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V-BASED CATALYSTS FOR THE ODH OF LIGHT PARAFFINS

The most recent results on the ODH of light paraffins over V-based catalysts are here reviewed. Process selectivity remains a key problem, especially for propane ODH. Olefin yield can be improved only by coupling a selective catalyst formulation, by optimising the reaction conditions and by proper process and reactor design.

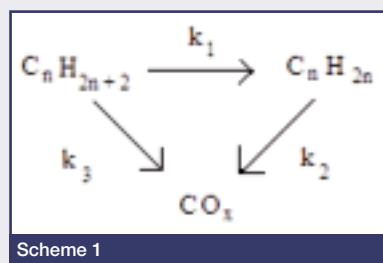
Light olefins are important building blocks for the polymers and intermediates industry [1]. Ethene and propene are mainly produced by steam cracking of naphtha or light hydrocarbons, which accounts for 95% of ethene and 70-75% of propene production in Western Europe. The remaining propene fraction comes from FCC units and dehydrogenation processes [2]. The need of light olefins is progressively growing, with a higher rate for propene, leading to the necessity of process

improvements [3]. This is particularly relevant also because steam cracking is one of the most energy demanding refinery processes and accounts for very high CO₂ emissions. Direct dehydrogenation can be an interesting alternative when low valued feedstocks are available. However, it is an endothermal reaction needing high energy input, it is equilibrium driven and the catalyst may be easily deactivated by coking. Nevertheless, it is a direct and sufficiently selective way to the desired olefin, decreasing the impact of the separation

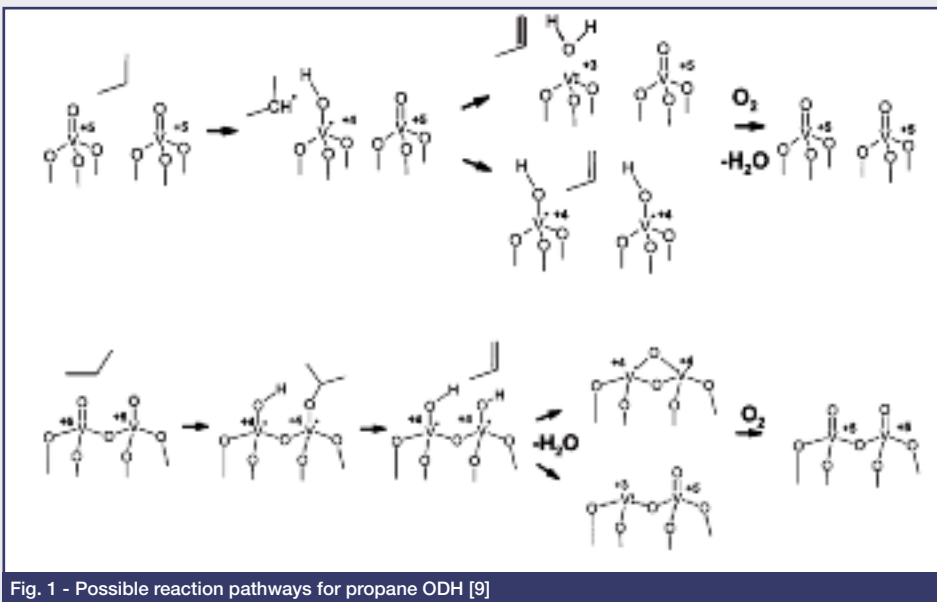
and purification section with respect to a steam cracking unit. The oxidative dehydrogenation (ODH) of light paraffins to the corresponding olefins has been proposed as a mean to overcome all these limitations. Indeed, it allows a direct supply of the required heat of reaction by coupling combustion to the endothermal dehydrogenation reaction, so leading to an autothermal process. Furthermore, it exceeds the equilibrium conversion by withdrawing H_2 and oxygen addition limits severe catalyst coking [4]. In spite of the considerable attention paid to this process and testified by a certain number of patents [see e.g. 5, 6 and references therein], the ODH technology can be hardly considered mature and it has not yet found commercial application due to selectivity issues. Indeed, oxygen should ideally consume H_2 , but paraffins and (most of all) olefins combustion are an unavoidable side reaction, which drives olefins yield below acceptable limits. Many efforts have been addressed to improve process selectivity. By examining the most recent investigations it clearly appears that olefin yield can be improved by using different strategies, *i.e.* by developing intrinsically more selective catalyst formulations (active phase, support and preparation procedure), by optimising the reaction conditions (temperature, contact time, O_2 /paraffin feeding ratio) and by suitable reactor and process design. This review focuses on the most recent developments on these topics.

