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A study of the reaction pathway upon propane oxidation over V–K/Al_2O_3 catalysts

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Abstract

The conversion of propane in the presence of oxygen on V–K/Al_2O_3 catalysts with different surface area and in different feed conditions has been investigated. The activation energy measured at low conversion is 21 kcal/mol (88 kJ/mol) and the reaction order of propane is 1. In order to propose a reaction pathway, complementary experiments have been performed with a K-free V/Al_2O_3 catalyst, and propene and 2-propanol oxidation tests have also been done. A reaction scheme for the propane oxidation process is proposed. Two different reaction regimes have been observed. Below 950 K true catalytic reaction occurs with propene, ethene, CO_2 and CO as the only detectable products. Both CO_x and ethene productions likely occur through a parallel-successive reaction scheme with respect to propene production. The key surface intermediate is thought to be the *sec*-propoxide species, that can give propene by elimination and either CO_x or ethene by oxidation. Above near 950 K a new regime involving gas-phase species is observed. In this range, where consumption of oxygen is already total or nearly total, the cracking of propane to ethene+methane becomes predominant. This reaction can be limited by filling the empty space of the reactor.

Keywords: Propane; Catalyst; Oxidation; Oxidative dehydrogenation; Propene; Vanadium oxide catalysts

1. Introduction

Propene is mostly produced industrially together with ethene and other light olefins by steam cracking of naphtha and/or of ethane [1,2]. The catalytic dehydrogenation of propane [3] is an alternative way to produce propene. Both processes are endothermic (with a consequent consumption of fuel to provide the needed reaction heat) and limited by thermodynamics. In recent years the demand of propene is growing faster than that of ethene, especially in USA [4]. For this reason alternative ways to produce propene or propene-rich mixture can be useful.

The oxidative dehydrogenation of propane, which has been the object of extensive investigation in recent years [5,6], represents another possible way to fulfil the propene demand. This reaction has no thermodynamic limitations and is exothermic. Promising results have been obtained using vanadia-based catalysts such as Mg vanadates [7–9] and supported and alkali doped vanadia [10–12]. However, still the performances are not sufficiently good to allow industrial exploitation. Actually, the best catalysts for oxidative dehydrogenation lack catalytic activity at low temperature, while at high temperature selectivity to propene is not sufficiently high. Main byproducts are reported to be CO and CO_2. It has been shown that reactions occurring in the gas-phase affect the catalytic performances [8,13,14]. New reactor design for this reaction could be useful [15].

An alternative approach is to convert propane with oxygen at very low contact times over metal-based catalysts. In this case ethene–propene mixtures are produced with olefin selectivities above 55% at total reactants conversion [16,17]. A coupling of the exothermic oxidative conversion of propane with its endothermic thermal cracking has been reported recently to occur on supported Sr–La oxides to give propene–ethene mixtures [18].

In this paper we report our results concerning propane oxidative conversion over V–K/Al_2O_3 catalysts. Catalytic materials with this composition have been reported to be among the best known today [11,19]. The aim of this work is to have a better knowledge of the byproducts pattern and of the reaction pathway in propane oxidative dehydrogenation. In order to have these data on the reaction intermediates, our experiments have been performed at quite low

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contact times with respect to most of the data reported in the literature.

2. Experimental section

Most of the experiments have been performed with a catalyst (hereinafter denoted as catalyst A) with the composition V_2O_5:K_2O:Al_2O_3 12:6:82 (w/w), prepared using 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%). Note that the potassium content used here is higher than usual. As for comparison other two catalysts have be prepared with the same V/K atomic ratio (2/1) and the same surface concentration of both elements (45.34 $Å^2$ per V atom, corresponding to 2.2 atoms/nm^2) but different surface areas. The coverage of the support by vanadium oxide can be evaluated to be near 40% of the theoretical monolayer coverage, that means that, including potassium the overall support surface coverage is near 60%. The catalysts have been prepared with one very high surface area support (γ-Al_2O_3 from Süd Chemie, 260 m^2/g), resulting in the composition V_2O_5:K_2O:Al_2O_3 17.3:8.7:74 (w/w, catalyst B), and another low surface area support (γ-Al_2O_3 containing 2% SiO_2 from Siralox, 38 m^2/g) resulting in the composition V_2O_5:K_2O:Al_2O_3 2.5:1.3:96.2 (w/w, catalyst C). The catalysts were prepared by sequential impregnation of the alumina supports with NH_4VO_3 water solution first and with KNO_3 water solution later. After impregnations the catalysts have been dried at 400 K and calcined at 773 K for 7 h. A K-free catalyst, corresponding to catalyst A, with composition V_2O_5:Al_2O_3 14:86 (w/w, denoted as catalyst D) has also been tested. The surface areas of the catalysts resulted to be less than 10% lower than those of the corresponding supports.

The catalytic tests were carried out at atmospheric pressure in a continuous fixed bed flow tubular quartz reactor (Ø 6.5 mm). 0.1 g of catalysts and 0.4 g of quartz (previously gently mixed mechanically) were loaded in form of fine powder (60–70 mesh) whose total volume was 0.477 cm^3. Blank experiment has been performed after loading the reactor with 0.5 g of quartz powder only. The normal feed composition was 3% of hydrocarbon, 3% of oxygen and 94% of helium. The total gas flow was 300 and 100 ml/min. 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 there were a nickel catalyst tube (HP) to reduce CO–CH_4. 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 propane itself, propene, ethene, ethane, 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:

$$S_A = \frac{nN_A^f}{3(N_P^0 - N_P^f)} \times 100$$

where N_A^f is the number of moles of the A product, n the number of carbon atoms in A and $N_P^0 - N_P^f$ the number of moles of propane 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:

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

3. Results and discussion

The data concerning the experiments of propane conversion in the reactor filled with 0.5 g quartz powder (i.e. empty from the catalyst) are reported in Fig. 1a. This experiment is performed with the feed flow condition of most of the catalytic experiments described below. In these conditions the residence time can be calculated to be, in the empty reactor volume, $\tau_R \sim 1.7$ s. No reaction is observed until above 950 K. The first products observed in these conditions are CO_2 and propene but, when propane conversion is above 10% ethene and methane are the main products and CO_2 production falls to zero and CO is produced. The consumption of oxygen indicates that propene is produced by oxidative dehydrogenation. The amount of ethene and methane produced on molar bases (remember that selectivity is calculated on the basis of carbon grammoatoms) is similar although a little more ethene is produced than methane. In Fig. 1b the result of a similar experiment performed with more critical conditions, by using a larger reactor, i.e. with residence time $\tau_R \sim 4.8$ s are reported. Here conversion starts well before, as expected, i.e. near 700 K, with propene as the largely predominant product. Oxygen conversion is total near 923 K and suggests that, at lower temperatures, oxidative dehydrogenation occurs. However, when conversion of oxygen is high (above 60% at 860 K) again ethene + methane are important products with a little excess of ethene with respect to the 1:1 molar ratio. These data suggest that the main thermal reactions observed in conditions similar to those of the below catalytic experiments, are the oxidative dehydrogenation of propane to propene and water and the cracking to ethene + methane. Perhaps a further way to ethene is also active. This reactivity starts above 700–900 K, depending on the residence time. These

