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Novel approaches for the improvement of selectivity in the oxidative activation of light alkanes

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Dedicated to Prof. Ferruccio Trifirò on his 65th anniversary.

Abstract

Selectivity is the key parameter for the practical application of oxidative activation of light alkanes, improving energy and raw materials utilisation efficiency and reducing CO_2 formation and emission. The intrinsic process complexity and the catalyst multifunctionality imply the need of a close control of many parameters (active centres nature, reactant composition, reaction mechanism, etc.) to improve the selectivity. Novel approaches to get this goal along three complementary directions, say: oxide nanocatalysts preparation by non-conventional routes (to tune the nature of the active centre), oxidant selection (to avoid overoxidation), and catalyst arrangement (to take advantage of the reaction mechanistic features), are presented and discussed by means of representative examples of their application. These include ODH of propane on nanosized molybdates, ODH of ethane with CO_2 on ceria- and MCM-41-based catalysts, and selective oxidation of light alkanes to unsaturated oxygenates over transition metal substituted MCM-41 catalysts.

Keywords: Selectivity; ODH of light alkanes; CO_2 use as selective oxidant; Isobutane oxidation to methacrolein; Propane oxidation to acrolein; Nanosized molybdate catalysts; Nanoxide catalysts; V-MCM-41; Co-MCM-41; Cr-MCM-41; Mesoporous redox catalysts

1. Introduction

Selectivity is the key parameter for the practical application of a catalyst in any type of catalytic reaction. A high selectivity is necessary for reaching a high efficiency in the use of raw materials and energy, as well as for reducing the costs of products separation downstream. The issue of improving the selectivity of a catalyst is even more critical in the case of selective oxidation of hydrocarbons. This is so because the thermodynamically most stable product is carbon dioxide, which release to atmosphere has an important effect in the climate change due to its properties as greenhouse effect gas, and which emissions have to be reduced as fixed in the Kioto Protocol. Therefore, an improvement in the selectivity of partial (selective) oxidation processes involves not only an improvement in the efficiency of the process but also a meaningful reduction of the emission of greenhouse effect gases, thus contributing to accomplish the Kioto Protocol.

The selective transformation of low molecular weight alkanes into more valuable products, such as olefins or unsaturated oxygenates, is still a challenging task. This is due to their low intrinsic chemical reactivity which demands a high energy input to activate them. Dehydrogenation of alkanes to light olefins shows some major disadvantages, i.e., a high tendency to coking and consequently short catalyst lifetime [1]. Oxidative catalytic processes such as oxydehydrogenation (ODH) are considered a promising alternative as limitations by the chemical equilibrium are removed by the coupling of dehydrogenation and hydrogen oxidation, and the presence of oxygen limits coking and extends, therefore, catalyst lifetimes [2]. However, in spite of the huge research effort devoted to the research of ODH of alkanes since the pioneering review by Centi and Trifirò [3], the only successful industrial process to date is maleic anhydride production by oxidation of *n*-butane. The main reason is the relatively higher reactivity of the desired

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product molecules, that can undergo rapid consecutive overoxidation in the presence of catalysts able to activate the much less reactive alkane molecule. In this situation, the selective activation of the alkane becomes a quite complex process that requires the catalyst to be intrinsically multifunctional, and makes necessary a fine control of catalytic properties. All these reasons may explain why this is still one unsolved industrial problem for most of the light alkanes.

Both the intrinsic process complexity and the catalyst multifunctionality imply the need of a close control of many parameters (active centres nature, reactant composition, reaction mechanism) in order to improve the selectivity of the oxidative activation of light alkanes. Therefore, we have developed, in cooperation with other groups, novel approaches to overcome these difficulties along three complementary directions: (1) oxide nanocatalysts preparation by non-conventional routes, to tune the nature of the active centre; (2) oxidant selection, to avoid overoxidation; (3) catalyst arrangement, to take advantage of the reaction mechanistic features. In this paper these strategies, and their combination, are presented and discussed by means of representative examples of their application to ODH and/or partial oxidation of ethane, propane and isobutane.

2. Oxide nanocatalysts preparation by non-conventional routes

Interest on oxide nanoparticles (<100 nm) is caused by their chemical and physical behaviour, unprecedented and remarkably different from those in bulk form. From the catalytic point of view, this is due to the increasing proportion of surface atoms, coordinatively unsaturated, when the particle size decreases down to the nano-scale. Most of the catalysts used in oxidative activation of light alkanes are constituted by mixed metal oxides [2–5]. Conventional methods of preparation of oxide catalysts face two types of drawbacks: a deficient control of the physico-chemical parameters of the final resulting solid and a low energetic efficiency. The most important step during these preparations consists in a solid-state reaction, one of which main specific difficulties is its slowness. To overcome it, in the conventional methods an intensive energy input is needed, usually by a thermal route, which involves relatively high temperatures and long treatment periods. This leads to sintering, big particle sizes and relatively low surface areas, making these methods unsuitable for nanoparticles preparation.

