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Reactivity of V/Nb mixed oxides in the oxidehydrogenation of propane under co-feed and under redox-decoupling conditions

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Abstract

V/Nb mixed oxides were prepared, characterized and tested as catalysts for the oxidehydrogenation of propane to propylene. The reactivity tests were carried out under co-feed and under redox-decoupling conditions, with alternate-feeds of propane and air (cyclic operation). The comparison between co-feed and alternate-feed operations evidenced that in the latter case a higher selectivity to propylene is achieved at low propane conversion. This was attributed to a reaction mechanism mainly involving propane dehydrogenation rather than oxidehydrogenation, occurring on the reduced catalysts. The selectivity to propylene, however, under both operating conditions decreased with increasing propane conversion. During reaction under redox-decoupling conditions $VNbO_5$ decomposed yielding vanadium oxide and V/Nb mixed oxides having V/Nb ratio lower than 1. The former compound played the major role in the reaction cycle.

Keywords: Oxidehydrogenation of propane; Redox-decoupling condition; V/Nb mixed oxides; Synthesis of olefins

1. Introduction

Oxidative dehydrogenation of alkanes constitutes one possible method for the synthesis of light olefins, alternative to the conventional industrial technologies which suffer from thermodynamic limitations, rapid catalyst deactivation and high energy consumption. A large number of papers published in recent years demonstrate the interest for this reaction, and the many catalytic, technological and engineering aspects of oxidehydrogenation have been widely discussed in several reviews [1–5].

Materials based on V and Nb mixed oxides have been investigated as catalysts for the dehydrogenation of light alkanes in the presence of molecular oxygen. The first papers on the use of V/Nb/O systems for propylene synthesis were published by Ross and coworkers [6–12], and later on analogous catalysts were studied by other authors [13–18]. Most papers deal with catalysts where V is diluted inside or dispersed over niobia, and analyze how the chemical–physical features of V, which is the active site for the reaction are modified by interaction with Nb. Niobia itself is poorly active in propane conversion, but is highly selective to propylene. The addition of V considerably improves the activity of the material, while maintaining high selectivity. Little work has instead been devoted to the study of the reactivity of intermetallic V/Nb oxides of definite composition [13]. The two elements, V and Nb, form a variety of mixed oxides, including compounds where Nb is in excess with respect to V and the latter is formally present as V^{5+} (i.e., VNb_9O_{25}, $V_3Nb_{17}O_{50}$,

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$V_4Nb_{18}O_{55}$), as V^{4+} (i.e., $V_2Nb_6O_{19}$), or in mixed valence states (i.e., $V_3Nb_9O_{29}$, $V_2Nb_{23}O_{62}$), or where V is in an equi-atomic amount with respect to Nb ($VNbO_5$ and $VNbO_4$). The main objective of the present work was to investigate the chemical–physical features and reactivity in propane oxidehydrogenation of V/Nb mixed oxides having different atomic ratios between the components, and prepared following different procedures.

A further objective of the investigation was to study the catalytic performance of V/Nb mixed oxides under: (i) stationary, co-feed conditions, and under (ii) non-stationary, redox-decoupling conditions (cyclic operation). The latter technology represents one important breakthrough in the field of selective oxidation of hydrocarbons, and has been applied successfully in the selective oxidation of *n*-butane to maleic anhydride [19] and of propylene to acrolein [20]. Specifically, the reaction is carried out by separating the two steps of the redox mechanism and carrying them out separately in two different reactors. One potential advantage is that exclusively bulk ionic oxygen of the lattice is involved in the reaction, and therefore no adsorbed oxygen species, which develop when the reaction is carried out with co-feed of reactants, can form.

In the case of propane oxidehydrogenation, it is known that one major limitation of the reaction consists of the decrease in selectivity which occurs when conversion of paraffin increases. Operation in the absence of molecular oxygen might limit the undesired consecutive combustion of propylene, if this is due to non-selective electrophilic oxygen species. Indeed, the way the reactants are put in contact with the catalyst may have a considerable effect on the selectivity to the product of partial oxidation, as demonstrated by the results achieved with the use of catalytic membrane reactors for oxidehydrogenation of ethane and propane [21–24]. A distributed feed of oxygen results in a marked increase in olefin yield with respect to the conventional co-feed of alkane and oxygen. Therefore, it appears that non-conventional reactor designs and operations can be used to improve performance. Cyclic operation has been claimed in several patents and papers for almost all selective oxidation reactions of hydrocarbons [5], and many have involved specifically the oxidehydrogenation of light paraffins [25–35].

2. Experimental

Catalysts were prepared by dissolving $NbCl_5$ and $VO(acac)_2$ in absolute ethanol, in the amounts necessary to reach the desired V/Nb atomic ratio. The solution was then dropped into water, buffered at pH 7. During the hydrolysis and precipitation of the oxohydrates the pH decreased; it was maintained at around 7 by controlled addition of ammonium hydrate. The solvent was then evaporated under light vacuum at 60 °C, and the solid obtained was first dried at 120 °C and then calcined either in chromatographic nitrogen flow, or in air flow, up to the maximum temperature of 700 °C, and with a final isothermal step of 3 h.

