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Oxidation of ethane over vanadia-alumina-based catalysts: co-feed and redox experiments

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Abstract

The conversion of ethane in mixture with oxygen and helium (or air) over a V_2O_5/Al_2O_3 12:88 (w/w) and a V_2O_5-K_2O/Al_2O_3 12:6:82 (w/w) catalysts has been studied. Results of co-feed experiments (with ethane–oxygen–He and with ethane–air feeds) and redox experiments, performed feeding pure ethane over fully oxidized catalysts, have been compared. Data concerning propane conversion over the same catalysts have also been considered. Over the heavily K-doped sample a direct combustion way to CO_2 parallel to the oxydehydrogenation way to ethylene is likely to exist. On the contrary, over undoped vanadia-alumina the main combustion way is successive and mainly gives CO. Similar yields have been obtained but at lower temperatures for co-feed than for redox experiments. However, in similar conditions the productivities can be definitely higher in redox than in co-feed experiments. Nevertheless the conversion of ethane in the empty reactor gives rise to definitely higher selectivities and yields, although at very high temperatures, than the catalyzed reactions.

Keywords: Ethane; Vanadia-alumina-based catalysts; Redox experiments; Oxidation of ethane; Co-feed experiments; Potassium doping

1. Introduction

The production of light olefins from alkanes separated from natural gas is a desirable option to limit the dependence from oil, and according to the low price of natural gas today. This can be obtained through endothermic reactions such as steam cracking [1] and thermal or catalytic dehydrogenation [2], or through an exothermic reaction such as oxidative dehydrogenation (ODH). In spite of the hard work done in this field by different groups [3–5] no sufficiently selective or active catalysts for oxidative dehydrogenation of light alkanes have been developed so far to allow process commercialization [6]. Oxide-supported vanadium oxides, in particular V_2O_5/γ-Al_2O_3, are considered among the best catalysts and have been tested by several groups [7–15]. K-doping can improve its performances in propane and butane ODH [16,17], but it seems that this does not occur in the case of ethane ODH [18].

The main by-reaction upon oxidative dehydrogenation is the catalytic combustion. The oxidative dehydrogenation of ethane and propane can occur thermally, i.e. in an empty reactor, at quite high temperature and is, in these conditions, quite highly selective to ethylene [12] and propene [19], respectively. Very active oxidation catalysts, such as manganese and iron oxides, actually allow high selectivities to olefins at low temperatures but only at very low conversion [20]. Less active materials (such as vanadium oxides and metal vanadates [21]) allow better but still insufficient yields in propene, but at quite high temperatures. In these conditions, gas-phase phenomena also occur, giving rise and to thermal dehydrogenation [22] and to cracking of propane to methane plus ethylene [19]. Propene/ethylene mixtures can be obtained selectively from propane at high temperatures. In previous studies, surface alkoxide species (2-propoxides from propane and surface ethoxides from ethane [4,19]) have been considered to be the surface key intermediates and the possibility of a direct parallel way to CO_x besides the successive one via olefin overoxidation has been evidenced [13,14,19].

New processes and reactor designs could allow to enhance the performances of catalytic oxidative dehydrogenation: for these reasons vanadia-based catalysts have also been tested in two-zone fluidized bed reactors [23], in membrane reactors [24,25] and in monolith-like reactors [25]. The oxidative dehydrogenation at short contact time on metal catalysts

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[26,27] is also apparently a promising option. This process is likely constituted by a gas-phase thermal dehydrogenation induced by the temperature rise generated by total catalytic combustion.

In recent years another type of selective oxidation process, i.e. the transport bed process has been developed, e.g. for maleic anhydride synthesis from *n*-butane [28]. In this case the pure hydrocarbon is converted into the product by the oxidized catalyst in an oxygen free atmosphere. The fluidized catalyst, reduced by the hydrocarbon, is continuously transported into a regeneration reactor where it is re-oxidized by air. Similar processes could also be proposed for oxidative dehydrogenation of alkanes [29].

In the present paper we report on the oxidative conversion of ethane on vanadia-alumina-based catalysts. The aim is to compare the results obtained in a typical laboratory experiment (packed bed flow reactor co-fed with ethane–oxygen–helium mixtures below the lower flammability limits) with those obtained still in laboratory reactors but in conditions approaching those of possible industrial processes, i.e. with a packed bed flow reactor co-fed with ethane-air in the interior of the explosion limits, and in redox conditions, i.e. by feeding the pure hydrocarbon over the fully oxidized catalyst. Data obtained with a heavily K-doped vanadia-alumina catalyst are also reported to check if the quite anomalous behavior of this catalyst observed for propane oxidative conversion also occurs with ethane.

2. Experimental

The tests below described have been performed with two vanadia-based alumina-supported catalysts, with compositions V_2O_5/Al_2O_3 12:88 (w/w) (VA) and V_2O_5-K_2O/Al_2O_3 12:6:82 (w/w) (VKA), prepared with a commercial γ-Al_2O_3 support from Akzo (surface area 180 m^2/g, pore volume 0.48 ml/g, medium pore radius 85 Å, Na <100 ppm, Si <0.2%).

The catalysts have been prepared by sequential impregnation of the alumina supports with NH_4VO_3 water solution first and with KNO_3 water solution later. After each impregnations the catalysts have been dried at 400 K and calcined at 773 K for 7 h. The surface area of the catalysts is 165 m^2/g.