Reaction pathways and kinetics

The following schematic reaction network has been proposed [7-9]:



with respect to the paraffin, which imposes to kinetically quench the desired product to limit its further oxidation. The contribution of k_3 is not univocal. Indeed, the extent of the direct combustion of the paraffin can be roughly estimated by extrapolation of the olefin selectivity curve at zero conversion and showed strongly dependent on the catalyst and on the paraffin. Direct propane combustion was considered negligible e.g. on 2.7 wt% VO_x /SBA-15 [11], whereas an extrapolated 80% ethene selectivity has been found for the ODH of ethane on 10 wt% VO_x / Al_2O_3 [12], indicating a non negligible direct ethane oxidation. However, similar conclusions have been drawn also for propane ODH on VO_x / Al_2O_3 catalysts [13]. In this case



propane conversion influenced more CO than CO_2 selectivity, suggesting that CO formation is likely due to the consecutive propene reaction. A substantial contribution of the direct paraffin oxidation has been confirmed for ethane and resulted negligible for higher hydrocarbons, according to [14].

Different possible reaction pathways have been proposed [8, 15], depending on the polymerisation degree of surface V species.

According to DFT calculations a one-electron reduction seems more likely for isolated V^{5+} species, leading to V^{4+} , which is readily reoxidised by O_2 (Fig. 1, top). The latter reaction is often very fast, leading to a zero apparent reaction order with respect to molecular oxygen [4, 11, 16], whereas, the apparent reaction order with respect to propane is usually one. A weak inhibition by H_2O has been also found for VO_x / Al_2O_3 samples [4]. However, a two-electron reduction mechanism is also proposed for dimeric V species, as depicted in the same Fig. 1 (bottom) [15]. It is not excluded also for the monomeric ones [8] and it is assumed as the preferred reaction pathway by some authors [16]. Also in this case a strong dependence on the support chosen is evidenced, the V^{4+}/V^{3+} ratio in the reduced catalyst depending on the possible delocalisation of unpaired electrons and on the amount of oxygen vacancies of the support (especially for TiO_2) [9]. Discrepancies are found in the literature on this point. Indeed, according to Koranne *et al.* [17] a preferential $V^{5+} \rightarrow V^{4+}$ reduction would occur when using Al_2O_3 as support, while a 70% $V^{5+} \rightarrow V^{3+}$ reduction has been calculated for silica supported samples. By contrast, other researchers [18, 19] report that the latter reduction path holds for VO_x / TiO_2 catalysts, whereas the former one, leading to V^{4+} , is active for Al_2O_3 and SiO_2 based samples. Furthermore, the vanadyl oxygen seems not to be responsible for the first oxidative formation of propene, but it is likely involved in its non selective complete oxidation. This explains the reason why stronger V-O bonds observed for some V-Si-O systems

with respect to V-Al-O ones may lead to higher selectivity to propene [20-22].

It seems consolidated [11, 15] that C-H bond cleavage represents the rate determining step for both olefin formation and combustion, lattice oxygen (vanadyl oxygen) playing an important role in the latter reaction [9]. Indeed, when using differently reduced catalysts with equal total oxygen availability one may observe an increase of olefin selectivity for the most reduced samples, attributed to a lower impact of the consecutive oxidation reaction [12]. Another interesting parameter, varying with the V oxidation state, is its acidic character, decreasing in the following scale $V^{5+} > V^{4+} > V^{3+}$. Therefore, a more reduced catalyst adsorbs the basic olefin to a lower extent and this unfavours its consecutive oxidation.