The controlling step in this reaction is the diffusion of the constituting cations through the reactant–product interface and the product phase, which rate decreases with the increase of the diffusion path (i.e., with the product particle size). The key objective of non-conventional methods is to increase this rate by decreasing the diffusion paths, thus reducing the time and temperature of thermal treatment [6]. These "soft" methods, i.e., with low energy input during the preparation, characterized by the decrease of the particle size of the starting reactants by the use of precursors, allow to overcome these inconveniences and provide a better control of the catalytic solid at the atomic (active centre environment), micro- (particle size, crystalline phases), and macroscopic (texture, surface area) scales. The ideal would be, similarly to the homogeneous catalysis approach, to determine by molecular engineering the nature and distribution of atoms constituting the active centre; however, this is not possible for oxides, as properties of the individual centre are partly a consequence of the collective properties at the crystal scale, thus making specially relevant the influence of particle size at the nano-scale.

The approximation closest to that ideal is the use of stoichiometric 'ordered' precursors. They are prepared by using heteronuclear complexes which contain, embedded in their anionic and cationic components, the cations constituting the catalyst active phase to be prepared. The location of component cations at the atomic scale vicinity minimizes the diffusion path, allowing to obtain highly homogenous crystalline phases at moderate temperatures. Thus, the formation of a monophasic perovskite $NdCoO_3$ can be completed at temperatures as low as 873 K by using the cobalt salt of the neodymium complex with DTPA (diethylen-triamin-penta-acetic acid) as the precursor [7]; the obtained perovskite shows a highly homogeneous composition (both XPS and EDX Nd:Co atomic ratios are practically 1), an average particle size of 40 nm and a specific surface area (10.8 m^2/g) among the highest reported in the literature for this compound. However, this approach is limited by the availability of complexes that allow to obtain the desired stoichiometry, and preparation of non-stoichiometric compositions is not possible.

The alternative is the use of 'disordered' precursors, where the component cations are randomly and statistically homogeneously distributed. This is their state in solutions. So, the issue is to avoid re-distribution of cations during the drying process, and several strategies have been described in the literature to keep the random distribution of cations. Among these, sol–gel techniques are very popular and their application to catalyst preparation has been object of several reviews [8–10]. However, they are limited by the availability of the corresponding metal alkoxides, and the difficulty to control the different hydrolysis rates to obtain bi- or multi-component oxides. Alternative ways to overcome these drawbacks are the evaporation of the solvent by sudden decompression (spray-drying) or by sublimation after freezing the solution (freeze-drying), which allow obtaining multicomponent precursors.

We have used the freeze-drying method to obtain amorphous precursors to prepare a variety of mixed oxide nanocatalysts. Compared with the 'ordered' precursor method, it requires slightly higher temperatures to complete the solid-state reaction and gives a lower homogeneity of the cationic distribution. Thus, $NdCoO_3$ prepared by freeze-drying of nitrates solutions requires calcination at 973 K to be monophasic, and shows a surface enrichment of Co and a slightly broader particle size distribution (30–50 nm) but a higher (a 60% increase) intrinsic catalytic oxidation activity [7].

The low calcination temperatures needed to prepare pure phases from precursors obtained by freeze-drying method allows to obtain compounds unreachable by conventional methods due to their low thermal stability. One example is the systematic loss of potassium in the preparation of K-containing perovskites by the ceramic method [11]. We prepared potassium substituted perovskites $Ln_{1-x}K_xMnO_{3+\delta}$ (Ln = La, Nd) with a substitution degree up to 25% ($0 < x < 0.25$) by freeze-drying, obtaining monophasic materials at just 873 K for the La perovskite [12] or 973 K for that of Nd [13]. Due to these low calcination temperatures, potassium is fully retained in the structure and the particle size, 30–50 nm, gives high specific areas, between 20 and 26 m^2/g depending on the substitution degree. The catalysts are active for the oxidation of ethane at 573–648 K, and the most interesting effect of potassium substitution over these perovskites is on selectivity. For the unsubstituted samples ($x = 0$), C_2H_4 selectivity remained constant ca. 2% in the temperature range studied, a behaviour typical of perovskites as combustion catalysts. However, in the case of catalysts with higher substitution degrees ($x > 0.10$), ethene selectivity at isoconversion increases as potassium substitution increases, and on each catalyst this selectivity increases also with increasing conversion, reaching 15–20% at 10% conversion, the later effect being much more marked in the Nd-containing samples [13]. This indicates that potassium favours either the formation and/or the desorption of ethene formed via ODH of ethane, and shows how non-conventional synthesis methods allow to observe unusual catalytic behaviours.

