ACADEMIC
PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 213 (2003) 95–102

JOURNAL OF
CATALYSIS

www.elsevier.com/locate/jcat

Oxydehydrogenation of propane catalyzed by V–Si–O cogels: enhancement of the selectivity to propylene by operation under cyclic conditions

Nicola Ballarini,[a] Fabrizio Cavani,[a,b,*] Maria Ferrari,[a] Roberto Catani,[c] and Ugo Cornaro[c]

[a] *Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy*
[b] *INSTM, Research Unit of Bologna, Bologna, Italy*
[c] *Snamprogetti SpA, Via Maritano 26, 20097 S. Donato Mi, Italy*

Received 13 June 2002; revised 18 September 2002; accepted 19 September 2002

Abstract

The selectivity to propylene in the oxydehydrogenation of propane is improved when the reaction is carried out under cyclic, redox-decoupled conditions rather than under stationary, co-feeding conditions, and using vanadium oxide dispersed in silica as the catalyst. However, the improvement in selectivity is possible only in samples having a V content which is lower than 10 wt% V_2O_5. This points out the importance of having dispersed vanadium oxide to limit the consecutive combustion of propylene.

Keywords: Oxydehydrogenation of propane; Vanadia–silica cogels; Redox decoupling; Propylene

1. Introduction

The oxidative dehydrogenation of light paraffins constitutes one possible synthetic route to olefins, an alternative to highly energy-intensive, endothermal catalytic dehydrogenation or steam cracking [1–5]. Of particular interest for possible industrial application is the oxydehydrogenation of propane and of ethane to the corresponding olefins. Several papers published in recent years have examined a variety of catalytic systems [1–3]. These systems can be roughly classified into two groups, the first including oxides of reducible transition metal ions, for which a mainly heterogeneous, ionic-type process is involved, provided temperatures below 550–600 °C are used, and the second including non-redox-type or hardly reducible oxides, which operate at temperatures higher than 600 °C and with radical mechanisms, usually beginning on the catalyst surface and then transferring into the gas phase. Amongst the former class of catalysts, vanadium oxide, either supported or in combination with other ions to form mixed oxides, is recognized to be a key component for the activation and oxifunctionalization of paraffins [6,7].

The main drawback of all catalytic systems for propane oxydehydrogenation, however, is the fact that the selectivity to propylene, sometimes very high for low paraffin conversion, rapidly falls for increasing values of propane conversion [1–3]. This is due to the fact that under the conditions which are necessary to activate the paraffin, propylene (more reactive than the alkane) undergoes consecutive reactions of combustion. It has also been recognised that one possible way to control the extent of undesired, consecutive combustion is the dosage of oxygen, which affects mainly the oxidation state of the active site under reaction conditions and finally may influence the catalytic performance. This can be achieved by suitable technologies such as catalytic membrane reactors [8–11].

The extrapolation of this concept is represented by the so-called redox-decoupling or cyclic technology, which operates by separation of the two steps included in the Mars–van Krevelen mechanism, i.e., (i) oxidation of the hydrocarbon by the catalyst, which has to be able to withdraw hydrogen and furnish oxygen, either for the formation of water or for the insertion onto the substrate, and which therefore undergoes simultaneous reduction (two-electrons reduced

---

[*] Corresponding author.
E-mail address: cavani@ms.fci.unibo.it (F. Cavani).

PII: S0021-9517(02)00015-5

per O^{2-} ion furnished) and (ii) oxidation of the reduced catalyst by molecular oxygen. Examples of successful application of this technology are the DuPont process for the oxidation of *n*-butane to maleic anhydride and the Atofina/DuPont process for the selective oxidation of propylene to acrolein [12,13]. In the past, however, this technology has been claimed in several papers and patents for practically all types of selective oxidation reactions, including ammoxidation, oxychlorination, and oxydehydrogenation of light paraffins [14–20].

For propane oxydehydrogenation, it has been reported that V/Mg/O catalysts are more selective to propylene when the reaction is carried out with cyclic operation [21–24]. It was demonstrated that the improvement in yield to propylene, occurring as a consequence of the improved selectivity, was due to the absence of molecular oxygen in the gas phase, and also that under a steady state, co-feeding operation it was possible to improve the yield by lowering the oxygen partial pressure, the variation of which for a low propane concentration (3% in the feed) had surprisingly no effect on alkane conversion. In this case the improvement in selectivity was attributed to an optimal reduction level of the catalyst in the presence of high propane-to-oxygen ratios in the feed.

In the present paper we compare the performance in propane oxydehydrogenation of vanadium-oxide-based catalysts where the active compound has been dispersed in a silica matrix by the “one-pot,” cogel procedure [25,26]. The reactivity was evaluated both under co-feeding, steady conditions and under redox-decoupling, cyclic conditions, i.e., with alternating feed of diluted propane and air.

