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Selective oxidation of light alkanes: interaction between the catalyst and the gas phase on different classes of catalytic materials

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Abstract

Some aspects concerning the chemistry of oxidative transformation of paraffins catalyzed by different classes of materials are examined. Attention is given mainly to: (i) the role of the redox properties of transition metal oxide-based systems, and (ii) the contribution of radical-type, homogeneous and heterogeneously-initiated homogeneous reactions over nonreducible metal oxide catalysts. Technological solutions aimed at the control of oxidizing properties of the catalyst are also examined. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Light alkanes; Redox properties; Homogeneous reactions; Heterogeneous oxidations

1. Introduction

Interest in the transformation of light alkanes to valuable oxygenated compounds and olefins by means of oxidation has been growing in recent years due to the possibility of developing new processes of lower environmental impact and of lower cost. Many reviews and monographs have been published [1–21] which analyze the fundamental aspects related to the oxidative activation and transformation of light alkanes over heterogeneous catalysts. The general picture that can be drawn on the basis of the most important factors which are examined in these reviews clearly shows that the problem of paraffin conversion and of selectivity to the desired product has to be solved within a complex framework of inter-related aspects. In particular, the interaction between the catalyst surface and the gas phase, and how surface phenomena are affected by homogeneous phenomena, plays an important role in conditioning the final performance in terms of product distribution.

In this paper, after a brief summary of the main aspects, which have been claimed as fundamental for the control of catalytic performance in the selective oxidation of alkanes, attention is focused on the following: (i) role of the redox properties of the active sites for catalysts based on reducible metal oxides, and (ii) role of the nonredox activation of hydrocarbons and of radical reactions in affecting the catalytic performance for catalysts based on nonreducible metal oxides. Technological implications which derive from these aspects are also discussed.

2. Key factors in selective oxidation of light alkanes

Examples of the points which have been considered as key factors in determining the pathway of alkane

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transformation to the product of selective oxidation are:

1. *The activation of oxygen and of the alkane*, and specifically:
    1.1. the role of adsorbed oxygen species [1–4,6, 7,11];
    1.2. the importance of the mode of alkane adsorption [1–3,5].
2. *The reactivity of the reactant and of the product(s)*:
    2.1. the mechanism of activation of the C–H bond (heterolytic vs homolytic activation) [11,13];
    2.2. the role of stability of the products [9,10,12].
3. *The mechanism of transformation of the reactant*:
    3.1. the importance of nondesorption of reaction intermediates [9,10];
    3.2. the importance of the relative ratio between intermediate olefin (oxy)dehydrogenation and oxygen insertion in affecting the selectivity to oxygenated products [9,10];
    3.3. the role of the nature of the reaction intermediate (hydrocarbon fragment) in determining the direction of oxidative transformation [11];
    3.4. the contribution of homogeneous reactions, especially for applications which require temperatures higher than 400–450°C [12];
    3.5. the effect of coadsorbates in facilitating the dissociative adsorption of saturated hydrocarbons [12].

A better understanding of each one of the above factors means a better comprehension of the overall process of alkane transformation, and hence an improved possibility of increasing the catalytic performance to make these processes more attractive from an industrial point of view.

3. Key bulk and surface properties of catalysts which affect performance

The following catalyst features have been considered as fundamental tools to control the catalytic performance:

1. *The surface of the catalyst*: the nature of the active sites, and how the surface is affected by the bulk features and specifically:
    1.1. the density of the active sites [3,9,10], which can be explained by the "site isolation" theory [23];
    1.2. the role of surface acidity [8,11];
    1.3. the need for intrinsic surface polyfunctionality [9,10].
2. *The structure of the catalyst*:
    2.1. the redox properties of the metal in transition metal oxide-based catalysts, in terms of reducibility and reoxidizability of the active sites, and the metal–oxygen bond strength [3,5];
    2.2. the reactivity of specific crystal faces in the different transformations which constitute the reaction network [3,2,6];
    2.3. the role of structural defects in favoring the mobility of ionic species in the bulk [1–3];
    2.4. the importance of cooperative effects of different phases in obtaining catalysts with improved performances [12,22];
    2.5. the importance of the interaction between the support and the active phase in modifying the catalytic properties of the latter [12].

Most of these aspects may be applied in general to hydrocarbon oxidation while some of them are specific for alkane transformations.

4. Survey of the reactions of oxidative transformation of paraffins

Table 1 summarizes the possible reactions of alkane selective oxidation which are of industrial interest, and their stage of development. Starting from the period following the oil supply crisis which steadily increased the interest in the use of natural gas components as the preferred raw materials, research in this area has been moving from *n*-butane exploitation, with the successful development of the process for maleic anhydride synthesis, towards lighter and less reactive alkanes [24–27] and towards the development of processes which make direct use of these components through exothermal processes. The challenge of trans-

Table 1
Industrial processes and processes under study or development for the oxidative transformation of light paraffins (C_1–C_6)

Raw material	Product	Stage of development
Methane	Methanol	Pilot plant
Methane	Syngas	Pilot plant
Methane	Ethylene	Pilot plant
Ethane	1,2-Dichloroethane, vinyl chloride	Pilot plant
Ethane	Acetaldehyde	Research
Ethane	Acetic acid	Research
Ethane	Ethylene	Research
Propane	Acrolein, acrylic acid	Research
Propane	Propyl alcohol	Research
Propane	Acrylonitrile	Demonstrative plant
Propane	Propylene	Research
n-Butane	Acetic acid	Industrial
n-Butane	Maleic anhydride	Industrial
n-Butane	Butadiene	Industrial, abandoned
Isobutane	Methacrylic acid	Pilot plant
Isobutane	Isobutene	Research
Isobutane	*t*-Butyl alcohol	Research
n-Pentane	Phthalic anhydride	Research
Cyclohexane	Cyclohexanol, cyclohexanone	Industrial
Cyclohexane	Cyclohexanone	Research

forming methane to liquid fuels was approached first with research on the oxidative coupling to ethane and ethylene (also with an interest in the pyrolytic dimerization of methyl chloride, the latter being produced by methane chlorination or oxyhydrochlorination) and on the oxidation to methanol. More recently the oxidation to syngas appears to be one of the most promising routes for methane employment [28–31].

The possibility of transforming *ethane* to acetic acid in one- step is conditioned by the high chemical stability of ethylene, one of the most favored products in ethane oxidative conversion [32–34]. For the same reason, one possible commercial exploitation of ethane consists in a reaction where the olefin itself becomes the raw material for the transformation to a valuable chemical, either in the same reactor (it is necessary that the second reaction can be carried out under conditions which are close to those necessary for ethane activation), or in an *integrated process*, where the ethylene-containing stream exiting from the first reactor is the feedstock (after necessary make-up) for the second reactor. An example is the single-step or two-step ethane oxychlorination to 1,2-dichloroethane and to vinyl chloride, where the ethylene produced may easily be transformed to the chlorinated products. This process was studied in the 1970s [35,36], but did not reach commercial application. Interest is now growing again, as documented by recent patents issued by companies which are PVC suppliers [37].

The second successful heterogeneous gas-phase process which has going reached the commercialization stage (besides the oxidation of *n*-butane), is the ammoxidation of *propane* to acrylonitrile, developed by BP America, for which fluidized-bed technology is employed [38–46]. Also in this case the stability of the product, which saves it from unselective consecutive reactions, has been a key factor for the process development.

Currently, papers are being published which describe attempts to transform *isobutane* into methacrolein and methacrylic acid in a single-step, a process that might replace the acetone–cyanohydrin technology, and *propane* to acrylic acid [47–55]. Interest from the industrial companies for this kind of reaction indeed goes back to the 1980s [56]. In these reactions a further problem arises due to the high reactivity of the desired products, which under conditions necessary for alkane activation are not stable and undergo unselective oxidative transformations.

