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The oxidative dehydrogenation of ethane and propane as an alternative way for the production of light olefins

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Abstract

The main aspects of ethane and propane oxydehydrogenation are discussed. The performance of the various catalysts described in the literature has been compared.

1. Introduction

The demand for olefins and products made from olefins is increasing, and the existing capacity might become insufficient to meet this demand. Until recently, light olefins (along with methane and aromatics) have been obtained from steam cracking of natural gas and of naphtha and from FCC in oil refining. These established processes are extremely capital-intensive; the products have to be separated and purified for use in downstream plants that require fairly pure feedstocks, and the supply and demand for each coproduct are rarely in balance. Consequently, the incremental future demand for olefins might be satisfied by direct productions of individual or specific cuts of olefins by selective processes. In addition, integration of these plants with downstream olefin conversion plants can be advantageous in many cases [1].

Commercial processes for the synthesis of light olefins through paraffins dehydrogenation are available, even though their main application is for isobutene synthesis. In the case of propane, a couple of plants are on service, while in the case of ethane thermodynamic constraints would force to operate at impracticable temperatures. The commercial catalytic dehydrogenation processes suffer from several limitations, especially: i) thermodynamic limitations on paraffin conversion; ii) side reactions such as thermal cracking; iii) strongly endothermic reactions to which large amounts of heat must be supplied at temperatures above the reaction temperature; iv) formation of coke on the catalyst which requires frequent regeneration. With the goal of overcoming these limitations, research is proceeding along some directions, of which the following are the most likely to be implemented: i) optimization of current dehydrogenation technologies, to obtain more selective, stable and environmentally safe catalysts and lower investments and utility costs; ii) dehydrogenation coupled with hydrogen oxidation, to supply the heat of reaction inside the catalytic bed while avoiding overheating and to shift the equilibrium toward the desired products; iii) oxidative dehydrogenation, to overcome thermodynamic limitations, operate at low temperature with an exothermic reaction, and avoid frequent catalyst regeneration; iv) membrane-assisted dehydrogenation and oxidative dehydrogenation,

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to obtain high conversion at low temperatures and to conduct the reactions and separations in the same equipment.

2. Oxidative dehydrogenation

Oxidative dehydrogenation takes place in the presence of an hydrogen acceptor such as molecular oxygen in the reaction medium. This process has the potential to overcome the major technical problems associated with pure dehydrogenation. However, other problems arise, related to the removal of the heat of reaction, control of selectivity due to the formation of undesired oxygenated by-products and carbon oxides, the flammability of the reaction mixtures, the possibility of run-away of the reaction. No commercial plants for the oxidative dehydrogenation of light paraffins are believed to be currently operational, although pilot or demonstration plants have been built and operated. A great variety of catalysts have been formulated and tested [1–42]. Curiously, best catalytic systems for ethane oxydehydrogenation are not the optimal ones for higher paraffins, and vice versa. This is likely due to the fact that the different features of both reactant paraffins and formed olefins make the mechanism of olefin formation and degradation different in the two cases.

2.1. Oxydehydrogenation of ethane

Some of the catalysts developed for the reaction of methane coupling are also active in the ethane oxydehydrogenation. In other cases, entirely new catalytic systems have been developed. The performances of catalysts reported in literature is summarized in Figs. 1 and 2, which report the highest achieved yields in a selectivity vs. conversion plot, and the levels of maximum productivity obtained at the average operative temperature for each system.

Generally, we can classify the catalysts into:

a) Catalysts based on ions and oxides of Group IA and IIA metals, which are also active for meth-

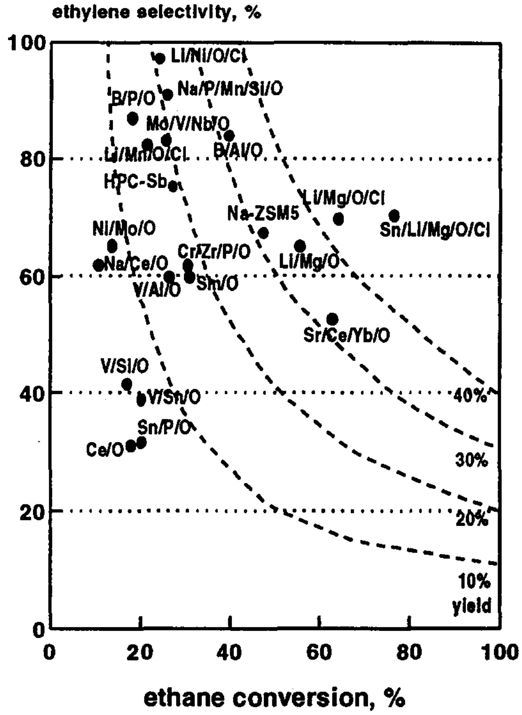

Fig. 1. Best yields of ethylene reported in literature for the various catalytic systems.