2. Experimental

Catalysts were prepared using the following procedure: $(NH)_4VO_3$ in the desired amount was completely dissolved in 40 ml water, and then 30 ml $Si(C_2H_5O)_4$ and 5 ml HCl 8 N were added; the sol was left at 40 °C under stirring. Under these conditions, the development of the gel was completed within 24 h. The gel was then carefully dried at 65 °C, left at this temperature for 5 h, heated to 500 °C with a heating rate not higher than 1 °/min, and finally left at 500 °C for 5 h. The thermal treatment was done in the presence of flowing air. Three catalysts were prepared, containing 6.8, 10, and 15 wt% V_2O_5 (with corresponding V/Si atomic ratios equal to 1/20.7, 1/13.6, and 1/8.6). The specific surface areas (as determined by the single-point, BET method) of the samples with increasing V content were equal to 490, 170, and 240 m^2/g, respectively.

Catalytic tests were carried out in a quartz fixed-bed reactor loading 1.5–2.0 cm^3 (0.7–1.0 g) of catalyst in powder form (30–40 mesh particles). Tests under both co-feeding (contemporaneous feeding of oxygen and propane) and cyclic, redox-decoupling (alternate feeding of diluted propane and air) conditions were carried out at 550 °C, atmospheric pressure, and gas residence times of 2, 4, and 6 s. The feed composition was 20% propane, 20% oxygen, and the remainder helium for co-feeding conditions, and 20% propane diluted in helium for the reducing half-cycle in the tests under redox-decoupling conditions. The oxidizing half-cycle was carried out by feeding air at 550 °C with a residence time of 2 s. The time for the oxidation half-cycle was always 30 min, which exceeded the time necessary to reach complete catalyst reoxidation. This period of time, however, was not optimized; thus, the minimum time necessary for catalyst reoxidation was not looked for. Tests under cyclic conditions were carried out by running the reaction between propane and the oxidized catalyst during the reducing half-cycle for different reaction times and by checking the instantaneous distribution of the products; before each test the catalyst underwent the oxidizing half-cycle. In addition to propylene, the reaction products were carbon monoxide, carbon dioxide, light hydrocarbons (ethane, ethylene, methane), water (not analyzed), and molecular hydrogen. No oxygenated compounds were found.

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 X-ray diffraction (Phillips PW 1050/81, radiation Cu K_α).

3. Results

Figure 1 shows the variation of instantaneous propane conversion as a function of the reaction time during the reducing half-cycle (tests under redox-decoupling conditions), i.e., the time the oxidized catalyst was left exposed to the reducing stream, for the three catalysts having increasing amounts of vanadium. In all cases the instantaneous conversion decreased with increasing reducing time, because of the progressive reduction of the vanadium ions and the cor-

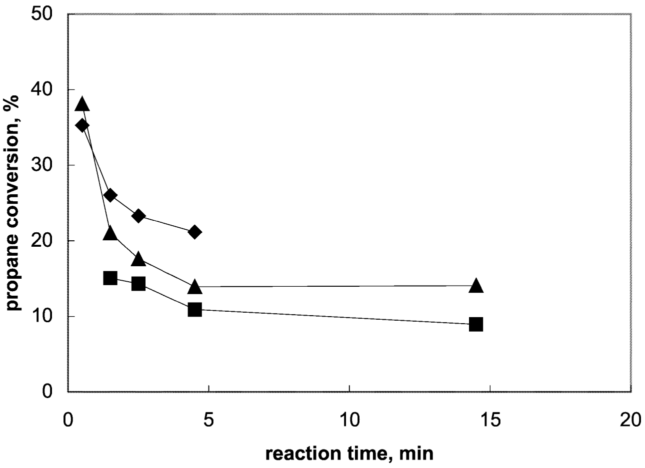

Fig. 1. Instantaneous conversion of propane as a function of the half-cycle reaction time. Catalysts: 6.8 wt% V_2O_5 (◆), 10 wt% V_2O_5 (▲), 15 wt% V_2O_5 (■). Gas residence time 4 s; temperature 550 °C.

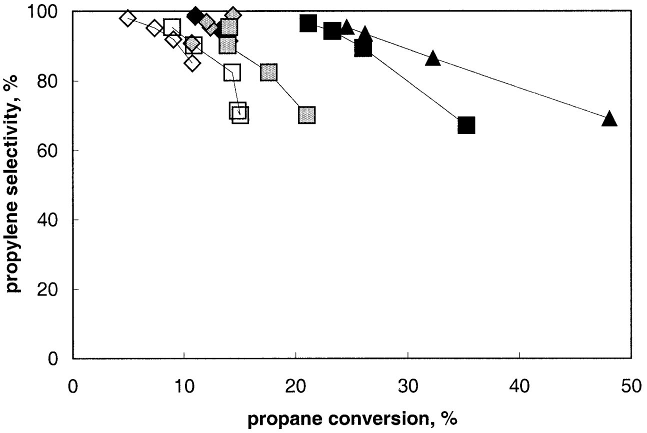

Fig. 2. Instantaneous selectivity to propylene as a function of instantaneous propane conversion. Catalysts: 6.8 wt% V_2O_5 (black symbols), 10 wt% V_2O_5 (grey-tone symbols), and 15 wt% V_2O_5 (open symbols). Data collected at 2 s (rhombs), 4 s (squares), and 6 s (triangles) residence times; temperature 550 °C.

responding decrease in the oxidizing activity of the catalyst. The initial activity, relative to the fully oxidized catalyst, was not simply proportional to the V content, since the surface areas of the three samples were different.