The IR spectra were recorded after activation at 673 K with a Nicolet Protégé instrument. Raman spectra were recorded after heating in dry oxygen with a Brucker FTS100 (Nd-YAG laser) instrument. UV diffuse reflectance spectra were obtained with a Jasco V-570 spectrophotometer.

The catalytic tests were carried out at atmospheric pressure in a continuous fixed bed flow tubular quartz reactor. Blank experiments have been performed in the empty reactor.

The reactants and the reaction products were analyzed using a on-line gas chromatograph (HP 5890) equipped with a PORAPLOT Q (HP) capillary column, connected to a TCD detector in series with a FID detector. Between them, CO was reduced to CH_4 by hydrogen on a nickel catalyst tube (HP). A six-port valve with a 0.5 cm^3 loop has been used for the gas sampling.

The reaction products detected and that will be quantified here are ethane itself, ethene, methane, CO and CO_2. Due to the possibility to produce the same product with different reaction stoichiometries, the selectivities have been calculated based on carbon atoms according to the following definition:

$$S_A = \frac{nN_A^f}{2(N_E^0 - N_E^f)} \times 100,$$

where N_A^f is the number of moles of the A product, n the number of carbon atoms in A and $N_E^0 - N_E^f$ the number of moles of ethane converted. The contact time τ has been defined as:

$$\tau = \frac{V_{CAT}t}{V_f} = \frac{V_{CAT}}{F_f},$$

where V_{CAT} is the apparent volume of the catalyst, excluded diluent, and F_f the total feed flow. When considering the thermal reaction we will refer to the residence time τ_R calculated on the basis of the empty volume of the reactor V_{react} as below:

$$\tau_R = \frac{V_{react}}{F_f}.$$

Four types of standard co-feed experiments have been performed, as summarized in Table 1. The same two catalysts have been tested in redox conditions as well, as summarized too in Table 1. In these experiments the catalyst was previously oxidized with pure oxygen for 15 min at the temperature of the experiment in order to reach the highest oxidation state of the active phase; later the line was purge

Table 1
Conditions for catalytic experiments

Notation	Total flow (ml/min)	Feed composition	Bed composition	τ (s)	Time on stream
Co-feed 1	300	3% C_2H_6, 3% O_2, He balance	0.1 g + 0.4 g quartz	0.02	Steady state
Co-feed 2	100	6% C_2H_6, 6% O_2, He balance	0.5 g	0.3	Steady state
Co-feed 3	30	17% C_2H_6, air balance	0.5 g	1.0	Steady state
Co-feed 4	24	17% C_2H_6, air balance	1 g	2.5	Steady state
Redox 1	48	Pure C_2H_6	2 g	2.5	1 and 3 min
Redox 2	12	Pure C_2H_6	2 g	10	1 and 3 min

for 3 min with He and later the catalyst was contacted by a stream of pure ethane. At each temperature two analyses have been performed at different times of stream (tos $= 1$ and 3 min). Sometimes, the carbon balance was not fulfilled by the gaseous products. Actually coke was formed on the catalyst. So, the carbon unbalance was attributed entirely to coke.

The activation energies were calculated taking into account the low-conversion data ($C < 10\%$), on the assumption that the conditions for a differential reactor are fulfilled.

3. Results

3.1. Spectroscopic characterization of vanadium-based catalysts

A deep characterization of vanadia-alumina catalysts has been already reported by several authors and is beyond the aim of this work. We want here to check on the effect of the heavy potassium doping on the nature of the surface vanadium oxide species (Figs. 1 and 2). The UV-Vis spectrum of vanadia-alumina (Fig. 1) presents an onset at 540 nm and an absorption increasing by decreasing wavelength down to near 300 nm where the maximum absorption occurs. Potassium doping causes a shift on the onset down to near 450 nm whereas the maximum is not shifted. According to previous studies [30], and in agreement with previous work [8,14,15] the main absorption centered in the region near 300 nm is attributed to the $O^{2-} \rightarrow V^{5+}$ charge transfer transition of isolated vanadyl species, while the tail at higher wavelengths is mainly associated to the $O^{2-} \rightarrow V^{5+}$ charge transfer transition of polymeric metavanadate species. The modification induced by K-doping, which accounts for a darker color of the undoped sample, can be attributed to a decrease of the partial polymerization degree of the surface vanadate species. The analysis of the spent catalysts shows, in the case of VA, a little shift down of the absorption edge with, however, a growth of the absorption in the visible region. This could agree with a partial reduction of vanadia centers and the appearance of absorption associated to V^{4+} d–d transitions. The spectrum of spent VKA is nearly unchanged with respect to that of fresh VKA, showing that potassium doping possibly also stabilizes V^{5+}.

The IR spectra of the fresh VA catalyst (Fig. 2) show the V=O stretching of isolated vanadyl species (1035 cm^{-1}) and its first overtone (2045 cm^{-1}). The Raman spectrum of the same catalyst after activation also shows the V=O stretching at 1030 cm^{-1}. As discussed elsewhere [31], the IR and Raman spectra are very likely more sensitive to “isolated” than to polymeric surface species. In any case, it is evident that the position of the bands of isolated vanadyls is shifted by potassium doping, down to below 980 cm^{-1} and to near 1850 cm^{-1} in the IR spectrum. The Raman spectrum of activated VKA shows two peaks at 930 and 975 cm^{-1}. The shift is due to the increase of the V=O bond order which results from the stronger equatorial $O \rightarrow V$ bond according to the increased basicity of the surface oxide ions in K-doped oxides, as previously discussed for vanadia-titania catalysts [32]. This perturbation could account for a higher stability of monomeric species with respect to the polymeric ones. In conclusions spectroscopic data suggest that VA is essentially characterized by a higher polymerization degree and a more reducibility of the V centers with respect to VKA.