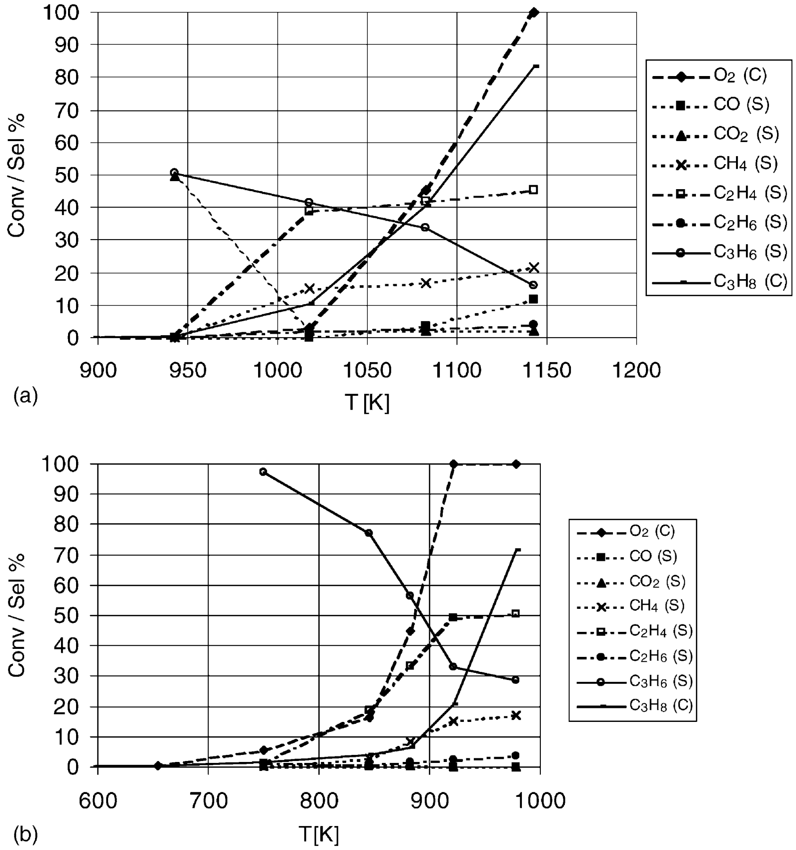


Fig. 1. (a) Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on quartz (0.5 g). Feed, 3:3:94 = C_3H_8:O_2:He; total flow, 300 ml/min; $\tau_R \sim 1.7$ s. (b) Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on quartz (0.5 g). Feed, 3:3:94 = C_3H_8:O_2:He; total flow, 300 ml/min; $\tau_R \sim 4.8$ s.

data roughly agree with those reported by Beretta et al. [17] for an empty reactor.

An estimation of the activation energy of propane conversion has been done by using the low conversion points: the value measured is near 70 kcal/mol (292.6 kJ/mol) which is a typical value for gas-phase radical reaction [8]. In the very early steps of the reaction the production of CO_2 suggests a role of the quartz particles as catalysts. On the contrary, the value for the activation energy measured for the range 1000–1050 K suggests that the reaction is, in these conditions, not diffusion limited and essentially occurring in the gas-phase.

The behavior of catalyst A is described in Fig. 2 (τ = 0.02 s). Note that in this experiments the reactor, the feed and

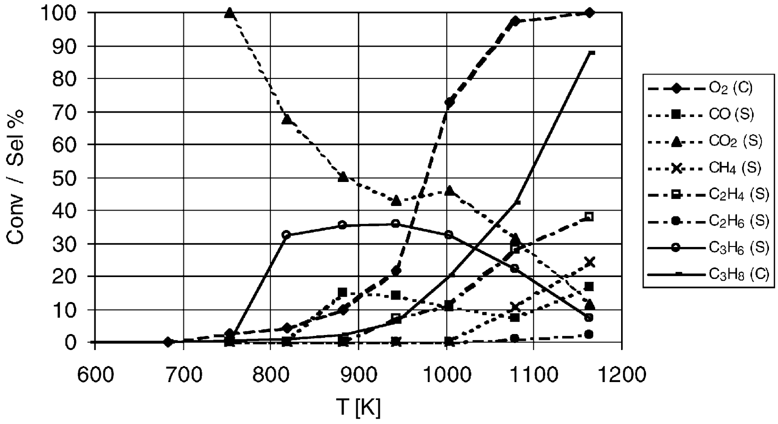


Fig. 2. Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Feed, 3:3:94 = C_3H_8:O_2:He; total flow, 300 ml/min.

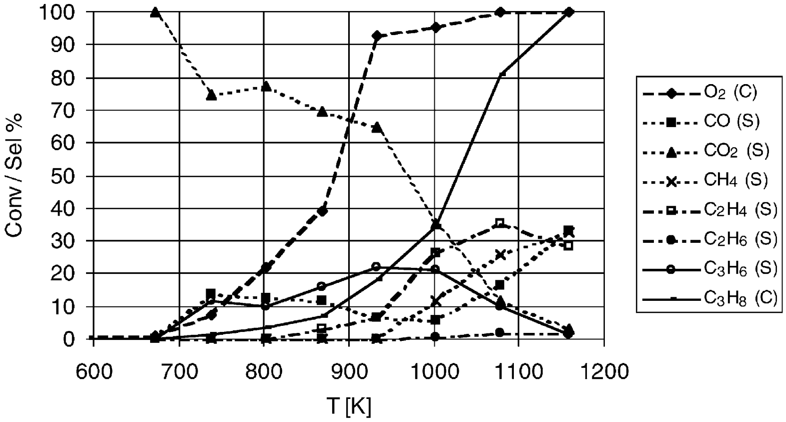


Fig. 3. Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Feed, 3:3:94 = C_3H_8:O_2:He; total flow, 100 ml/min.

