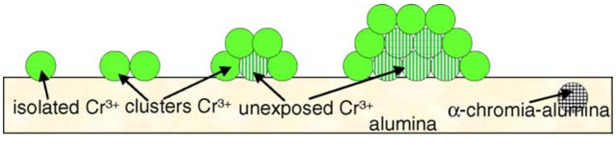

Fig. 3. Model of the chromia–alumina interaction.

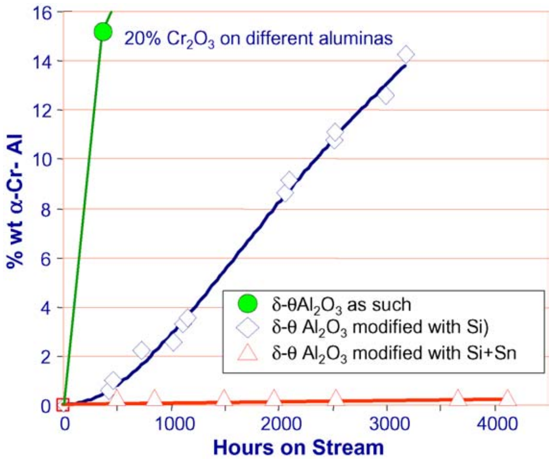

Fig. 4. Effect of carrier surface modification on the rate of α-chromia alumina formation.

undergo a cycle during which it will be exposed to a hydrocarbon atmosphere, followed by a period in the presence of oxygen (and/or some steam). It must therefore keep its morphological, structural, chemical stability under severe hydrothermal conditions. The length of the time on hydrocarbon stream is distinctive of the selected active phase: typical values are ‘‘minutes/hours’’ for Cr catalysts and ‘‘hours/days’’ for the Pt ones.

Irreversible deactivation due to sintering, volatilization of catalyst components and morphological or phase transformations of the support determines the active life of the catalyst, which usually is expected to be a few years.

3.2. *Reaction engineering constraints*

Heat must be supplied to the process stream at temperature above 550 °C in such a way that it reduces the reactor ΔT within the range of catalyst activity (<50–60 °C).

The conceptual choices for the *heat supply* are:

(a) Heat directly to the reacting mixture:
  - Tubes in fired furnaces.
  - Adiabatic reactors in series with interstage re-heating.

(b) Use of catalyst as a heat storage to be transferred to reactants:
  - Batchwise.
  - Circulating the catalyst itself.

Regeneration of ‘‘coked’’ catalyst in the presence of air can be achieved:

(a) Alternating gas atmospheres in the same reactor (several reactors in parallel are required).

(b) Moving or circulating the catalyst between different vessels (a reactor and a regenerator).

The integration of such concepts with the choice of catalyst is the basis for the commercial dehydrogenation technologies.

3.3. *Commercial dehydrogenation technologies*

Catofin (*Houdry technology*) commercialized by ABB Lummus [16,17]. The catalyst is Cr/Alumina by SuedChemie in adiabatic, fixed-bed reactors. Heat is stored on the catalyst during the regeneration step and released by the catalyst to the reagents during the reaction period. The reactors operate batchwise under vacuum, in cycles, quickly alternating between reaction, purging and regeneration (heating) periods. Continuous operation is achieved by using several reactors in parallel (conceptual scheme in Fig. 5a).

The reactor temperature profile is complex due to the alternating reaction taking place, but in principle, during the reaction period the temperature is expected to decrease with the time on stream and from the reactor inlet to the outlet.

Oleflex commercialized by UOP [18,19]. The catalyst is Pt/Sn on Alumina. The reactors are adiabatic, mobile beds in series with interstage re-heating in fired furnaces. Recycle of hydrogen helps reduce the coke formation on the catalyst.

For regeneration, the catalyst slowly downflows, and it is collected at the end of the last reactor, conveyed to the regenerator and then transferred back to the first reactor (conceptual scheme in Fig. 5b).

The reactor temperature profile is a typical sequence of re-heating steps.

STAR (*steam activated reforming*) by Krupp Uhde (formerly developed by Phillips) [20]. The catalyst is Pt/Sn on Mg/Zn Aluminates in tubular, fixed-bed reactors. The heat is supplied in the same way as a steam-reforming process by burning fuel in a fired furnace. Steam dilution is used at a total operating pressure of a few bar. For regeneration, more reactors in parallel are used (conceptual scheme in Fig. 5c).

The T-profile of the reactor is quasi-isothermal according to the balance of exchanged heat and the furnace temperature profile.

A new concept introduced by K–U consists of pushing paraffin conversion with a secondary reactor which is O_2/air blown for selectively burning the H_2 from the 1st reactor.