The conversion reached an almost constant value for increasing values of reduction times. On the other hand, if the propane activation and oxidation were exclusively due to the oxidized V sites under these conditions, zero conversion of propane should soon be reached. This means that other reactions may contribute to the conversion of propane on the reduced catalyst. It is worth mentioning that a sample made only of silica, prepared with the same procedure as the V/Si/O cogels, gave less than 2% conversion under redox-decoupling conditions, in the entire range of half-cycle reduction times, with a selectivity to propylene around 60–80%, the by-products being lighter hydrocarbons and coke. Under the same conditions and with the reactor filled with only inert material, no propane conversion was observed under anaerobic conditions.

For the three catalysts the instantaneous selectivity of propylene is plotted in Fig. 2 as a function of instantaneous propane conversion for different values of gas residence times. The selectivity was calculated considering only the C-containing products found in the outlet stream of the reactor: propylene, carbon monoxide, carbon dioxide, and lighter hydrocarbons (methane, ethylene, ethane). However, an additional product was coke, the formation of which was indirectly evaluated from the atomic C balance applied to the reactor. For tests carried out at 2 and 4 s of residence time, the C balance was in general close to 100% for short reduction times (e.g., for times shorter than 5 min), while it became worse, e.g., in the 70 to 80% range, for increasing reaction times. We thus infer that the oxidized catalyst transforms propane exclusively to gaseous products, while the progressively more reduced catalyst is less active and transforms a fraction of the propane to coke. In a hypothetical cyclic process where the reducing and oxidizing steps are alternated over the catalysts (e.g., in a circulating fluidized-bed reactor), the coke deposited on the catalyst during the former step has to be burnt to carbon oxides in the latter step; therefore, the coke has to be considered a true reaction product. Tests carried out at 6 s residence time, instead, gave a 70 to 80% C balance even for short reaction times.

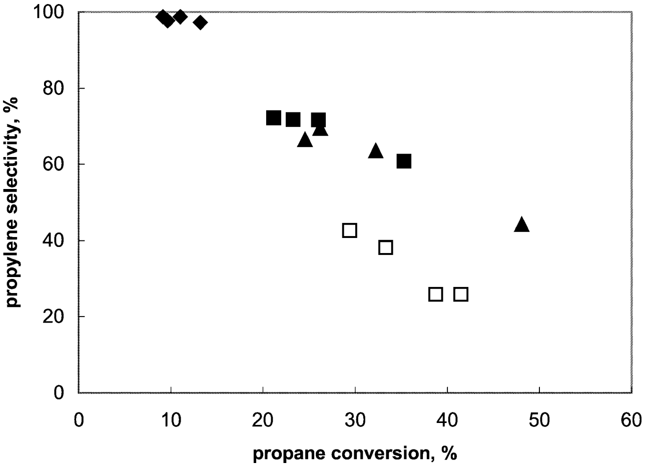

Fig. 3. Instantaneous selectivity to propylene (including coke formation) as a function of instantaneous propane conversion under redox-decoupling conditions at residence times 2 s (◆), 4 s (■), and 6 s (▲) and under co-feeding conditions (□, residence times 2 and 4 s). Temperature 550 °C; catalyst 6.8 wt% V_2O_5.

The overall selectivity to propylene, calculated also including the formation of coke, is reported in Fig. 3 for the catalyst containing 6.8 wt% V_2O_5. In the same figure, the selectivity to propylene achieved under steady conditions, thus with co-feeding of propane (20%) and oxygen (20%), is also reported; under the latter conditions total oxygen conversion was reached. Considerable improvement in selectivity to propylene was obtained when operation was carried out under redox-decoupling conditions instead of the traditional co-feeding conditions. The improvement was achieved at relatively high propane conversion (i.e., higher than 30%), indicative of the decreased contribution of the consecutive reaction of propane combustion when the reaction is carried out under anaerobic conditions. On the other hand, no difference in selectivity to propylene was found between the two operations when the two catalysts containing 10 and 15 wt% V_2O_5 were used.

Under co-feeding conditions the three catalysts behaved similarly at 550 °C, all of them reaching total oxygen conversion and a selectivity to propylene lower than 30% (specifically, 25, 22 and 19% selectivity at 39–41% propane conversion for the three catalysts with increasing vanadia contents).

In Fig. 4, a comparison is made among the three catalysts of the time-averaged yields to propylene under cyclic conditions as a function of the time of the reducing half-cycle with the yield obtained for the same conditions (temperature 550 °C and gas residence time 4 s) under co-feeding

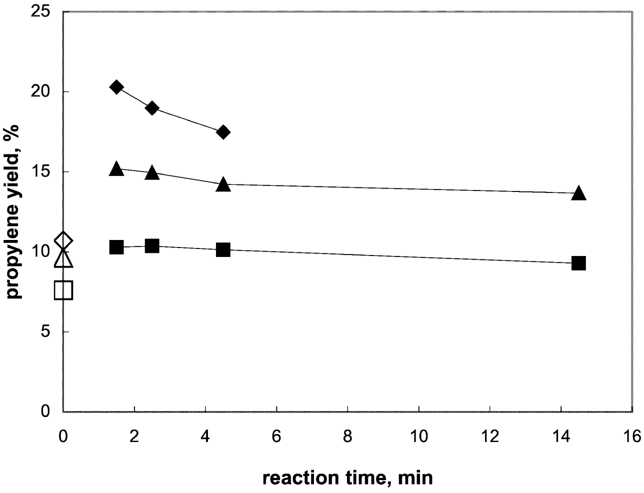

Fig. 4. Time-average yield of propylene as a function of the half-cycle reaction time under redox-decoupling conditions (solid symbols) and steady yield to propylene under co-feeding conditions (open symbols). Residence time 4 s; temperature 550 °C. Catalysts: 6.8 wt% V_2O_5 (rhombs), 10 wt% V_2O_5 (triangles), 15 wt% V_2O_5 (squares).