the empty reactor volume are the same as for Fig. 1a. The reaction starts definitely earlier in this case, i.e. near 800 K, so providing evidence for catalyst activity. The main product at the lowest temperature is CO_2, whose selectivity declines in favor of propene by increasing temperature. This result seems to contradict most of literature data, that showed that (over different catalysts) CO_2 is a final product. We have carefully confirmed this. We will discuss further this below. Propene is produced with selectivities ranging between 32 and 36% in the range 820–1000 K, when propane conversion progressively grows up to near 20%. In this range CO_2 (selectivity $> 40\%$) and CO (selectivity near 15%) are the only significant byproducts. Starting from 950 K the selectivity to propene decreases while ethene is also produced with selectivity up to 35%. Starting from above 1000 K, methane is produced in increasing amounts and becomes (on molar bases) the predominant product at 1150 K. These data suggest that at least three different reactions occur in the region below 950 K, i.e. the combustion to CO_x, the oxydehydrogenation to propene and an oxidative conversion to ethene. Above 950 K the cracking to methane + ethene becomes predominant although the more reactive product, ethene, burns in part, in contrast to methane which is recovered as a product. This explains why more methane than ethene is obtained. The coincidence of the temperature range at which the production of methane occurs in the reactor without the catalyst and with the catalyst (with the same flow and empty volume conditions) suggests that cracking to ethene + methane is essentially a gas-phase reaction.

By using the points at low conversion reported in Fig. 2, it is possible to calculate the activation energy for propane conversion over this catalyst. The value measured is 21 ± 1 kcal/mol (88 ± 4 kJ/mol). This value shows that our experiments are performed in conditions where the reaction rate is controlled by a chemical phenomenon. In other words, diffusion limitations and gas-phase phenomena should not be relevant at least at low temperature in the conditions of Fig. 2. The measured activation energy is also in the range typical of propane selective and non-selective oxidation over different catalysts [20–24].

Incidentally, we remark here that the catalytic activity of the materials studied here appears to be essentially stable only if they are used at temperatures not above near 900 K. When used above this temperature they lose activity if they are later tested in a successive run, even after previous reoxidation. So, we have to mention that a modification of the catalysts occur associated to surface area loss at or above this temperature limit.

To have more information on the reaction path we performed experiments with the same catalyst A but with tripled contact time (Fig. 3, $\tau = 0.06$ s). As expected the propane and oxygen conversion increases with increasing contact times. Below 950 K the conversion of propane is proportional to the contact time, while above this temperature the increase of conversion is lower than the increase of contact time. Note however that in these conditions also the residence time in the empty space of the reactor is nearly tripled, i.e. it is a little higher than that of the experiment described in Fig. 1b. Actually, the conversion of oxygen and propane are in these two experiments very similar being perhaps even higher without than with the catalyst. However, the product selectivities are very different here. In particular, at very low propane conversion, combustion predominates in the presence of the catalyst, while oxydehydrogenation prevails in the empty reaction. The catalyst is evidently not “selective” for oxydehydrogenation in these conditions. At higher conversions however while in the gas-phase cracking predominates, combustion and oxydehydrogenation are both relevant in the presence of the catalyst.

The very different product distributions further suggests that below 950 K true catalytic reactions occur. Above this temperature, where gas-phase phenomena could become relevant, oxygen is also totally converted and this also certainly affects the conversion. The increase of contact time causes, in the “catalytic” range, a definite increase of the production of CO_2 and a decrease in the production of propene, while CO production is nearly constant. Ethene starts to be detected already at 870 K while the production of methane still occurs only above 950 K (i.e. in the range where non-catalytic phenomena certainly predominate). This is likely due to the higher residence time obtained also in the empty space of the reactor, according to the lower reactants flow. The increase in the CO production with the corresponding decrease in propene production suggests that most of CO is formed by burning of propene. This process, successive to oxidative dehydrogenation, is obviously favored at higher contact times. We also remark that at these higher contact times the activation energy measured for propane conversion (16 kcal/mol, 67 kJ/mol) is a little lower than that observed at lower contact times. This suggests that diffusion limitations could become to have effect in these conditions, but also demonstrates that gas-phase phenomena do not predominate in the range below 950 K even at these low flow experiments.

The comparison of the results reported in Figs. 2 and 3 show that, at the same propane conversion degree (in the range 1–15%) the CO_2 selectivity increases with increasing contact time, while propene selectivity decreases by increasing contact time. Also ethene selectivity increases a little bit by increasing contact time while the behavior of CO is not clear. This also occurs at the same reaction temperature (but different conversion). This suggests that actually part of the propene product is allowed to burn by increasing contact time if oxygen is available.

If both propane concentration and catalyst amount are tripled with respect to the experiment of Fig. 2 (Fig. 4) oxygen is definitely in high defect, and is totally consumed already near 870 K. Methane production starts at 870 K. At 940 K methane and ethene are produced nearly 1:1 on molar bases but methane selectivity grows later while ethene selectivity drops, likely due to its burning. This shows that the production of methane, which can be taken as indicative of the starting of gas-phase cracking, actually becomes relevant when oxygen is fully consumed. This reaction is consequently competitive with oxidation reactions and slower at least below 950 K. On the other hand a way to ethene different from cracking could exist before total oxygen consumption is reached.

Experiments with higher oxygen concentrations have also been performed, as shown in Fig. 5. The effect of increasing oxygen pressure on CO_2, CO and propene production is slight, while ethene production is enhanced. On the other hand the temperature for methane production is shifted up in agreement with the shift up of the temperature for total oxygen consumption. In the temperature range 950–1020 K the total selectivity to olefins (propene + ethene) is near 40% without any production of methane. In this range propane conversion grows from 10 to 50%.

To define whether ethene (which can be in principle an interesting byproduct) is a parallel or a successive product with respect to propene, we have also investigated the oxidation of propene, whose results are reported in Fig. 6. It is evident that the main reaction of propene is its combustion to CO_2 and CO. However, small amounts of ethene are also produced from propene oxidation, although less than from propane oxidation in the same conditions. This suggests that a way from propene to ethene should exist but that the main way to ethene from propane does not involve propene as an intermediate. Also methane is not produced from propene, as expected. The activation energy measured for propene conversion is 26 kcal/mol which is in the typical range for propene oxidation over oxide catalysts [24,25].