A Mars van Krevelen reaction mechanism is usually proposed for the ODH reaction on V based catalysts [11, 23]. An intrinsic activation energy of 140 kJ/mol has been estimated for propane ODH on a VO_x /SBA-15 catalyst, much higher than what reported by Malleswara *et al.* [23], who calculated an activation energy of 50-60 kJ/mol for propene formation on V-Mo oxides supported on alumina and titania. However, the same authors found that active sites reoxidation was characterised by rather high activation energy. Furthermore, when changing catalyst composition they did not observe a substantial variation of activation energy, the difference in reaction rates being attributed to a variation of the frequency factors. Similar conclusions have been also reported when comparing the ODH of ethane and propane over VO_x/Al_2O_3 samples [4]. The authors reported similar activation energy for both reactions and the much lower reaction rate obtained for the former reactant was attributed to a lower frequency factor or to a lower number of active sites. A lower value of the preexponential term would then imply a larger negative formation entropy of the transition state for ethane than for propane.

A detailed kinetic analysis has been also proposed for the ODH of propane on $VO_x/\gamma-Al_2O_3$ [24]. A first set of kinetic equations has been analysed, concluding that direct propane oxidation seemed negligible, oxygen partial pressure did not influence sensibly the rate determining step and the O_2 /propane ratio was important for selectivity and active sites regeneration. The authors also proposed different microkinetic models following LHHW, Eley-Rideal or Mars van Krevelen reaction mechanisms, the latter seeming more suitable to interpret the kinetic data. A Mars van Krevelen mechanism was also supported by isotopic exchange experiments [13], confirming that surface oxygen was responsible for propane ODH and gaseous oxygen was only involved in active sites regeneration. Furthermore, in the presence of V_2O_5 propene selectivity decreased more quickly with increasing propane conversion, indicating bulk vanadia as active phase for non selective oxidation. Finally, when cofeeding propane and propene, the conversion of the former species decreased, showing that both reactants were in competition for the same active sites [13].

Catalyst formulation

Three main V-based catalysts families can be found in the literature: supported vanadium oxide catalysts, V-P catalysts [see e.g. 25] and V-containing polyoxometallates [26]. Here the attention is focused on the former class of materials.

Mono- or bi-metallic (especially V-Mo, [23, 27]) formulations have been proposed for this application, differing for the support employed, for V loading and for the preparation procedure. All these elements concur to a different arrangement of the VO_x active sites, ending in marked differences of activity and selectivity. A detailed assessment of the nature of V-containing species can be done by coupling many different characterisation techniques, among which Raman, FT-IR, UV-Vis spectroscopies, XRD and TPR, the latter to assess a mean V^{n+} oxidation state. Four types of V-containing species have been identified in supported VO_x catalysts: (1) isolated surface VO_4 species containing one terminal V=O bond and three bridging V-O-support bonds, (2) polymeric surface VO_4 species containing one terminal V=O bond and three bridging V-O-V/V-O-support bonds, (3) crystalline V_2O_5 and (4) mixed oxide compounds with the oxide support, usually forming upon calcination at high temperatures (e.g. $Zr(V_2O_7)_2$, $AlVO_4$, $V_xTi_{1-x}O_2$, $NbVO_5$, $Mg_3(VO_4)_2$, $Mg_2V_2O_7$) [16]. Naked acid sites due to the support can be also present, depending on V loading and support nature, which deeply influence catalyst selectivity [28].

Many different supports have been tested, such as SiO_2 [16, 29, 30], $\gamma-Al_2O_3$ [4, 10, 13, 16, 24, 28, 31, 32], TiO_2 [10] and ZrO_2 [16, 33]. V-substituted zeolites or silicalites [34] have been also proposed, with particular attention in the last years to mesoporous materials, such as MCM-41 and SBA-15 [35]. A mesoporous framework can allow reaching a higher V dispersion during traditional catalyst preparation by impregnation, with consequent high activity and selectivity (*vide infra*). Furthermore, a mesoporous pore network facilitates propene diffusion back to the gas phase with consequent lower impact of its consecutive oxidation on selectivity. Isomorphous V substitution for the host framework cations seems less effective for this kind of materials, lowering catalyst selectivity, likely due to the formation of acidic sites.

