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Some aspects that affect the selective oxidation of paraffins

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Abstract

This paper examines the most important factors that affect the functionalization of light alkanes by means of selective oxidation. The state-of-the-art in paraffin oxidation and the main features that affect the choice of the reactor and the process configuration are discussed.

Keywords: Selective oxidation; Paraffin; Functionalization

1. Introduction

Catalytic oxidation is a very important technology, widely employed for the functionalization of alkenes and aromatics, the most important raw materials for the petrochemical industry [1]. In future, however, the petrochemical industry will probably directly use alkanes, which are more economical than the corresponding olefins, comprising readily available raw materials with low toxicity as compared to aromatics. Moreover, the demand for olefins is increasing, and the existing capacity (principally from steam-cracking of naphtha and FCC in oil refining) may well become insufficient to meet this demand. Consequently, the increased future demand for olefins is likely to be satisfied mainly by direct production in plants dedicated to individual olefins.

This review examines some fundamental aspects in the conversion of paraffin hydrocarbons to oxidized products. Particular attention will be given to those aspects that are related to the choice of the reactor technology and process configuration. Some aspects in the reaction network that may affect the selectivity to the desired product are also discussed, by making a comparison with the only process of selective alkane oxidation that has been commercialized up to this time, namely the oxidation of *n*-butane to maleic anhydride [2].

2. State-of-the-art and challenges in the oxifunctionalization of paraffins

Many examples of catalysts, active in the selective oxidation and oxidehydrogenation of paraffins, have been reported in patents and in scientific literature [3,4]. However, low yields in the final product are frequently observed and, in almost all cases, the productivity of these processes is far from that of industrial interest. Indeed, many problems in the oxidation of paraffins, concerning the activation of the saturated organic substrate and its selective transformation to the desired product, remain to be solved. For example, one of the main problems concerns the reactivity of the product of partial oxidation, which is higher than that of the reactant itself. This makes it

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Table 1
Industrial processes and processes under study or development for the oxifunctionalization of light paraffins (C_1–C_6) in the petrochemical industry

	Raw material	Product	Phase	Stage of development
1	Cyclohexane	Cyclohexanol, one	Liquid, hom[a]	Industrial
2	*n*-Butane	Acetic acid	Liquid, hom	Industrial
3	*n*-Butane	Maleic anhydride	Gas, het[b]	Industrial
4	Methane	Chloromethanes	Gas, het	Industrial
5	Methane	Methanol	Gas, het/hom[c]	Pilot plant
6	Methane	Syngas	Gas, het/hom	Research
7	Methane	Ethylene	Gas, het/hom	Pilot plant
8	Ethane	1,2-Dichloroethane, vinyl chloride	Gas, het	Research
9	Ethane	Acetic acid	Gas, het	Research
10	Ethane	Ethylene	Gas, het/hom	Research
11	Propane	Acrylic acid	Gas or liquid	Research
12	Propane	Propyl alcohol	Liquid, het or hom	Research
13	Propane	Acrylonitrile	Gas, het	Demonstration plant
14	Propane	Propylene	Gas, het	Research
15	*n*-Butane	Butadiene	Gas, het	Industrial, abandoned
16	Isobutane	Methacrylic acid	Gas, het	Pilot plant
17	Isobutane	Isobutene	Gas, het	Research
18	Isobutane	*t*-Butyl alcohol	Liquid, het or hom	Research
19	*n*-Pentane	Phthalic anhydride	Gas, het	Research
20	Cyclohexane	Cyclohexanone	Liquid, het or hom	Research

[a] hom – homogeneous.
[b] het – heterigenous.
[c] het/hom – the likely presence of a mechanism initiated on the catalyst surface and transferred in the gas phase.

difficult to stop the reaction at the desired product and avoid its further nonselective oxidation under the conditions at which the reactant is activated.

Table 1 summarizes the reactions of oxidation of alkanes which are actually employed in the petrochemical industry, as well as those that are under study and development (for the synthesis of intermediates and of base building blocks, i.e., olefins).