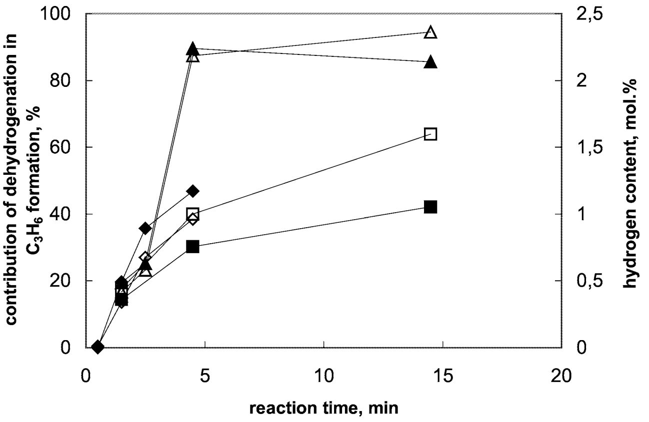

Fig. 5. Concentration of hydrogen in the exit stream (right scale, solid symbols) and contribution of dehydrogenation in propylene formation as calculated from the concentration of hydrogen (left scale, open symbols) as functions of the reaction time under redox-decoupling conditions. Catalysts: 6.8 wt% V_2O_5 (rhombs), 10 wt% V_2O_5 (triangles), 15 wt% V_2O_5 (squares). Gas residence time 4 s; temperature 550 °C.

conditions. In the former case, to reduce the error in extrapolation of data at zero reaction time, the values of conversion and selectivity were integrated starting from the experimental result at 1.5 min reaction time. Therefore the data are indeed to be considered slightly underestimated. The value of the time-averaged yield was calculated without considering the time necessary for the catalyst reoxidation. This is a reasonable simplification, since in a circulating fluidized-bed reactor the reduced catalyst is transported to a second vessel for the reoxidation with air, and therefore the half-cycle time necessary for catalyst reoxidation only affects the rate at which the catalyst is circulated and the catalyst hold-up in the two vessels, but is not used for the calculation of the productivity. For all catalysts the average yield declined slightly with increasing reaction time, due to the combination of the opposite effects of increasing instantaneous selectivity and decreasing instantaneous conversion. Also, the behaviour shown derives from the particular trend relative to conversion as a function of reaction time, which did not become nil with increasing reaction time (Fig. 1). The catalyst having the lowest V_2O_5 content gave the highest yield, because of the contribution of the higher conversion (a consequence of its higher surface area) and of the higher selectivity to propylene. For all catalysts, the yield to propylene achieved was higher than that obtained under co-feeding conditions. However, in the latter case the conversion of propane was limited by the availability of oxygen, which already at 550 °C and 2 s residence time was fully converted.

The productivity of propylene achieved under redox-decoupling conditions can be estimated to be approximately 0.14 $kg_{propylene}/(kg_{cat}\,h)$ for a feed containing 20% propane, with the time-average yield equal to 20% obtained for a reaction time of 1.5 min and gas residence time of 4 s, for the catalyst containing 6.8 wt% V_2O_5. The productivity under steady conditions (approximately 0.07 h^{-1}) was lower than that under redox-decoupling conditions because of the lower yield to propylene achieved. The productivity value of 0.14 h^{-1} is comparable to the values which can be calculated from most data reported in the literature for steady, co-feeding conditions and for several different catalysts [3]. On catalysts having higher than 15 wt% V_2O_5, the productivities of propylene calculated under the two different configurations were more similar, since the yields of propylene were closer (see Fig. 4).

The concentration of hydrogen in the exit stream as a function of reaction time, for the three catalysts examined, is reported in Fig. 5. The same figure also shows the contribution of dehydrogenation to propylene formation, as calculated on the basis of the hydrogen concentration. In practice, it represents the ratio between the concentration of hydrogen and that of propylene; thus, it is assumed that all the hydrogen is produced by the dehydrogenation of propane to propylene. Of course, this is an oversimplification, since it does not take into account that a fraction of the hydrogen produced may have reacted to form water (especially on oxidized catalysts) and that hydrogen may form by other reactions as well. In fact hydrogen may be (i) co-generated with coke, the latter being formed on more reduced catalysts; (ii) formed by steam-reforming of the hydrocarbons (water is present in the reaction medium); (iii) co-produced with CO in the partial oxidation of the hydrocarbons; or (iv) co-generated with CO_2 in the water-gas-shift of CO. Nevertheless, the plot of Fig. 5 is useful to compare the relative amount of hydrogen formed with that of propylene and to understand the progressive change in catalyst performance with increasing levels of catalyst reduction. For increasing reaction times, the contribution of dehydrogenation increased, until it became the prevailing one in propylene formation for strongly reduced catalysts. Dehydrogenation may be catalyzed by either the reduced V species, or by the coke which accumulates on the catalyst