The availability of C_5 paraffins, as a consequence of environmental regulations which require a lower vapor pressure of gasolines, and the discovery that *n-pentane* can be transformed with unexpected selectivity to valuable compounds, i.e. maleic anhydride and phthalic anhydride, can open new prospects in the exploitation of saturated raw materials [57–68]. In this case, the key factor for industrial commercialization is the achievement of a high selectivity to phthalic anhydride, possibly close to that obtained from *o*-xylene.

The huge number of papers devoted to the *oxidative dehydrogenation* of paraffins is an indication of the scientific and industrial interest for alternatives to catalytic and thermal dehydrogenation/cracking, reactions which suffer from energetic drawbacks [5,9,17–20]. In these cases, the advantage gained from the use of a cheaper raw material and of an exothermal process must be weighed against the drawbacks such as the loss of valuable hydrogen (coproduced in dehydrogenation and in stream-cracking), the difficulty in separation of CO from the paraffin (in the case of ethane oxydehydrogenation, but also of methane oxidative coupling to ethylene), and the formation of traces of corrosive by-products. While in the case of ethane the problem mainly concerns the low reactivity of the molecule (the selectivity to the olefin which is achieved is usually high, due to the low ethylene reactivity and to the nature of the mechanism involved), the selectivity problem is of main concern in the case of oxydehydrogenation of propane and of *n*-butane to the corresponding olefins. With the latter molecules, the formation of allylic oxygenated compounds is the reason for the low selectivity achieved since these are transformed to carbon oxides.

5. Classes of catalysts for selective oxidation of alkanes

We shall now analyze aspects associated with the catalyst properties and the nature of the interaction between the gas phase and the catalyst only for those reactions which are catalyzed by solid materials, and where reactants and products are present in the gas phase (heterogeneous gas-phase processes). Three main classes of catalysts will be discussed:

1. catalysts based on reducible metal oxides (typically, transition metal oxides), for which a heterogeneous, redox-type mechanism is operating (a particular case is that where the reaction indeed consists of a first step occurring in the gas phase, and a second step which occurs on the surface of the catalyst);
2. catalysts based on nonreducible metal oxides (or sometimes, systems which are very difficult to reduce under the reaction conditions), for which the mechanism is initiated on the catalyst and then transferred into the gas phase (or at least, in the close proximity of the catalyst surface);
3. noble metal-based catalysts, which are usually considered as nonselective oxidation systems (i.e. they are typically used for combustion), but which under particular reaction conditions may become selective catalysts.

5.1. Redox-type catalysts: interaction between the gas phase and metal component, and role of the redox properties of the latter under reaction conditions

It is well known that the oxidation state of transition metal ions which constitute the active component of mixed oxide-based catalysts is a function of the operating conditions for the reaction, since the surface of the catalyst is in dynamic interaction with the gas phase [2,21]. If operation is carried out under fuel-rich conditions (thus under conditions in which molecular oxygen is the limiting reactant) the active component has a lower oxidation state than under fuel-lean conditions. This also affects the catalytic performance in terms of activity and selectivity. Indeed, more oxidized surfaces usually result in more active but less selective catalysts, while the opposite is true for more reduced surfaces. This has been the fundamental driving force for the development of processes which operate in the presence of very low amounts of oxygen in the gas phase; other advantages are related to the absence of hazards associated with the possible formation of flammable mixtures (which are instead present when the combustible and the oxidant are co-fed).

A lower oxidation state for the metal ion corresponds to a surface which is poorer in oxygen ions, and thus exhibits either a lower number of O^{2-}-insertion sites or possibly an electron-richer surface where the metal–oxygen bond strength is different from that of the fully oxidized surface, this resulting in sites with modified oxidizing properties. All this in practice corresponds to the well known ''site-isolation'' theory, developed many years ago by Callahan and Grasselli [23], which claims the importance of having a statistically controlled number of surface oxidizing sites in order to favor selective oxidation reactions over combustion reactions.

In general, the mechanism which operates is completely heterogeneous and includes the formation of an intermediate alkoxy species (or alkyl radical species). This occurs preferentially at lower temperatures (i.e. less than 450–500°C for ethane, the temperature being a function of both (i) the reaction conditions, such as pressure and reactant concentration, and (ii) the alkane reactivity), and is often found for transition metal oxide-based catalysts. Either the olefin or other oxygenated products can be the prevailing product, depending on the nature of the alkane. The ratio of the rates of further reaction of this intermediate with activated oxygen, to give carbon oxides, and alkoxy evolution to the desired products, determines the selectivity of the reaction.

Some examples can be found in the literature where the importance of the redox properties of the active sites in determining the catalytic performance is emphasized. These will be discussed in the following Chapters.

5.1.1. *Oxidation of propane to acrylic acid and of isobutane to methacrylic acid over Keggin-type heteropolymolybdates*

Heteropolycompounds are currently being studied intensively for the oxidation of hydrocarbons with molecular oxygen [9,69–74]. The oxidation of isobutane to methacrylic acid and of propane to acrylic acid are examples of possible industrial applications. It is claimed that a lower average oxidation state for molybdenum results in a higher selectivity to methacrylic acid. In particular, it has been reported that particularly designed preparation procedures may lead to more reduced compounds, exhibiting enhanced selectivity properties in the oxidation of propane and of isobutane. For example, in patents claimed by Asahi Chem. Ind. [56,75–77] the two essential requirements for catalysts of superior performance are: (i) a partial degree of reduction, and (ii) a cubic crystalline structure. These two properties are achieved by calcination of ammonium salts of 12-molybdophosphoric acid (Keggin-type heteropolycompound $H_3PMo_{12}O_{40}$) in a nitrogen atmosphere. The partial reduction of molybdenum can also be achieved by treatment with isobutene at 450°C. It is known [78] that ammonium may be released from the heteropolycompound structure in the form of molecular nitrogen, leaving reduced sites. Asahi has also claimed an improved performance in isobutane oxidation to methacrylic acid by operation in two reaction vessel: (i) a vessel where the catalyst is put in contact with isobutane and where methacrylic acid is produced, and (ii) a regeneration vessel where the reduced catalyst is restored to its original oxidation state by contact with air.

Highly reduced heteropolycompounds have been obtained by heat treatment of pyridinium or quinolium salts of 12-molybdophosphoric acids under a nitrogen stream at 420°C [55]. The authors demonstrated that the reduced state of the catalyst was stable even under catalytic conditions, and yielded acrylic acid from propane with 50% selectivity at 12% paraffin conversion. A reduced state could also be achieved by treatment of the ammonium salt of 12-molybdophosphoric acid $(NH_4)_3PMo_{12}O_{40}$, but the molybdenum was reoxidized under reaction conditions. The reduced state achieved by treatment of the pyridinium salt could therefore be stabilized even under conditions which favor the reoxidation of molybdenum. On the contrary, the oxidized catalyst was not selective in the oxidation of propane, and mainly yielded propene and carbon oxides. Mizuno et al. [53] have also pointed out the importance of partially reduced molybdenum in heteropolycompounds, in achieving the best performance in isobutane and propane oxidation.

All these data indicate that the best reaction conditions are those which may favor a lower oxidation state of molybdenum. In fact, in most papers and patents, compositions on the fuel-rich side of the flammability region for isobutane/oxygen/inert mixtures are used; under these conditions, oxygen is the limiting reactant, and hydrocarbon conversions not higher than 15% are obtained.