In most cases, which are still at the research stage, the main problem is the development of a catalyst with good catalytic performance, in terms of both activity and selectivity to the desired product, in order to obtain acceptable levels of productivity and reduce the operating costs associated with the purification of the product and possible recycling of the unconverted reactant. The second problem is associated with the catalyst lifetime, which is sometimes limited by the presence of the irreversible phenomena of deactivation.

In some cases the technology is already available, but has not yet been industrially exploited, as in the case of the oxidation of isobutane to methacrylic acid, and oxidative coupling of methane to ethylene. One reason for this, besides the reluctance to substitute reliable and profitable technologies, is the lower performance generally obtained when starting from paraffin, as compared to the processes based on traditional raw materials which lower the profit due to the low cost of paraffin. It is generally agreed that the possibility of wide industrial development of processes from light alkanes is strictly related to the following technical and economic conditions:

1. development of a technology which can conveniently manage the high exothermicity of the reaction;
2. construction of the plant in a country where natural gas is available at low cost, or at least not far from the deposit, in order to lower the high penalty associated with transportation costs;
3. an even more profitable ratio between the costs of natural gas and oil; and

4. the availability of low-cost oxygen for those applications that require recycling of the unconverted hydrocarbons.

On the other hand, in some cases, the greatest opposition to the development of new oxidative processes arises on account of the loss of valuable coproducts, as in the case of oxidehydrogenation as an alternative to dehydrogenation. The increasing demand for hydrogen for refinery applications is a convincing reason for improving existing dehydrogenation technologies rather than developing alternative ones which do not yield hydrogen.

Finally, some cases are no longer of industrial interest, such as that of the synthesis of butenes and butadiene from *n*-butane (there is presently an excess supply of these olefins with respect to the market demand, and interest is now directed more towards hydrogenation of the olefins to *n*-butane), or of the synthesis of 1,2-dichloroethane and vinyl chloride through direct oxychlorination of ethane. In the latter case, problems that exist are associated with the high ethane-to-HCl ratio which must be fed in order to achieve complete conversion of HCl (and avoid the use of expensive corrosion-resistant materials downstream from the reactor), with consequent costs associated with the recycling of unconverted ethane, and the lower selectivity obtained with respect to the process from ethylene. The oxychlorination of methane also has been industrially applied, even though interest in this reaction is rapidly decreasing due to the ban on toxic halomethanes. The reaction has however been proposed as an intermediate step in the conversion of methane to liquids [5].

Moreover, it has to be mentioned that in some cases, the advantage in the development of a process of direct paraffin oxidation would not only lie in the lower cost of the raw material, but also in the process simplicity and the use of less harmful raw materials and intermediates. This is the case of the synthesis of methyl methacrylate, which is now produced at a relatively low cost, with completely damped investment costs, but with a rather complex process, and high negative environmental impact due to the use of toxic chemicals.

Following are the targets, which, if reached, would allow transfer of the reactions under research to industrial exploitation:

1. *Achievement of high productivity and/or high selectivity to the desired product.* The most striking example in this direction is the synthesis of ethylene by means of methane oxidative coupling, where a yield of 30 mol% with 70–80 mol% selectivity has been claimed as the minimum to make the process economically feasible with respect to steam cracking of naphtha; at the moment, yields <22–24 mol% under stationary conditions have only been reported [6].
2. *Development of stable catalysts*, which exhibit industrially acceptable lifetimes, and can be easily regenerated. This is the case of catalytic systems that possess intrinsic multifunctional properties, which have demonstrated the ability to activate the saturated organic substrate and to insert oxygen in it (or abstract hydrogen in the form of water). These peculiar properties are reached through the formation of crystalline structures that are often thermodynamically non-stable, due to:

(a) A structural organization into ionic molecular-like entities, containing both electron-acceptor oxidizing metal moieties and a second metal responsible for the formation of the ionic charge, which tend to decompose into separate oxide components. Heteropolycompounds belong to this class of compounds. The development of a structurally stable heteropolycompound (or of a heteropolycompound stabilized through doping or supporting) would open many possibilities in the field of oxifunctionalization of alkanes. Heteropolycompounds have been claimed for the selective oxidation of isobutane to methacrolein and methacrylic acid [3,7].