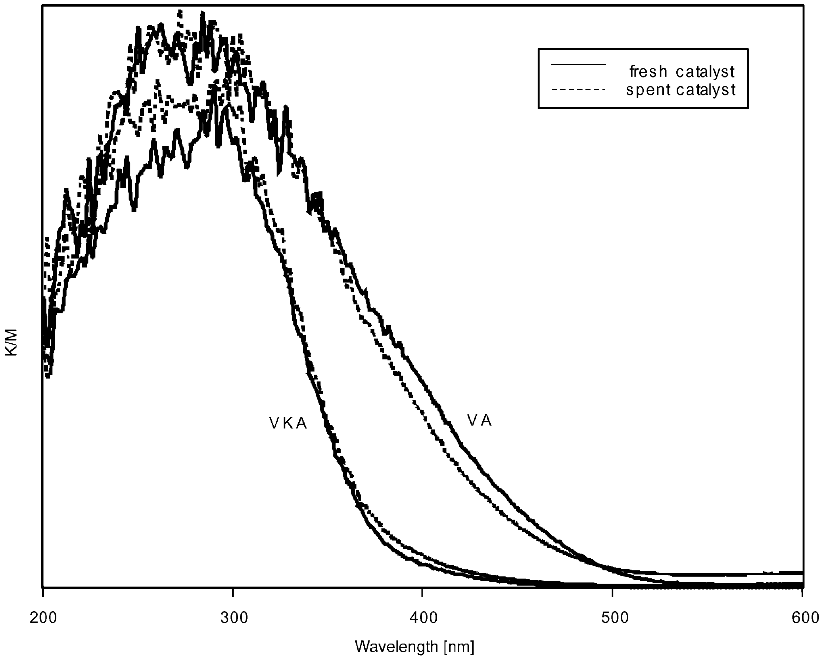

Fig. 1. UV-Vis spectra of VA and VKA catalysts fresh and spent.

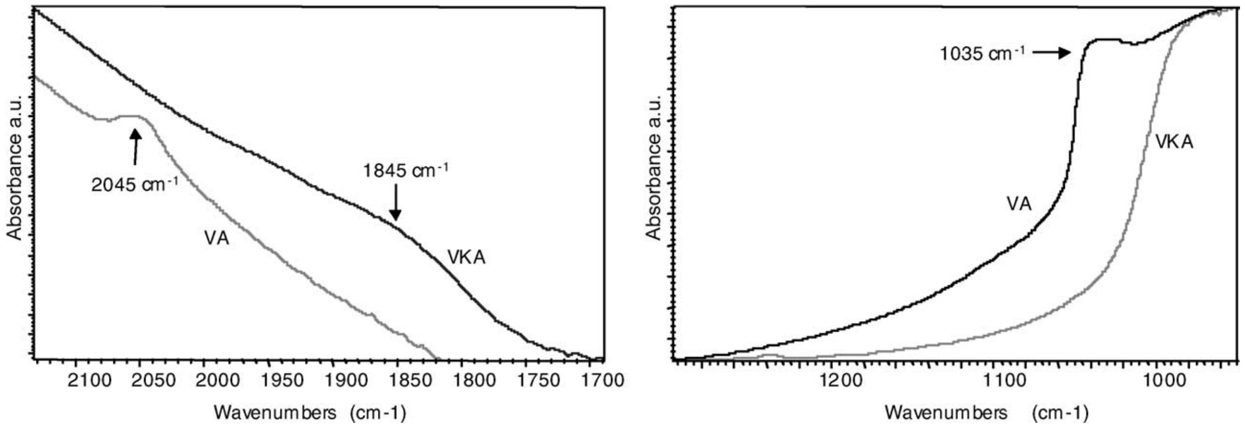

Fig. 2. IR spectra of VA and VKA catalysts. V=O stretching of isolated vanadyl species (right) and its first overtone (left).

3.2. Co-feed tests

In Fig. 3 the results of the conversion of ethane in mixture with oxygen and helium in the empty reactor are reported. The residence time is 5.4 s. We can evaluate that the residence time in this experiment is similar to the residence time of the reacting mixture in the empty volume of the catalytic reactor. The conversion of ethane is detected well above 1000 K giving rise to ethylene as the main product. The conversion of oxygen agrees with the occurrence of an oxidative dehydrogenation, as for the stoichiometry is concerned. CO is produced in increasing amounts by increasing temperature whereas CO_2 is produced in traces. Above 1000 K methane is also observed. A rough evaluation of the apparent activation energy gives more than 300 kJ/mol in agreement with what is expected for a gas-phase phenomenon. The data are consistent with those reported by Beretta and Forzatti [33] and by Mulla et al. [12] for experiments performed without catalysts at different residence times.