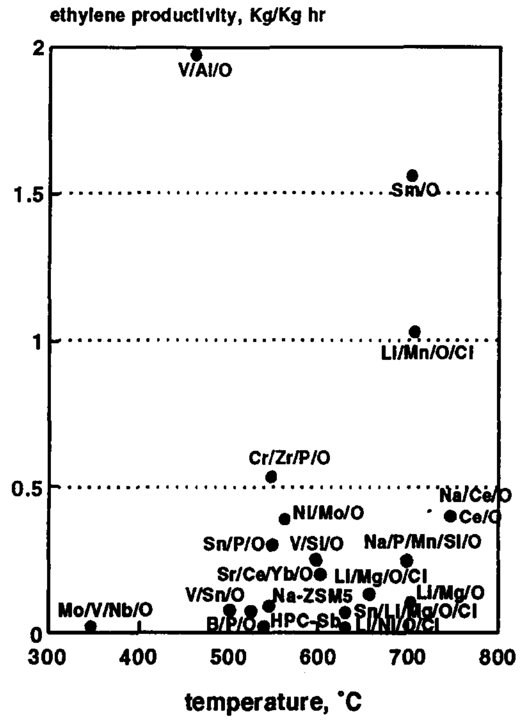

Fig. 2. Ethylene productivity on the various catalytic systems.

ane coupling [2–10]; these activate ethane at temperatures usually higher than 600°C to form ethyl radicals, which then further react in the gas phase. The most successful of these catalysts is the Li/Mg/O one. The mechanism does not involve a classical redox-type cycle; thus, no furnishing of bulk oxygen occurs, and the catalyst only is involved in C–H heterolytic scission with radical formation, analogously to that occurring with methane. The role of the generation of Li^+–O^- centers capable of abstracting a H· and forming the ethyl radical. However, a progressive loss of Li occurs at temperatures higher than 700°C. Such catalysts could be employed after a methane coupling reactor, in order to increase the yield to ethylene through oxydehydrogenation of formed ethane. Catalysts for coupling operate at 700–800°C, and the hot outlet stream could be fed to a downstream catalytic or thermal oxydehydrogenation reactor.

High selectivities and yields to ethylene can be achieved with this catalytic system, above all when chlorine-containing compounds are also fed to the reactor, or when the catalyst is doped with halides [9,10]; the promoter effect is maintained by continuous feeding of the chlorine, which modifies the catalyst surface [11]; chlorine radicals are thought to favour the homogeneous decomposition of ethyl radicals to ethylene. Yields as high as 34% to ethylene could be achieved [3,10]; however, the use of chlorine is limited by problems related to equipment corrosion.

The selectivity to ethylene is increased with temperature; this is due to the fact that the formed ethyl radical at high temperature (600–700°C; above 700°C homogeneous overoxidation of ethylene decreases the selectivity) desorbs and forms ethylene in the gas phase via reaction with molecular oxygen; the high stability of ethylene and the contribution of the heterogeneously-initiated homogeneous reactions lead to the observed high selectivity. At lower temperatures the formation of a surface ethoxy species is preferred, precursor of CO_x formation.

A further aspect of this system is the formation of H_2 under oxidative conditions [7,12]. H_2 can be formed either via thermal or catalyzed dehydrogenation; also, a contribution was proposed due to water gas shift equilibrium (over rare earth oxides) or of intermediate ethoxy species decomposition to CO, C and H_2. Recently [13], it was found that catalysts like Ca/Ni/K/O and Li/Mg/O are active in the water gas shift at the temperatures at which ethane oxydehydrogenation occurs.

Other systems that are active at temperatures higher than 600°C are Li_2O/TiO_2, LiCl/NiO, $LiCl/MnO_2$ and $LiCl/Sm_2O_3$. Dopants other than Li^+ have been reported: SnO_2, Na_2O, lanthanides (mainly CeO_2) [14].

b) Catalysts based on transition metal oxides [15–23]. Rare earth oxides are remarkably active [12,15], and yield ethylene with high productivity and good selectivity. In addition, they exhibit a very high stability even at high temperature. Doping Sm_2O_3 with alkali metals gives the best performances. These systems are believed to operate with a mechanism similar to that of Li/Mg/O catalysts.