(b) A structural organization into acid or neutral frameworks which host in their lattice guest ions with redox properties, and under severe reaction conditions tend to be eliminated from the lattice. Crystalline metal silicates belong to this class of compounds. Vanadium silicalite is known to be active and selective in the oxidehydrogenation of propane to propylene [3], but under certain reaction conditions the vanadium can be eliminated and the catalyst loses its peculiar properties. The same occurs for titanium silicalite, which is known to catalyze the liquid-phase oxidation of paraffins with H_2O_2 [3].

Problems of this kind might be overcome by developing particularly active catalysts, which are capable of activating the paraffin substrate at relatively mild reaction conditions, under which the catalyst itself is structurally stable. This is the case of $(VO)_2P_2O_7$, the only catalytic system active and selective in the oxidation of *n*-butane to maleic anhydride [2]. The structural organization into a mixed oxide with a peculiar combination of acid and redox properties allows the paraffin to be activated selectively under conditions at which the catalyst is stable.

3. *Development of oxidation catalysts which quickly furnish high amounts of oxygen* to the activated paraffin substrates without undergoing structural collapse and are able to recover quickly the original oxidation state by contact with oxygen. This would allow two-stage oxidation of the organic substrate, thus achieving better control of the selectivity.
4. *Absence of CO among the by-products.* In the oxidehydrogenation of light paraffins to olefins, the by-products CO_2 and CO can be easily separated from the paraffin/olefin mixture by absorption in basic water and a demethanizer column under pressure, respectively. However, in case of methane oxidative coupling or ethane oxidative dehydrogenation, the separation of CO from the unreacted paraffin and the olefins thus produced, may become rather expensive. In case CO is not immediately separated, as for instance in an integrated process of production of the olefin followed by its transformation to some other chemical, the production of CO has to be minimized. In fact, the formation of a minimum amount of inert gases makes it possible to decrease the purge stream in case the unconverted paraffin is recycled. Therefore, the absence of CO, through the development of a suitable catalyst and optimization of the reaction conditions, would allow a considerable decrease in investment and operating costs.
5. *Absence of traces of corrosive by-products* (i.e., organic acids) when the reaction is aimed at the synthesis of products which are themselves noncorrosive, i.e., olefins. This might allow considerable saving in the cost of materials for construction of reactors and downstream apparatus.
6. *Use of the same reactor and separation technology which are now used for the conventional process*, with only minor expenses for revamping. This is the case of the ammoxidation of propane to acrylonitrile, where comparable reaction conditions might allow the use of the same reactor as for propylene ammoxidation, and a similar distribution of products might lead to minor modifications in the separation section.
7. *Integration of the oxidation plant* with a process that employs the product of partial oxidation, and can operate without purification of the effluent stream of the oxidation reactor. This might facilitate the process flow-sheet, with less investment and operating costs. Some cases will be discussed in the following sections.

3. Thermodynamics of the oxifunctionalization of paraffins

One of the most convincing arguments about the importance of developing oxidative processes for the functionalization of paraffins is illustrated in Fig. 1, which gives a comparison of the heat of reactions for some technologies presently employed and for the corresponding alternative oxidative processes, aimed at the synthesis of some specific intermediate for the petrochemical industry. Examples are given for:

1. the synthesis of methanol by the conventional technology of methane steam-reforming, followed by syngas conversion to methanol, and the alternative direct oxidation of methane to methanol;
2. the steam-cracking of natural gas to yield ethylene, converted to acetaldehyde through the Wacker process and then oxidized to acetic acid, and the alternative one-step oxidation of ethane to acetic acid; and
3. the synthesis of acrylonitrile by means of propane dehydrogenation, followed by ammoxidation of the olefin, compared to the direct ammoxidation of propane.