In Fig. 4 the behavior of VA catalyst in the conditions of experiment 1 (see Table 1) is described. In these conditions, the reaction starts at 700 K, conversion of ethane increases by increasing temperature, reaching a maximum (60%) at 900 K when oxygen is almost completely converted. Up to 900 K, in presence of oxygen, ethylene is the main product, whose selectivity decreases from 100 to 45% and remains constant at higher temperatures. In the same range of temperature selectivity to CO increases reaching a maximum 45% at 900 K; the selectivity to CO_2, does not exceed 15% at 1030 K. The apparent activation energy measured for ethane conversion here (Table 2) is 114 kJ/mol, which indicates that the kinetic regime is limited by a catalytic phenomenon. This apparent activation energy is similar to that

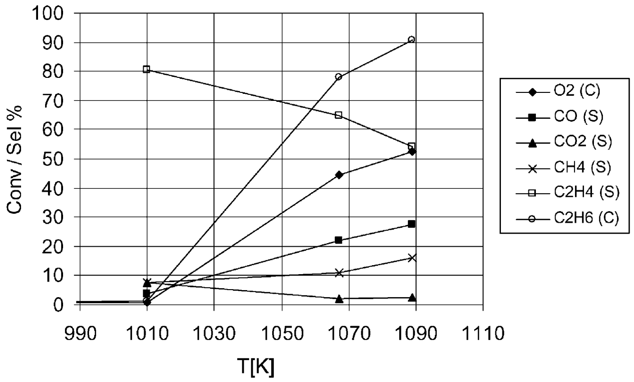

Fig. 3. Variation of the conversion (*C*) of ethane and oxygen and the selectivities (*S*) to the main reaction products in the empty reactor. Feed, 6:6:88 = C_2H_6:O_2:He; total flow, 100 ml/min.

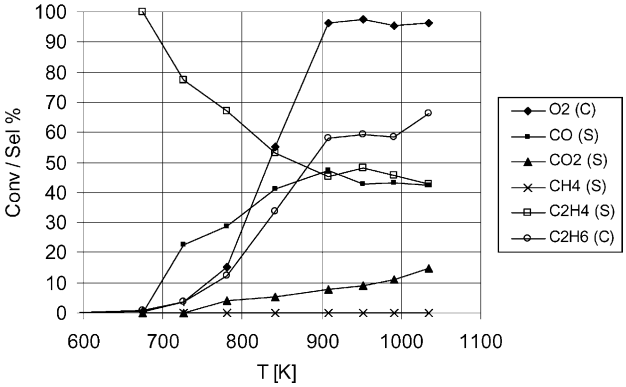

Fig. 4. Variation of the conversion (*C*) of ethane and oxygen and the selectivities (*S*) to the main reaction products on VA catalyst (0.1 g of catalyst and 0.4 g of quartz). Feed, 3:3:94 = C_2H_6:O_2:He; total flow, 300 ml/min.

Table 2
Apparent activation energies (E_{att}) and turnover frequencies (TOF) for light alkane conversion over VA and VKA

	Ethane		Propane	
	E_{att} (kJ/mol)	$TOF_{823\,K}$ (s^{-1})	E_{att} (kJ/mol)	$TOF_{823\,K}$ (s^{-1})
No catalyst	>300		293	
VA	114	0.0057	88	0.0130
VKA	151	0.00016	90	0.00025

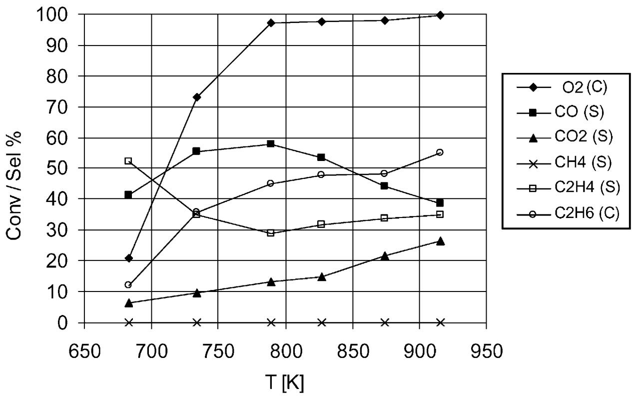

Fig. 5. Variation of the conversion (*C*) of ethane and oxygen and the selectivities (*S*) to the main reaction products on VA catalyst (0.5 g of catalyst). Feed, 6:6:88 = C_2H_6:O_2:He; total flow, 100 ml/min.

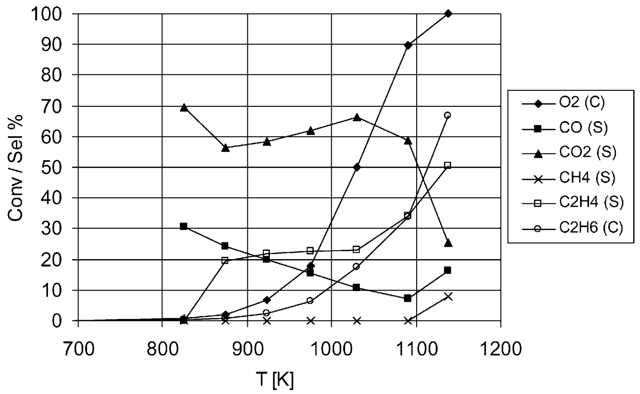

Fig. 7. Variation of the conversion (*C*) of ethane and oxygen and the selectivities (*S*) to the main reaction products on VKA catalyst (0.1 g of catalyst and 0.4 g of quartz). Feed, 3:3:94 = C_2H_6:O_2:He; total flow, 300 ml/min.

measured on similar catalysts for ethane oxidation [7,14,34]. The turnover frequencies measured compare well with those reported for similar catalysts in similar conditions [15].