At low V loading isolated monovanadate species are usually present, which progressively oligomerise and polymerise with increasing V concentration up to a monolayer and beyond this point V_2O_5 segregation occurs. Different V loadings and V surface densities corresponding to monolayer completion characterise each support [16, 31, 36, 37]. For example, the extent of polymerisation follows the trend $Al_2O_3 > ZrO_2 > SiO_2$ [16]. Isolated VO_x species can be found on SiO_2 up to ca. 2 V/nm² surface density, whereas alumina- or titania-supported samples showed higher surface density (7-8 V/nm²), corresponding to polymeric vanadyl species. With the latter supports, it was difficult to attain high V dispersion, unless by excessively decreasing V loading, detrimental for activity.

The oxide support cation interferes with the reactivity of surface VO_4

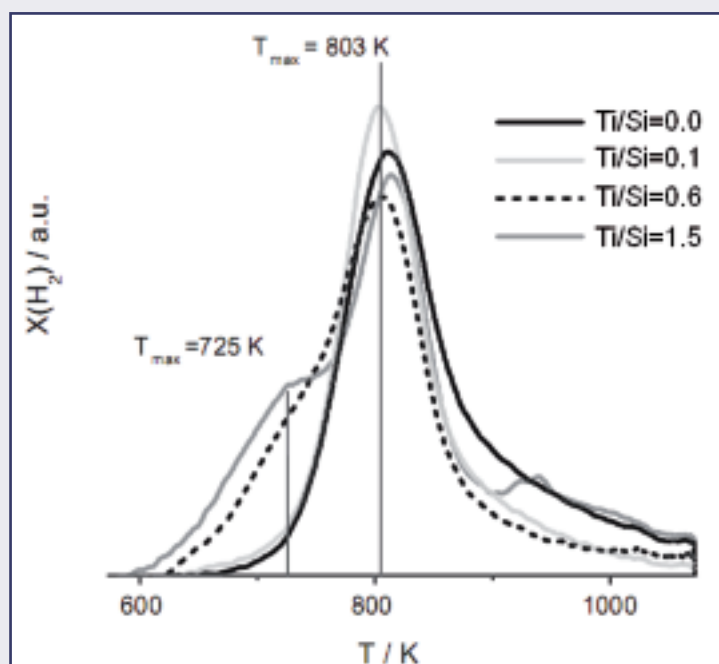


Fig. 2 - Temperature programmed reduction of V-(Ti-Si)O₂ catalysts. Readapted from [43]

species by affecting the electron density or basicity of the bridging V-O-support bond. The reactivity of the latter is related to the support cation electronegativity, a low value of such parameter increasing the electron density of the V-O-support bond [16].

High reaction rates for the ODH of C₂-C₄ paraffins are found with polymerised vanadate species, up to the formation of a VO_x monolayer, while lower activity and selectivity are usually associated with the presence of bulk V₂O₅ [11, 12, 38]. Furthermore, when the support has a strong Lewis acidity [13] the formation of a compact VO_x monolayer completely covering the support acid sites is welcome to improve selectivity.

Sometimes mixed metal oxide phases form, such as AlVO₄ with alumina supported samples and CeVO₄ with CeO₂ supported ones [31]. In both cases no particularly positive effect of such phases is reported on activity, nor on selectivity.

Usually, the higher the reducibility of VO_x species, the higher is catalytic activity for the ODH reaction. No univocal interpretation is found also from this point of view. Indeed, according to some researchers [39] the ease of reduction follows the sequence: defective coordinatively unsaturated surface V ion > isolated vanadyls > bidimensional polymeric vanadyls > three-dimensional clusters or crystalline V₂O₅. By contrast, it was reported elsewhere [40] that the surface polymerised vanadia species are more easily reduced than isolated surface vanadia species (in the presence of ethane or *n*-butane). The reason of this contradiction can be found in the support adopted, in the possible incorporation of part of V into the lattice and, ultimately, in the preparation procedure, confirming that activity and selectivity do not depend on the V aggregation state only, but also on the V-O-support interaction. An increased reducibility has

been indeed observed when increasing V loading on Al₂O₃ up to a monolayer [31].