It is evident that using endothermal processes (steam-reforming, steam-cracking and dehydrogenation) for the production of chemical building blocks, followed

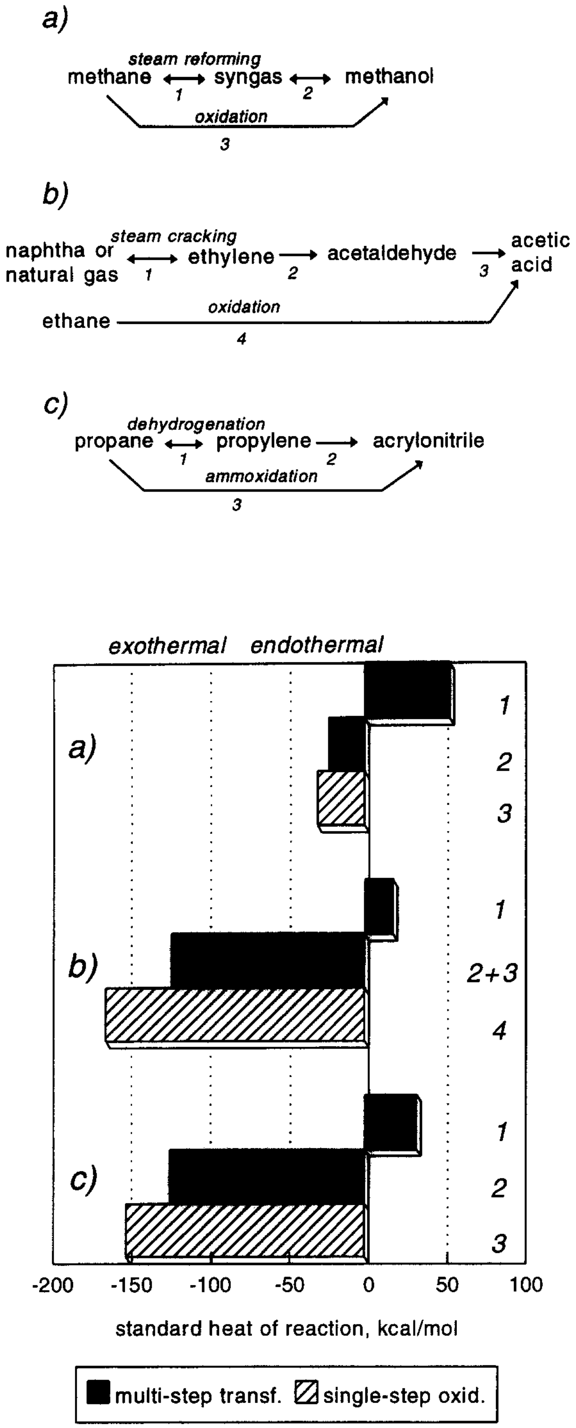

Fig. 1. Industrial multi-step transformations of paraffins to intermediates for the petrochemical industry for (a) alternative single-step oxidative transformations and (b) corresponding heats of reaction.

by the exothermal transformation to other chemicals is less logical than a direct single exothermal step of transformation. However, this is a simplistic approach to the problem, because other factors have to be taken into account, and also because the olefin intermediates are employed for a variety of applications. It is therefore necessary to have processes aimed at their production. Nevertheless, there are some further considerations which have to be taken into account:

1. The endothermal, energy-intensive processes for the production of building blocks for the petrochemical industry (syngas and olefins) require very large plants, with high investment costs. Therefore, when there is a market demand for some compound, it is worthwhile to set up a specific, middle-sized plant for its production with new technology which directly transforms natural gas components.
2. The refinery is now undergoing dramatic changes, as a consequence of the changes in market demand for reformulated gasolines and diesel fuels. Modifications in the severity in FCC and catalytic reforming are changing the supply of olefins and aromatics for the petrochemical industry to face increasing demand for isobutene, high purity olefins and hydrogen, and decreasing demand for aromatics. These modifications have had a considerable effect on the market value of olefins, with variations that are hardly predictable in the near future.

The possibility of developing a process that does not depend on the olefin supply, i.e., starting directly from the natural gas components, would allow the problems associated with these price variations to be avoided.