The freeze-drying method has also been used to prepare nanosized selective oxidation catalysts, such as Ni and Co molybdates [14,15]. Calcination of the amorphous precursors, prepared by freeze-drying of mixed solutions of nitrates of Ni or Co and ammonium heptamolybdate, at temperatures as low as 573 K gives monophasic molybdates of different M:Mo (M = Co, Ni) ratios, with particle sizes below 50 nm and BET areas between 20 and 40 m^2/g. The stoichiometric molybdates were tested for the ODH of propane at 673–800 K (feed molar ratio propane: O_2: He = 1:2:17; $W/F = 70$ g h/mol C_3) and their behaviour compared with that of their corresponding homologous molybdates prepared by the conventional citrate method to obtain similar surface areas (Fig. 1). Within experimental error, the apparent activation energy for the ODH of propane is the same for all the samples (Table 1), but meaningful differences appear depending on the nature of the cation (Ni or Co). While for the Co molybdate system the surface intrinsic rate is lower for the sample prepared by freeze-drying than that of the citrate sample (cp), for the Ni molybdate system the reverse is true (Fig. 1). Nevertheless, the most relevant finding is that, in both systems, nanosized molybdates show a much higher selectivity to olefin at isoconversion (20–25% points), a two-fold increase in the case of Ni molybdate. This produces a 30–40% increase of the olefin yield per pass compared to the conventional counterparts. The method has been recently applied to obtain isomorphically substituted $Co_xNi_{1-x}MoO_4$ in the

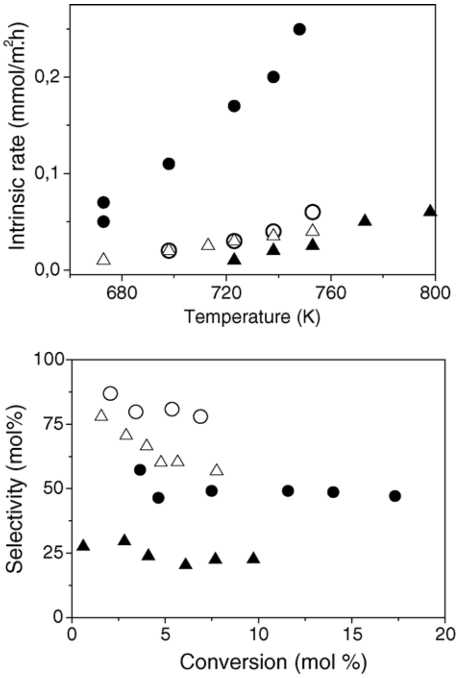

Fig. 1. Comparison of the catalytic behaviour $CoMoO_4$ (circles) and $NiMoO_4$ (triangles) prepared at 673 K from freeze-dried precursors (hollow symbols) and their homologues prepared by citrate method (full symbols): effect of reaction temperature on the surface intrinsic rate (top) and propene selectivity as a function of propane conversion (bottom).

Table 1
Surface properties of the molybdate catalysts and activation energy (E_a) of propane ODH

Catalysts (T_C)	EDX M/Mo atomic ratio	BET surface area (m^2/g)	E_a (kcal/mol)
$CoMoO_4$ (cp)	0.86[a]	10	17 ± 1
$CoMoO_4$ (573)	2.0	30	20 ± 3
$CoMoO_4$ (673)	1.5	18	22 ± 5
$NiMoO_4$ (673)	2.33	39	19 ± 1
$NiMoO_4$ (773)	1.26	42	20 ± 2
$NiMoO_4$ (cp)	1.16[a]	46	

[a] Measured by XPS.

whole $0 \leq x \leq 1$ range [15]. The catalytic behaviour of these new nanosized molybdates are presently under study.

It may be summarized that the use of amorphous precursors prepared by freeze-drying allows to obtain high surface area, monophasic nanosized oxides, more selective for ODH than their homologues prepared by conventional methods.

3. Oxidant selection

The main difficulty for the practical application of the ODH of alkanes comes from the further (and easier) oxidation of the produced olefin, which causes a quick drop of the selectivity to the desired olefin with the increase of alkane conversion, leading to low yields and productivities. One alternative to tackle this problem could be the use of oxidants with less oxidising power than molecular oxygen and, thus, more selective to partial oxidation products. From this point of view the use of carbon dioxide looks promising as it is an inexpensive raw material, available in great amounts (specially in petrochemical processing environments), its use instead of O_2 eliminates the risks of flammability of the reacting mixtures, and the main product of its reduction, CO, can be easily used as raw material with present technologies. This allows to imagine ideal processes in which 100% of the reactants' carbon content could be converted into useful products. However, the low chemical reactivity of CO_2 makes its activation difficult, which usually implies the need of high reaction temperatures. This drawback could make the use of CO_2 as a selective oxidant well suited for the activation of ethane, which also requires high temperatures.

A clear example of the advantage of CO_2 as a selective oxidant is found with ceria-based catalysts. The oxidation of ethane with molecular oxygen over low surface ceria, prepared by ceramic method, produces carbon dioxide with a selectivity near 100%. Our initial study of the reaction of ethane with CO_2 over this catalyst [16] reported for the first time that CeO_2 is effective for the ODH of ethane with CO_2, with ethene selectivities of 58–65% in the temperature range 953–1023 K, and proposed the redox couple Ce^{4+}/Ce^{3+} can activate CO_2 to produce active oxygen species for the reaction [16,17]. The key point of this hypothesis, the (re)oxidation of partially reduced ceria by CO_2 was later evidenced by Sharma et al. [18]. It should be noted that, as homogeneous reactions may become relevant at such high reaction temperatures, reaction conditions were selected to minimize gas phase reactions in order to evidence the catalytic nature of the reaction. We found that the homogenous reaction in the absence of the catalyst is a mere dehydrogenation where CO_2 acts as an inhibitor [17], which allows to analyse separately the catalytic reaction, and that the catalytic CO formation rate is always higher than that of ethene. No carbon formation is observed on the catalyst surface, and no hydrogen was observed in the gas products. Therefore, besides the catalytic ODH of ethane by CO_2:

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O \qquad (1)$$

another unselective catalyzed oxidation reaction:

$$C_2H_6 + 5CO_2 \rightarrow 7CO + 3H_2O \qquad (2)$$

must be considered to explain such results.