Different solutions have been proposed to mitigate surface acidity, such as the direct use of MgO as support (leading to propene yield up to 30% [41]) or its addition to SBA-15 to increase the basic character of the support and limit olefin adsorption [6, 41, 42]. In such way an overall increase to 23% butenes yield has been reached with respect to the unmodified support [41]. The addition of a second metal oxide increased propene yield with alumina-based catalysts, whereas the addition of alkali or P to TiO₂ increased selectivity at the expenses of activity [23]. Furthermore, the addition of Ti to SiO₂ improved the selectivity to propene. By combining *in operando* UV-Vis spectroscopy and TPR analysis the authors attribute the high activity to a higher V⁵⁺ reducibility when V sites are bound to Ti rather than to Si (Fig. 2). Therefore, a lower V-O bond strength is observed with Ti-Si oxide with respect to Si, which favours both the first reaction step (propene formation) and the consecutive propene oxidation reaction, however leading to an overall increase of olefin yield [43]. Different synthesis procedures have been proposed. Usually V is added by impregnation of commercial oxidic supports, but in some cases a coprecipitation technique has been used to increase V dispersion. The same procedure has been adopted to add simultaneously V and Mo oxides to a commercial P25 TiO₂ sample [23]. According to these results, molybdenum oxide is inactive for propane ODH, it does not influence catalyst acidity or V reducibility, but it has a promoting effect for catalyst activity, though its excess can depress selectivity. Optimal results were reached with ca. 3.5 wt% V e 0.5 wt% Mo. Inverted proportions are reported in [27] where a catalyst constituted by 8 wt% Mo and up to 3 wt% V, supported on Al₂O₃ is described.

Some less common preparation methods were also reported, such as atomic layer deposition [5], used to obtain thin metal oxide layers on different supports. A 50% propene selectivity has been obtained at 16% propane conversion between 400 and 430 °C, selectivity did not vary with the addition of niobia and decreased with the addition of WO₃, leading to an increase of CO₂ concentration in the outlet gas. Another unconventional preparation procedure is flame spray pyrolysis (FP), which allows to achieve a higher dispersion of VO_x supported on silica with respect to conventional methods [20-22]. This technique allows to obtain nanoparticles characterised by higher site isolation (considered beneficial) with respect to the common impregnation of V at the same V content. Furthermore, V incorporation into the support in a sufficiently stable structure may be useful especially for SiO₂ samples, because V-O-Si bonds may be easily hydrolysed with consequent V₂O₅ segregation during the reaction [3].

The V local structure was studied by means of many complementary techniques, such as electron paramagnetic resonance (EPR) and X-ray absorption (XAS). The limit of the former technique is that it is sensitive to the V⁴⁺ ion only, which however represent a possible reaction intermediate. Furthermore, it can evidence the aggregation

state of V^{4+} ions, which can be considered as an index of the overall V dispersion, since it is sensitive to the formation of ferromagnetic aggregates. According to EPR results, the V^{4+} ion is accommodated in the centre of a planar array of oxygen atoms, with a perpendicular V-O bond, which length (and therefore bond strength) depends on the support used and on the preparation procedure adopted [22]. XAS analysis confirmed the dependence of V local structure on such parameters and underlined different V-O bond length in the case of VO_x/MgO catalysts [44]. The V-O bond strength has been correlated to catalyst activity and selectivity for different supports and reaction conditions [20-22].

An extremely useful conversion vs. selectivity chart has been proposed in a recent review by Cavani *et al.* [3], where the performance of many different catalyst formulations was summarised. The comparison between ethane and propane ODH immediately evidenced that though for the former reaction important yields can be achieved, in some cases higher than 60%, the results are less encouraging for the latter application. Indeed, the reported propene yields over V-based catalysts were always lower than 30%, due to the predominant contribution of the consecutive combustion reaction. However, together with yield, productivity should be taken into account. Data reported in the same review revealed that if ethene productivity higher than $5 \text{ g}_{\text{ethene}}/\text{g}_{\text{cat}} \text{ h}$ can be achieved by using different catalyst formulations, the highest propene productivity is reached over V-based catalysts [3, 45, 46].

Process optimisation

A suitable optimisation of the reaction conditions can improve olefin yield. Usually, paraffin conversion increases with reaction temperature, however accompanied by a decrease of selectivity to the corresponding olefin.