In the conditions of experiment 2 (Fig. 5), the ethane conversion on VA is significant above 650 K reaching a maximum of 55% at 920 K, whereas oxygen conversion is almost total already at 800 K. On the other hand, ethylene selectivity decreases by increasing temperature at least up to temperatures near 800 K. In this range of temperatures CO is produced much more than CO_2. Above 800 K, CO_2 and ethylene selectivities grow and CO selectivity decreases. No production of methane has been observed up to 920 K.

Experiments of ethane conversion in air with $\tau = 1$ and 2.5 s have been performed to approach the conditions of a possible commercial process. The results obtained are similar, see Fig. 6 for experiment 3, $\tau = 2.5$ s. A comparison of the results showing the effect of contact time are reported in Table 2. At these quite high contact times still the ethane conversion and the selectivity to CO_2 increase with increasing contact time while selectivity to ethylene and CO decrease. We can mention here that the spent catalysts generally retain catalytic activity upon further runs if they have been used at no more than 800 K. At higher temperatures the catalyst lose activity slowly.

Comparing the results so obtained it is possible to conclude the ethane ODH to ethylene is largely predominant on VA at low contact time and low temperatures, whereas at higher contact times and temperatures the selectivity to ethylene is significantly reduced and an increasing of CO, the main product, and CO_x is observed. The data reported here for VA appear to be substantially comparable with those reported previously by several authors on vanadia-alumina catalysts and in similar conditions [7,8,14,15].

In the same conditions, experiments have been performed also over the catalyst denoted as VKA. In Fig. 7 results of the ODH of ethane over VKA catalyst at the lowest contact time (0.02 s) are reported. The curves here reported show that the reaction starts at temperature above 850 K, more than 100 K higher than the same reaction over VA. Oxygen conversion is total above 1100 K. Ethane reaches the maximum conversion (65%) above 1100 K. The main product is CO_2 having a slight increase of selectivity, from 55 to 65%

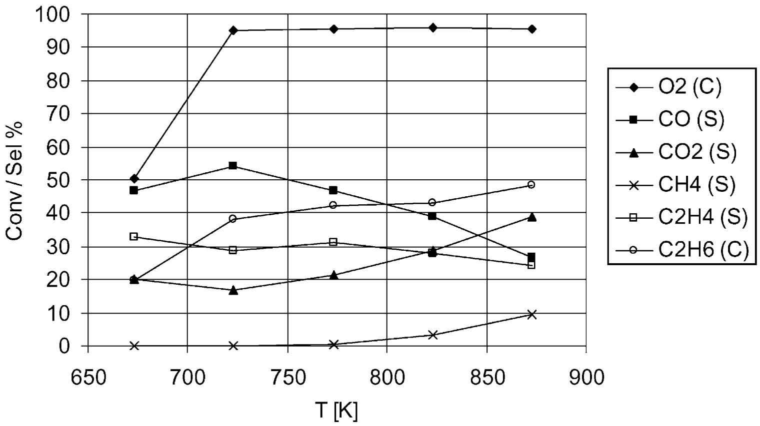

Fig. 6. Variation of the conversion (*C*) of ethane and oxygen and the selectivities (*S*) to the main reaction products on VA catalyst (1 g of catalyst). Feed, 17:17:66 = C_2H_6:O_2:N_2; total flow, 24 ml/min.

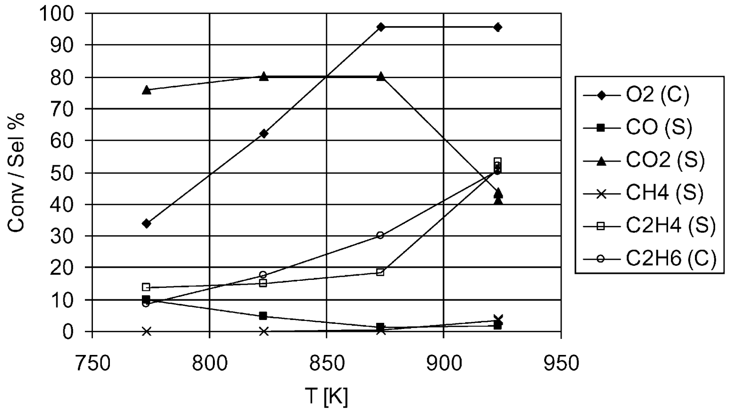

Fig. 8. Variation of the conversion (*C*) of ethane and oxygen and the selectivities (*S*) to the main reaction products on VKA catalyst (1 g of catalyst). Feed, 17:17:66 = C_2H_6:O_2:N_2; total flow, 24 ml/min.

in the range 850–1020 K, whereas in the same temperature range CO selectivity shows a slight decrease from 25 to 10%. As for ethylene selectivity, is constant at a little more than 20%. Above 1050 K reactants conversion is significantly enhanced, selectivity to CO_2 decreases drastically, because of oxygen total conversion, whereas an increase of selectivity to ethylene up to 50% is observed; above 1100 K an higher CO production and methane is detected, indication of the occurrence of gas-phase reactions.