As already noted, our experiments (Figs. 2–5) show that CO_2 is the main product of propane oxidation at low temperature. This suggests that a direct way from propane to CO_2 could exist (without propene as an intermediate). This substantially agrees with what has been reported by Khodakov et al. [26,27] and Chen et al. [28] over different oxide supported vanadia catalysts. However, high selectivities to CO_2 appear at very low propane conversion, i.e. when the number of moles produced is very low and error in their

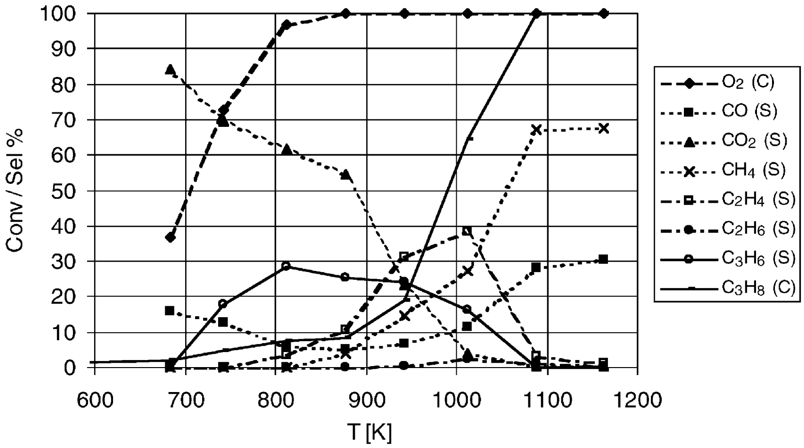


Fig. 4. Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.3 g of catalyst and 0.2 g of quartz), surface area 180 m^2/g. Feed, 9:3:88 = C_3H_8:O_2:He; total flow, 100 ml/min.

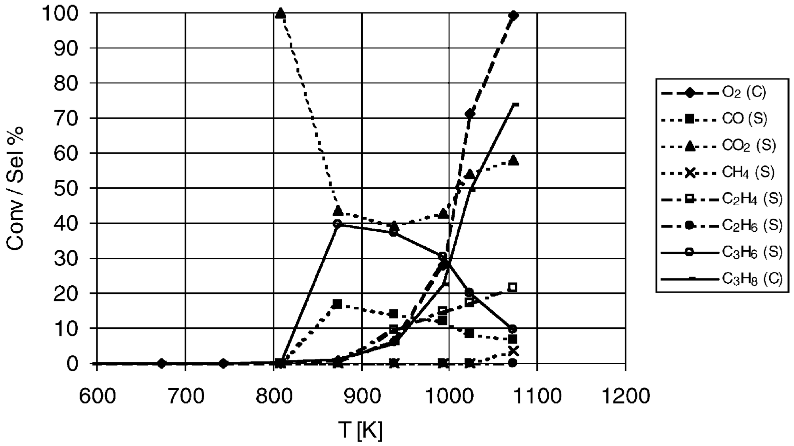


Fig. 5. Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Feed, 3:9:88 = C_3H_8:O_2:He; total flow, 300 ml/min.

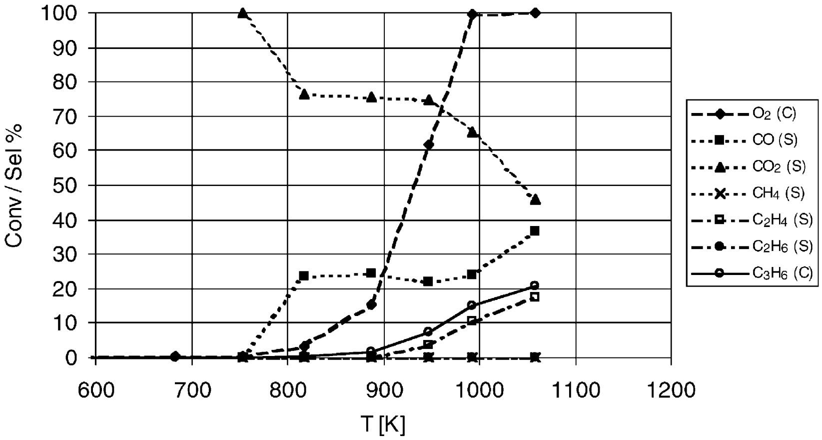


Fig. 6. Variation of the conversion (*C*) of propene and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Feed, 3:3:94 = C_3H_6:O_2:He; total flow, 300 ml/min.

measure can be high. In other words, this could be an artifact. To have a confirmation of this, we investigated in the same conditions also a K-free catalyst. The results of propane oxidation experiments in the same conditions with K-free and K-containing catalysts are compared in Table 1. The data show that the additional of potassium hinders propane conversion and favors the formation of CO_2 at low conversion. Actually we have determined that the relatively high amount of K in our catalyst is associated to high CO_2 selectivity at low temperature.

Table 1
Comparison of propane conversion (*C*) and product selectivities (*S*) on V/Al and V–K/Al catalysts

Catalyst V/Al				Catalyst V–K/Al			
T (K)	Propane (*C*)	C_3H_6 (*S*)	CO_2 (*S*)	*T* (K)	Propane (*C*)	C_3H_6 (*S*)	CO_2 (*S*)
$\tau = 0.33$ s; propane:oxygen = 1:1							
624	0.5	100	0	624	0.3	0	100
674	2.1	72.6	9.1	673	0.7	32.3	67.7
727	6.3	55.2	13.7	723	2.1	35.1	50.2
777	17.5	34.1	18.3	774	6.0	35.7	43.2
$\tau = 0.167$ s; propane:oxygen = 1:5							
625	0.3	100	0	624	0		
675	2.3	53.1	28.8	674	0.6	0	100
718	6.4	55.1	19.4	722	5.3	48.5	27.7

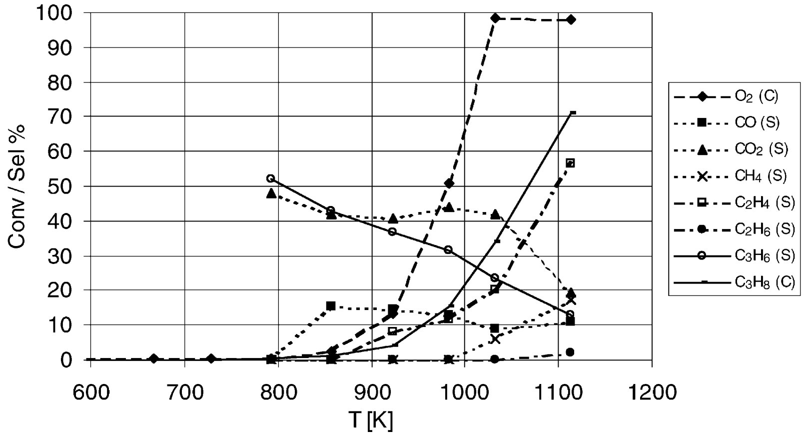


Fig. 7. Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Reactor filled with quartz wool. Feed, 3:3:94 = C_3H_8:O_2:He; total flow, 300 ml/min.