A different strategy can be followed by decreasing as much as possible the contact time. Of course this inhibits the consecutive oxidation of the product, but it limits the overall reaction rate and a compromise has to be found also in this case. A different approach has been followed by Beretta *et al.* [47-50], who studied ethane and propane ODH in a short contact time autothermal reactor over a Pt/Al_2O_3 oxidation catalyst. Time factors as low as 10^{-6} - $10^{-7} \text{ kg}_{\text{cat}}/\text{h}/\text{L}(\text{NTP})$ could be reached under these conditions. The analysis of the homogeneous phase reaction and of the catalytic one allowed to conclude that the chosen catalyst was active for the unselective oxidation only, but that this could be coupled with the gas phase homogeneous reaction to supply the required heat. Selectivity to olefins (ethene+propene) as high as 50 mol% have been achieved at 90% propane conversion. A detailed description of optimal reaction conditions and of products distribution can be found in the cited references, together with a comparison between gas phase pyrolysis and the catalytically promoted process. In addition, the same active phase has been deposited on a FeCrAlloy support and loaded in a tubular reactor. The small amount of active

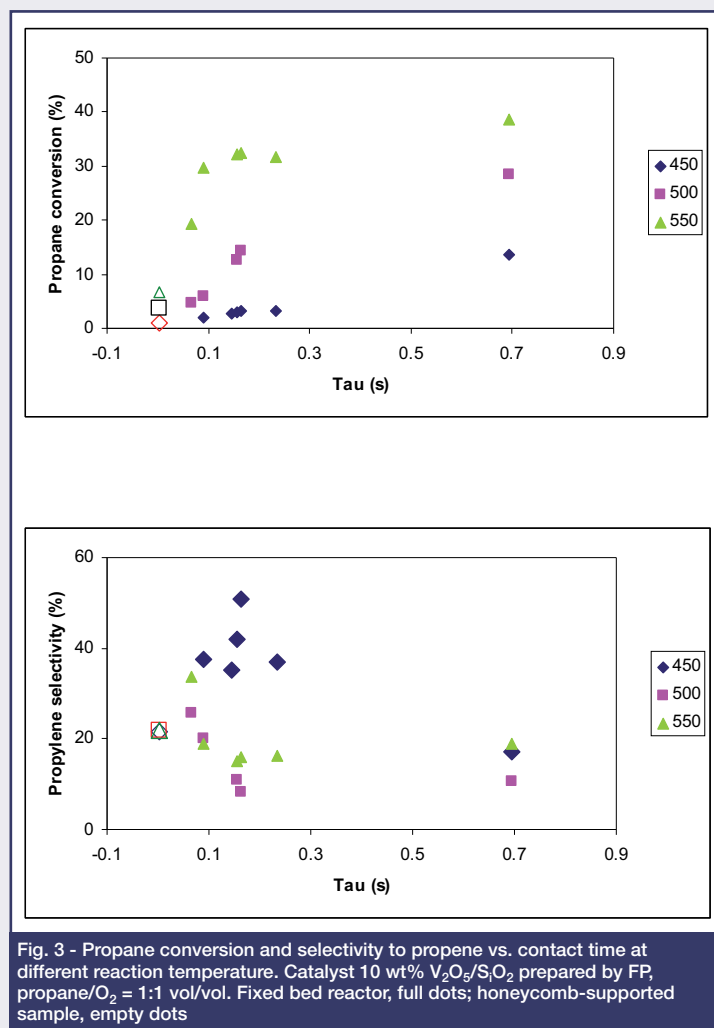


Fig. 3 - Propane conversion and selectivity to propene vs. contact time at different reaction temperature. Catalyst 10 wt% V_2O_5/SiO_2 prepared by FP, propane/ O_2 = 1:1 vol/vol. Fixed bed reactor, full dots; honeycomb-supported sample, empty dots

phase allowed to reach very high space velocity and the metallic support guaranteed optimal thermal exchange. Also in this case, however, the catalyst was used only to help the light off of the homogeneous reaction and to thermally support the process through complete oxidation.