The catalysts were characterized before and after reaction by Raman spectroscopy (Renishaw 1000 instrument, equipped with a Leika microscope, Ar laser at 514 nm, power 25 mW), and by X-ray diffraction (Phillips PW 1050/81, Cu Kα radiation). Ex situ characterization on unloaded catalysts was done by cooling the samples in an inert flow from reaction to room temperature.

Catalytic tests under co-feed conditions were carried out using the following reaction conditions: temperature 550 °C, residence time 2 s (the amount of catalyst loaded was 1.8 cm^3, or less for tests at lower residence time), feed composition 20 mol% propane, 20 mol% oxygen, remainder helium. Tests under redox-decoupling conditions were carried out at residence times equal to 2 and 4 s, and at the temperature of 550 °C. Half-cycle reducing periods of variable time-length, with a feed containing 20% propane in helium were alternated with the half-cycle oxidizing period, lasting 30–40 min (feed air, residence time 2 s, temperature 550 °C). Since the aim of tests was to develop a selectivity vs. conversion plot, to be compared with results achieved under co-feed conditions, the cycle split ratio was changed. To achieve this, the reducing step was carried out for increasing periods of time, typically 1.5, 2.5, 4.5 and 14.5 min. Before each test the catalysts were re-oxidized as described above.

Reactants and products were analyzed by means of gas-chromatography. Propane, propylene, acetic acid and acrolein were separated with a Porapak Q column (FID), while hydrogen, oxygen, carbon monoxide and carbon dioxide were separated with a Carbosieve S column (TCD). The carbon balance was determined by comparing the effective propane conversion with the sum of the yields as inferred from GC analysis. Missing C thus corresponds to the C-unbalance. Blank tests were done by carrying out the reaction with an inert component (acid-washed corindone) filling the reactor. Tests made by feeding only diluted propane led to a very low conversion of propane (between 0.2 and 0.4% at 550 °C), while tests made by feeding 20% propane and 20% oxygen led to a propane conversion of 2.5% at 550 °C, mainly yielding propylene and carbon dioxide.

3. Results

3.1. *Characterization of samples after the thermal treatment*

Table 1 reports the surface area of the samples after the thermal treatment, and the atomic ratio between V and Nb used for the preparation. A reference sample made of Nb_2O_5 is also reported (sample 6); this was prepared following the same procedure as used for the V/Nb mixed oxides. The reference V_2O_5 was instead a commercial sample (sample 1). Samples 2–5 were calcined in N_2 at 700 °C, samples 6 and 7 were calcined in air at 700 °C, and sample 3ox was calcined first in N_2 at 700 °C and then in air at 550 °C. Samples 2–3 had high specific surface area when calcined in N_2. For low V/Nb atomic ratios (i.e., in sample 5), the surface area approached that of niobia. Sample 7 (calcined in air) instead had a very low surface area.

Table 1
Samples prepared and characterized

Sample *n*	V/Nb, atomic ratio	Atmosphere of thermal treatment	Specific surface area (m^2/g)
1 (commercial)	1/0	–	9
2	1/0.5	N_2	112
3	1/1	N_2	48
3ox	1/1	N_2, then air	<5
4	1/2	N_2	16
5	1/5	N_2	8
6	0/1	Air	8
7	1/1	Air	<5

Fig. 1 reports the X-ray diffraction patterns of samples 1–7. Sample 1 shows the pattern typical of V_2O_5, and sample 6 shows the pattern corresponding to that of $Nb_{16.8}O_{42}$. Niobia crystallizes in several forms [36], and the pattern found was very similar to that of the TT-phase (JCPDS-ICDD file 27-1312), which is reported to be stable at 700 °C, that is the temperature used for the thermal treatment of samples. Samples 3–5 exhibit a pattern corresponding to the overlapping of rutile-type $V^{3+}NbO_4$ and of niobia.

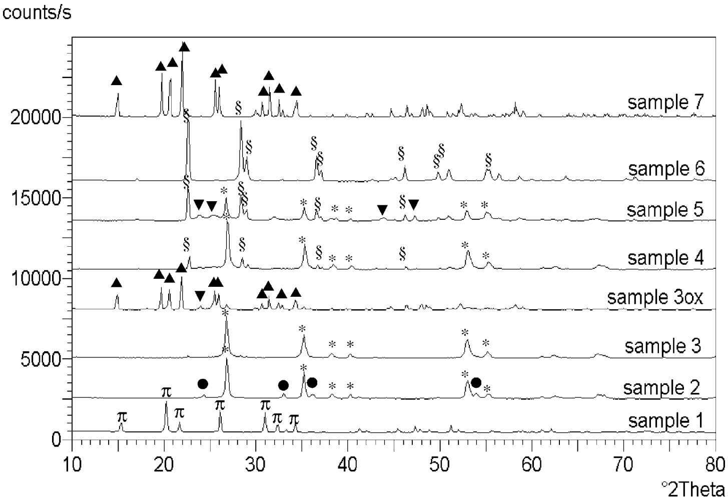

Fig. 1. X-ray diffraction spectra of samples 1–7 after calcination. V_2O_5 (Shcherbinaite, JCPDS-ICDD file 41-1426) (π); rutile (*); V_2O_3 (JCPDS-ICDD file 34-0187) (●); $Nb_{16.8}O_{42}$ (JCPDS-ICDD file 71-0366) (§); $V_3Nb_9O_{29}$ (JCPDS-ICDD 38-0959) (▼); $VNbO_5$ (orthorhombic, JCPDS-ICDD file 46-0046) (▲).