To confirm that the production of methane mainly involves gas-phase cracking we performed an experiment in the same conditions as those of Fig. 2 but with the empty reactor section filled with quartz (Fig. 7). Below 950 K the data of Fig. 2 are perfectly reproduced (except the first point) but above 950 K the conversion of both reactants is lower and the production of methane is definitely lower when the reactor is partly filled. This confirms that the empty reactor space takes a role in the reactants conversion above 950 K and that methane is produced by gas-phase cracking giving rise to ethene too. Part of ethene burns to CO under these conditions, so that the ethene to methane molar ratio is lower than 1.

To have further data on the role of the catalyst surface area, we have repeated the experiment of Fig. 2 with the same amounts of catalyst but with catalysts B (Fig. 8) and C (Fig. 9). This is equivalent to change the surface area of the catalyst without changing its weight. Actually the higher is the surface area the higher is the propane conversion. However, the conversion is not proportional to the surface area. The measured activation energy over catalyst B is lower than that catalyst A (16 kcal/mol, 67 kJ/mol). This suggests that, due to the higher catalyst area available, diffusional effects are no more negligible. More combustion (in particular more CO at low temperature) is found, and lower selectivity to propene. These effects agree with the higher surface area of the catalyst and with the consequent longer contact of the reactants with the catalyst surface. On the contrary, the selectivity to ethene in the "catalytic range" apparently grows significantly and is higher than selectivity to propene above 980 K. Total selectivities to olefins of near 40% without methane production are obtained but at near 10% conversion only. Cracking to methane is enhanced but again is observed only above 950 K.

With the low surface area catalyst C the measured activation energy for propane conversion is similar as for catalyst

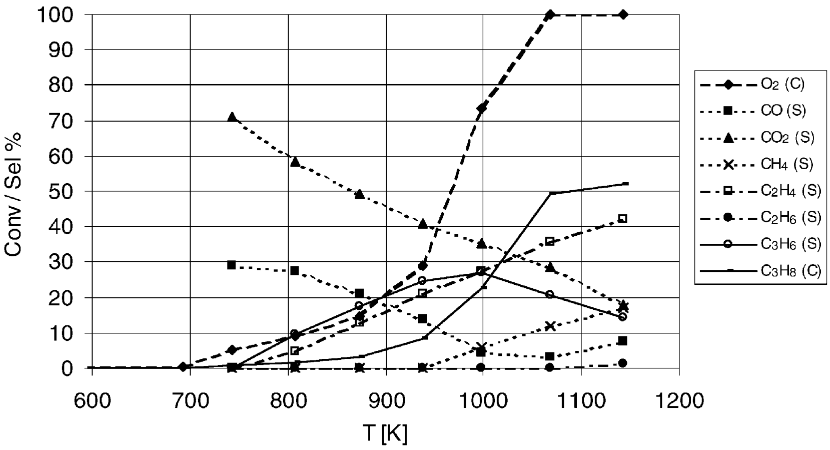


Fig. 8. Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (17.3 wt.%) and K_2O (8.7 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 260 m^2/g. Feed, 3:3:94 = C_3H_8:O_2:He; total flow, 300 ml/min.

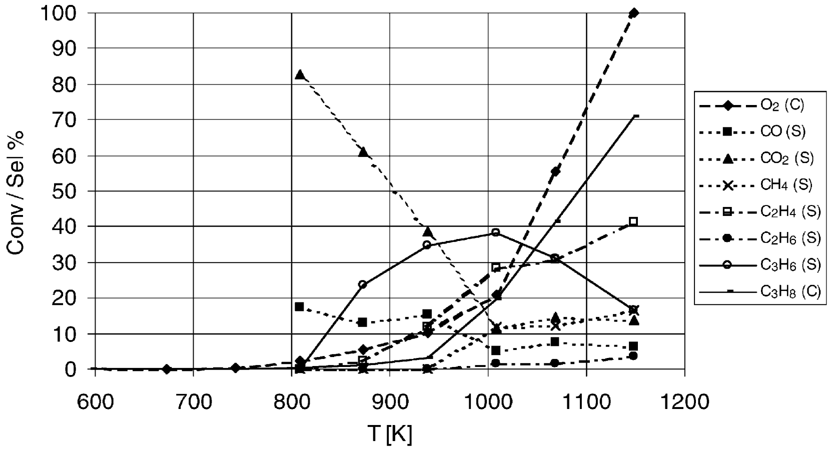


Fig. 9. Variation of the conversion (*C*) of propane and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (2.5 wt.%) and K_2O (1.3 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 38 m^2/g. Feed, 3:3:94 = C_3H_8:O_2:He; total flow, 300 ml/min.

A (22 kcal/mol, 92 kJ/mol). Change in product selectivities is also not very evident.

In previous studies we proposed that surface 2-propoxy-groups could be intermediates in propane total oxidation and oxydehydrogenation over metal oxide catalysts [29,30]. To check this hypothesis we studied the adsorption and the conversion of 2-propanol over the catalyst A in conditions similar to those used for propane conversion (Fig. 10).

2-Propanol conversion starts at much lower temperature (450 K) than propane and propene conversion, as expected indeed. Acetone is the largely predominant product up to very high conversions of 2-propanol. Propene is produced in minor amounts (10% selectivity or less). Above 550 K the selectivity to acetone decreases down to 80% and CO_2 is formed by its combustion (near 10% selectivity). Above 600 K oxygen (which is in stoichiometric slight excess with respect to 2-propanol oxydehydrogenation, but obviously in large defect with respect to its combustion) is totally consumed in this experiments due to the partial overoxidation of acetone.

To investigate the possible further evolution of acetone, we also performed an experiment of oxidation of 2-propanol over VKA in presence of excess oxygen (Fig. 11). We find now that above 550 K due to the large availability of oxygen, acetone burns more and more and CO_2 production grows correspondingly. Under these conditions propene is still observed and its selectivity is quite constant near 10%. This shows that the oxidation of 2-propanol through acetone is definitely faster than that of propene over A catalyst when oxygen is available above 550 K. These results again agree with those concerning propene oxidation over A. In fact propene in the presence of oxygen is not converted over A until 800 K (see Fig. 6).