Also $Na_4P_2O_7/MnO_x/SiO_2$ catalyst operates at very high temperature; such system is claimed for cyclic operation with ARCO [16] or Phillips [17] technology in circulating-bed applications, where higher selectivities are achieved by dividing the reaction into two stages: i) oxydehydrogenation of the paraffin in the absence of molecular oxygen and ii) regeneration of the catalyst by treatment with air.

In vanadium oxide-based systems the catalyst is reduced by interaction with the hydrocarbon, through a classical redox cycle [18–23]. These systems can activate ethane at temperatures as low as 400°C, and the entire reaction is heterogeneous, hence controlled by the catalyst; the contribution of homogeneous reactions only occurs at the highest temperatures. Mixed oxides of Mo/V/Nb were shown to be active in ethane oxidation at temperatures as low as 250°C, with selectivity to ethylene higher than 80%. However, the reported experimental conditions lead to an ethylene productivity which appears to be too low to have practical application. Mo/V/Nb/O also forms considerable amounts of acetic acid. Alumina-

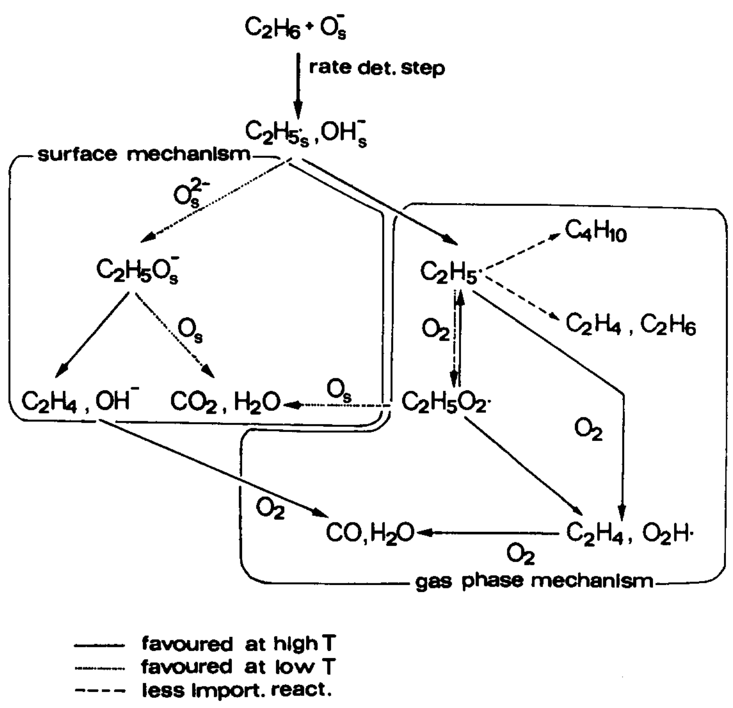

Fig. 3. Summary of the mechanisms proposed in the literature.

supported vanadium oxide exhibits an high activity in ethane conversion, with fairly high productivity.

Fig. 3 summarizes the mechanisms proposed in the literature for the two classes of catalysts, operating at low and high temperature.

2.2. *Oxydehydrogenation of propane*

Most catalysts described in the literature are based on vanadium oxides as the main component [24–38]; particular attention has been given to the magnesium vanadates. A summary of the catalytic performance described in literature is given in Figs. 4 and 5.

A general feature of most catalytic systems is that the selectivity to propylene is decreased on increasing the propane conversion (Fig. 6). This is likely due to the presence of labile allylic hydrogen atoms in the formed propylene which acts as a center for consecutive oxidative attacks. This conversion/selectivity trade-off is one of the main differences between ethane and propane (as well as other higher paraffins).