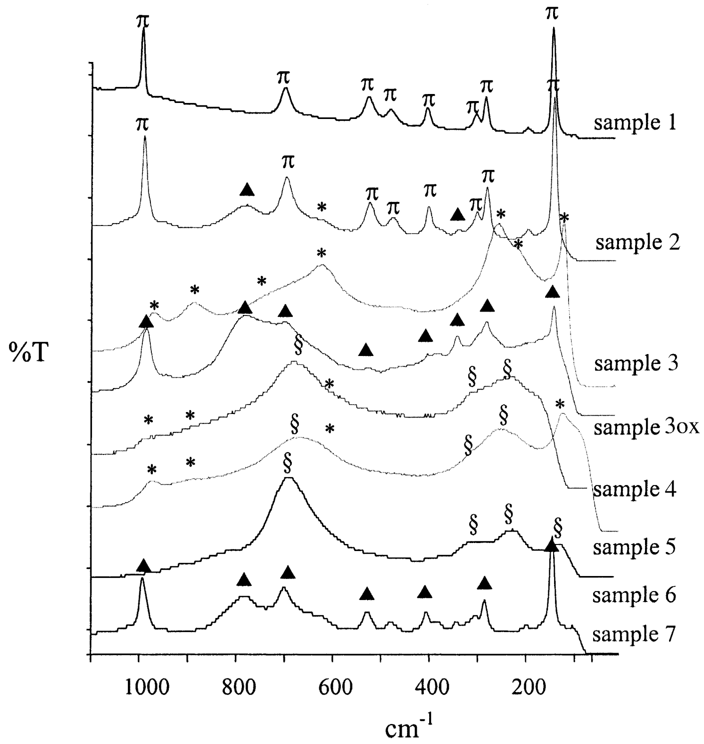

Fig. 2. Raman spectra of samples 1–7 after calcination. Symbols indicate vibrations attributable to specific crystalline compounds (symbols are same as given in Fig. 1).

The relative intensity of the reflections attributable to the latter compound increased with decreasing V/Nb ratio. In sample 5, additional reflections were also present which were attributed with some uncertainty to $V_3Nb_9O_{29}$. In sample 2, instead, besides the reflections attributable to $VNbO_4$, also those corresponding to V_2O_3 were present. Sample 7 shows the pattern attributable to $V^{5+}NbO_5$.

Raman spectra of samples 1–7 are shown in Fig. 2; spectra were in good agreement with XRD patterns. Bands attributable to vibrations in the rutile compound are those falling at the Raman shifts 970–980, 890, 630 and 250–260 cm^{-1}, while those falling at 680–690, 320–340 and 220–230 cm^{-1} (observed in samples 4 and 5, having V/Nb ratios lower than 1, and in sample 6) are attributable to niobia. With increasing Nb content, the relative intensity of the bands changed accordingly. In sample 2, the bands attributable to V_2O_5 were present; this can be attributed to the re-oxidation of V_2O_3 (the compound detected by XRD in sample 2) under the laser beam during spectrum recording.

Reactivity tests under redox-decoupling conditions were carried out by first treating the catalysts in air at 550 °C. The same treatment was applied after each of the half-cycle reducing steps at increasing reaction times, to restore the initial oxidation state and to remove carbon deposits before carrying out the following reducing step. Therefore, it is useful to check the features of the catalysts after this treatment, since this was the material which then effectively underwent the catalytic cycles under redox-decoupling conditions. Figs. 1 and 2 report the XRD pattern and Raman spectrum of sample 3 after the oxidizing treatment (the sample is referred to as 3ox in Figs. 1 and 2 and in Table 1). The rutile compound $VNbO_4$ transformed to $VNbO_5$, i.e., the same compound obtained by direct calcination of the precipitate in air at 700 °C (sample 7). Also the Raman spectrum of sample 3ox was very similar to that of sample 7. Sample 3ox, however, appeared not to be very homogeneous: some particles were clear, while others were grey or black (which is the color typical of $VNbO_4$ particles). When the beam was focussed on these latter particles, some bands attributable to rutile were also observed. This indicates that the oxidation of V^{3+} to V^{5+} and the transformation of $VNbO_4$ to $VNbO_5$ had not been complete. The specific surface area of sample 3ox was lower than $5\,m^2/g$; therefore, the transformation of $VNbO_4$ into $VNbO_5$ led to a decrease of the surface area.

3.2. *Characterization of samples after catalytic tests*

Samples were characterized after reaction under co-feed operation and under redox-decoupling operation; in the latter case samples were unloaded after the half-cycle reducing step.