3. Interest is now growing in processes for the production of base chemicals that might overcome thermodynamic barriers associated with strongly endothermal processes. As shown in Table 1, exothermal partial oxidation of CH_4 to CO/H_2 as an alternative to methane steam-reforming, and oxidehydrogenation of paraffins as an alternative to dehydrogenation are transformations which take advantage of more favourable equilibria and can occur at much lower temperatures.

4. Choice of the reactor

The high exothermicity of oxidative reactions poses the problem of removal of the heat released. The overall amount of heat is affected considerably by the selectivity obtained. This is because the unselective combustion reactions are much more exothermal than the selective reactions. Fig. 2a shows the heat of reaction as a function of the selectivity to ethylene, synthesized by means of ethane oxidehydrogenation. Three cases that were considered are: CO as the by-product; CO_2; and equimolar amounts of CO and CO_2. The values reported were calculated at 550°C. Also given in the figure are the approximate heat ranges for which the different types of reactors (fixed-bed, multitubular fixed-bed, and fluid-bed) operate efficiently. It is shown that if a theoretical 100% selectivity were achieved, the fixed-bed reactor could be satisfactorily employed. More realistically, however, it is necessary to choose fluid-bed technology, which is more suitable for efficient heat removal and maintenance of isothermal conditions in the catalytic bed. Choice of the fluid-bed reactor also allows the danger associated with the possibility of run-away to be minimized.

Fig. 2b gives the same evaluation in the case of the ammoxidation of propane to acrylonitrile. In this case, a further variable to be considered is the side combustion of ammonia to nitrogen, which is not highly exothermal but can be the cause for the start-up of highly exothermal hydrocarbon combustion, with danger of run-away. It is known that when ammonia is lacking in the gas phase due to its transformation to nitrogen and under the reaction conditions necessary for the ammoxidation of propane, the propane and propylene (intermediate product in the one-step transformation of paraffin to acrylonitrile) are quickly burned to carbon oxides. In this case, therefore, the key factor in control of the reaction is the development of a catalyst that is not active in the combustion of ammonia, and allows operation with ratios between the reactants close to stoichiometric ones. However, it is shown that the high exothermicity of the reaction