Doping the ceria with a 10 mol% of CaO (catalyst 10CaCe) further improved the olefin selectivity (Fig. 2, right), as well as the CO_2 efficiency, defined as the percentage of CO_2 used in the selective ODH reaction (1), reaching 88–94 and 60–75%, respectively, in the same temperature range. The maximum catalytic yield of ethane obtained was around 7–8%, partly due to the low surface areas (1–2.3 m^2/g) obtained by the ceramic method used.

To improve activity and ethene productivity, catalysts with those compositions, say CeO_2 and ceria doped with

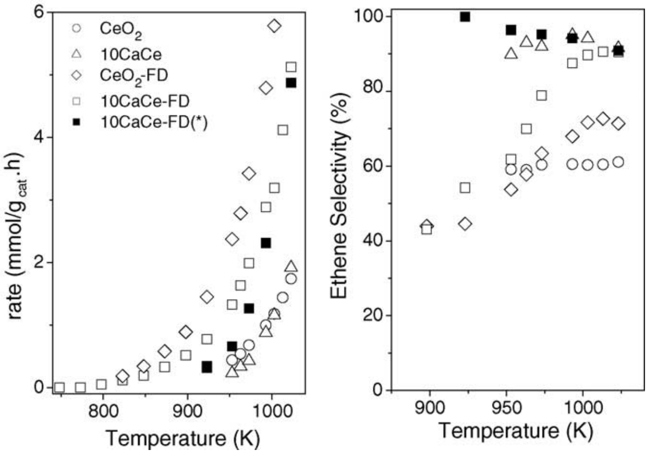

Fig. 2. ODH of ethane with CO_2 over ceria-based catalysts: ethene formation rate (left) and ethene selectivity (right) of the catalytic reaction vs. reaction temperature. The asterisk (*) indicates runs after catalyst operation at 1023 K. Reaction conditions: feed C_2H_6:O_2:He = 1:2:17, total flow 200 ml/h, catalyst load 1 g.

10 mol% CaO (hereinafter denoted as CeO_2-FD and 10CaCe-FD, respectively) were prepared by the freeze-drying method [19]. After calcination at just 573 K, both samples were monophasic and nanostructured (formed by agglomeration of spherical particles of near 7 nm diameter) with very high specific surface areas (117 m^2/g for CeO_2-FD and 91 m^2/g for 10CaCe-FD). Their catalytic tests were made stepwise at increasing temperatures, after keeping the catalyst 1 h at each reaction temperature. On CeO_2-FD, CO formation is detected already at 723 K, while ethene is detectable starting at 773 K. The yield of ethene increases with reaction temperature up to 30.3% (selectivity 71.4%) at 1023 K. The catalyst activity was stable when operated up to 873 K, and only after operation at 1023 K showed a 50% decrease (without modification of selectivity).

The activity of 10CaCe-FD was lower (Fig. 2, left), with much lower differences in the formation rates of CO and ethane, i.e., higher olefin selectivity (Fig. 2, hollow squares). The highest ethene yield was 22.6% (selectivity 90.5%) at 1023 K. At a variance of CeO_2-FD, the interaction with the reaction mixture above 953 K modified the features of catalyst behaviour of 10CaCe-FD. Thus, catalytic tests of the 10CaCe-FD sample after reaction at 1023 K show that while rate of ethene formation decreased slightly, that of CO had decreased drastically. As a consequence, the selectivity to ethene improved markedly, reaching 95–99% (with CO_2 efficiencies of 75–95%) in the 923–1000 K range (cf. solid and hollow squares in Fig. 2, right). Further tests of this sample showed no variations of activity within the experimental error (less than 10%), indicating a stabilisation of the new state of the catalyst reached upon reaction at the high temperatures. This may be indicating that, besides its role as selective oxidant, CO_2 may play a role in the formation of highly efficient phases and/or surface states.

As the main drawback of the use of CO_2 as an oxidant is the need of high temperatures for its activation, looking for catalysts active at lower temperatures we have just explored for the first time the use of transition metal containing M-MCM-41 catalysts (M = Ni, Co, Cr), prepared by direct hydrothermal synthesis, for the ODH of ethane with CO_2 [20]. The catalytic behaviour depends on the nature of the transition metal. Cobalt-containing MCM-41s are little active, showing activity only above 873 K, but the reaction is mostly a non-oxidative dehydrogenation, without the participation of CO_2. On the contrary, the main product over Ni-MCM-41 is CO, which is formed already at 723 K, but the catalyst deactivates due to coking.