When unloaded after reaction under co-feed conditions, sample 3 had the same XRD pattern and Raman spectrum, typical of rutile, as for the corresponding sample before reaction. The same occurred when sample 3 was subjected to reaction under anaerobic conditions but without preliminary oxidation treatment. This means that under our co-feed conditions (i.e., 20% oxygen and 20% propane at 550 °C), or in the absence of oxygen as well (i.e., 20% propane in helium), $VNbO_4$ was stable, while if treated in air at the same temperature it was oxidized to $VNbO_5$ already at 550 °C (sample 3ox).

Different was the case for samples unloaded after preliminary oxidation and reaction under redox-decoupling (anaerobic) operation. Fig. 3 shows the XRD patterns relative to: (i) sample 1 unloaded after reaction with propane at 550 °C for 14.5 min; (ii) sample 3 after reaction with propane at 550 °C for 1.5 and 14.5 min; (iii) sample 3 after reaction with propane for 14.5 min and subsequent re-oxidation in air at 550 °C; (iv) sample 7 after reaction with propane at 550 °C for 14.5 min. The pattern of sample 1 corresponds to that of V_2O_3. The patterns of samples 3 and 7 correspond to the overlapping of patterns attributable to $V_4Nb_{18}O_{55}$ and $V_3Nb_{17}O_{50}$ (indeed, the presence of crystalline V_6O_{13} cannot be excluded, since most reflections relative to this compound are coincident with those of $V_3Nb_{17}O_{50}$). The re-oxidation of the latter samples at 550 °C led to the appearance of reflections relative to V_2O_5, while those relative to the V/Nb mixed oxides were left unchanged.

3.3. *Catalytic performance in propane oxidehydrogenation under co-feed conditions*

Samples 1, 3, 3ox and 7 were tested as catalysts for propane oxidehydrogenation under co-feed conditions. The results obtained are summarized in Table 2. In the case of sample 1, total oxygen conversion was achieved already at a temperature lower than 300 °C, while for the other samples total oxygen conversion (with a corresponding propane conversion around

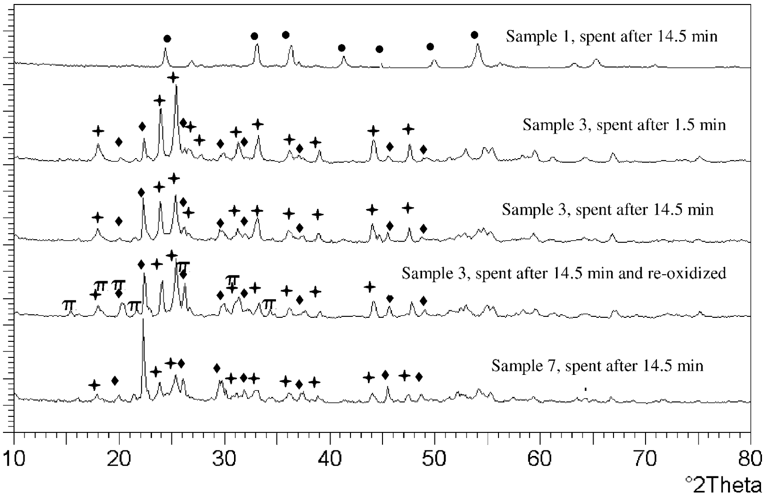

Fig. 3. X-ray diffraction patterns of selected catalysts unloaded after reaction under anaerobic conditions for different reaction times. Symbols are same as given in Fig. 1. Additional symbols: $V_4Nb_{18}O_{55}$ (JCPDS-ICDD file 46-0087) (◆); $V_3Nb_{17}O_{50}$ (JCPDS-ICDD file 19-1397) (✚).

Table 2
Summary of catalytic performance in propane oxidehydrogenation under co-feeding conditions

Sample *n*	*T* (°C), τ (s)	Propane conversion (%)	Selectivity to propylene (%)
1	255, 2	32	5
3	435, 0.2	9	11
3	550, 0.2	27	7
3	552, 0.5	34	11
3ox	435, 2	15	7
3ox	485, 2	38	9
7	550, 2	33	6

30–40%) was reached above 450–500 °C. All catalysts yielded propylene with a very low selectivity, lower than 15%, for propane conversions between ≈10 and 40%; the selectivity to propylene was not much affected by the reaction temperature. In the case of sample 3 acetic acid and small amounts of acrolein were also obtained, with an overall selectivity around 25–30%. Oxygenated products did not form with samples 3ox and 7.

Molecular hydrogen also formed, especially under conditions of high temperature, that is of high oxygen conversion; in this case the amount of hydrogen corresponded to a large fraction of the propylene produced. This means that under conditions of oxygen starvation the mechanism of propylene formation is a dehydrogenative one, and oxygen is consumed for the combustion of propane; hydrogen itself is not (at least, not completely) burnt to water.

In the case of the tests carried out on sample 1, no hydrogen was detected below 300 °C, while for higher temperatures, at conditions at which complete oxygen conversion was reached, a considerable amount of hydrogen formed, higher than that corresponding to the amount of propylene formed. This suggests that molecular hydrogen may form through mechanisms other than the dehydrogenation of propane, such as the formation of coke (but the balance upon C was always close to 100%) or the partial oxidation of propane to CO and H_2. The selectivity to propylene remained very low (around 7%) over the entire range of temperature.