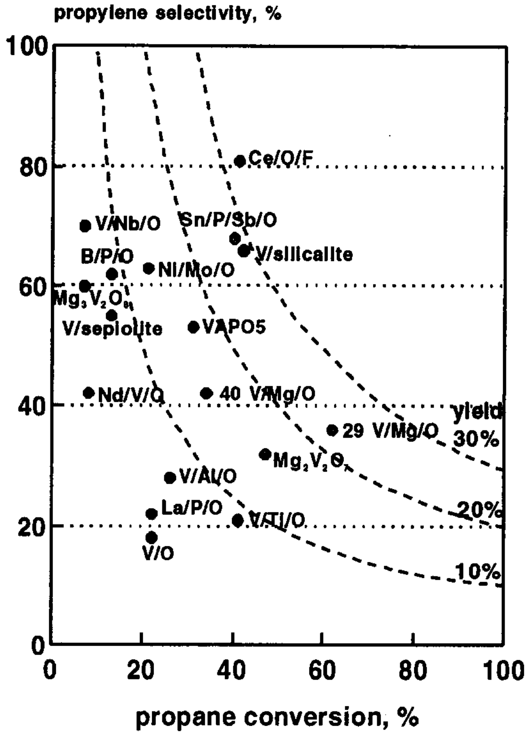

Fig. 4. Best yields of propylene reported in literature for the various catalysts.

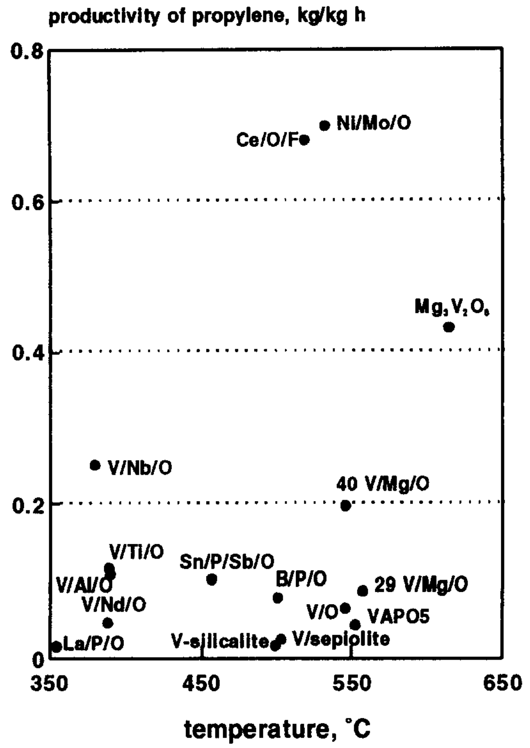

Fig. 5. Propylene productivity on the various catalysts.

Recently [32], it has been pointed out that the non-catalyzed thermal oxidative pyrolysis of propane gives an overall yield to olefins (ethylene and propylene, approximately 1/1) in a quartz apparatus higher than that achieved by whichever catalytic system, and at a temperature only 50–100 degrees higher than that usually employed for the catalyzed reaction. This makes doubtful whether is really advantageous to develop a catalyst for this reaction. However, it has to be pointed out that in the author's apparatus the operating mechanism is a surface-initiated homogeneous reaction. Other authors have pointed out that higher yields to propylene can be achieved with a post-catalytic homogeneous reaction [34].

The following is a summary of the catalytic performances of the various systems.

a) V_2O_5 is not a good catalytic system for the paraffins oxydehydrogenation, but the spreading of the oxide onto a support with basic features (such as sepiolite) or over alumina, with the formation of centers with peculiar chemical–physical features and reactivity lead to a more selective catalyst [25,29]. Oxygenated compounds are not formed. These catalysts are active at relatively low temperature (in the 350–450°C range); however, selectivity not higher than 40% were obtained, and only at low levels of conversion, with low overall productivity and yield (not higher than 8–9%).

b) Mg/V/O catalysts have been the object of several investigations in recent years. This system is active in the 500–600°C temperature range, and with respect to V_2O_5 are characterized by improved basicity and surface area [26–28,30–33]. This catalyst also leads to the formation of oxygenated by-products. Selectivity to propylene as high as 60% can be reached, with yields of 20% and fairly high productivity. The selectivity generally decreases with conversion.