Fig. 1 shows the effect of the hydrocarbon content of the feed for a fixed amount of oxygen on the overall rate of isobutane consumption and on the selectivity to

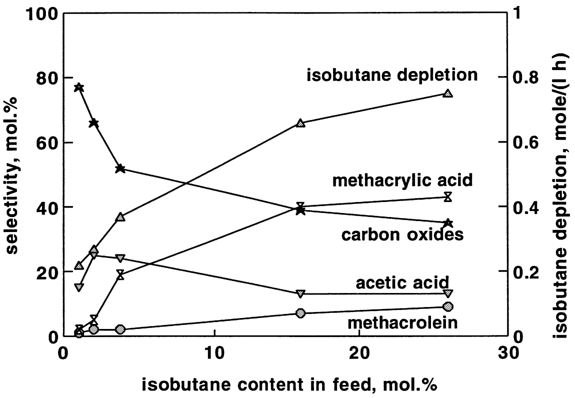

Fig. 1. Rate of isobutane depletion and selectivity to the products in isobutane oxidation as a function of the paraffin content in the feed over a Sb-doped Keggin-type heteropolycompound. Reaction conditions: temperature 350°C, residence time 3.6 s, feed composition: 13 mol% O_2, 12 mol% H_2O, He balance.

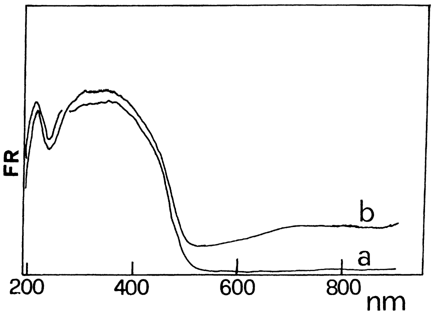

Fig. 2. UV-Vis-DRS spectra of a heteropolycompound catalyst $(NH_4)_3PMo_{12}O_{40}$ after use for isobutane oxidation under the following conditions: (a) 1% isobutane, 13% O_2, 12% H_2O, rest He; temperature 350°C, residence time 3.6 s; (b) 26% isobutane, 13% O_2, 12% H_2O, rest He; temperature 350°C, residence time 3.6 s.

the products for a doped Keggin-type heteropolycompound. The isobutane consumption increases on increasing the isobutane concentration and the selectivity to the products of interest increases as the isobutane content in the feed increases.

Fig. 2 shows the ex situ UV-Vis-DRS spectrum of a $(NH_4)_3PMo_{12}O_{40}$ heteropolycompound after reaction (cooled in helium and immediately characterized). Fig. 2(a) shows the spectrum for a sample after operation at the fuel-lean side (1 mol% isobutane and 12% oxygen in the feed), while Fig. 2(b) shows spectrum for a sample unloaded after operation under isobutane-rich conditions (26 mol% isobutane and 12% oxygen). The band at 700 nm is typical of Mo^{5+} in heteropoly-blues, and its intensity is approximately proportional to the extent of molybdenum reduction [79]. The catalyst which operates under fuel-lean conditions is less reduced than the catalyst which operates under hydrocarbon-rich conditions.

These data confirm the importance of the degree of molybdenum oxidation in heteropolycompounds used as heterogeneous catalysts for the selective oxidation of propane and of isobutane. Since the oxidation state of molybdenum is a function of the gas-phase composition, the optimal situation might be theoretically reached if a reduced, more selective catalyst oxidation state could be maintained even under oxidizing conditions (i.e. at low hydrocarbon-to-oxygen ratio), thus under conditions which are typically less favourable for selectivity [55].

5.1.2. Oxydehydrogenation of paraffins to olefins over vanadium oxide-based catalysts

Amongst the factors which affect the selectivity to olefins in the oxydehydrogenation of paraffins over vanadium oxide-based catalysts, particular importance has been attributed to the average oxidation state of the vanadium [5]. In fact, the degree of reduction of the active site in magnesium vanadates affects the metal–oxygen bond strength (and hence the reducibility of metal cations), finally influencing the ratio between the olefin and carbon oxides produced. In the case of alumina-supported vanadium oxide, a catalyst for the oxydehydrogenation of *n*-butane to butenes and butadiene, the results of pulse tests showed that the selectivity to the desired product increased rapidly as the catalyst was progressively reduced (i.e. with increasing hydrocarbon pulse number) [80,81]. For the same reason, supported vanadium oxide systems in which partly reduced vanadium phases develop, stabilized by the interaction with the underlying support, are more selective in the formation of olefins. On the contrary, bulk V_2O_5 (found, for instance, at high vanadia loading in supported systems) has a considerably lower selectivity to olefins [82–85].

5.1.3. Oxidation of n-butane and n-pentane over vanadyl pyrophosphate

The role of different vanadium phosphate phases, and of the valence state of vanadium in the selective oxidation of *n*-butane to maleic anhydride has been widely studied [9,16,61,86–95]. In general, the fundamental role of the vanadyl pyrophosphate $(VO)_2P_2O_7$ as the active phase is recognized but it is generally believed that oxidized V^{5+} sites, present as dispersed $VOPO_4$ phases at the surface of the vanadyl pyrophosphate, or in the form of domains at the basal (100) face of $(VO)_2P_2O_7$, are directly involved in the formation of maleic anhydride. The simultaneous presence of V^{4+} and V^{5+} seems to guarantee the best catalytic performance. However, Guliants et al. [87], who proposed that the best catalytic system is the one which only contains vanadyl pyrophosphate with well ordered stacking of the (200) planes.

The oxygen species which are involved in the multi-electron transformation of *n*-butane are both bulk oxygen ions (even though probably limited to a few surface atomic layers) and chemisorbed species

[94–97]. It seems that even though the vanadyl pyrophosphate is very well crystallized and formally contains no V^{5+} species, "patches" or dispersed V^{5+} species develop in the reaction environment (either by chemical adsorption of oxygen, or by oxidation of vanadyl pyrophosphate layers to form $VOPO_4$ phases, namely δ-$VOPO_4$), which make a fundamental contribution to the mechanism of formation of maleic anhydride. In some cases, $VOPO_4$ phases are already present in the catalyst, especially when the compound has been calcined in air prior to the reaction [61]. In addition, the formation of oxidized $VOPO_4$ phases in the reactor will be affected by: (i) the reaction conditions, i.e. temperature and gas phase composition (differences in the average oxidation state of vanadium in the equilibrated catalyst unloaded from a fixed bed may be expected between that of the catalyst placed at the reactor inlet, where the hydrocarbon-to-oxygen ratio is the highest, and that at the exit, where the ratio is the lowest); and (ii) the bulk features of the vanadyl pyrophosphate, such as its crystallinity and P/V ratio [9]. In fact, well crystallized $(VO)_2P_2O_7$ exhibits a tendency towards oxidation which is different with respect to badly crystallized or microcrystalline vanadyl pyrophosphate. It is worth mentioning that spent equilibrated catalyst may exhibit a vanadium valence state which varies from 4.00 [60,61,87], to 4.02 [95], or be even higher [93,98].

The important role of the valence state of vanadium in affecting the catalytic properties in *n*-butane and butene oxidation over V–P–O catalysts has also been demonstrated by means of pulse tests and by an ex situ characterization of catalysts unloaded after reaction at different reaction conditions (i.e. different hydrocarbon-to-oxygen ratios in the feed) [99,100]. It was found that at low *n*-butane conversion (i.e. under conditions in which the consecutive contribution of maleic anhydride combustion is negligible) the selectivity was proportional to the hydrocarbon-to-oxygen ratio, and that at high *n*-butane conversion the selectivity to maleic anhydride rapidly decreased as the average degree of oxidation of vanadium increased. It was proposed that a limited amount of surface V^{5+} is necessary to obtain the highest selectivity to maleic anhydride but that excessive vanadium oxidation leads to an enhancement of the consecutive combustion of maleic anhydride.