Interestingly, Cr-MCM-41 catalysts are active already at 723 K (Fig. 3), the main products being ethene (with a high selectivity, always higher than 96%) and CO, with an apparent activation energy of around 20 kcal/mol. Similar results on ODH of propane on this type of catalyst were simultaneously reported by Takehira et al. [21].

The Cr-MCM-41 catalytic activity was stable for at least 25 h on stream when operated at 873 K, but decreased to one half upon operation at 1000 K. However, it was recovered by treatment under oxygen (15 mol% in He) at 873 K for 2 h. So, this deactivation could be due either to carbonaceous deposits or to over-reduction of the catalyst at the highest temperature. Recent studies show that CO_2 can keep the surface of supported Cr_2O_3 in a state of oxidation slightly higher than that in its absence during the dehydrogenation of light alkanes [22], and that higher oxidation state species are considered key for activity of Cr/H-ZSM-5 for this reaction [23].

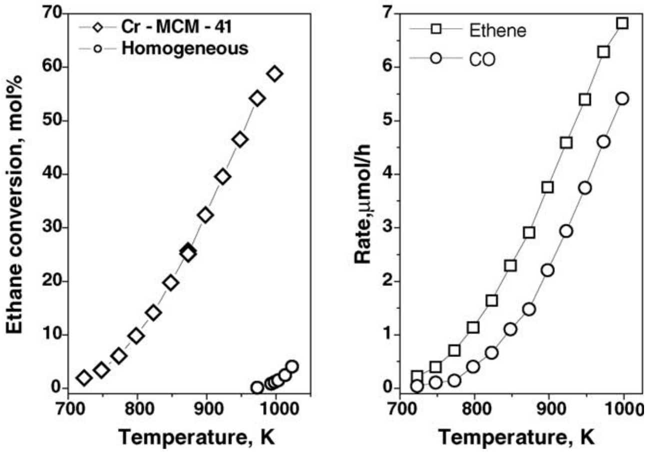

Fig. 3. ODH of ethane with CO_2 on 14 at.% Cr-MCM-41 catalyst. Left: effect of temperature on ethane conversion in the presence (rhombs), and absence (circles, homogeneous reaction) of catalyst. Right: rates of formation of ethene and CO on Cr-MCM-41 catalyst. Reaction conditions: 0.5 g catalyst, feed composition C_2H_6:CO_2:He = 1:2:17 and total flow 6 l/h.

At the contrary that over ceria-based catalysts, the ethene formation rate is always higher than that of CO, but the ratio between both rates decreases as temperature increases. This means that both, oxidative and non-oxidative, dehydrogenations are produced simultaneously. This is confirmed by tests of dehydrogenation in the absence of CO_2, which evidence the dehydrogenating activity of the Cr-MCM-41 catalyst, but the ethane conversion is lower and the catalyst deactivates very fast. This seems to indicate that, over Cr-MCM-41, CO_2 may play a multiple role: it can dissociate on the catalyst surface to produce active oxygen species, as on ceria-based catalysts [17], it stabilizes the active higher oxidation state of chromium [22], and it inhibits the coke formation on the catalyst surface, probably by the reverse Boudouart reaction ($C + CO_2 \rightarrow CO$), thus keeping stable the catalytic dehydrogenating activity.

These promising results seem to point out the feasibility of using CO_2 as a selective oxidant at moderate temperatures.

4. Catalyst arrangement

Compared to the most successful results of ODH of C_2–C_4 alkanes into their corresponding olefins, or their selective oxidation to unsaturated acids (such as isobutane to methacrylic acid) or anhydrides (such as *n*-butane to maleic anhydride), few significant breakthroughs have been made in their selective oxidation into unsaturated aldehydes [5,24]. In fact, most of the data reported for the latter reaction come from its formation as by-products in the oxidation to unsaturated acids [25–30], the aldehyde selectivity being often lumped with that of the acid [30].

In particular, in the case of propane partial oxidation to acrolein (POA), for almost one decade the maximum yield of the desired product reported, obtained over Ag/Bi/V/Mo mixed oxides by Moro-oka and coworkers, did not exceed 10% [31].

As Cavani and Trifirò pointed out [24], one of the key factors in determining the pathway of the alkane transformation to the selective oxidation product is the mechanism of such transformation, including the importance of the ratio between the intermediate olefin (oxy)dehydrogenation and oxygen insertion and the contribution of homogenous reactions. So, for each particular process, kinetic analysis is required to elucidate if homogeneous steps are just side reactions or they take part in the main route and play an important role in the formation of the desired products [32]. Sinev and coworkers demonstrated that the size factor, i.e., the characteristic size of the free gas space, may have a substantial effect on the features of the overall reaction when it has a complex heterogeneous–homogeneous nature [33]. In our collaborative work on isobutane ODH over multicomponent V-based catalysts [34], we found that isobutane conversion, olefin selectivity and olefin yield are strongly dependent on the catalyst particle size and the postcatalytic void volume of the reactor, showing a meaningful improvement (up to two-fold) in those conditions favouring the participation of homogeneous reactions. These results strongly suggest that parameters of the overall process depend on the combination of heterogeneous and homogeneous factors, which opens a new way to selectivity improvement by taking advantage of these mechanism features.