The concept of operating at low contact time was extended to a V-based catalyst more selective for propylene production rather than for complete combustion [I. Rossetti, unpublished results]. A 10 wt% V/SiO_2 catalyst for propane ODH, prepared by FP and described in [20, 22] was loaded on a 400 cpi cordierite monolith. A primer was necessary to provide suitable grafting of the active phase. SiO_2 was selected as primer and its deposition on the monolith was achieved by repeated wash coating from a TEOS solution and subsequent calcination. The active phase has been added by dip-coating from an aqueous suspension of the catalyst. The optimal amounts of primer and active phase to guarantee a uniform and stable coating were found 0.4 wt% for SiO_2 and 0.15 wt% for the active phase. A higher loading ended in the formation of deep cracks in the coating. This catalyst amount allowed to reach a contact time of 2.3 milliseconds in our testing apparatus, ca. two

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orders of magnitude lower than the lowest value used for our standard fixed bed tests. The decrease of contact time brought about a decrease of propane conversion, as expected. However, this catalyst formulation revealed more selective for the complete oxidation of the substrate, rather than for its selective oxi-dehydrogenation, as shown in Fig. 3. Indeed, though the conversion attained with the honeycomb supported sample (empty symbols in Fig. 3) is fairly in line with the level expected with the very short contact time attained, the selectivity to propene falls well below the expectations. High CO_2 selectivity was observed and coke formation revealed significant. This was partly due to the exposure of the primer on the monolith surface, due to the very low catalyst loading, in turn determined by coating stability. Therefore, a compromise between the stability of the supported primer and catalytic layers and catalyst performance should be reached.

A completely different approach has been followed elsewhere [6]. A microchannel reactor has been developed for propane ODH, leading to ca. 20% propene yield at 30% conversion (propane/ $\text{O}_2=1$, $T=580^\circ\text{C}$). This configuration couples dehydrogenation channels with ODH ones, to achieve autothermal conditions. A $\text{V}_2\text{O}_5/\text{MgO}$ catalyst is loaded on ceramic or metallic alloy, to obtain a suitable thermal control and to efficiently quench the products. Furthermore, very low contact time is usually achieved in this configuration. These results contradict what reported by different authors [51], who did not observe any substantial difference among fixed bed and microchannel reactors. However, it should be underlined that interesting selectivity values have been observed only in the presence of an inert gas, which substantially decreases the volumetric efficiency of the system.

Since partially reduced catalysts show lower oxygen availability, or, better, the residual oxygen is more tightly bound to V, it is possible to achieve, at least in principle, a higher selectivity with respect to fully oxidised catalysts [12]. This also suggested the use of a different oxidising agent, e.g. N_2O , which led to an increase of propene selectivity at isoconversion. However, it demonstrated less effective than O_2 in coke removal [42]. Another possible process configuration is constituted by alternate feeding of the reactants (redox decoupling), which is also interesting to address safety issues. Propane is fed for a certain time lapse to a fixed bed reactor, containing a fully oxidised catalyst. Then catalyst regeneration is accomplished by feeding oxygen or air. Interesting results have been obtained for V-Si and V-Al catalysts [20-22, 52-54], obtaining up to 10.7% propene yield at 550°C (14% conversion, 76% selectivity) with 10 wt% VO_x/SiO_2 prepared by flame pyrolysis [22]. The same catalyst

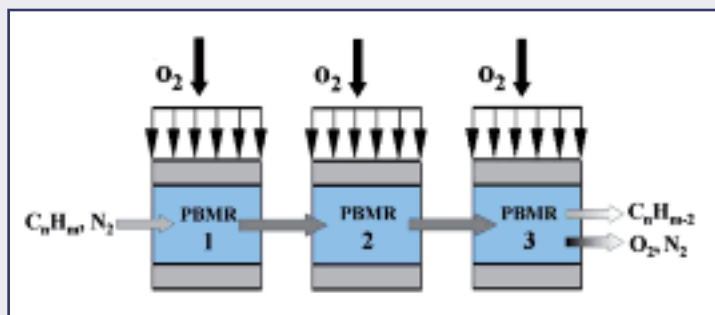


Fig. 4 - Partialisation of oxygen feed in a three stage membrane reactor. Readapted from [55]

tested in standard cofeed mode led to 32% propane conversion and 27% selectivity to propene with an overall 8.6% yield to the desired product at the same temperature. The FP prepared catalysts likely allowed to obtain an improved selectivity in the redox decoupling mode due to a higher dispersion of V sites, a qualifying attribute for this operating mode [3, 4].