The existence of a limited amount of beneficial V^{5+} corresponds, in practice, to the necessity for discrete amounts on the catalyst surface of O-insertion sites which may favor the transformation of intermediates (i.e. olefin species) to the final product. Also in the case of *n*-pentane oxidation over V–P–O catalysts, the distribution of the products is affected considerably by the availability of O-insertion sites. In this case, the hydrocarbon-to-oxygen ratio in the feed not only modifies the relative ratio between the products of selective oxidation and of carbon oxides, but also the ratio between maleic and phthalic anhydrides [60–63]. Results concerning the oxidation of *n*-pentane over an equilibrated vanadyl pyrophosphate catalyst are shown in Fig. 3, where the overall rate of paraffin consumption and the selectivity to the products are reported as functions of the paraffin content in the feed, for a fixed amount of oxygen [62]. The results obtained can be summarized as follows:

1. For amounts of hydrocarbon which increase in the range 0–2 mol% (Fig. 3(a)), the rate of transformation of the paraffin is proportional to the hydrocarbon content. In this range, the conversion of *n*-pentane decreases (but the rate of hydrocarbon depletion increases), the overall selectivity to maleic plus phthalic anhydride increases, and the ratio phthalic-to-maleic anhydride also increases. This means that under conditions under which the catalyst surface is not saturated, a decrease in the oxidizing power of the gas phase leads to a more favorable surface situation, in terms of specific centers for the transformation to the final stable products. This is the same phenomenon as the one displayed in Fig. 1 for isobutane oxidation over an heteropolycompound-based catalyst.
2. Things change considerably under conditions of surface saturation, thus under conditions at which the rate of *n*-pentane transformation levels out, i.e. above 2% paraffin content in the feed (Fig. 3(b)). The selectivity to products of interest is lowered to 10–15%, while the formation of carbon oxides becomes largely kinetically favored. At the same time, other by-products (aldehydes, ketones, hydrocarbon fragments) appear, which, on the contrary, are not observed at all for low *n*-pentane

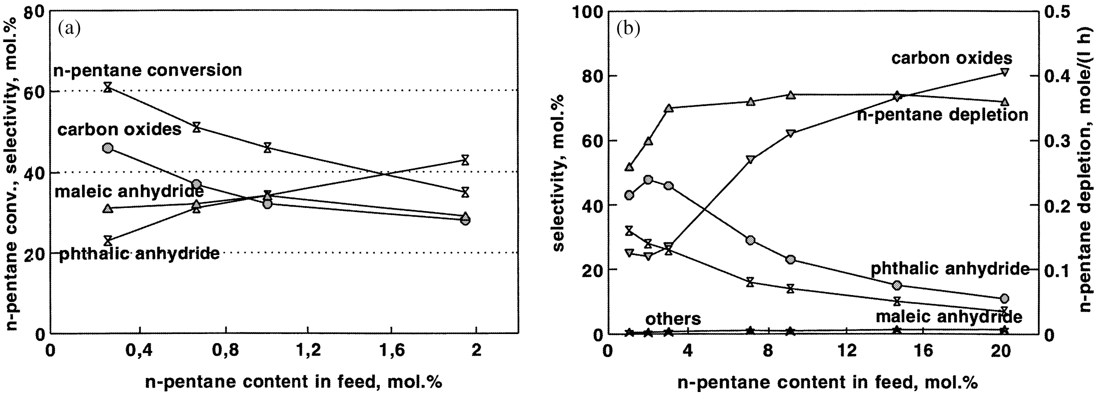

Fig. 3. *n*-Pentane conversion (a), rate of *n*-pentane depletion (b) and selectivity to the products as functions of *n*-pentane content in the feed over an equilibrated vanadyl pyrophosphate catalyst. Reaction conditions: (a) W/F 3 g s ml^{-1}, temperature 340°C, 20% O_2 in feed; (b) W/F 1 g s ml^{-1}, temperature 340°C, 16% O_2 in feed.

concentrations in the feed. Therefore, when the surface is saturated with adsorbed species, the formation of the final stable products (maleic and phthalic anhydrides) is hindered, due to the scarcity of O-insertion sites. Under these conditions, the reaction becomes nonselective because intermediate olefinic species desorb into the gas phase or are attacked by unselective oxygen species either in the gas phase or directly in the adsorbed state. The main difference with respect to data reported in Fig. 1 therefore concerns the lower availability of active sites on the vanadyl pyrophosphate for the oxidation of *n*-pentane relative to those on heteropolycompound as the catalyst for isobutane oxidation.

It is interesting to note that when 1 mol% of 2-pentene in air is fed to the reactor, the same distribution of products is observed as in the case when a high concentration of *n*-pentane (i.e. 20 mol%) is oxidized [101]. This is shown in Fig. 4 which compares the selectivity to the products from the two reactants under the two different reaction conditions. It is shown that the overall selectivity to maleic plus phthalic anhydride from 2-pentene is around 10–15%, the remainder being mainly carbon oxides and other unsaturated products of partial oxidation (the overall selectivity of which is around 15%). This indicates that when the olefin is used as reactant, surface saturation occurs at much lower hydrocarbon partial pressure than with *n*-pentane, due to the high nucleophilicity of the olefinic reactant which makes easier interaction with the Lewis acid centers of the vanadyl pyrophosphate. Under these conditions, the situation on the catalyst surface is the same as when high concentrations of *n*-pentane are fed. An increase in the oxygen partial pressure favors the selectivity to the anhydrides, even though the selectivity with the olefin never reaches the same values that are obtained with *n*-pentane [62,101].

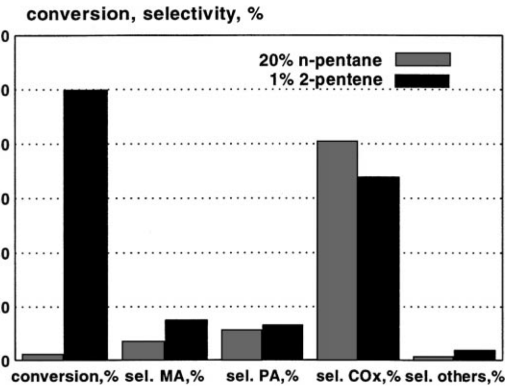

Fig. 4. Hydrocarbon conversion and selectivity for *n*-pentane (20% pentane and 16% oxygen in feed, temperature 340°C, W/F 1 g s ml^{-}1) and 2-pentene (1% 2-pentene, 20% O_2, temperature 340°C, W/F 1 g s ml^{-1}) oxidation over an equilibrated vanadyl pyrophosphate catalyst.

5.2. Mixed homogeneous/heterogeneous reactions on redox-type catalysts

Particular cases, which can be considered as intermediates between completely heterogeneous mechanisms and homogeneous reactions are those reactions which, even though they occur on redox-type catalytic systems, include a first step which occurs in the gas phase. An example has been reported by Moro-oka and coworkers [102,103] for the oxidation of propane to acrolein over Ag/Bi/V/Mo mixed oxides, where the contribution of homogeneous reactions was found to play a fundamental role and to lead to substantially higher yields with respect to completely heterogeneous mechanisms. In particular, under the conditions employed (temperature around 500°C), the thermal dehydrogenation of propane in the gas phase led to the formation of propene, which was then selectively converted to acrolein on the catalyst surface by O-insertion sites.