Sample 3 was also tested as a dehydrogenation catalyst, thus with only diluted propane in the feed, at 550 °C and residence time 2 s. A propane conversion of 12% was obtained after 15 min reaction time, with a selectivity to propylene around 25%, the remaining being constituted of traces of cracking products and, mainly of C residues (indirectly determined as C-unbalance) which accumulated on the catalyst surface during this initial period of reactivity.

3.4. Catalytic tests under redox-decoupling conditions

Tests under cyclic conditions were carried out at 550 °C, by measuring the concentration of products in the outlet stream in correspondence with different half-cycle reduction times, thus in correspondence with different times of exposure of the catalyst to the stream containing diluted propane. Before each test, the catalyst was re-oxidized by exposure to an air flow at 550 °C (half-cycle oxidizing step). An example of the plot achieved is shown in Fig. 4, which reports the conversion of propane and the distribution of the products as functions of the reaction time, for sample 3. It is worth recalling that the preliminary oxidation treatment in air at 550 °C transformed the rutile compound $VNbO_4$ to $VNbO_5$ (as evidenced by the characterization of sample 3ox).

The results plotted in Fig. 4 are the instantaneous values obtained at that specific reaction time. Time-averaged values, which are those of interest in a possible industrial application with transport-bed-type reactors for the reducing step and for the re-oxidation step, have to take into account the integrated values as inferred from the curves from nil reaction time to a specific reaction time.

The conversion of propane was initially relatively high, around 35%, and rapidly decreased with increasing reaction time, thus with increasing extent of catalyst reduction. This clearly indicates that the active V species is that one having the highest degree of oxidation, and that a progressive reduction of V ions is accompanied by a decrease in activity. Concerning the distribution of products, a decrease in conversion led to an increase in selectivity to propylene and to a decrease in selectivity to carbon dioxide and, mainly, to carbon monoxide. For 10% propane conversion, the selectivity to propylene was around 40%, that to carbon dioxide was 7% and to carbon monoxide was 2%. Light hydrocarbons (ethane, ethylene, methane) also formed, with an overall selectivity which, though increasing with increasing reaction time was always lower than 1%. No formation of oxygenates was detected.

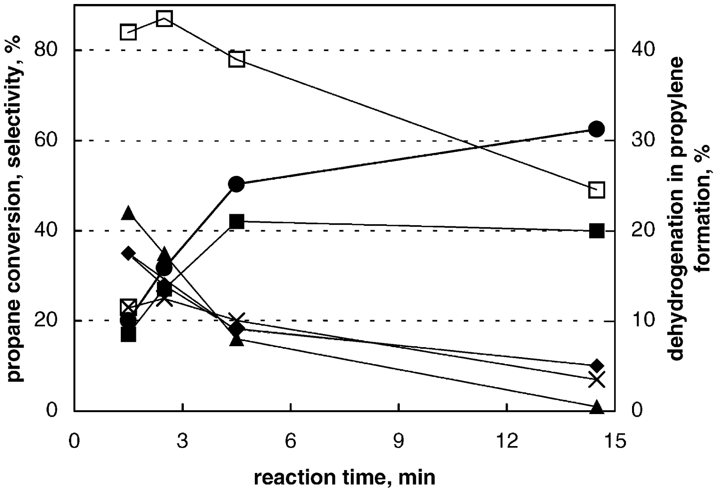

Fig. 4. Catalytic performance of sample 3 under cyclic operation as a function of the half-cycle anaerobic reaction time. Propane conversion (◆), selectivity to propylene (■), to carbon monoxide (▲) and to carbon dioxide (×), carbon balance (□). Right scale: contribution of dehydrogenation in the formation of propylene (i.e., H_2 concentration/C_3H_6 concentration in the exit stream, %) (●). Residence time 2 s, temperature 550 °C, feed 20 mol% propane in helium.

The C balance (also shown in Fig. 4) was fairly good for the fresh catalyst, thus for the compound which had been exposed for short times to the propane feed, and became very low as reaction times increased. This was due to the formation of coke. The analysis of the C residue in the catalyst unloaded after 1.5 min yielded less than 0.1 wt.% C, while after 14.5 min the amount was 0.3 wt.% C. Therefore as long as the catalyst had a relatively high number of oxidizing sites, it was able to convert propane with good efficiency, without formation of coke, but the prevailing products of propane transformation were carbon oxides. With increasing degrees of V reduction, the catalyst progressively lost its activity, becoming more selective to propylene and much less selective to carbon oxides. Under these conditions, however, the formation of coke was relevant. The contribution of dehydrogenation in the formation of propylene (reported in Fig. 4) increased with increasing level of catalyst reduction. The values were calculated assuming that hydrogen was produced exclusively in the dehydrogenation of propane to propylene.