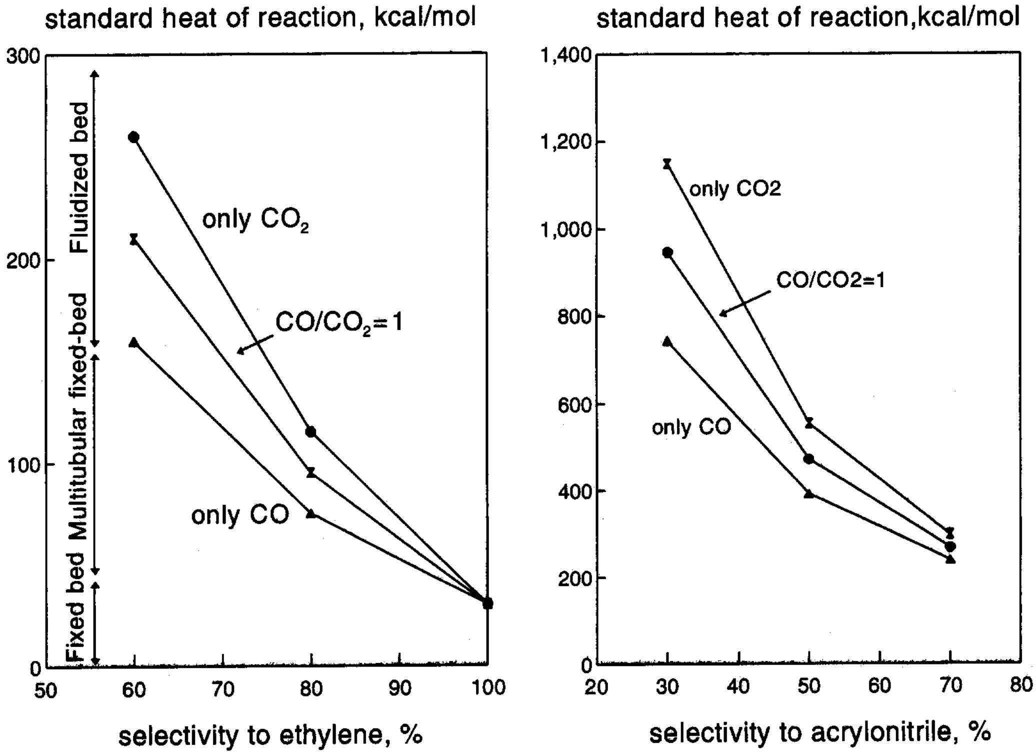

Fig. 2. Heat of reaction as a function of the selectivity for (a) the oxidehydrogenation of ethane to ethylene and (b) the ammoxidation of propane to acrylonitrile.

makes the choice of the fluid-bed reactor compulsory. The data reported in Fig. 2b were calculated at 470°C, taking into account the formation of propylene and the combustion of ammonia.

The problem of selectivity is very important, as it affects the economics of the reaction. Higher selectivities mean better exploitation of the reactant, lower operating costs associated with separation and recycling of unreacted reactants, and lower plant volumes. In the case of oxidative coupling of methane to ethylene, for example, it has been reported that for a fixed target yield of 25%, the cost of production of ethylene would be competitive with that from steam-cracking only if selectivity to ethylene >68% were achieved [6].

5. The process technology

Different process configurations that have been proposed for the oxifunctionalization of paraffins are illustrated schematically in Fig. 3. They differ in the composition of the feedstock fed to the oxidation reactor. Each solution offers some advantages and presents some disadvantages.

(1) The first solution consists in the co-feeding of all reactants, hydrocarbon and air (or oxygen) for oxidation, and ammonia or HCl for ammoxidation and oxychlorination, respectively. This classical solution has the advantage of technical simplicity with low investment costs. Operation can be carried out either at the lean side of the flammability bell, or at the fuel-rich side. In the former case, the reaction is once-through, and the operating conditions are tuned in order to achieve hydrocarbon conversion, as high as possible. The problem in this case is associated with the development of a catalyst which is able to operate in the presence of low hydrocarbon-to-oxygen ratios, thus under conditions unfavourable for the achievement of high selectivities to the products of partial oxidation. When operation is carried out at the fuel-rich side, instead, the oxidizing agent fed in the fresh feed together with the make-up hydrocarbon is oxygen, and only moderate conversions of the hydrocarbon are obtained due to the hydrocarbon-to-oxygen ratio, which is higher than the stoichiometric requirement. The unconverted hydrocarbon is recycled, and under these conditions, higher selectivities to the products of partial oxidation are usually obtained. In addition, due to the better heat conductivity proper-