5.3. Nonredox-type catalysts; the contribution of radical-type homogeneous reactions

A considerable amount of research work has been done on the use of nonreducible metal oxides as catalysts for the oxidation of light paraffins. The most important is the case of methane oxidative coupling, where most active catalysts are those based on alkaline earth oxides, such as MgO and CaO, doped with alkali metal ions, but the same class of catalysts has also been found to be active and selective in the oxydehydrogenation of ethane to ethylene [17,104–115]. Since these compounds lack bulk-O-insertion properties, they are not used when the reaction is aimed at the production of oxygenates.

Systems which are known to operate a nonredox-type activation of molecular oxygen and/or of paraffin are [17]:

- *Alkaline earth oxides.* Alkaline earth oxides, doped with various components aimed at increasing the contribution of surface defects in hydrocarbon and oxygen activation [31,104]. These are essentially p-type semiconductors, at least at the temperatures used for paraffin activation. Alkali metal-doped and rare earth-doped alkaline earth compounds are amongst the most effective catalysts for methane oxidative dimerization [104–115]. Promotion by chlorine, either fed directly to the reactor as chlorine-containing compounds or added in the catalyst composition, lowers the reaction temperature considerably and increases the selectivity to ethylene in methane oxidative coupling and in ethane oxydehydrogenation [116–121]. The halogen has to be fed continuously to the reactor in order to maintain the best catalytic performance. The effect of chlorine can be different: (i) gas-phase reactions involving chlorine radicals can contribute measurably to the activation of the paraffin and to the formation of ethylene from ethane, thus increasing both conversion and selectivity; (ii) chlorine-modified active sites may be involved in the reaction; in particular, chlorine may inhibit the centers responsible for total oxidation. In these systems, the role of alkali metal dopants is fundamental in the creation of the surface defects able to activate molecular oxygen. Alkali metals are also important promoters for TiO_2 [122] and for MnO_2. The $Na_4P_2O_7/MnO_2/SiO_2$ system is the catalyst claimed by ARCO for the process of methane oxidative coupling and for the oxydehydrogenation of ethane under cyclic operation, where the catalyst is continuosly withdrawn from the hydrocarbon contact zone and passed to the oxidation zone for coke removal [123–126].
- *Rare earth oxides.* Rare earth oxides, which are p-type semiconductors (La_2O_3, Sm_2O_3, Dy_2O_3), even though ionic-type conductivity can contribute in some cases [127–136]. Cerium and praseodymium oxides (which instead are n-type semiconductors, and also exhibit remarkable ionic conductivity) are nonselective to C_2 from methane, and in paraffin oxydehydrogenation as well [137], due to the high activity in methyl radical attack by active oxygen species which leaves less time for methyl radical dimerization [138]. Alkaline earth metal-doped or alkali metal-doped rare earth oxides are particularly effective catalysts [139,140].
- *Boron oxide-based catalysts.* Boron oxide has been described to be an efficient catalyst for the oxidation of ethane to acetaldehyde or to ethylene [141–145], and of propane to propylene [146]. The

main problem of this material is its high volatility which makes the catalyst lose activity rapidly due to the loss of the active component. However, it can be stabilized by interaction with a support or by formation of stable compounds, typically phosphates. The mechanism which has been proposed to occur consists of the generation of alkyl radicals at the boron oxide surface, which are then released to the gas phase, while dissociatively adsorbed oxygen is mainly responsible for the formation of carbon oxides.

- *Tin oxide-based catalysts.* Tin oxide, a n-type wide-gap semiconducting oxide, supported on silica or alumina and doped with alkali metals catalyzes the oxidative coupling of methane. It is effective mainly as a dopant for the Li/MgO system, since it reduces the loss of lithium under reaction conditions and also promotes activity [147]. However, tin oxide alone as well as SnO_2–P_2O_5 activate ethane and yield ethylene with good selectivity especially at superatmospheric pressures [148,149]. The formation of an ethoxy intermediate was postulated.
- *Silica.* Silica also exhibits unexpected oxidizing properties. It has been found to be active in the oxidation of methane to formaldehyde [150]. Silica also is active in the ammoximation of cyclohexanone to cyclohexanone oxime, intermediate in the synthesis of caprolactam [151–153]. In these cases it has been proposed that surface defects (reduced sites) are the sites for the generation of active oxygen species [152,153]. The formation of O_2^- species, which are initiators of radical reactions occurring on the solid surface, was detected by means of EPR and measurements of surface potential.

The contribution of homogeneous radical reactions in alkane oxidation can in general be neglected for those catalysts which typically operate at lower temperatures. On the contrary, gas-phase reactions may play a fundamental role when operation is carried out at higher temperatures, thus typically on nonredox-type catalysts [5,12,104,154–159]. Rare earth oxides and alkaline earth oxides, and in general nonreducible metal oxides, activate methane and ethane only at temperatures higher than 500–600°C. Besides the high temperatures used, reactant mixtures are often used with compositions which fall inside the flammability region; in the case of more reactive alkanes, the temperatures used are close to the autoignition temperatures. In these cases, the contribution of homogeneous reactions becomes fundamental.

The mechanism which operates in these cases usually involves a fundamental contribution of alkyl radical species which are generated at the catalyst surface and then: (i) react quickly in the adsorbed state (for instance, by being transformed to the corresponding olefin via β-elimination, or by undergoing non-selective oxidative attack by adsorbed oxygen species), (ii) react further in the close proximity to the catalyst surface (i.e. in the boundary layer), or (iii) become transferred into the gas phase where the reaction proceeds.

The further evolution of alkyl radical fragments in the gas phase is known to be a function of temperature. In general, the reaction between $C_nH_{2n+1}^{\bullet}$ and O_2 below 330–350°C proceeds mainly by a simple, reversible addition process with formation of a peroxide $C_nH_{2n+1}O_2^{\bullet}$ species that is thermally stable. Under these conditions, the adduct may either be converted to oxygenated products (aldehydes or others, which may also be precursors of carbon oxides):

$$2C_nH_{2n+1}O_2^{\bullet} \leftrightarrows H_{2n+1}C_nOOOOC_nH_{2n+1}$$

$$H_{2n+1}C_nOOOOC_nH_{2n+1} \leftrightarrows 2C_nH_{2n+1}O^{\bullet} + O_2$$

$$C_nH_{2n+1}O^{\bullet} + C_nH_{2n+2} \leftrightarrows C_nH_{2n+1}^{\bullet} + C_nH_{2n+1}OH$$

$$H_{2n+1}C_nOOOOC_nH_{2n+1} \rightarrow C_nH_{2n}O + O_2 + C_nH_{2n+1}OH$$

$$C_nH_{2n+1}O^{\bullet} \leftrightarrows C_{n-x}H_{2(n-x)+1}^{\bullet} + C_xH_{2x}O$$

$$C_nH_{2n+1}OH + C_nH_{2n+1}^{\bullet} + O_2 \leftrightarrows C_nH_{2n}O + C_nH_{2n+2} + HO_2^{\bullet}$$

etc. or be converted directly to CO_2, possibly also by oxygen species adsorbed on the catalyst surface. Only minor amounts of olefin are formed (for $C_{>1}$ alkanes), via direct H abstraction from the $C_nH_{2n+1}^{\bullet}$ by oxygen:

$$C_nH_{2n+1}^{\bullet} + O_2 \leftrightarrows C_nH_{2n} + HO_2^{\bullet}$$

The selectivity to C_nH_{2n} is therefore low.