Fig. 8 shows the trend of conversion/selectivity versus temperature curves related to the reaction over VKA catalyst at $\tau = 2.5$ s, in air. Over this catalyst, except for very high temperatures, CO_2 is always the predominant product, while selectivity to ethylene is always below 30% also at very low conversions. The apparent activation energy for ethane conversion over VKA has been calculated (taking low-conversion–low-temperature data) in these conditions to be 151 kJ/mol (Table 2), i.e. definitely higher than on VA but still typical of catalyzed phenomena.

The data reported here show again the very different behavior of VKA with respect to VA and most ODH catalysts, as already noted in the case of propane conversion [19] but also in the case of ethane [18]. On VKA in fact the selectivity to ethylene tends to increase with temperature or be nearly constant and CO_2 is produced as the predominant product also at very low conversions. This is more evidenced in Table 3 where data taken in air show that CO_2 is certainly a secondary product on VA while it could be a primary product over VKA. In fact by increasing contact time at constant reactant partial pressure and temperature CO_2 selectivity increases on VA while it is quite constant on VKA.

The data recorded at very high temperature for VKA, to push conversion, show that a bad catalyst can only apparently become a very selective one at very high temperature. In such conditions in fact the gas-phase reaction also starts and, as shown in Fig. 3, gas-phase reaction is highly selective to ethylene.

3.3. Redox tests

VA and VKA catalysts have been tested also in redox conditions. As for VA catalyst, in Fig. 9a results of experiment at $\tau = 2.5$ s and times on stream (tos) of 1 min are shown. A decrease of selectivity to ethylene related to an increase of the selectivity to methane (which is produced in much larger amounts than for co-feed experiments) and to an increase of coke, coating the catalyst surface. CO selectivity shows a 20% maximum at 923 K, whereas very low CO_2 concentrations (less than 10%) have been detected. Fig. 9b shows the trend of the ethylene yields (at $\tau = 2.5$ s) at different temperatures and 1 and 3 min times of stream. Ethane conversion increases by increasing temperature, as expected, and by decreasing of time of stream. Selectivity to ethylene increases by increasing tos. However, after 3 min only slight deactivation and increase in selectivities are observed.

Experiments have also been performed at $\tau = 10$ s (Fig. 10a). Conversion of ethane is definitely higher, while ethylene selectivity is definitely smaller. Additionally, in

Table 3
Effect of contact time on ethane conversion and product selectivities

Catalyst	*T* (K)	τ (s)	*C* ethane (%)	*C* oxygen (%)	*S* ethylene (%)	*S* CO (%)	*S* CO_2 (%)
VA	720	1.0	29	66	35	50	15
	720	2.5	39	94	28	54	18
VKA	770	1.0	4	15	12	10	78
	770	2.5	9	32	13	10	78

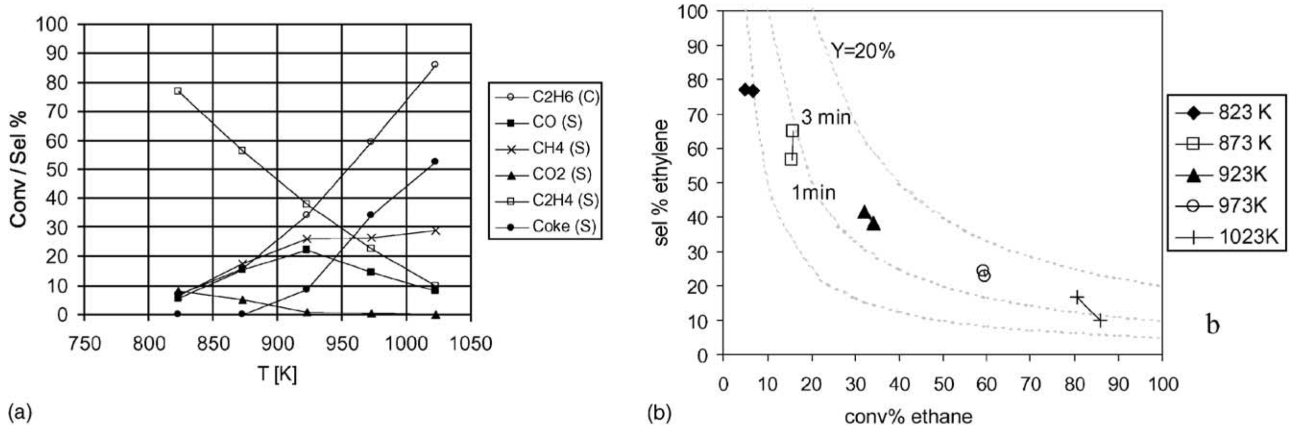

Fig. 9. Redox test over VA catalyst (2 g of catalyst, $\tau = 2.5$ s): (a) conversion/selectivity (%) vs. temperature curves, tos = 1 min; (b) ethylene selectivity (%) vs. ethane conversion (%).