To check this concept, and considering that propane POA could be a result of the sequential ODH to propene and selective oxidation of propene to acrolein, we tried a novel approach for the POA, based on the combination of two catalysts: a mixed VSbBiBa oxide supported on alumina (Cat. 1), highly efficient for ODH of light alkanes [34] and a MoBiCoFe complex oxide (Cat. 2), highly efficient for propene selective oxidation, in various arrangements in a single reactor [35].

Three catalyst arrangements, schematically shown in Fig. 4, were tested: a mechanical mixture of Cat. 1 and Cat. 2 in separate particles (A), an intraparticular mixture, prepared by grinding together both catalysts and making particles of the resulting mechanical mixture (B), and two separate, consecutive layers of Cat. 1 and Cat. 2 (C). It should be noted that a big gap does exist between the optimal conditions required for the two steps: the most efficient propane ODH proceeds at elevated temperatures (>773 K), short residence times (<0.1 s), and high propane-to-oxygen ratios; on the contrary, propene POA over the most efficient catalysts requires relatively low temperatures (<673 K), long residence times (several seconds) and excess of oxygen in

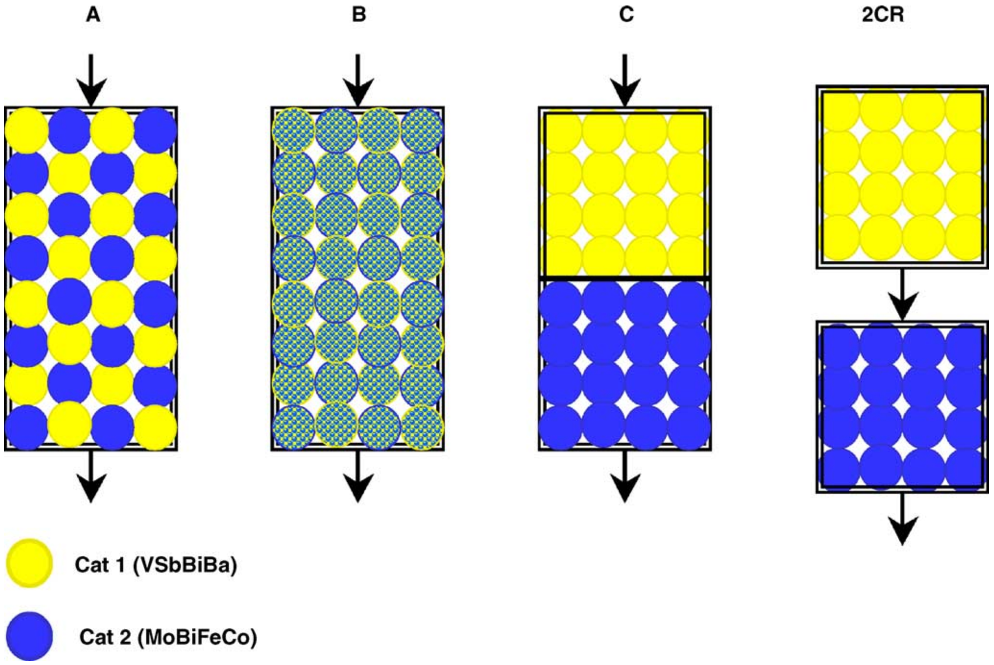

Fig. 4. Catalysts arrangements for the partial oxidation of propane (see text): (A) physical mixture of particles of each catalyst; (B) particles composed of intraparticular mechanical mixtures of both catalysts; (C) two separate consecutive layers. 2CR represents the theoretical two reactors model used to estimate the results assuming propane ODH and propene selective oxidation are sequential reactions.

the feed. Tested individually, Cat. 1 catalyzes propane ODH to propene and combustion of propene and acrolein, while over Cat. 2 propane and acrolein reactivity are low but propene is efficiently oxidized to acrolein (acrolein yield $\geq 85\%$ at ≤ 573 K with contact time ~ 10 s). Based on the results of separate tests of propane ODH over Cat. 1 and of propene oxidation over Cat. 2, an estimation of the expectable result in the reaction conditions used for the combined arrangements was made assuming a two consecutive reactors model (2CR in Fig. 4).

Both mixed catalysts arrangements A and B give quite similar results (Table 2), with propane conversion and acrolein yield (1.4%) about one half of the estimated by the 2CR model with acrolein selectivity (10–12%) equal to that estimated by the model (Table 2). At a variance, the consecutive layers arrangement C gives a higher propane conversion (18%) and, more interestingly, a much higher acrolein yield (11.3%) with a quite high selectivity (62%). No acrylic acid was detected in any case.

Furthermore, by varying either temperature or contact time with the separate consecutive layers arrangement C, acrolein yield passed through a maximum, an effect not observed with mixed catalysts arrangements A or B. As a result, acrolein yields up to 13% are obtained, values among the highest ever reported in the open literature for the direct propane oxidation to acrolein.