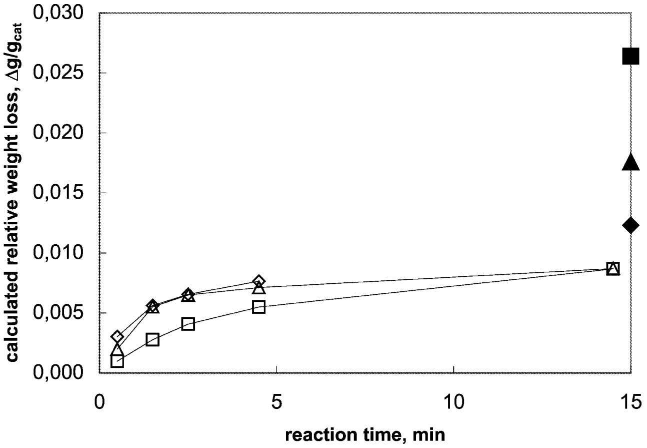

Fig. 6. Integral catalyst weight loss referred to the unit weight as calculated from the distribution of products as a function of the reaction time under redox-decoupling conditions at residence time 4 s and temperature 550 °C (open symbols) and theoretical values of maximum weight loss (solid symbols). Catalysts: 6.8 wt% V_2O_5 (rhombs), 10 wt% V_2O_5 (triangles), 15 wt% V_2O_5 (squares).

surface for long reaction times. It is worth mentioning that even under co-feeding conditions a nonnegligible amount of hydrogen was detected, and thus a fraction of propylene was likely produced by means of propane dehydrogenation even in the presence of molecular oxygen.

In Fig. 6 is plotted the integral weight loss of the three catalysts referred to the unit weight, as calculated from the stoichiometries for the formation of each product, and assuming that no bulk oxygen species is required in the formation of coke or hydrogen. Also given in the figure are the theoretical reference values, as calculated by hypothesizing that vanadium is present exclusively as V_2O_5 and that it can be reduced completely to V_2O_3. The sample having 6.8 wt% V_2O_5 reached a reduction level for vanadium (weight loss: 0.88%) very close to the theoretical one. The same occurred for tests at a residence time of 2 s (not shown in the figure), and the trend in Fig. 6 suggests that $\Delta g/g \approx 0.9\%$ represents a limit value. Different was the case for samples having higher vanadia loading, for which the weight loss reached under these conditions was far lower than the theoretical one for complete reduction of V_2O_5 to V_2O_3. This suggests that the degree of dispersion of vanadia in the samples is a function of the vanadia loading. For the catalyst having the lowest vanadia content, the higher degree of dispersion and the higher surface area of the catalyst make almost all vanadium sites virtually accessible to reactants, and all of them are reduced under anaerobic conditions. In contrast, in samples having higher vanadia content and lower surface area, a fraction of the vanadium ions are not accessible to the reactants, and are not reduced, at least under the reaction conditions used.

Raman spectra of calcined catalysts are shown in Fig. 7. Silica prepared with the sol-gel method gave no band. It has been reported that silica gel gives vibrations at 975 cm^{-1} (Si–O stretching of Si–OH group), 820–800 cm^{-1}, 605 cm^{-1}, and in the range 350–550 cm^{-1} (vibrational mode of Si–O–