PDH (*propane dehydrogenation technology*) by Linde-BASF-Statoil [21,22]. The catalyst was originally Cr on alumina, now it is supposed to be Pt based on Mg(Al)O [23].

The reaction section includes three identical gas fired dehydrogenation reactors of the steam-reformer type (conceptual scheme in Fig. 5d). Two of these reactors operate under dehydrogenation conditions, while the third reactor is regenerated by combustion of the coke deposit on the catalyst with a steam/air mixture. The T-profile of the reactor is conceptually similar to the previous one.

FBD (*fluidized bed dehydrogenation*) by Snamprogetti-Yarsintez [24,25]. The catalyst is Cr on alumina, and the reaction system includes a fluidized bed reactor and a regenerator.

The reaction heat is supplied by the heat capacity of the ‘‘hot’’ (>650 °C) circulating catalyst, continuously moving to the reactor top from the bottom of the regenerator. The catalyst cools down again (<560 °C) from the bottom of the reactor to the top of the regenerator through a transfer line system.

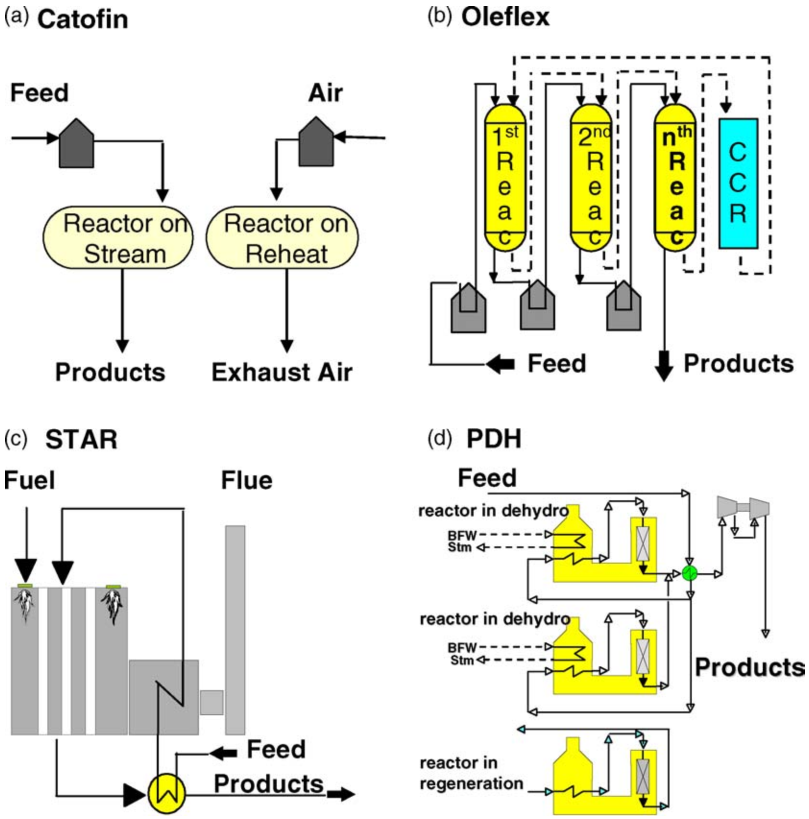

Fig. 5. Conceptual scheme of different reactor configurations.

A countercurrent flow of gas and solid both in the reactor and in the regenerator is obtained. Fig. 6 shows the catalyst cycle between reactor and regenerator and the sequence of involved chemical steps.

A bubbling fluidized bed shows typically a low pressure drop, uniform temperature, efficient heat exchange and a CSTR-like behavior. As a consequence, a significant spreading of gas contact times would be expected. Since consecutive reactions decrease the selectivity at increasing conversion, a widespread distribution of gas contact time would lower the selectivity at constant total conversion. A way to control backmixing is to ‘‘stage’’ the fluidized bed, approaching a series of CSTR, and a global PFR-like behavior. A higher number of ideal stages results in a behavior closer to a plug flow reactor. Staging is achieved by insertion of properly designed internal baffles.

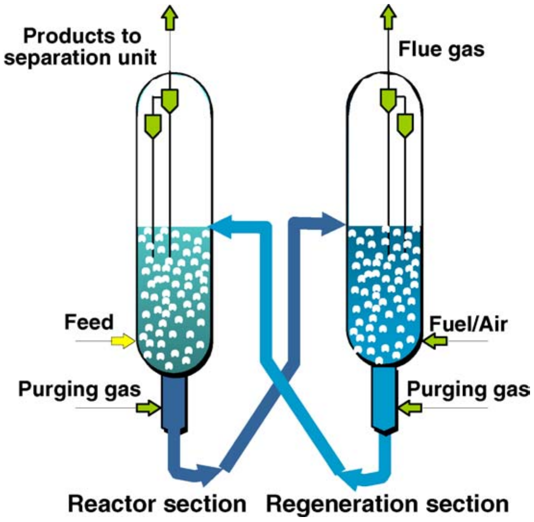

Fig. 6. The FBD reactor–regenerator system.