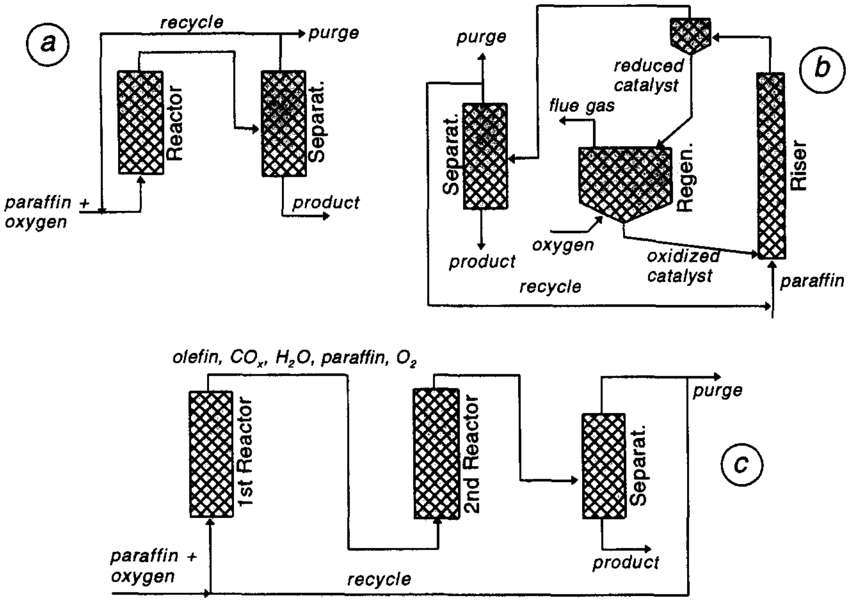

Fig. 3. Schematic processes for the oxifunctionalization of paraffins: (a) one-step (amm)oxidation, (b) two-step (amm)oxidation with cyclic reduction/oxidation and (c) two-step (amm)oxidation with integration of the paraffin (oxi)dehydrogenation and olefin (amm)oxidation.

ties of the hydrocarbon with respect to nitrogen (in case air is used as the oxidizing agent, as in the once-through reaction), a better control of the temperature in the catalytic bed is achieved.

(2) The second solution, shown schematically in Fig. 3, consists in the separation of the oxidation reaction into two steps: the first step where the hydrocarbon is kept in contact with the catalyst (which furnishes oxygen to the reactant), with formation of the product and simultaneous reduction of the catalyst, and the second step, where the reduced catalyst is re-oxidized by contact with air. The catalyst is continuously transported from the first section (the reactor, usually a riser) to the second one (the regenerator).

Advantages of this technology include the higher selectivity achieved in the absence of molecular oxygen and the better control of the heat of reaction, because the overall exothermal reaction is divided into two less exothermal steps. On the other hand, the main problem of this technology is in the development of a catalyst capable of sustaining wide variations in the average metal oxidation state without undergoing structural collapse. Moreover, the productivity of the process is related to two factors: (a) the amount of bulk oxygen available in the catalyst that can be readily furnished to the organic substrate, and (b) the rate at which the reduced compound can be re-oxidized by molecular oxygen. Usually, the second reaction is much slower than the first, and this causes very different contact times for the two sections of the plant lay-out. In addition, the amount of oxygen that can be furnished by the catalyst is usually relatively small, due to a slow diffusion of bulk oxygen to the surface, or the fact that over-reductions can lead to structural collapse. All these factors lead to reactor configurations like those shown in the figure, with a riser-type vessel for the reaction (similar to that employed for FCC), where the catalyst has a very high linear velocity and short contact times, and a large regenerator, where the catalyst slowly flows down under the influence of gravity. The drawback of this system is therefore related to the mechanical stress that the catalyst undergoes, and the high amounts of the catalyst that are re-circulated.

Nevertheless, this solution has been developed for at least three different reactions of paraffin oxidation: (a) by Du Pont, for the selective oxidation of *n*-butane to maleic anhydride, on a V–P–O-based catalyst, (b) by Atlantic Richfield, for the methane oxidative coupling on a Mn–B–P–Mg–Na–O/SiO_2-based catalyst, and (c) by Monsanto, for the ammoxidation of propane to acrylonitrile on a Sb–U–Fe–W–O-based catalyst.

(3) In the third solution, the feedstock to the reactor for the synthesis of the oxygenated compound, is a stream containing paraffin, the corresponding olefin, oxygen, an inert gas (nitrogen, carbon oxides), and water. This stream is the effluent of a first reactor where the paraffin is converted to the corresponding olefin by means of dehydrogenation, or better still, oxidehydrogenation. The advantage of this configuration lies in the reduction of costs associated with separation of the olefin, because the entire outlet of the first reactor is fed to the second reactor without any separation. The final transformation of the olefin can be carried out in the presence of the paraffin (which under these conditions is left unaltered), carbon oxides, and water. The same by-products are obtained in the oxidation of the olefin as well.