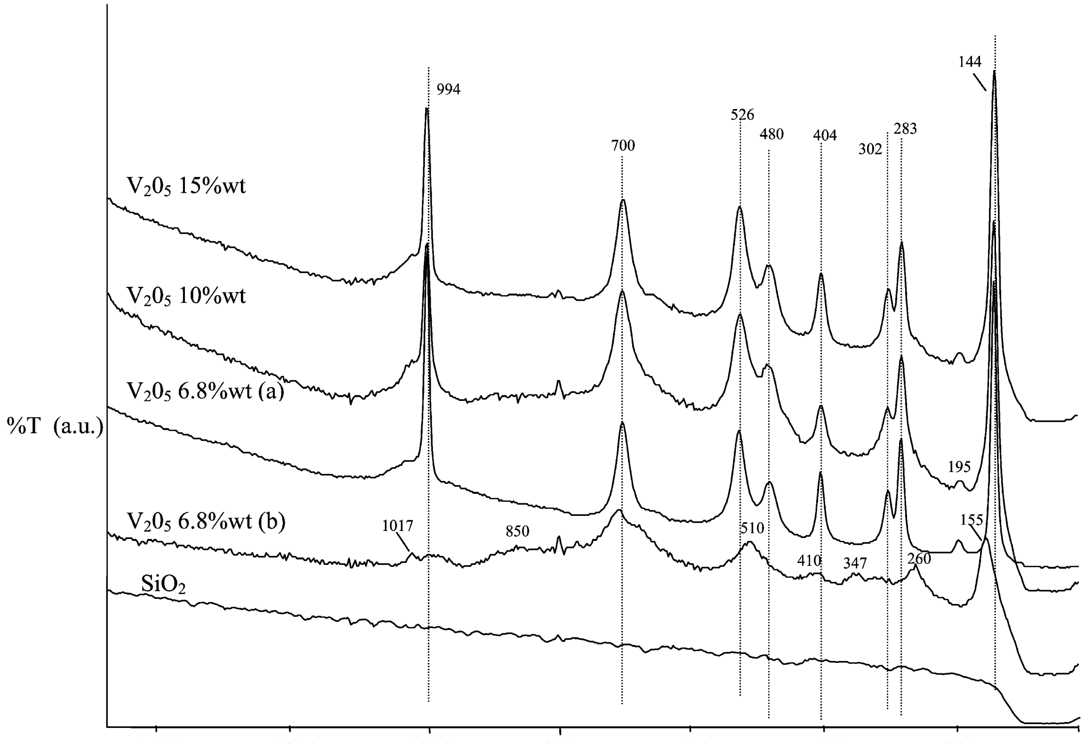

Fig. 7. Raman spectra of calcined samples.

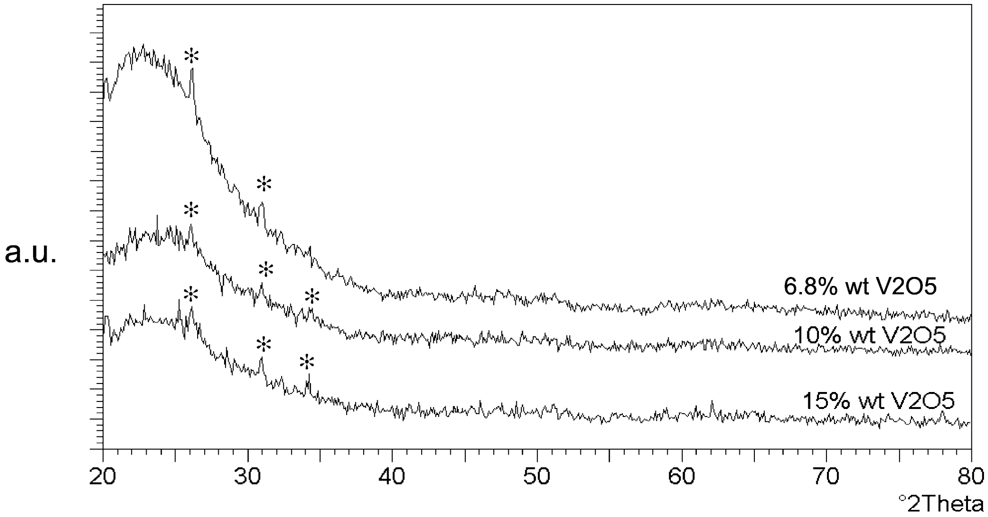

Fig. 8. X-ray diffraction spectra of calcined samples. *, crystalline vanadia.

Si bridges) [25,27]. In the case of catalysts with vanadium content of 10 and 15 wt% the sample was homogeneous, and only one type of spectrum was recorded when the beam was focussed on several different particles. Bands at 994, 700, 526, 480, 404, 302, 283, 195, and 144 cm^{-1} are characteristic of crystalline V_2O_5 [25,28,29]. The catalyst having the lowest vanadia content (6.8 wt% V_2O_5), instead, was more heterogeneous, and two different types of spectra were obtained when focussing on different particles. One spectrum (spectrum a in the figure) is typical of crystalline V_2O_5 (similar to those observed for the two catalysts having higher vanadium content), while the other spectrum (spectrum b in the figure) does not show any bands attributable to crystalline V_2O_5, thus indicating that a part of the vanadium consists of isolated species. A similar spectrum has been reported by Wang et al. [26], for a 1% vanadia–silica cogel sample; this sample is reported to give rise to Raman bands at 150, $\sim$ 260, 310, 410, 520, 648–761, and 990–1016 cm^{-1}, which are characteristic of the hydrated surface vanadia species on silica, and which are also observed in spectrum b of our sample. The band at 1017 cm^{-1} is characteristic of the hydrated terminal V=O bond; a shoulder at the same Raman shift is present also in the spectra of our catalysts with 10 and 15 wt% vanadium. The bands at 200–300 and 500–800 cm^{-1} are assigned to V–O–V vibrations and the band at 150 cm^{-1} is due to lattice vibration [26].

X-ray diffraction spectra, reported in Fig. 8, confirm the presence of crystalline vanadia in all samples.

4. Discussion

The data reported in Fig. 1 show that the conversion of propane reached an almost constant value with increasing reaction time, despite the considerable extent of reduction which was reached after 15 min exposure to the propane-containing stream. This can be explained by hypothesizing that a change in mechanism occurs as the extent of vanadium reduction increases. Thus, while the oxidized catalyst is able to oxydehydrogenate propane (or, alternatively, to dehydrogenate the paraffin and burn hydrogen to water, since no hydrogen formed for short reduction times), the reduced catalyst dehydrogenates propane to propylene. In oxydehydrogenation, the catalyst yields mainly propylene and carbon oxides (at relatively high propane conversion) and progressively gives its bulk ionic oxygen, while in dehydrogenation the catalyst mainly yields propylene, cracking products, coke, and hydrogen (with only minor amounts of carbon oxides). Under the latter conditions, the catalyst does not continue to lose weight, since no oxygen is transferred from the catalyst to the reactants or products. Figure 6 shows that the catalyst weight loss, as calculated on the basis of the distribution of products, tends towards a limiting value which is close to the theoretical one only for the catalyst having the lowest vanadium content. In the region of the plateau (for longer reaction times) the catalyst nevertheless converts propane to propylene, mainly through a dehydrogenation mechanism which no longer requires withdrawal of oxygen from the catalyst.