Above 350°C, for the case of methane and ethane oxidation over rare earth oxides and alkaline earth oxides, the formation of the olefin is preferred with respect to other oxygenated compounds. Since at high temperature the equilibrium:

$$C_nH^{\bullet}_{2n+1} + O_2 \leftrightarrows C_nH_{2n+1}O^{\bullet}_2$$

is strongly in favor of the hydrocarbon, consumption of the radical to yield the olefin must be accounted for by a different mechanism. Direct H abstraction by O_2 may occur, or alternatively, the elementary addition produces an excited alkylperoxy species which, at high temperature, is quickly decomposed to the olefin and $HO^{\bullet}_2$ via an intermediate alkylhydroperoxy species [160].

$$C_nH^{\bullet}_{2n+1} + O_2 \leftrightarrows C_nH_{2n+1}O^{\bullet}_2{*}$$

$$C_nH_{2n+1}O^{\bullet *}_2 \leftrightarrows C_nH_{2n}O_2H^{\bullet *}$$

$$C_nH_{2n}O_2H^{\bullet *} \rightarrow C_nH_{2n} + HO^{\bullet}_2$$

The contribution of homogeneous reactions in heterogeneously-initiated alkane oxidation thus can easily explain the increase in the selectivity to the olefin which is usually observed with increasing temperature. This has been observed with ethane because ethylene is a stable product. With higher paraffins, however, the high reactivity of the allylic methyl group in the olefins produced causes the selectivity to decrease with increasing temperature.

Other reactions involving the alkyl radical are the dimerization pathway (which is fundamental for the methyl radical), and chain branching occurring by decomposition of hydrogen peroxide to hydroxy radicals $OH^{\bullet}$, very active species that initiate a chain mechanism by reacting with the alkane:

$$2C_nH^{\bullet}_{2n+1} \leftrightarrows C_{2n}H_{2(2n+1)}$$

$$C_nH_{2n+2} + O_2 \leftrightarrows C_nH^{\bullet}_{2n+1} + HO^{\bullet}_2$$

$$C_nH_{2n+2} + HO^{\bullet}_2 \leftrightarrows C_nH^{\bullet}_{2n+1} + H_2O_2$$

$$H_2O_2 \leftrightarrows 2OH^{-}$$

$$2HO^{\bullet}_2 \leftrightarrows 2OH^{\bullet} + O_2$$

$$C_nH_{2n+2} + OH^{\bullet} \leftrightarrows C_nH^{\bullet}_{2n+1} + H_2O$$

In the case of *methane*, after the methyl radical species has been formed at temperatures higher than 600°C at the catalyst surface and has desorbed from the surface, the formation of $CH_3O_2^{\bullet}$ is highly unfavored thermodynamically. The two reactions of methyl radical dimerization to produce ethane and of methyl radical oxidation to give formaldehyde by reaction with $HO^{\bullet}_2$ (or with atomic oxygen) are favored. Since methyl radicals can also interact with gas-phase oxygen, leading to the formation of carbon oxides, control of the gas-phase composition, and the ability of the catalyst to convert oxygen rapidly into surface selective species are factors which determine the control of the process selectivity [31].

In the case of *ethane* oxydehydrogenation, the mechanism can also include the fundamental contribution of gas-phase radical reactions [17,18,111,154–156,161] and also in this case, at high temperatures the formation of ethylene by evolution of the ethyl radical is the preferred reaction. The selectivity of the process is therefore affected considerably by the nature of the intermediate species (either an ethoxy species or an ethyl radical species) which is generated on the catalyst surface.

In the case of *propane* oxidation, the higher reactivity of the C–H bond makes the contribution of homogeneous reactions more likely than in the case of ethane. (However, lower temperatures are usually needed to activate this paraffin.) Indeed, the activation of propane with generation of the propyl radical may occur either on the catalyst surface or even in the gas phase by a thermal (pyrolysis) process. Moreover, due to the presence of the activated methyl group in the propylene produced, this olefin is much more reactive than ethylene. Contributions of homogeneous reactions have been found for the reaction of propane oxydehydrogenation to propylene when operating at temperatures higher than 450°C [154,162–164].

In the case of *n-butane*, butene may be produced in the gas phase at high temperatures via cracking of the butyl radical, while at low temperatures the butyl radical is preferentially transformed to oxygenated products (mainly aldehydes and ketones, such as methylethylketone, methylvynilketone, crotonaldehyde and butanal). Oxygenates can also decompose yielding lower oxygenates such as formaldehyde and acetaldehyde [165]:

$$C_4H_8O \rightarrow {}^{\bullet}CHO + {}^{\bullet}C_3H_7$$

$$CHO^{\bullet} + H^{\bullet} \rightarrow HCHO$$

or can be burnt to carbon oxides.

The lighter oxygenates may also arise from rearrangement and decomposition of the C_4 alkyl peroxy radical. The nature of the products evolving from the alkyl radical species (either oxygenates or olefins) is therefore once again mainly a function of temperature.

A further reaction, intramolecular H abstraction, is made possible by the molecule length (mechanism of "back-biting") [166,167]:

$$CH_3-CH_2-HC^{\bullet}-CH_3 + O_2 \leftrightarrows CH_3-CH_2-HC(OO^{\bullet})-CH_3$$

$$H-CH_2-CH_2-HC(OO^{\bullet})-CH_3 \leftrightarrows {}^{\bullet}CH_2-CH_2-HC(OOH)-CH_3$$

The hydroperoxy species is the precursor of acetone formation.

An increase in the number of carbon atoms makes the mechanism of intramolecular rearrangement of alkylperoxy radicals and of radical fragmentation more important.

In the case of *isobutane* oxydehydrogenation to isobutene over P/W, Keggin-type heteropolycompounds, the contribution of homogeneous radical processes has also been postulated to play a fundamental role [168,169]. In particular, it has been found that the conversion of isobutane increased with increasing isobutane concentration in the feed, thus corresponding to a formal order of reaction for isobutane disappearance higher than 1 (Fig. 5). The selectivity does not decrease with increasing isobutane partial pressure, thus leading to a remarkable increase in the overall yield to the olefin. The same phenomenon was observed by Buyevskaya et al. [146] for propane oxydehydrogenation over boria–alumina catalysts, and for propane oxidation over boron phosphate catalysts [170]. In all cases, it was proposed that the mechanism begins on the catalyst surface, with generation of alkyl radicals, and that the reaction is then transferred into the gas phase. The order of reaction higher than 1 has been attributed to the presence of homogeneous bimolecular reactions between the paraffin and $RO_2^{\bullet}$, leading to the regeneration of the chain carrier $R^{\bullet}$ and of RO_2H which is then decomposed to the olefin and to oxygenated compounds (propionaldehyde, acetone and acrolein from propane) [170]. Alternatively, the phenomenon can be attributed to an autocatalytic effect, brought about by the olefin formed which may interact with the catalyst surface, generating more active surface centers, or may contribute in chain propagation due to its weaker allylic C–H bond than that in isobutane [168]. In any case, there are indications in the literature that when the reaction mechanism for the oxydehydrogenation of light paraffins includes a contribution of gas-phase reactions, operation at high hydrocarbon concentrations may lead to a considerable increase in the rate of reaction with improvement of both conversion and yields.

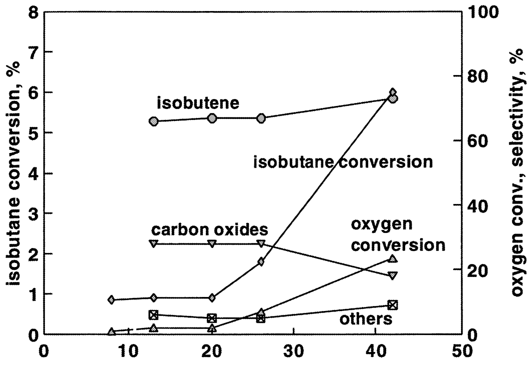

Fig. 5. Isobutane and oxygen conversions and selectivities to the products as a function of the isobutane content in feed over a Wells–Dawson heteropolycompound catalyst, $K_6P_2W_{18}O_{62}$. Reaction conditions: temperature 470°C, residence time 1 s, feed composition: O_2 13 mol%, H_2O 12 mol%, balance He.