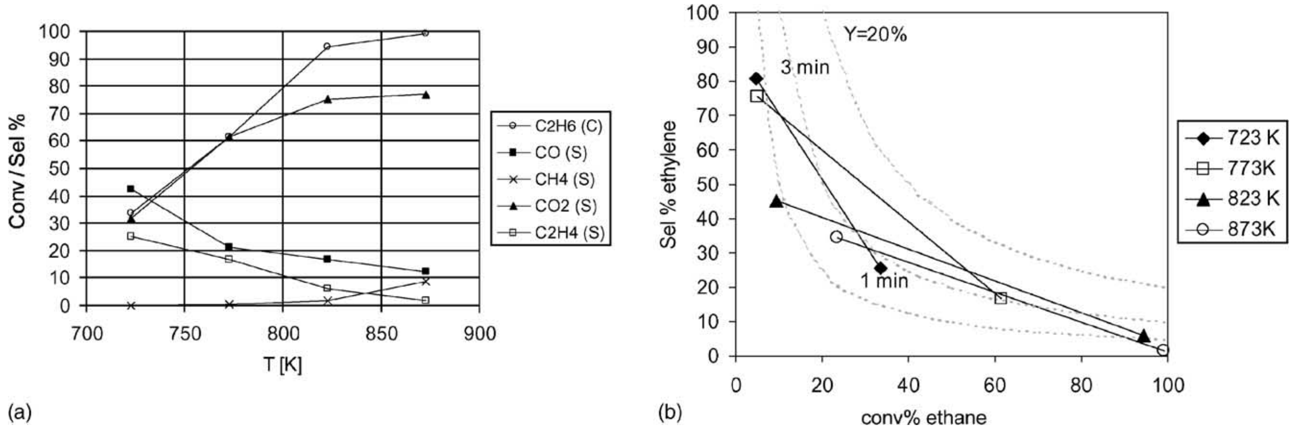

Fig. 10. Redox test over VA catalyst (2 g of catalyst, $\tau = 10$ s): (a) conversion/selectivity (%) vs. temperature curves, tos = 1 min; (b) ethylene selectivity (%) vs. ethane conversion (%).

these conditions the effect of tos is much stronger, with a fast deactivation. On the other hand, the ethylene yield is always below 15% here while with shorter τ the yields are between 15 and 20% at 900–1000 K.

The same experiments have been done with VKA. It is evident that, also in redox conditions, VKA is less active than VA (compare Fig. 11a with Fig. 9a, and Fig. 12a with Fig. 10a). However, the selectivities obtained at $\tau = 2.5$ s

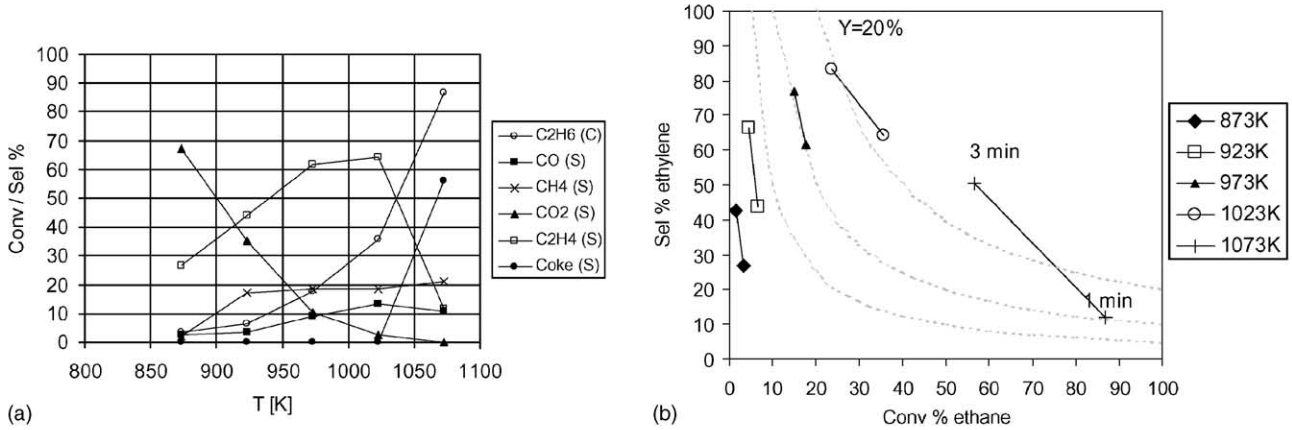

Fig. 11. Redox test over VKA catalyst (2 g of catalyst, $\tau = 2.5$ s): (a) conversion/selectivity (%) vs. temperature curves, tos = 1 min; (b) ethylene selectivity (%) vs. ethane conversion (%).