Comparison of the data plotted in Figs. 2 and 3 suggests the following considerations.

(1) Figure 2 shows that as the extent of propylene conversion increases, the selectivity to propylene decreases, due to the corresponding increase in the formation of carbon monoxide and carbon dioxide. The steepest decrease in selectivity was with the catalyst having the highest V content, while in the case of the sample having 6.8 wt% V_2O_5 the selectivity remained above 70% up to 30% propane conversion. It is interesting to observe that for instantaneous conversions less than 10% (which were achieved with the longer reduction times) the selectivity to propylene (as calculated from the reactor effluent) was very high (close to 100%), because of the very low amount of carbon oxides which formed (on the other hand, the true selectivity was

lower, around 75–85%, due to the formation of coke, which accumulated on the catalyst surface). This means that under these conditions there is no contribution of the parallel propane combustion. This may be for the following different reasons:

(a) The reaction mechanism changes from an oxydehydrogenative one (or from a dehydrogenative mechanism followed by hydrogen combustion), occurring on the oxidized catalyst for shorter reaction times, to a dehydrogenative one, occurring on the reduced catalyst for longer reaction times.
(b) In the absence of molecular oxygen the parallel reaction of propane combustion is made nil. This implies that this reaction is mainly caused by electrophilic oxygen species which develop in the presence of molecular oxygen under co-feeding conditions.
(c) A reduced catalyst (i.e., the one which develops with prolonged exposure to the reducing stream under redox-decoupling conditions) is intrinsically more selective than a more oxidized one and does not burn propane.

The first hypothesis is the most likely, as also suggested by the different nature of the by-products which are obtained with increasing times of half-cycle reduction.

(2) The comparison of the selectivity vs conversion plots for the three catalysts, shown in Fig. 2, evidences that the rate of the consecutive reaction of propylene combustion is a function of the number of active sites in the catalyst. Raman spectra (Fig. 7) indicate that indeed catalysts are substantially made of two different vanadium species: (a) crystalline vanadia, observed in all samples, which is either occluded in the silica gel, or dispersed over it, and (b) vanadium ions, likely dispersed in the silica gel, which have been detected only in the sample having the lowest vanadium content. The effect on selectivity to propylene shown in Fig. 2 may be due to the fact that a system in which vanadia crystallites are more diluted makes the readsorption of propylene and the consecutive combustion less likely to occur. Higher densities of V sites (in the catalysts having 10 and 15 wt% V_2O_5) lead to to an higher contribution of the consecutive reaction of propylene combustion. This also points out the important role of site isolation in this reaction, at least under anaerobic conditions [30].

(3) Figure 3 also reports the values of selectivity which were obtained when the reaction was carried out under co-feeding conditions, for the catalyst having 6.8 wt% V_2O_5. In the case of catalysts having 10 and 15 wt% V_2O_5, the selectivity to propylene achieved under co-feeding conditions and with total oxygen consumption (reached in correspondence to 35–40% propane conversion) was comparable to that obtained when operating under anaerobic conditions for the same level of conversion. Therefore for these catalysts there is no advantage when the reaction is carried out under redox-decoupling conditions rather than under co-feeding conditions. This also implies that the mechanism occurring under redox-decoupling and co-feeding conditions is the same, and thus involves the same type of active oxygen species (at least so long as the mechanism is an oxidative one rather than a dehydrogenating one). Thus, it is reasonable to assume that the O^{2-} species is involved in both propane oxydehydrogenation and propylene combustion. Different was the case of the catalyst having 6.8 wt% V_2O_5 (shown in Fig. 3), since in this case there was a considerable difference between the values of selectivity to propylene obtained in the two cases. Thus, operation under redox-decoupling conditions led to a substantial improvement in the yield to propylene. Therefore, propylene may be saved from consecutive combustion only provided that the two conditions are fulfilled at the same time: (i) the surface density of active V species is relatively low, and (ii) there is no oxygen in the gas phase. This cannot be explained simply by hypothesizing that in the absence of molecular oxygen the species responsible for propylene combustion is not formed (otherwise the same effect would be observed even in catalysts having the highest vanadia content), nor can it be attributed exclusively to the lower concentration of active sites in the catalyst having the lowest vanadia content (otherwise a greater difference in selectivity at isoconversion between the three samples would be also observed under co-feeding conditions). It is possible to hypothesize that under co-feeding conditions the working catalyst has an average oxidation state for V active sites which is higher than that which develops when the same catalyst gives the same instantaneous conversion under anaerobic conditions. Thus the reduction of vanadium and the low surface density of oxidized V^{5+} sites provide a further opportunity for propylene to avoid re-adsorption and consecutive combustion.