4. Future of olefin technologies

An impressive number of attempts by R&D are devoted to the development of improved or new routes to olefins. Only a few have real chances of being developed into commercial technologies because of the intrinsic technical difficulties as well as the economics connected with the feedstock.

4.1. Improvements of current technologies

Improvements of the dehydrogenation route involve new catalytic formulations and/or new reactor concepts. As *new catalysts* in ‘‘conventional’’ catalytic dehydrogenation, several possibilities are under consideration:

- Zeolite-type catalysts. Several ways have been claimed: modified, substituted, impregnated. Some examples are the use of Pt or Pt–Sn in ZSM-5 [26], Gallium in/on mordenite [27], SAPO-11 [28], MCM-41 [29].
- Gallium on oxides like TiO_2 [30], Al_2O_3 [31–33].
- Alternatively or together with new catalysts, new *reactor concepts* are evolving within catalytic dehydrogenation.

- Interstage H_2 combustion to overcome the equilibrium limits [34].
- Simultaneous dehydro-isomerization of *n*-butane to isobutylene [35].
- Membrane reactor via selective H_2 permeation. Several R&D groups (at Alcoa, Laval Univ., Salford Univ., USC, Waseda Univ.) are active in a ‘‘wide’’ approach that includes the catalytic membrane reactor with and without permeate H_2 combustion [36].

4.2. Alternative routes to olefins

New routes to olefins are under investigation:

- The catalytic dehydrogenation of ethane to ethylene as an extension of the ‘‘conventional’’ C_3–C_4 technologies has to face the low thermodynamic conversion below 700 °C (above the predominant thermal route) and the consequent low ethylene concentration in the reactor outlet. Therefore, the economics depend upon the selected separation route. Two different proposals are: (a) new separation techniques, like the complexation with silver salts [37], or the integration with downstream direct use of ‘‘diluted’’ ethylene (e.g., by alkylation of benzene to ethylbenzene) [27,38,39].
- Non-conventional cracking processes to ethylene are being studied, such as the use of fluidized bed reactors (Lurgi Sand Crackers), a catalytic steam cracking on KVO_3/In_2O_3 (Vniios), on Ca–Fe aluminates (Toyo), and on various zeolites (Asahi).
- Oxidative dehydrogenation of paraffins by burning the produced H_2, pushes forward the thermodynamic limit. As O_2 source both molecular and ‘‘structural’’ oxygen are proposed [40]. Several groups [41–44] are investigating the ethylene formation via short-contact-time (millisecond) catalytic partial oxidation.
- Considerable interest is associated with the production of olefins from methane. The ‘‘old’’ studies of the direct route via the methane oxidative coupling are largely abandoned due to the low yields, and much more attention is paid to the ‘‘indirect’’ routes through methanol-DME, like in the newly commercialized technologies MTO (UOP, Norsk Hydro [45]) and MTP (Lurgi [46]).
- To be considered is the route of methanol homologation to ethanol, further dehydrated to ethylene (old work by Gulf and Shell [47]). New studies (1990s) involve the use of Co, Ru, Rh–Ru.
- Another way to ethylene from syngas is through a modification of the high temperature Fischer–Tropsch applied in Mossel Bay, or as in the studies in the 1980s by Dow/UCC syngas to EtOH and higher alcohols on MoS_2 [48] or the Ruhrchemie (1970s–1980s) on Fe/Ti/Zn [49].

5. Challenges to olefins: drivers and limits

When evaluating new approaches for the production of propylene from propane, it has to be taken into account that the economic breakeven will be determined by the cost of refinery propylene. New catalyst and/or reactor configurations should reach selectivities above 95% at conversion so high as to significantly reduce the separation and recycle costs.

Mandatory in any case is ‘‘low cost’’ propane that is more likely to be available at a ‘‘remote’’ location. The competition from emerging technologies like Metathesis, Olefin Interconversion, MTP has also to be considered.

Alternative ethylene processes have to show very significant reduction of capital and utility costs in order to compete with the mature steam cracking economics and reliability.

The potential of oxidative dehydrogenations has to overcome the limit of selectivities and it is actually a difficult task. Furthermore, the cost of oxygen has to be considered in chemicals consumption.

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