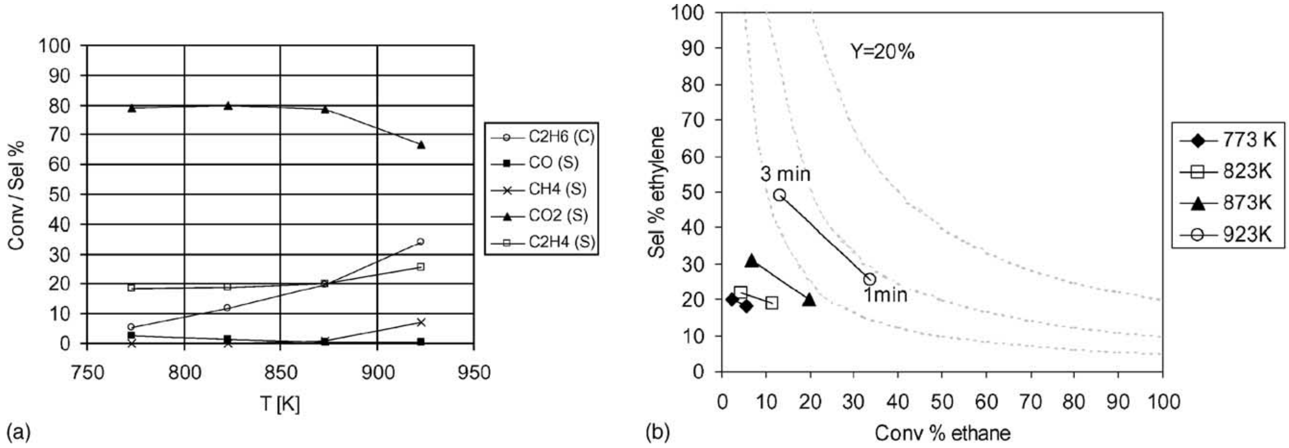

Fig. 12. Redox test over VKA catalyst (2 g of catalyst, $\tau = 10$ s): (a) conversion/selectivity (%) vs. temperature curves, tos = 1 min; (b) ethylene selectivity (%) vs. ethane conversion (%).

are remarkable and give yields exceeding 20%. Again, however, this occurs at very high temperatures when gas-phase phenomena likely are also involved.

4. Conclusions

The data reported here confirm that the undoped VA catalyst is more active than the heavily K-doped VKA catalyst, as previously observed for propane [19] as well as for ethane [18] conversion. The activation energies measured for the ethane conversion agree with those reported in the literature for similar catalysts [7,14] and also the turnover frequencies roughly agree with those reported by Bañares et al. [15] (Table 3). The comparison with our previous data show that ethane activation is harder than propane activation and that VA is more active than VKA. This higher activity can be due to the lowered polymerization degree of surface vanadyl species and to the strongly perturbed nature of the isolated species evidenced by UV-Vis and IR spectroscopies. Although this contradicts the data of Argyle et al. [14], who obtained similar activation energies for ethane and propane conversion, the lower apparent activation energies we found for propane conversion with respect to those for ethane conversion are in line with the bond energies of the weakest C–H bonds in the molecules, where carbon is secondary for propane and primary for ethane.

Also in the case of ethane conversion, like for propane conversion, the different olefin/CO$_x$ selectivity pattern observed in the two catalysts strongly suggests a quite different reaction path. A direct way burning the alkane to CO$_2$ without passing through the olefin must occur on VKA, accounting for the unusual increasing selectivity to ethylene with temperature over this catalyst.

In Fig. 13 a comparison of co-feed and redox experiments is given, in terms of yields in ethylene. The comparison is made with the same contact time (2.5 s), although this comparison must be taken with care because for co-feed experiments much lower ethane partial pressure is used. As for redox experiments, the results taken after tos = 3 min is used. We can likely suppose that two regimes exist, as determined for propane conversion over the same catalysts [19]. Below a temperature (870 K for co-feed experiments, 1000 K for redox experiments) true catalysis (or surface reactions) occur while above these temperatures gas-phase reactions likely predominate. It is evident that selectivity to ethylene is better at higher temperatures in the region where gas-phase phenomena occur, both for co-feed and redox experiments. Similar yields are obtained in the “catalytic region” in both experiments (note that the time on stream in the range 1–3 min has not much effect on yields in the case of redox experiments) but at definitely lower temperatures for co-feed than for redox experiments for both catalysts, in spite of the definitely higher ethane partial pressure (1 atm) used in the redox experiments.

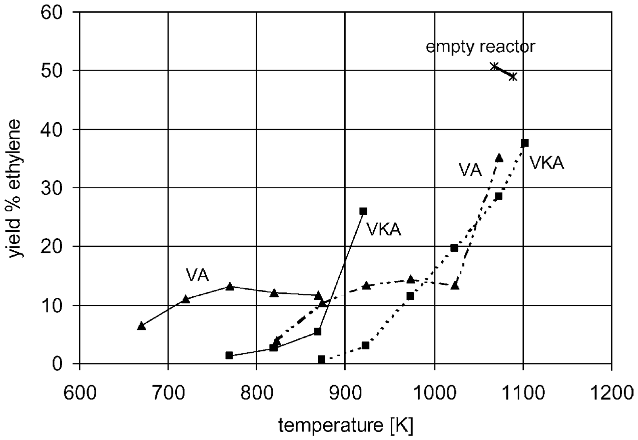

Fig. 13. Yield (%) to ethylene vs. temperature over VA and VKA catalysts ($\tau = 2.5$ s) in co-feed (full lines; feed, 17:17:66 = C_2H_6:O_2:N_2; total flow, 24 ml/min) and redox (broken lines; feed, pure ethane; tos = 3 min) conditions and in the empty reactor (feed, 6:6:88 = C_2H_6:O_2:He; total flow, 100 ml/min).

Due to the higher ethane flow used in the redox experiment, however, similar yields in ethylene correspond to much higher productivities in the redox experiments. The ethylene amount per gram of catalyst (productivity) produced on VA in the experiments in the range 800–900 K is definitely higher for redox (2.4 ml/(min g catalyst) at 873 K at $\tau = 2.5$ s) than for co-feed experiments (0.49 ml/(min g catalyst) at 873 K at $\tau = 2.5$ s). The productivities obtained in redox conditions can be also higher than those obtained on metal catalysts at "short contact times" but using diluted feeds [27].

The redox technique, although does not allow to increase ethylene yields, allows to avoid explosion problems (ethane and air are not mixed), to work with undiluted flows and to obtain high productivities.

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