In conclusion, when the mechanism of paraffin oxidation also involves homogeneous reactions, the selectivity to olefins may become considerably higher than for completely heterogeneous mechanisms provided that the olefin is stable enough to resist consecutive degradation reactions. From this point of view, therefore, the contribution of homogeneous reactions can be highly desired even though the coupling of heterogeneous processes (needed to accelerate the generation of the alkyl radical species) and of homogeneous oxidative transformations may give rise to serious problems from the technological and engineering points of view. A problem may arise in trying to avoid the consecutive reactions of combustion of more reactive olefins ($C_{>2}$) and oxygenates since high temperatures also favor homogeneous degradation of these products. In these cases, as pointed out by Goetsch et al. [165], it is necessary to quench the product gases rapidly to enable the olefins or oxygenates to survive. Monolith-type reactors can be favored since considerable differences in temperature may be found between the catalyst surface and the gas phase in the reactor void fraction under laminar-flow conditions. In this way, very rapid paraffin activation and transformation are provided due to the high local temperature at the catalyst surface and the consecutive reactions of combustion of products are minimized by quenching the latter with the cooler gases. On the other hand, those systems which are characterized by relatively high mass transfer rates may favor radical termination via interactions with the surface rather than nonselective homogeneous chain-branching reactions and decomposition reactions of the oxygenates. High flow rates increase the mass transfer of reactants towards the catalytic surface by decreasing the thickness of the boundary layer. In this way, the diffusion of radicals formed in the gas phase towards the surface (which acts as a radical scavenger) is also favored, thus preventing undesired consecutive reactions in the gas phase.

5.4. Noble metal-based catalysts

In view of the results described above, the results of Schmidt and coworkers [14,165,171–176], who have made an extensive study of paraffin oxydehydrogenation and methane partial oxidation in monolith-type reactors under autothermal conditions, should be mentioned . Noble metal (Pt, Pd, Rh) coated ceramic foam monoliths were used. These catalysts are usually considered as being nonselective for the oxidation of alkanes (i.e. they are used in combustion of hydrocarbons); however, control of the oxygen-to-hydrocarbon ratio as well as the high surface temperature reached on the very active metal surface allowed the reaction pathway to be directed towards the formation of olefins. In fact, the key point of this reactor type is the large temperature difference between the catalyst surface (where temperatures are as high as 1000°C) and the gas phase due to the limitation of the heat exchange through the boundary layer. Moreover, the residence time with respect to the thin layer of the catalytically active component in these reactor configurations is a few milliseconds. Very slow deactivation due to coke deposition was observed and the selectivity to olefins (ethylene from ethane, propylene and ethylene from propane and from *n*-butane, propylene and isobutene from isobutane) was in most cases higher than 60% with a very high fuel conversion.

6. Technologies aimed at control of the oxygen supply to the catalyst

In the case of redox-type catalysts, it is clear that control of the redox properties of the catalyst is fundamental in order to obtain the best catalytic performance. Examples exist in the literature which describe the use of reactor technologies aimed at control of the oxygen supply to the reaction medium for the selective oxidation of paraffins. In particular, there is considerable interest in the use of catalytic membrane reactors, where the oxygen supply is controlled either via selective ionic diffusion (dense membranes), or through control of molecular diffusion (inorganic porous membranes) [177–179].

With porous inorganic membranes, the hydrocarbons and oxygen are fed separately to the core and shell sides of the membrane reactors. One advantage lies in the possibility of supplying oxygen to the reaction zone (where the catalyst is placed) in a distributed fashion over the entire reactor length, instead of feeding it together with the hydrocarbon at the reactor entrance (Fig. 6). The supply of the oxidant to the reactor medium is therefore governed by the laws of mass transport through the porous membrane. In this way, the concentration of dioxygen all along the reactor can be kept sufficiently low to favor kinetically the partial oxidation reactions instead of complete hydrocarbon combustion and by keeping the catalyst at a desired average oxidation level. A further advantage of this configuration is that the reactants are kept separate, thus avoiding any flammability hazard; it is thus possible to feed undiluted fuels.

Most publications which describe the use of membrane reactors deal with methane oxidative coupling [180–183] but a few papers have described the oxydehydrogenation of propane to propylene [184–186]. In the latter case, either a V–Mg–O based catalyst [184] or a γ-Al_2O_3/V_2O_5 based catalyst [185,186] was used; in both cases, the active component was coated in the form of a thin layer over the ceramic α-alumina membrane. No significant membrane effect was found with these mesoporous materials since they do not act as effective gas barriers. In the case of the V–Mg–O system, no difference in performance was observed between the cofeeding mode and the separate feeding mode [184]. On the contrary, an improvement in

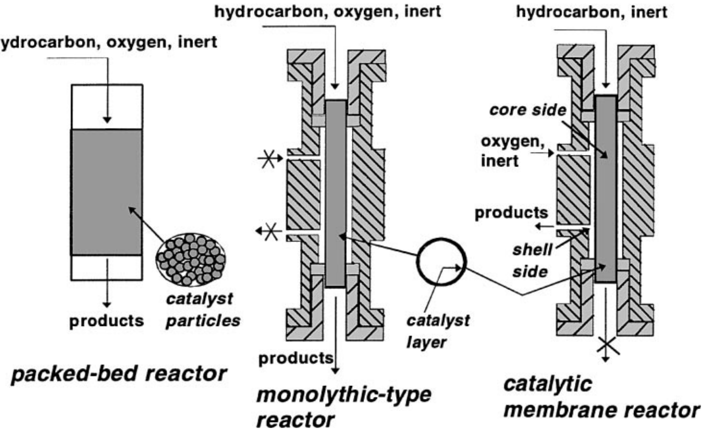

Fig. 6. Laboratory reactor configurations for the selective oxidation of paraffins.

selectivity was observed when a hybrid membrane configuration was adopted with separate feeding in a case when a V–Mg–O catalyst bed was enclosed in a microporous zeolitic membrane reactor. Analogously, no differences between the cofeeding configuration and separate feeding were observed in the case of the γ-Al_2O_3/V_2O_5 based catalyst dispersed on a ceramic membrane [185,186]. However, an improvement in selectivity to proylene, due to a lower contribution of the consecutive reaction of propylene oxidation to carbon oxides, was observed when the performance obtained with the membrane reactor was compared with that of a packed bed reactor (Fig. 7). Furthermore, the turnover number was substantially improved. This effect may be attributed either to a distribution of the oxygen along the reactor (thus achieving a more favorable hydrocarbon-to-oxygen ratio all along the catalytic bed) or to a more efficient transport mechanism (i.e. convection instead of diffusion) [179] as a consequence of the very low residence time of gaseous components with respect to the thin layer of active component (in the order of few milliseconds). A very low residence time of the hydrocarbon in the catalytically active material has also been claimed to be beneficial for selectivity in the dehydrogenation of methanol to formaldehyde due to a more narrowly distributed residence time of reactant and product in the narrow pore size distribution of the catalytically active layer with respect to the bulk particle of the same active component [187].