The possibility to feed separately the paraffin and the oxidising agent opens the way to the use of membrane reactors. An interesting comparison between the performance of a traditional fixed bed and a membrane reactor has been proposed [55]. The $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst has been supported on a ceramic $\alpha\text{-Al}_2\text{O}_3$ membrane, coated by $\gamma\text{-Al}_2\text{O}_3$, with a final 10 nm pore size. The catalyst was loaded in the internal part of the reactor, where propane is fed, whereas oxygen flows in the shell and is forced through the membrane since no gas outlet is provided on the shell side. Semi-pilot scale activity tests have been performed for both the ethane and propane ODH reactions, focusing on the effect of contact time, temperature and comparing the oxygen cofeeding vs. radial dosage operating modes (Fig. 4). Reactor simulations allowed to predict the concentration profiles along the proposed reactors (Fig. 5). The main advantage of the membrane configuration was the possibility to feed a higher overall oxygen amount with respect to the fixed bed, keeping conversion at higher level without penalising so much selectivity. However, the advantage of a membrane layout was more evident for ethane than for propane ODH.

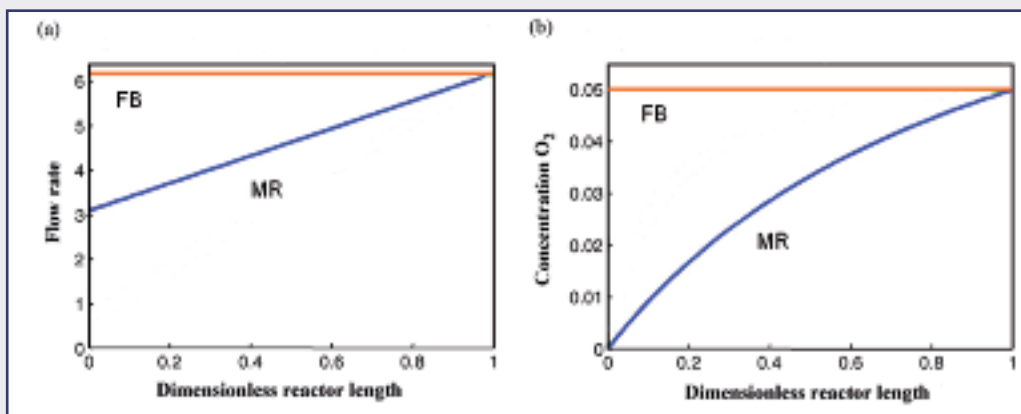


Fig. 5 - Total flow rate (a) and oxygen concentration (b) profiles in a fixed bed reactor (FB) and in a membrane one (MR). Readapted from [55]

Conclusions

V-based catalysts showed interesting catalytic activity and selectivity for the oxidative dehydrogenation of light paraffins. Better yields were generally reported for ethene than for higher olefins. Catalyst selectivity remains a key problem, especially for propene. This problem should be addressed by selecting a proper catalyst formulation (active phase(s) and support) and carefully controlling the nature of active sites with suitable synthesis procedures. The development of selective reactor designs or operating procedures may help to further increment olefin yield.



Born in 1974, Ilenia Rossetti got her PhD degree c/o Università di Milano, where she is presently senior researcher since 2002. Her research interests focus on heterogeneous catalysis, mainly in the fields of environmental catalysis and energy conversion. She is co-author of ca. 40 papers, 60 congress presentations and one book.

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RIASSUNTO

Catalizzatori a base di V per la deidrogenazione ossidativa di paraffine

Vengono esaminati i più recenti risultati ottenuti per la produzione di olefine leggere mediante deidrogenazione ossidativa delle corrispondenti paraffine. La selettività del processo resta un punto cruciale, in particolare nel caso dell'ODH del propano. Un significativo aumento della resa si può ottenere solo combinando la scelta di catalizzatori intrinsecamente selettivi, l'ottimizzazione delle condizioni operative e sviluppando nuove configurazioni reattoristiche.