The same configuration can be used even when the first reaction is a dehydrogenation reaction, but in this case it will be necessary to take care of the presence of H_2 in an oxidizing environment in the second reactor. The outlet stream of the second reactor can then be conveniently treated to separate the oxygenated compound. The paraffin can be recycled to the first reactor. Different kinds of process integrations are under study or development; some examples are as follows:

$$\mathrm{C_2H_6} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{C_2H_4} + \mathrm{H_2O};\ \mathrm{C_2H_4} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{HCl} \rightarrow \mathrm{C_2H_4Cl_2} + \mathrm{H_2O}\,(1,2-\text{dichloroeth.})$$

$$\mathrm{C_3H_8} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{C_3H_6} + \mathrm{H_2O};\ \mathrm{C_3H_6} + \frac{1}{2}\mathrm{O_2} + \mathrm{NH_3} \rightarrow \mathrm{C_3H_3N} + 3\mathrm{H_2O}\,(\text{acrylonitrile})$$

$$\mathrm{i-C_4H_{10}} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{i-C_4H_8} + \mathrm{H_2O};\ \mathrm{i-C_4H_8} + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{C_4H_6O_2} + \mathrm{H_2O}\,(\text{methacrylic acid})$$

6. Some aspects in the reaction network that affect the selectivity to the desired product

At least two steps can be distinguished formally in the mechanism of the single-stage transformation of a paraffin to oxygenated compounds: (i) the first step of paraffin functionalization with H_2 abstraction and formation of a double bond, and (ii) the second step of transformation of this more reactive hydrocarbon to the final desired compound. The entire mechanism may occur on the catalyst surface, and it can be reasonably hypothesized that the first step is slower than the second, on the basis of the lower reactivity of the paraffin with respect to the olefin. However, this is not always true; in the case of ethane compared with ethylene, the C–H bond is stronger in the olefin than in the paraffin.

C–H bonds in allylic carbon atoms are more labile than C–H bonds in the corresponding paraffins. Therefore, assuming a slower rate for the first step, there is no desorption of the intermediate olefin because under the conditions at which the adsorbed olefin-like compound is formed, it is soon converted to the final product. This is the case of the oxidation of *n*-butane to maleic anhydride, where the reaction mechanism involves the likely formation of a butene- or butadiene-like intermediate compound, but no olefin is detected among the reaction products.

There are however some cases where this does not occur. For instance, in the case of the ammoxidation of propane to acrylonitrile, propylene is always obtained among the reaction products [8], and in the oxidation of ethane to acetic acid, ethylene is also obtained. Whereas in the latter case the low reactivity of ethylene can be responsible for its desorption, in the former case it would be expected that the propylene were completely transformed to the acrylonitrile.

This aspect is very important because desorption of the intermediate olefin, and its low reactivity under the conditions employed, may constitute a limit to the maximum achievable selectivity to the desired product. In addition to the problems associated with the presence of consecutive reactions of oxidative degradation upon the desired product (from this point of view, the formation of stable molecules, such as anhydrides or nitriles, rather then aldehydes or acids, is a more favourable situation), and the undesired contribution of parallel reactions of paraffin combustion, the third aspect affecting selectivity is the desorption of the olefin-like intermediate (Fig. 4).

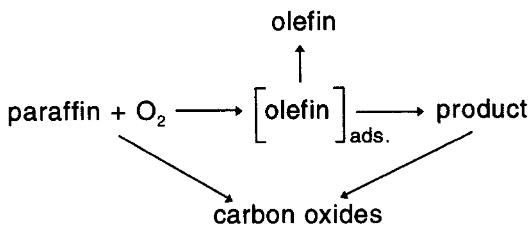

Fig. 4. The points in the network of alkane oxifunctionalization which are responsible for the decrease in selectivity.

The surface properties of the catalyst play an important role in affecting these aspects. For instance, an acidic surface may be important in the desorption of acids, while basic surfaces are necessary to accelerate the desorption of a nitrile and avoid its consecutive combustion. However, those properties that may favourably affect the final desorption of the desired product may also favour the desorption of the basic olefin, and avoid its further adsorption and conversion. This may justify the presence of propylene among the reaction products in the synthesis of acrylonitrile, and may explain the absence of olefins among the products in the synthesis of maleic anhydride from *n*-butane. The well-known surface acid properties of vanadyl pyrophosphate, the active catalyst in this reaction, favour the interaction of the surface with the intermediate butene-like compound and its further evolution to the final product.

Acknowledgements

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