Some disagreement exists in literature about the nature of the preferred structure, exhibiting the best catalytic performance. The published results can be summarized as follows:

- $Mg_3(VO_4)_2$ (Mg orthovanadate) spread over MgO is considered by some authors to be the most active and selective composition in n-butane oxydehydrogenation (propane

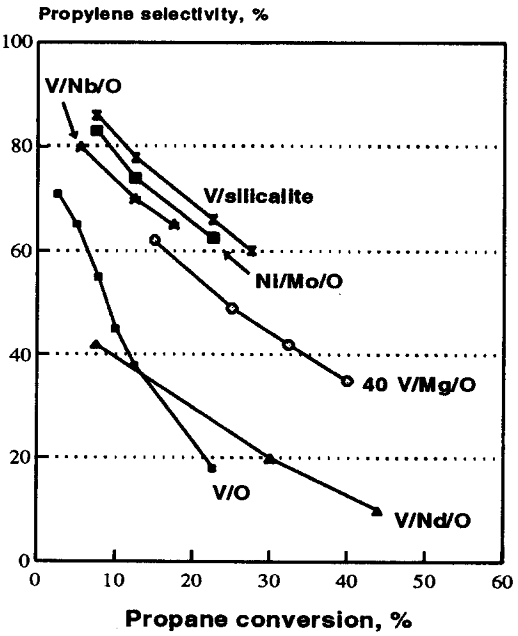

Fig. 6. Selectivity vs. conversion plot for various catalysts.

was instead much less sensitive to the catalyst structure), due to the presence of isolated VO_4 units which are not active in oxygen insertion onto activated hydrocarbon (oxygenated hydrocarbons are precursors of CO_x formation) [26–28,33].

- $Mg_2V_2O_7$ (Mg pyrovanadate) was reported to exhibit a superior catalytic performance in terms of selectivity; the scale of selectivity was consistent with the vanadates redox properties: the highest the cation reducibility (the redox couple V^{4+}/V^{5+} is supposed to be the one catalytically operating), the highest the selectivity [30,31].

Indeed, it is likely that factors other than the crystalline structure of the vanadates can contribute in affecting the catalytic performance, i.e.: i) the presence of small undetected amounts of V_2O_5 (the preparation of pure reference phases is indeed a hard task); ii) the presence of alkali metals impurities coming from the raw materials employed for the preparation; iii) the surface enrichment in either magnesium or vanadium; iv) particle size and morphology, which can be affected by the thermal treatment; v) the method of preparation employed.

c) V/Nb/O catalysts operate at 380–450°C; they exhibit good productivity to propylene and apparently no formation of oxygenates [35–37]. Nb_2O_5 itself is a selective catalyst, and the addition of vanadium improves the activity while maintaining the selectivity high. The active sites are assumed to be vanadium ions in the form of small clusters, and neighbouring surface Nb ions improve the selectivity. Selectivities as high as 90% could be reached at low propane conversion in samples prepared by 'melt method' (solid state reaction between NH_4VO_3 and hydrated niobia).

d) Metal-zeolites [38,39]; isolation of oxidizing sites is realized by dispersion of vanadium ions inside matrixes catalytically inert, such as zeolites or zeolitic-like compounds. V–silicalite exhibits relatively high yields, but low productivity; in VAPO-5 isolated VO_4 tetrahedron structures have been proposed to be the active and selective sites in paraffins oxydehydrogenation.

e) Molybdates. Bismuth molybdates and vanadomolybdates are known to successfully operate in the oxidation and ammoxidation of propane to acrolein, acrylic acid and acrylonitrile [40]. Nickel molybdates exhibit a very high activity, with 60% selectivity to propylene; oxygenated products also form [41]. Magnesium molybdates are claimed by Dow Chem. Co. for butane oxydehydrogenation in two steps, with 80% overall yield to butadiene plus butenes [42].

3. Conclusions

The problem of propylene stability towards consecutive unselective oxidative attack makes the finding of a suitable catalyst for propane oxydehydrogenation a hard task: several systems have been found that can activate the paraffin, but not one able to save the formed olefin. It is likely that best conditions might come from the coupling of i) an heterogeneous system able to activate propane at (relatively) high temperature, and ii) an homogeneous decomposition of desorbed radical species to propylene; in fact, low temperatures favour the surface-catalyzed further oxidation of propylene. This happens because the activation energy for the gas-phase dehydrogenation is higher than that one for the heterogeneous combustion.

In the case of ethane oxydehydrogenation, a surface-initiated, homogeneous mechanism leads to high selectivities to ethylene. The possibility of development of a process competitive to the steam-cracking of ethane likely depends on the development of stable catalytic systems able to operate in the absence of corrosive or toxic gas-phase promoters, giving the olefin with high selectivity and acceptable productivity. However, it is obvious that hard operating conditions (more favourable to the selectivity) might render the paraffin oxydehydrogenation less competitive with the other conventional processes. The minimization of CO, the most difficult by-product to separate, is also an important task.

4. Acknowledgements

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