The values of propane conversion are plotted in Fig. 5 as functions of the half-cycle reduction time, for samples 1–7. Considerable differences between samples were observed. The initial activity, as inferred from the conversion measured at 1.5 min reaction time (that corresponds to the activity of the pre-oxidized catalyst, since all samples were treated in air at 550 °C before each test) was proportional to the V/(V + Nb) atomic ratio. Under the hypothesis that the surface density of oxidizing sites is proportional to the V fraction in the catalysts, thus it is proportional to the V/(V + Nb) ratio (this hypothesis is valid provided the bulk and surface compositions are similar), a direct relationship indicates that only V sites are involved in the rate-determining step, and that Nb does not affect the redox properties of V sites. This is in line with that reported by Watling et al. [13], who claimed that in co-feed experiments the TOF was substantially independent of the vanadia content in V/Nb mixed oxides; variations in the chemical environment of V ions due to the presence of Nb did not cause significant changes in the specific activity.

The selectivity to propylene is plotted in Fig. 6 as a function of propane conversion for samples 1–7. In the same figure the values of selectivity obtained under co-feed conditions for samples 3 and 3ox are also reported (similar values were obtained with the other catalysts). All catalysts exhibited similar trends, and the selectivity obtained at low conversion under redox-decoupling conditions was higher than that

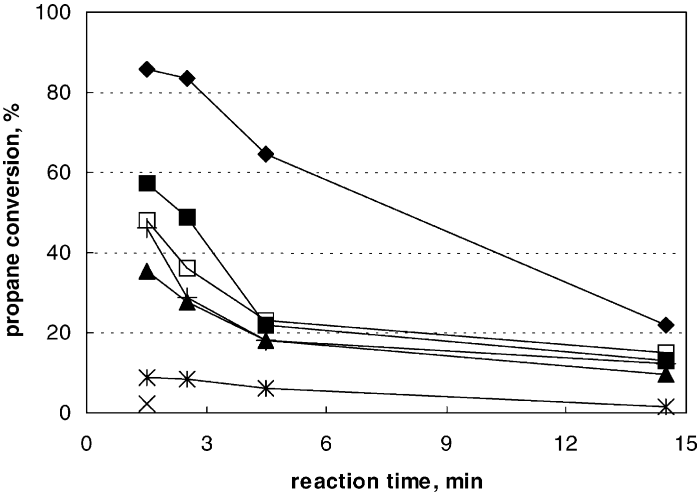

Fig. 5. Conversion of propane as a function of the half-cycle anaerobic reaction time at T 550 °C and residence time 2 s. Samples 1 (◆), 2 (■), 3 (▲), 4 (+), 5 (✳), 6 (×) and 7 (☐).

obtained with the same catalysts under co-feed conditions. This indicates a much lower contribution of the parallel reaction of propane combustion. Therefore operation in the absence of oxygen made it possible to achieve a much higher selectivity to propylene than under aerobic conditions.

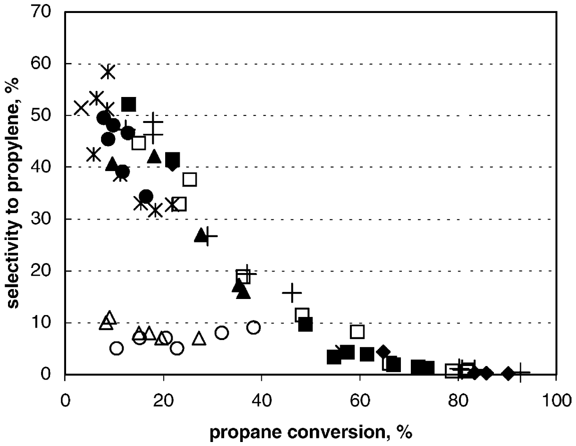

Fig. 6. Selectivity to propylene as a function of propane conversion under redox-decoupling conditions (temperature 550 °C, residence time 2 and 4 s, feed composition 20% in helium), and under co-feed conditions. Redox-decoupling tests: samples 1 (◆), 2 (■), 3 (▲), 3ox (●), 4 (+), 5 (✳), 6 (×), 7 (☐). Co-feed tests: samples 3 (△), 3ox (○).

With the exception of samples 1 and 6, for all V/Nb/O catalysts reported in Fig. 6 the formation of carbon oxides under redox-decoupling conditions was almost nil for very low propane conversions. In other words, if the selectivity to propylene is calculated exclusively based on the concentration of products at the reactor outlet (i.e., without considering the C-unbalance), it was almost total. For all catalysts, however, at high propane conversion the selectivity to propylene was similar under the two different operating conditions (under co-feed conditions this occurred for total oxygen conversion).

The characterization of sample 3 after reaction under redox-decoupling conditions evidenced that $VNbO_5$ had decomposed into vanadium oxide (easily re-oxidized to V_2O_5 during the oxidation half-cycle) and to V^{5+}/Nb/O mixed oxides having V/Nb ratios lower than 1. The catalytic performance of sample 1 (which during reaction was reduced to V_2O_3) was very similar to that of V/Nb mixed oxides, being as selective as the latter catalysts at low propane conversion, and unselective at high propane conversion. This further supports the hypothesis that the catalytic performance of V/Nb mixed oxides was governed by the reactivity of vanadium oxide which developed by decomposition of $VNbO_5$. Also sample 6 (niobia) was selective to propylene, but the catalyst reached a very low conversion of