The same 2-propanol conversion experiment carried out over catalyst D, which has the same composition in terms

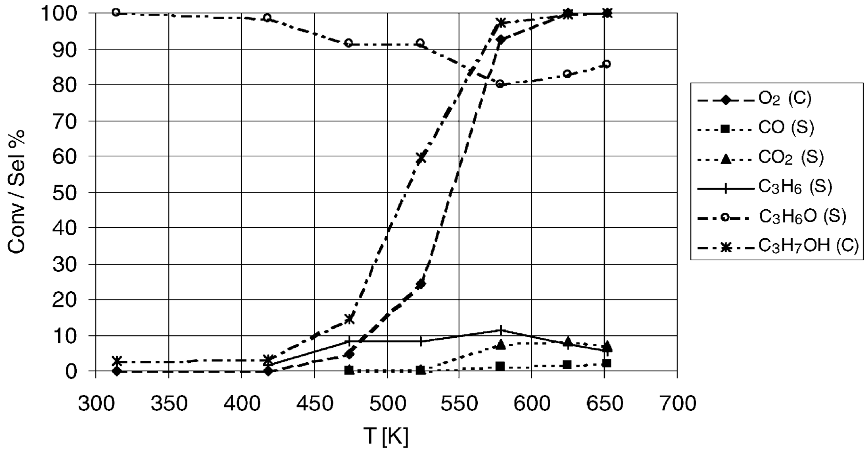


Fig. 10. Variation of the conversion (*C*) of 2-propanol and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Feed, 3:3:94 = C_3H_7OH:O_2:He; total flow, 300 ml/min.

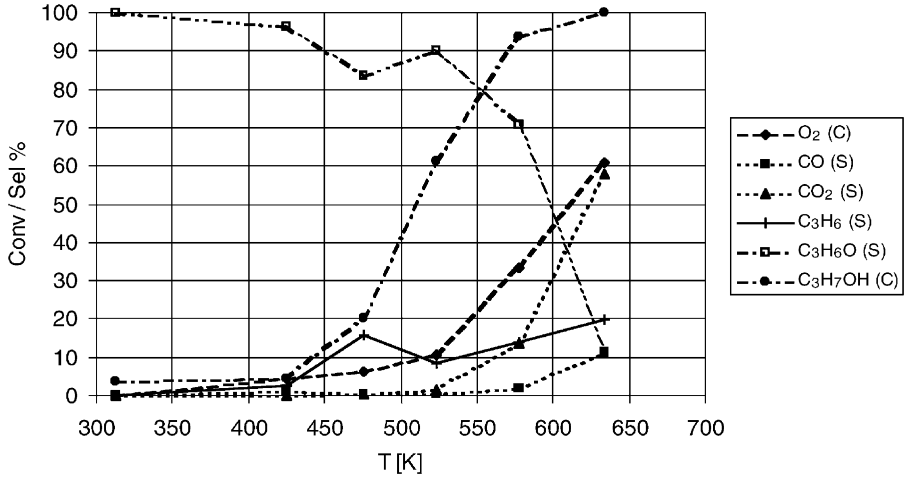


Fig. 11. Variation of the conversion (*C*) of 2-propanol and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (12 wt.%) and K_2O (6 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Feed, 1:5:94 = $C_3H_7OH:O_2:He$; total flow, 300 ml/min.

of vanadium and alumina but lacks of K, has also been performed (Fig. 12). In this case almost no 2-propanol oxidation is obtained, but propene (i.e. the dehydration product) is the largely predominant product, the selectivity to propene from 2-propanol is not significantly affected by oxygen concentration, in fact oxygen is almost not converted.

2-Propanol adsorption experiments carried out in an IR cell show in agreement with previous data that 2-propoxides are formed at the catalyst surface at room temperature over both catalysts A and D, and convert, in excess oxygen, to CO_x via acetone–acetates + formates over catalyst A and to propene over catalyst D [31]. IR studies showed that 2-propoxide species can also be formed by interaction of propene over our catalysts [31] as observed previously for V_2O_5/TiO_2 catalysts [32].

These data support the hypothetical role of 2-propoxide species for propane oxidation. In fact we note that, at the temperature at which propane begins to be converted (and oxygen is consequently still largely available), 2-propanol is totally converted on catalyst A. At this temperature CO_2 is the main product starting both from propane and from 2-propanol, propene being a minor product in both cases, if any. So, the same intermediate (i.e. 2-propoxy-group) could be involved. On the other hand, both propane conversion experiments (see Table 1) and 2-propanol conversion experiments (see Figs. 10–12) show that potassium (in the big amounts characterizing catalysts A–C) has a main role in orienting the selectivity towards CO_2 with respect to towards propene at low conversions.

On the other hand, GC–MS analyses show that acetone is a byproduct, although in very small amounts, of propene oxidation over our catalyst. Experiments performed cofeeding water show that the amount of acetone produced is definitely increased, although still weak.

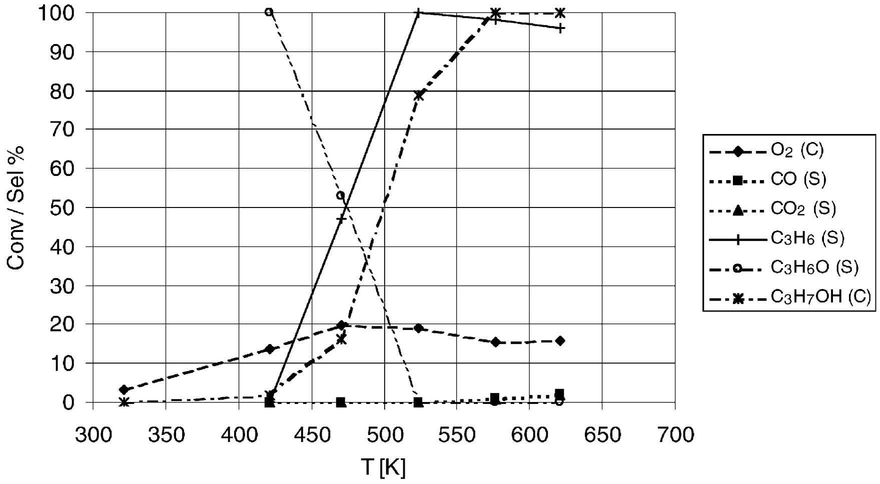


Fig. 12. Variation of the conversion (*C*) of 2-propanol and oxygen and the selectivities (*S*) to the main reaction products on V_2O_5 (13 wt.%)/γ-Al_2O_3 catalyst (0.1 g of catalyst and 0.4 g of quartz), surface area 180 m^2/g. Feed, 3:3:94 = $C_3H_7OH:O_2:He$; total flow, 300 ml/min.