Noteworthingly, quite similar results for the oxidation of isobutane to methacrolein were later reported by Obana et al. [36]. They used a combination of $Ni_2P_2O_7$, the catalyst effective for isobutane ODH, and $Bi_1Mo_{12}F(1)_iCo_6Ni_2Cs_{0.14}$ oxide, the catalyst effective for selective oxidation of olefins. Methacrolein was formed with the selectivity as high as 65% in a reactor with two catalyst beds in series. A mixed catalyst consisting of a mixture of the powders of both catalysts was effective for isobutene formation, although the conversion was reduced, whereas a mixture of granules was less effective.

The increase of propane conversion and acrolein yield in the two layers arrangement C, not explainable by the two sequential ODH and POA reactions or the redox mechanism, reveals new mechanistic features for the process. Their variation with temperature and contact time points to a short-living intermediate species, as it was not detected by GC, that may leave easily the Cat. 1 layer. The results were interpreted assuming the formation of a highly reactive, surface-generated gas-phase radical C_3H_7 over the ODH catalyst [35]. This could be later transformed either in the gas phase back to propane, on the ODH catalyst surface to give propene or on the POA catalyst surface to give acrolein. The two steps, formation of highly reactive intermediate from the relatively inactive propane and formation of the much more reactive product (acrolein), presumably proceed in different “reaction zones”. This spatial separation allows to preserve acrolein from sequential transformations and to achieve elevated selectivities at moderate conversions.

One may assume that, if the mechanism proposed above is correct in general outline, it could be used as a guideline for the further development and optimisation of the process [35].

A way to apply this new approach to alkane partial oxidation, i.e., integration of the homogeneous–heterogeneous processes in a controlled manner and separation of each reaction step’s location, is the use of mesoporous MCM-41-like catalysts, as they allow to reveal an influence of the reactivity inside the confined space of the mesopores. In this line, we have investigated the oxidative activation of isobutane on V- and Co-substituted MCM-41 materials [37,38]. To ensure a homogenous active site distribution and to overcome the practical limit of the transition metal contents found in the direct hydrothermal route, the catalysts were prepared by the so-called atrane route [39]. This method, based in the use of atrane complexes of the component cations to homogeneize the hydrolysis rates during the formation of the mesostructured intermediate material, allows to obtain quite high transition metal (V, Co) contents without segregation of bulk oxidic phases.

Thus, V-MCM-41 catalysts with ratios Si/V = 49–70, BET areas around 1100 m^2/g and BJH pore diameter around 2.5 nm, were prepared and tested between 700 and 800 K with a isobutane:oxygen:He feed (27.0:13.5:59.5 mol ratio) [37]. The catalysts are very efficient for ODH: the overall selectivity to (oxy)dehydrogenation products varies between 71 and 50% in the conversion range obtained, 2–25% (Table 3). Besides, selectivity to CO_x is very low and there is a moderate portion of oxygenated products, mainly methacrolein (MAL). The formation of oxygenated products during the propane ODH over V-MCM-41 prepared by other methods has been reported [40–42], but in those cases they came mostly from the oxidative degradation, as previously observed on SiO_2-supported vanadia catalysts, and no meaningful amounts of the olefin selective oxidation product, acrolein, are found. The most remarkable result

Table 2
Propane partial oxidation to acrolein with different catalysts arrangements

Catalysts arrangement	Conversion (%)		Selectivity (%)		Yield (%)	
	C_3H_8	O_2	C_3H_6	Acrolein	C_3H_6	Acrolein
Mechanical mixture (A)	13.5	65	16.3	10.0	2.2	1.35
Intraparticle mixture (B)	11.5	50	22.6	12.2	2.6	1.4
Consecutive layers (C)	**18.0**	**85**	**10.5**	**62.8**	**1.9**	**11.3**
2CR model (estimated)	24.5	>95	4.8	13.3	1.15	2.8

Experimental conditions: 673 K, 0.6 g Cat. 1, 0.2 g Cat. 2, 20 ml/min of mixture C_3H_8:O_2:He in molar ratio 1:1:8.

Table 3
Selective oxidation of isobutane over V-MCM-41 catalysts[a]

Catalyst Si/V ratio	Reaction temperature (K)	Conversion (%)		Selectivity (%)								Yield (%)	
		iC_4H_{10}	O_2	iC_4H_8	MAL[b]	ACT[c]	C_3H_6	HCHO	CO	CO_2	Others[d]	iC_4H_8	MAL
49	698	2.7	7.6	48.1	26.3	8.8	2.5	1.9	5.7	4.8	1.9	1.3	0.7
	723	5.6	21.1	40.5	28.5	8.6	3.5	3.0	7.1	5.5	2.3	2.3	1.6
	748	10.6	41.6	35.1	28.7	8.0	4.4	4.4	8.9	6.7	3.8	3.7	3.0
	773	17.1	41.6	30.6	26.8	7.3	5.4	5.5	11.9	7.9	4.6	5.2	4.6
	798	25.2	99.5	30.7	22.9	6.6	5.7	5.0	14.0	8.0	7.1	7.7	5.8
59	773	12.4	45.6	34.8	21.0	6.3	7.8	7.4	11.8	6.9	4.0	4.3	2.6
70	773	11.5	38.6	38.7	16.9	5.6	7.9	7.8	11.6	7.8	3.7	4.4	1.9