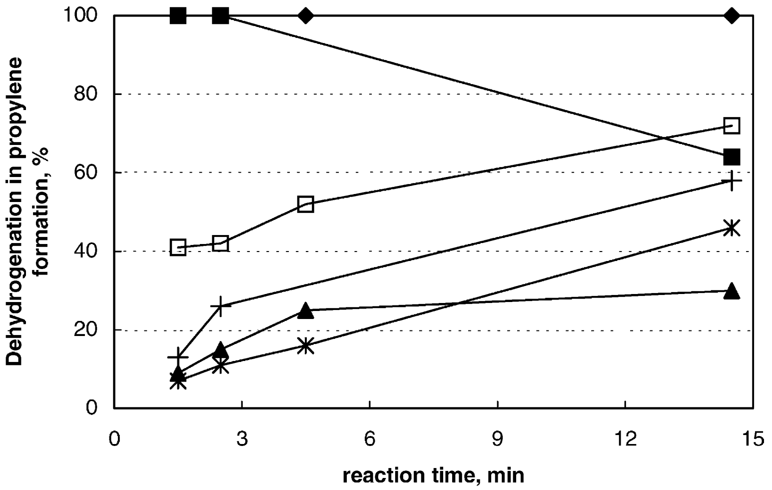

Fig. 7. Contribution of dehydrogenation in the formation of propylene (i.e., H_2 concentration/C_3H_6 concentration in the outlet stream, %) as a function of half-cycle anaerobic reaction time for tests under redox-decoupling conditions. Conditions are same as in Fig. 4 and symbols are same as given in Fig. 5.

propane; initial conversion at 1.5 min reaction time was 2.5%.

The theoretical contribution of dehydrogenation in propylene formation (as calculated from the hydrogen concentration in the exit stream) as functions of the half-cycle reduction time is reported in Fig. 7. The limitation of the data elaboration as reported in Fig. 7 is that it does not take into account: (i) the possibility that the hydrogen produced may in part be oxidized to water by bulk oxygen (and this is more likely to occur for short reaction times, thus with oxidized catalysts), and that propylene produced may in part be consecutively transformed to carbon oxides; (ii) the possible contribution of other reactions to hydrogen formation.

The contribution of dehydrogenation increased with increasing the reaction time. However, it is evident from Fig. 7 that on decreasing the V/Nb ratio the contribution of dehydrogenation in propylene formation became lower, due to the fact that the formation of hydrogen decreased. This means that on decreasing the V content either the catalyst became less active in propane dehydrogenation and more active in propane oxidehydrogenation (this however seems unlikely, since the degree of V reduction for a defined propane conversion reasonably was the highest just in samples having the lowest V/Nb ratio), or the hydrogen combustion to water became more favored, or V catalyzed the formation of hydrogen through other reactions. With sample 2, the concentration of molecular hydrogen in the exit stream was comparable with the concentration of propylene, over the entire range of reduction times, while with sample 1 the concentration of hydrogen was much higher than that of propylene, especially for shorter reduction times, thus on more oxidized catalysts. The high level of hydrogen formation with samples 1 and 2 under both co-feed and redox-decoupling conditions at high temperature might be explained with the contribution of other reactions for the formation of H_2, catalyzed by vanadium oxide (which in fact was the prevailing component in both samples).

4. Discussion

The procedure adopted made it possible to obtain the rutile compound $VNbO_4$ with a relatively high surface area (Table 1). It is worth mentioning that the procedures described in the literature for the synthesis of $VNbO_4$ are more complex than the one adopted in the present work [37,38]. A solid state reaction between NbO_2 and VO_2 at temperatures above 1000 °C under vacuum is one typical preparation [37]. When excess of one element is used, solid solutions $V_{1-x}Nb_xO_2$ are claimed to develop, which when $0.5 < x < 1$ (excess of Nb) in practice correspond to a solid solution between NbO_2 and $VNbO_4$ [$V^{3+}_{1-x}Nb^{5+}_{1-x}Nb^{4+}_{2x-1}O_2$], but when $0 < x < 0.5$ (excess of V) correspond to a solid solution between VO_2 and $VNbO_4$ [$V^{3+}_{x}Nb^{5+}_{x}V^{4+}_{1-2x}O_2$], all these compounds being isostructural [37]. Therefore our procedure, i.e., co-precipitation of salts from an alcohol solution, made it possible to avoid fractional precipitation of metal oxohydrates, and obtain a more homogeneous precursor, the thermal treatment of which, when carried out in nitrogen flow, led to the reduction of V^{4+} to V^{3+} and to the development of the rutile compound even under relatively mild conditions. On the other hand, under our conditions apparently it was not possible to develop solid solutions having V/Nb ratios other than 1/1, even when the V/Nb preparation ratio was considerably lower than 1.