Table 2
Results of thermodynamic calculations on the reactions potentially involved in the propane oxidation process

	Reaction	ΔH°_{298} (kJ/mol)	$\Delta G^\circ(T)$ (J/mol)
Combustion of propane	$C_3H_8 + 7/2O_2 = 3CO + 4H_2O$	−1194	$\Delta G^\circ \ll 0$ (always)
	$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$	−2043	$\Delta G^\circ \ll 0$ (always)
Oxidative dehydrogenation of propane to propene	$C_3H_8 + 1/2O_2 = C_3H_6 + H_2O$	−117.672	$-1.227 \times 10^5 + 72.569T + 0.035T^2 - 7.403 \times 10^{-6}T^3 + 6.976 \times 10^{-10}T^4 - 26.119T \ln T$
Pure dehydrogenation of propane	$C_3H_8 = C_3H_6 + H_2$	124.326	$1.164 \times 10^5 + 89.830T + 0.031T^2 - 4.798 \times 10^{-6}T^3 + 2.046 \times 10^{-10}T^4 - 35.074T \ln T$
Dehydrogenation of propane by CO_2	$C_3H_8 + CO_2 = C_3H_6 + CO + H_2O$	165.526	$1.561 \times 10^5 + 131.737T + 0.078T^2 - 2.284 \times 10^{-5}T^3 + 3.631 \times 10^{-9}T^4 - 51.244T \ln T$
Cracking of propane	$C_3H_8 = C_2H_4 + CH_4$	81.337	$7.682 \times 10^4 + 21.246T + 0.049T^2 - 1.452 \times 10^{-5}T^3 + 2.160 \times 10^{-9}T^4 - 27.28T \ln T$
Oxidative conversion of propane and propene to ethene	$C_3H_8 + 3/2O_2 = C_2H_4 + CO + 2H_2O$	−438.365	$-4.504 \times 10^5 + 148.929T + 0.079T^2 - 1.632 \times 10^{-5}T^3 + 1.545 \times 10^{-9}T^4 - 61.215T \ln T$
	$C_3H_6 + O_2 = C_2H_4 + CO + H_2O$	−320.692	$-3.277 \times 10^5 + 76.359T + 0.0446T^2 - 8.917 \times 10^{-6}T^3 + 8.47210^{-10}T^4 - 35.096T \ln T$

4. Thermodynamic considerations

To better understand the behavior observed in our experiments we have also attempted some thermodynamic calculations [33] and considerations. We have taken into consideration the reactions potentially occurring in our system, summarized in Table 2.

The two strongly exothermic and irreversible propane combustion reactions occur in part already starting from near 670 K in the presence of V–K–Al_2O_3 catalysts. This shows that the oxydehydrogenation catalysts are also active for the combustion of propane. We already remarked that part of these reactions occur as a parallel way with respect to oxidative dehydrogenation. On the other hand it is also clear that propene produced by oxydehydrogenation is also burnt catalytically as a successive step. The reactions are also observed in the “empty” reactor near 950 K but they become rapidly negligible.

The oxidative dehydrogenation of propane to propene (exothermic but much less than the previous ones) is also totally shifted towards the products at any temperature. It is clear that this reaction is competitive with total oxidation in the presence of the catalyst. On the other hand, in the empty reactor this reaction appears to be faster than total oxidation. In fact no CO_x are observed in the empty reactor in the range 1000–1100 K at low contact time, and not at all at higher contact time. It seems likely that propane oxydehydrogenation is the main oxygen-consuming reaction in the empty reactor.

The pure dehydrogenation of propane could occur in particular after the total consumption of oxygen. This reaction is, in absence of fed hydrogen and with no consumption of the produced hydrogen, expected to be shifted towards the products above 930 K or even at lower temperature due to our low reactants pressure. This reaction can contribute to the production of propene in particular in the range above 900 K. However, it is likely not occurring below this temperature.

The dehydrogenation of propane by CO_2 is favored thermodynamically above 950 K (when $\Delta G^\circ \sim 0$) and is possible to occur in our temperature range. This reaction could be involved in the production of propene [34] in our conditions, although no clear evidence of this is found here.

The cracking of propane is favored ($\Delta G^\circ < 0$) above near 600 K. However, we have evidence of this reaction only above 950 K, when this reaction occurs also in the reactor empty from the catalyst. We suppose consequently this reaction occurs thermally. This is confirmed by the decrease of the production of methane by filling the empty space of the reaction with quartz. Methane is observed as a product above 950 K even when oxygen is still not totally consumed, while it is observed below this temperature only after total oxygen consumption. This seems to indicate that this reaction is definitely slower than catalytic oxidative dehydrogenation but competes with thermal oxidative dehydrogenation.

The oxidative conversions of propane and propene to ethene are largely favored in all our temperature range. They are obviously favored even more if CO_2 instead of CO is considered as a product. So they could explain the production of ethene in aerobic conditions from both propane and propene. However we observed more ethene from propane than from propene. This suggests that propene is not intermediate to give this reaction from propane. A common intermediate could be involved.

5. Conclusions

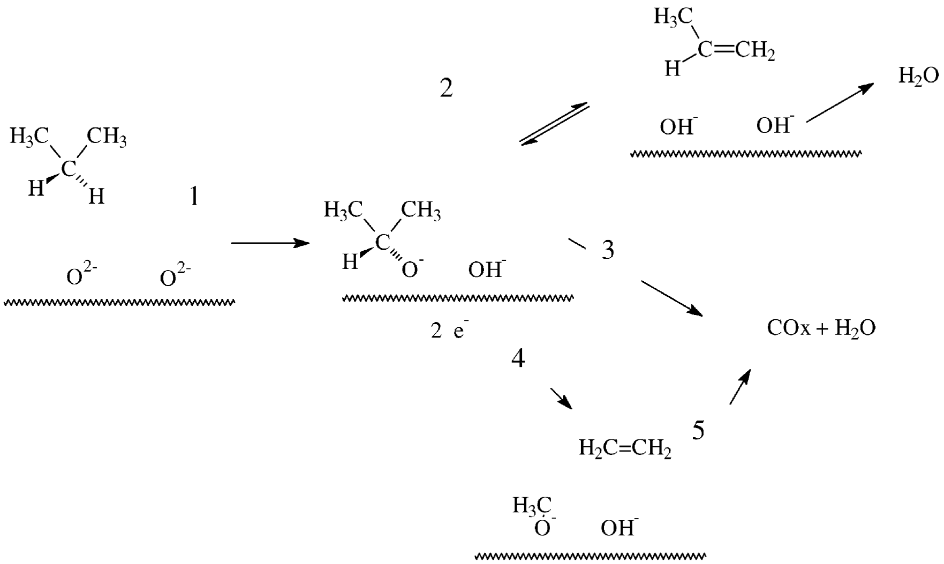
The data described above allow us to propose some conclusions concerning the reaction pathway upon propane oxidative conversion over V–K/Al_2O_3 catalysts. Evidence is provided for the existence of two well defined temperature ranges for the reaction regime in our conditions where the contact time is smaller than usual and the K-content in the catalyst is very high. At low temperature (i.e below ~950 K) a true catalytic reaction certainly predominate whereas above ~950 K gas-phase reactions certainly play a main role. In the “catalytic range” four products are observed, i.e. propene, CO, CO_2 and ethene. The data show that, by decreasing contact time, the selectivity to propene increases while that to CO_2 and to $CO+CO_2$ decrease. This result is actually consistent with most of the previous literature, showing that propene is a primary product and can later be overoxidized. This has been discussed recently, for example, by Stern and Grasselli [35] for nickel–cobalt molybdate catalysts, where this way is assumed to be the only one.