5. Conclusions

Systems based on vanadium oxide dispersed in silica gel through the one-pot, co-gelation procedure were tested as catalysts for the oxydehydrogenation of propane to propylene under co-feeding and under cyclic (redox-decoupling) conditions. Evidence was obtained showing that an important factor for the achievement of better selectivity to propylene in oxydehydrogenation of propane is the amount of vanadium oxide, and thus the degree of dispersion of the active sites, specifically V ions, in an inert matrix. Higher dispersion provides the necessary isolation of active sites, which is one fundamental factor in selective oxidation reactions to avoid the occurrence of consecutive reactions on the desired product. However, the improvement in performance is achieved only when the reaction of propane oxydehydrogenation is carried out under redox-decoupling conditions. This positive effect on selectivity is instead very low when the reaction is carried out under co-feeding, steady conditions. The improvement in selectivity to propylene, with a catalyst made of 6.8 wt% V_2O_5 dispersed in silica, when operation is carried out under redox-decoupling conditions with respect to the traditional co-feeding operation, is around 25 percentage points (50% selectivity against 25%) for a propane conversion of 40%.

Acknowledgment

Snamprogetti is gratefully acknowledged for financial support.

References

[1] E.A. Mamedov, V. Cortes-Corberan, Appl. Catal. A 127 (1995) 1.
[2] M. Bettahar, G. Costentin, L. Savary, J.C. Lavalley, Appl. Catal. A 145 (1996) 1.
[3] F. Cavani, F. Trifirò, Catal. Today 24 (1995) 307.
[4] G. Centi, F. Cavani, F. Trifirò, Selective Oxidation by Heterogeneous Catalysis, Kluwer Academic/Plenum, New York, 2001.
[5] P. Arpentinier, F. Cavani, F. Trifirò, The Technology of Catalytic Oxidations, Technip, Paris, 2001.
[6] S. Albonetti, F. Cavani, F. Trifirò, Catal. Rev. Sci. Eng. 38 (1996) 413.
[7] K. Chen, A. Khodakov, J. Yang, A.T. Bell, E. Iglesia, J. Catal. 186 (1999) 325.
[8] A. Pantazidis, J.A. Dalmon, C. Mirodatos, Catal. Today 25 (1995) 403.
[9] M. Tellez, M. Menendez, J. Santamaria, AIChE J. 43 (1996) 777.
[10] A.L. Tonkovich, J.L. Zilka, D.M. Jimenez, G.L. Roberts, J.L. Cox, Chem. Eng. Sci. 51 (5) (1996) 789.
[11] G. Capannelli, E. Carosini, F. Cavani, O. Monticelli, F. Trifirò, Chem. Eng. Sci. 51 (10) (1996) 1817.
[12] E. Bordes, R.M. Contractor, Top. Catal. 3 (1996) 365.
[13] R.M. Contractor, M.W. Anderson, D. Campos, G. Hecquet, R. Kotwica, C. Pham, M. Simon, Patent WO 99/03809, assigned to Elf Atochem and DuPont, 1999.
[14] A.D. Eastman, J.H. Kolts, US Patent 4,370,259, assigned to Phillips Petroleum, 1983.
[15] C.A. Jones, J.J. Leonard, J.A. Sofranko, US Patent 4,737,595, assigned to Atlantic Richfield, 1988.
[16] B. Khazai, G.E. Vrieland, G.B. Murchison, US Patent 5,258,347, assigned to Dow Chemical, 1993.
[17] G.E. Vrieland, C.B. Murchison, Appl. Catal. A 134 (1996) 101.
[18] G.E. Vrieland, B. Khazai, C.B. Murchison, Appl. Catal. A 134 (1996) 123.
[19] V.P. Luk'yanenko, L.P. Shapovalova, M.Yu. Kutnyaya, V.S. Solodkaya, J. Appl. Chem. USSR 60 (5) (1987) 1169.
[20] V.A. Doroshenko, L.P. Shapovalova, L.P. Dolya, J. Appl. Chem. USSR 59 (5) (1986) 1176.
[21] D. Creaser, B. Andersson, R.R. Hudgins, P.L. Silveston, Chem. Eng. Sci. 54 (1999) 4365.
[22] D. Creaser, B. Andersson, R.R. Hudgins, P.L. Silveston, Chem. Eng. Sci. 54 (1999) 4437.
[23] D. Creaser, B. Andersson, R.R. Hudgins, P.L. Silveston, Appl. Catal. A 187 (1999) 147.
[24] D. Creaser, B. Andersson, R.R. Hudgins, P.L. Silveston, J. Catal. 182 (1999) 264.
[25] D.C.M. Dutoit, M.A. Reiche, A. Baiker, Appl. Catal. B 13 (1997) 275.
[26] C.-B. Wang, G. Deo, I.E. Wachs, J. Catal. 178 (1998) 640.
[27] Q. Sun, J.-M. Jehng, H. Hu, R.G. Heman, I.E. Wachs, K. Klier, J. Catal. 165 (1997) 91.
[28] A.J. Huuhtanen, M. Sanati, A. Andersson, S.L.T. Andersson, Appl. Catal. A 97 (1993) 197.
[29] B.A. Khodakov, B. Olthof, A.T. Bell, E. Iglesia, J. Catal. 181 (1999) 205.
[30] R.K. Grasselli, Topics Catal. 15 (2001) 93.