Rutile $VNbO_4$ (sample 3) was stable under our co-feed conditions or in the absence of oxygen, thus could withstand reducing environments, while if treated in air it was oxidized to $VNbO_5$ already at 550 °C (sample 3ox). On the contrary, $VNbO_5$ (samples 3ox and 7) when exposed to the feed of diluted propane under redox-decoupling conditions was decomposed into amorphous vanadium oxide plus V^{5+}/Nb/O compounds having $V/Nb < 1$. Thus $VNbO_5$ is not able to withstand the reduction of V^{5+}, and segregation of vanadium oxide occurs under these conditions. The latter is then oxidized to crystalline V_2O_5 when the same catalyst is exposed to air for the oxidizing half-cycle. Therefore, the V species which indeed plays the main role in the redox cycle is the one belonging to segregated vanadium oxide. The same also occurred with samples containing $VNbO_4$, since the latter was transformed to $VNbO_5$ before running catalytic tests, during the pre-oxidation treatment at 550 °C.

The reactivity data performed under co-feed conditions pointed out that $VNbO_4$ and $VNbO_5$ are not good catalysts for the oxidative dehydrogenation of propane, since they produce propylene with a very low selectivity; the prevailing products were carbon oxides. The olefin is formed mainly via a dehydrogenative mechanism under conditions of high oxygen conversion, while it is produced via oxidative dehydrogenation under conditions of oxygen availability in the gas phase. Moreover, $VNbO_4$ has no ability to furnish oxygen for the abstraction of hydrogen from propane and the co-generation of water, and only acts as a dehydrogenating catalyst when propane is the only reactant.

Under redox-decoupling conditions the catalysts were more selective than under co-feed conditions for low propane conversion, while they were poorly selective at high propane conversion. This suggests that the oxygen species responsible for the consecutive combustion of propylene is likely a bulk species, and therefore even in the absence of molecular oxygen this reaction becomes the prevailing one at high propane conversion (this occurred for short reduction times, thus with the more oxidized catalysts). The high selectivity to propylene achieved for low propane conversions can be due to different reasons:

(1) The absence of molecular oxygen makes the rate of the parallel reaction of propane combustion become practically nil. This means that the oxygen species responsible for the reaction of propane combustion under co-feed conditions is a surface, electrophilic one, generated in the presence of molecular oxygen [39].
(2) Since the low conversion values were obtained for longer reaction times, thus on more reduced catalysts, the development of a catalyst surface which is more reduced leads to active sites which are more specific in oxidehydrogenation than in combustion of propane. This effect has been proposed to play an important role with other vanadium oxide-based catalysts [22]. The improvement in selectivity and yield to propylene was achieved by operating at steady-state conditions, with careful control of the propane-to-oxygen ratio in the feed [33]. This indicates the importance of having a discrete number of oxidizing sites in order to develop a selective catalyst [40]. Since in our redox-decoupling tests the oxidation state for V which was reached during the reducing step is likely to be lower than that which developed under stationary, co-feed conditions, this difference in the nature of V sites caused the difference in performance found for the two operations at low propane conversion.
(3) A change may occur in the operating mechanism, from an oxidehydrogenation to a dehydrogenation, with increasing degree of catalyst reduction. One aspect which is in favor of this hypothesis is that in all cases the formation of coke (as

determined by the lack in C balance) became relevant for increasing values of reduction time (i.e., for decreasing degrees of propane conversion), pointing out the progressive decrease of the number of oxidizing sites in catalysts. This hypothesis is also supported by the results plotted in Fig. 7, which reports the contribution of dehydrogenation in propylene formation. The curves suggest a change in the reaction mechanism with increasing reaction time, likely related to the different nature of the V sites involved for short and for long reduction times.

Concerning the role of Nb in V/Nb/O systems, literature evidences exist that Nb may affect the selectivity to propylene through the action of its Lewis acidity [13–18]; the interaction between V and Nb leads to the formation of V active sites having acidity and redox properties different from those of bulk vanadium oxide. However, literature data indicate that one condition to obtain good performance is the dispersion of V sites in the niobia matrix, achieved by either impregnation or co-precipitation [13]. This may lead to a co-operation effect between the acidity of the Nb sites and the redox properties of the V sites. On the contrary, this co-operation is missed in systems having a higher V/Nb ratio, like in intermetallic compounds studied in the present work. Under these conditions Nb did not substantially play any specific role neither on catalyst activity nor on selectivity to propylene.

5. Conclusions

Operation under redox-decoupling conditions made it possible to achieve an higher selectivity to propylene with respect to operation under co-feed conditions, but only for low levels of propane conversion. This occurred with both vanadium oxide and with V/Nb mixed oxides. However, this improvement in selectivity was likely related to a change in the reaction mechanism from an oxidative to a dehydrogenative one, due to the low valence state of V which developed during prolonged contact with propane in the absence of molecular oxygen. It is also proposed here that this might explain the improvement in selectivity described in the literature with other vanadium oxide-based catalysts when operation is carried out under cyclic conditions. On the contrary, no advantage was obtained under anaerobic conditions with oxidized catalysts; in this case high instantaneous conversions of propane were accompanied by a very low selectivity to propylene.

The characterization of V/Nb/O compounds evidenced that rutile $VNbO_4$ withstands reducing environments (e.g., 20% propane in helium), but is irreversibly oxidized to $VNbO_5$ in air at 550 °C. On the contrary, $VNbO_5$ does not withstand reducing environments, since under the latter conditions it is irreversibly transformed to Nb-rich V/Nb/O compounds and to vanadium oxide. The latter plays the major role in catalytic activity.

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