[a] Reaction conditions: $iC_4:O_2:He = 27.0:13.5:59.5$ (mol%), $W/F = 12\ g_{cat}\ h/(mol_{C_4})$.
[b] MAL = methacrolein.
[c] ACT = acetone.

with our catalysts is the relatively high selectivity to MAL, which allows to obtain yields per pass up to 5.8%, to our knowledge the highest reported for the direct oxidation of isobutane, above those reported for this reaction for complex Mo–V–Sb oxides, i.e., ca. 3% yield with 30% selectivity on $Mo_1V_1Sb_{10}O_x$ [43] and 1.7% with 28% selectivity on $Mo_{10}V_{10}Sb_{80}O_x$ [44], and on Re–Sb oxides, 3.15% yield with 40% selectivity for $SbRe_2O_6$ [45]. The characterization results show that accessible vanadium atoms are tetrahedrically coordinated in isolated and dimeric or oligomeric species. Noticeably, at similar isobutane conversions, the higher the V content in the V-MCM-41 material, the higher the conversion and MAL selectivity and the lower the isobutene selectivity (Table 3). These results seem to support the mechanism features discussed above: each type of vanadium centre would be responsible of one of the two reaction steps involved (alkane activation, methacrolein formation).

While in V-MCM-41 the vanadium incorporation up to a Si/V ratio of 49 does not modify the symmetry and order of the mesopores system, the increase of Co incorporation to Co-MCM-41 brings along a progressive loss of symmetry. For this reason we studied the performance of Co-MCM-41 with Si/Co ratios of 49 and 98, both with hexagonal array (partially disordered for Si/Co = 49) [38]. In the reaction conditions used for V-MCM-41 catalysts, these Co-MCM-41 catalysts give a similar range of products (carbon oxides but also isobutene, methacrolein and other oxygenates were formed), although with lower activity and lower selectivity to (oxy)dehydrogenation products (40–48%). At similar conversion levels, the increase of Co content does not modify the olefin selectivity but decreases the selectivity to MAL, at a variance of what is observed with V-MCM-41.

The dehydrogenated products may not be due to the non-catalysed gas-phase homogeneous reaction as, in the absence of catalyst, conversion was roughly one order of magnitude lower. UV–vis diffuse reflectance spectra indicate that catalysts Co-MCM-41 with Si/Co ≥ 23 present a unique tetrahedral coordination of the Co(II) centres. This type of Co^{2+} species are present in CoH-containing zeolites BEA, MFI, MOR and FER, reported to be active for the ODH of ethane and propane [46], but no product of the selective oxidation of the olefin was detected. Therefore, to explain the formation of MAL and its evolution, an additional factor, besides the nature of the cobalt centre, must be influencing the catalytic behaviour, that could be analysed in terms of heterogeneously initiated, radical gas-phase homogenous reactions, according to the model above described for the propane POA [35].

In this way, activation of the alkane molecule would take place on centres located on the inner pore wall, generating radical species that would either react either in the gas phase inside the void volume of the mesopores (acting as ‘‘nano-reactors’’) or interact with another centre of the pore wall. The decrease of the methacrolein selectivity with the Co content increase could be explained by the higher number of active centres, that will increase the probability of further oxidation of the formed methacrolein. Further studies are in progress to clarify the role of nature and number of active centres as well as the pore volume and dimensions in the mechanism.

Summarizing, partial oxidation of alkanes to insaturated oxygenated compounds seem to involve the participation of different, separate active centres and the contribution of heterogeneously-initiated, gas phase radical intermediates. This seems to imply that catalyst arrangements, both intraparticular (pore volume and dimensions) and inter-particular (particle size, interparticular void volume, catalytic bed arrangement, reactor void volume) are relevant to the efficiency of the catalytic process, which brings a new route to selectivity improvement.

5. Concluding remarks

The industrial transformation of light alkanes into more valuable products via catalytic oxidative reactions such as ODH and selective oxidation is, with a few exemptions, still not solved. Selectivity is the key issue for the successful implementation of such processes. However, the intrinsic complexity of the reaction mechanisms involved makes selectivity to be dependent on a broad number of factors, ranging from catalyst and active centre design, oxidant nature, reactants–catalyst interaction, reaction mechanism, etc. until reactor and process design. So, along with the conventional approaches of catalyst design, screening and selection, novel approaches to overcome the difficulties to improve selectivity and productivities of the desired product are needed. The approaches presented here, oxide nanocatalysts preparation, oxidant selection and catalyst arrangement, are complementary ways to improve selectivity by tuning the nature of the active centre, avoiding overoxidation and taking advantage of the reaction mechanistic features.

Hopefully, new approaches to obtain a fine control of the catalytic performance through catalyst synthesis design, the use of alternative reactants and reactions, mechanistic studies and catalyst arrangement configuration will provide new steps forward to the implementation of such industrial processes.

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