Solid-electrolyte membranes for the ionic diffusion of oxygen (via O^{2-}) are made of ZrO_2, CeO_2, ThO_2, Y_2O_3-ZrO_2, or $SrCeO_2$ [188]. Perovskite solids (La/Sr, Y/Ba/Cu mixed oxides), are materials exhibiting superior conduction rates as those can transport oxygen with a rate of 10^{-11}–10^{-9} mol cm^{-2} s^{-1} through a vacancy diffusion mechanism, this being several orders of magnitude higher than for conventional solid electrolytes. The mechanism of diffusion consists of dissociative chemisorption of dioxygen followed by ionization of the atoms and transport of the latter

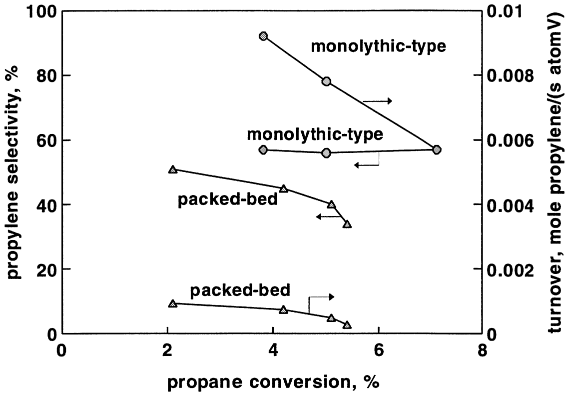

Fig. 7. Selectivity to propylene and turnover rate in propane oxidehydrogenation as functions of propane conversion over a V_2O_5/γ-Al_2O_3 catalysts in two different reactor configurations. Reaction conditions: temperature 450°C, feed composition: 9.2 mol% propane, 1.6 mol% O_2, balance He. Residence time was varied.

through the crystalline lattice to the opposite surface where they lose their charge and again form oxygen. The driving force for the diffusion of the O^{2-} species can be either a difference of pressure between the two sides of the membrane or an electrical potential gradient obtained by electrodes deposited on the sides of the membrane. The possibility of pumping specific ionic oxygen species at a controlled rate directly to the catalytically active surface of the catalyst may allow very specific oxidation reactions to be carried out, thus with a very high theoretical selectivity to specific products. The limitation of these materials is however the low rate of permeation and thus the low productivity which can be achieved; permeation can be facilitated by operation at high temperature (higher than 600°C). In addition, one technological limit is the problem of sealing these membranes into devices which have to operate at high temperature.

Different applications in the field of oxidation have been claimed which make use of oxygen-conducting electrolytes, especially in the oxidative transformations of methane [189,190]. In this case, a further advantage is the rejection of nitrogen (when air is fed to the shell side of the membrane). In this way it is possible to overcome the problem associated with separation of nitrogen from the products and from unconverted reactant in the process of methane oxidative coupling.

An electrochemical reactor using yttria-stabilized zirconia (YSZ) as a solid electrolyte and gold and silver as the anode and the cathode respectively has been used for the oxidation of alkanes at temperatures lower than 475°C [191,192] and for the partial oxidation of methane to syngas [193]. It was reported that ethane, propane, butane and isobutane can be oxidized with good specificity to aldehydes and ketones (acetaldehyde from ethane, acetone, propylene oxide and acrylaldehyde from propane, methylvinylketone, methylethylketone and butyraldehyde from *n*-butane, methacrolein from isobutane) even though at rather low conversion.

Another remarkable example of a reactor technology aimed at the control of oxygen supply is the CFBR (Circulating Fluid Bed Riser) reactor developed by DuPont for the oxidation of *n*-butane to maleic anhydride, and which is now commercially available [194–198]. Similar technologies for alkane oxidation have been developed (but not yet made commercial) by ARCO for methane oxidative coupling and for paraffin oxydehydrogenation [199] and by Monsanto for propane ammoxidation [200] . Indeed, the first example in the field of hydrocarbon selective oxidation was developed for the ammoxidation of *m*-xylene [201]. All of these processes have a first step which operates under (almost) anaerobic conditions and a second step in which the reduced catalyst undergoes reoxidation by contact with molecular oxygen. It is thus possible to decouple the two-steps of the redox reaction in two separate reactors and make the hydrocarbon (HC) interact with the catalyst in the absence of gas-phase oxygen to yield the oxidized product (HCO):

$$\mathrm{HC} + \mathrm{cat}_{\mathrm{ox}} \rightarrow \mathrm{HCO} + \mathrm{cat}_{\mathrm{red}}$$

$$\mathrm{cat}_{\mathrm{red}} + \mathrm{O}_2 \rightarrow \mathrm{cat}_{\mathrm{ox}}$$

Continuous catalyst reactivation by transport from the reaction vessel to the regeneration one is achieved. In addition, very fast exothermic reactions can be managed better than in fluidized-bed reactors. The operation becomes intrinsically safe since the hydrocarbon and oxygen are not fed together but separately in the two vessels. Other advantages with respect to fixed bed technology or conventional fluidized-beds are [16] as follows:

1. High flexibility of the plant, since the two sections can be designed and optimized separately by choosing the best conditions for each. Only the oxidation processes involving oxygen ion transfer from the catalyst surface to the organic substrate occur, while undesired reactions involving molecular oxygen in the gas phase (i.e. homogeneous reactions of combustion) do not occur.
2. Higher throughput because of the higher gas velocity and the possibility of independently optimizing the kinetic conditions for the two stages.
3. Excellent intragrain and interphase heat and mass transfer because of the fine solid particles used and of the high gas velocity relative to the solid. Consequently, very high catalyst efficiencies can be achieved and the thermal gradients inside the particle can be considered to be minimal.
4. Higher product concentration, and hence fewer recovery problems.
5. As in turbulent fluidization, gas–solid contacting is improved with respect to the bubbling/slugging regime.

6. The possibility of achieving better control of temperature in the riser by efficient cooling (quenching) through injection of cold gas along the reaction pathway.

On the other hand, the disadvantages are:

1. The need for a catalyst with particular properties: high attrition resistance and high availability of active centers even in the absence of one reactant (i.e. ready availability of bulk oxygen).
2. Significant uncertainty in scale-up due to radial and axial gradients of the solid and the lack of a model that allows for geometric parameters and discontinuity at the inlet and outlet of the riser to be foreseen.

Using a pilot CFBR reactor, 75% selectivity to maleic anhydride at up to 50% *n*-butane conversion, for hydrocarbon concentrations up to 50%, were claimed. The rate of catalyst circulation is affected by the amount of active oxygen available on the catalyst surface. It was calculated that the available oxygen corresponds to one surface monolayer arising by oxidation of vanadium. When the rate-determining step is catalyst reoxidation, a long residence time in the reoxidation vessel is required, and therefore, in order to achieve acceptable productivies of maleic anhydride, very high energy costs for circulating large amounts of catalyst are required [202].

7. Conclusions

Three main classes of catalysts have been described for the selective oxidation of light alkanes, and those, due to their very different characteristics, operate under different temperature conditions and give rise to different reaction mechanisms:

1. Redox metal oxide-based catalysts, which are active below 400–450°C and for which the mechanism can be considered as completely heterogeneous (except when temperatures higher than 450–500°C are used). For less reactive catalysts, temperatures higher than 500°C can lead to thermal, uncatalyzed dehydrogenation of the paraffin followed by a catalyzed O-insertion into the olefin.
2. Nonredox metal oxide catalysts which are active above 500°C and are employed for the oxidation of methane and ethane. Under these conditions, the reaction begins on the catalyst surface, with generation of alkyl radicals, which then react in the homogeneous phase.
3. Noble metal-based catalysts which under particular conditions (temperature higher than 700°C, very low residence time) may become selective in alkane oxidation. In this case, the mechanism also occurs in part on the catalyst surface, in part in the proximity of the catalyst surface, (in the boundary layer) and in part in the gas phase.

Acknowledgements

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