On the other hand, in the low temperature and very low conversion region, the selectivity to propene tends to increase and the selectivity to CO_2 tends to decrease by increasing temperature over our V–K–alumina catalysts. This contrasts what we found over the K-free catalysts where selectivity to propene grows by decreasing reaction temperature. This suggests that CO_2 can also act as a primary product over V–K–alumina catalysts. In this case CO_x can be formed both by a parallel way and by a consecutive way with respect to propene. This is consistent with the results reported recently over other supported vanadia catalysts [26–28]. Our data on K-free V/Al_2O_3 show that the peculiar behavior is associated with the big amount of doping potassium. When potassium is absent, the parallel way to CO_2 vanishes, and CO_2 is likely only produced by successive propane overoxidation. CO_2 is always in large excess with respect to CO in the lower temperature range, CO selectivity being also quite stationary near 10%. It is consequently not clear if CO is an intermediate in CO_2 production at higher temperature.

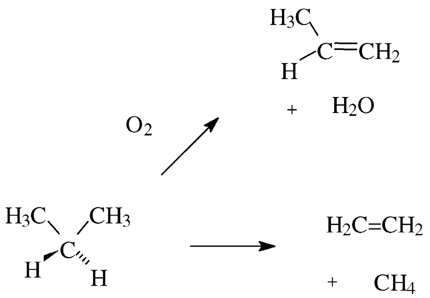
In the temperature range 850–950 K relevant amounts of ethene are also formed without any formation of methane. The lack of detection of methane in these conditions excludes that ethene arises from cracking of propane. This allows us to suppose that ethene is in this range produced by a true catalytic oxidation. Evidence has been provided that ethene can be also produced by oxidation of propene but it is mostly produced directly from propane oxidation. So, also for the production of ethene some kind of parallel-consecutive way with respect to production of propene should be proposed. The analysis of the data suggests that ethene is likely coproduced with CO_x.

The experiments of 2-propanol oxidation over both K-containing and K-free catalysts show some parallelism with those of propane oxidation. In fact, acetone at low temperature and CO_2 at high temperature are the largely predominant products of 2-propanol conversion over our V–K–alumina catalyst. On the contrary, propene is the largely predominant product of 2-propanol conversion over K-free V–alumina. This suggests that surface 2-propoxides can be the intermediates in both reactions. This agrees with previous studies performed over very active oxidation catalysts that supported the idea that the activation of alkanes over metal oxides occurs through the oxidative cleavage of their weakest C–H bond forming surface alkoxides [19,29,30,36,37]. This step is possibly common to the selective and to the non-selective oxidation ways (see Scheme 1). To this common step, which is very likely rate determining, can be attributed the activation energy of near 21 kcal/mol (near 88 kJ/mol) we measured.

2-Propyl alkoxide formed by oxidation of the weakest C–H bond of the propane molecule (way 1 in Scheme 1), that in the position C_2, can evolve by elimination to give rise to propene (way 2). However, IR studies showed that this way is reversible, i.e. 2-propoxides can also be formed by propene over the catalyst OHs. 2-Propoxides can also evolve by oxidation to acetone–acetate + formate species, finally giving rise to carbon oxides (a mixture of $CO+CO_2$, way 3). This way and the reversibility of the propene producing step account for a parallel-consecutive way to CO_x with respect to propene production.



Scheme 1. Reaction pathway for the truly catalyzed reactions upon propane oxidative dehydrogenation over $V–K/Al_2O_3$ catalysts.



Scheme 2. Reaction pathway for the main gas-phase reactions competing with catalytic reaction at high temperature upon propane oxidative dehydrogenation over V–K/Al_2O_3 catalysts.

On the other hand it is also possible to hypothesize that this species can also break into ethene + methoxides (way 4). The last, in agreement with previous methanol oxidation studies [38,39], would be easily oxidized to CO_x. Again the reversibility of the propene adsorption/desorption step accounts for a parallel-successive way to ethene with respect to propene (see scheme below).

The catalytic oxydehydrogenation of propane over these catalysts competes not only with its catalytic total oxidation but also, at higher temperature, with gas-phase reactions. Our data suggest that the main gas-phase reactions, occurring mainly after oxygen total consumption and/or above 950 K, are the gas-phase oxidative dehydrogenation to propene and the cracking to ethene + methane (Scheme 2). In these conditions the best yields to propene or to ethene + propene can be obtained, but with methane as a main byproduct.

The data reported here (Table 1) show that our heavy K-doping of vanadia–alumina decreases the selectivity to propene at very low conversion. However, it increases a little bit the selectivity with respect to propene at conversions of the order of 20% with respect to K-free vanadia–alumina. Additionally, it provides a new way to ethene which is not found over K-free vanadia–alumina.

On the other hand the gas-phase reaction can be more selective to propene than the catalytic one on our heavily doped catalysts, at least when partial conversion is obtained with quite high residence times. In terms of yields to propene it is evident that the thermal not catalyzed conversion of propane is competitive with those obtained on most “oxydehydrogenation catalysts”, reported so far. The data obtained on our catalysts allowed to provide evidence for the parallel-consecutive ways to CO_2 and ethene which can affect the behavior also of other more performant catalysts. The reaction pathway we proposed here is the base for a kinetic modeling study which is now in progress.

Acknowledgements

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