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Selective heterogeneous oxidation of light alkanes. What differentiates alkane from alkene feedstocks?

G. Centi

Department of Industrial Chemistry and Materials, V. le Risorgimento 4,
40136 Bologna, Italy

Some aspects of the reactivity of vanadyl pyrophosphate catalysts in *n*-butane and *n*-pentane oxidation and propane ammoxidation are discussed in order to illustrate differences and peculiarities of the catalysts for the selective oxidation of alkanes in comparison to the catalysts for the selective oxidation of alkenes. The formation of alkenes as reaction intermediates, the catalytic and mechanistic differences in alkane and alkene conversion, their different effects in changing the active surface configuration, the relationship between surface concentration of adspecies and catalytic behavior, and the problem of the surface isolation of the active intermediates are discussed. Some brief economic considerations about the advantages of the various processes of alkane oxidation as compared to alkene or aromatic oxidation are also given.

Keywords: *n*-butane and *n*-pentane oxidation; propane ammoxidation; vanadyl pyrophosphate; oxyfunctionalization; surface concentration of adspecies and catalytic behavior

1. Introduction

The development around the sixties of various processes of selective oxidation of alkanes has constituted a significant breakthrough for the large scale production of chemicals and intermediates. Today most of the monomers for the manufacture of plastics and synthetic fibers are produced by selective catalytic oxidation of hydrocarbons and include large volume products such as ethylene oxide, acrylonitrile, vinyl chloride, maleic and phthalic anhydrides. In addition, the world market for oxidation catalysts may be estimated as around 200–250 million US dollars, about half of which is in Europe.

On the average, the costs for a chemical product produced by oxidation processes can be allocated as follows: 60% to raw materials, 20% to capital costs, and 20% to other costs such as labor, utilities, catalysts, etc. Therefore, a larger economic impact for chemical oxidation processes may be realized by technologies using alternate, less-expensive raw materials. The substitution of expensive alkenes or other hydrocarbons (for example, aromatics) with a less expensive alkane feedstock can thus represent a breakthrough for the realization of shut-down economics [1], i.e. technologies able to reduce the transfer price of a product in a fully amortized plant as compared to the existing competitive technologies. In most cases, in fact, the price of light (C_2–C_6) alkanes is the same as that of fuel, due to the reduced number of non-energy applications for these hydrocarbons. Furthermore, the functionalization of alkanes in the presence of oxygen (*oxyfunctionalization* which includes oxidation, ammoxidation, oxidative dehydrogenation, oxychlorination and oxidative dimerization processes) in comparison to other possible competitive petrochemical processes of alkane conversion is the more interesting process option to obtain selectively high value chemicals.

However, the possible utilization of alkane feedstocks for selective oxidation reactions requires the discovery of a selective catalyst for the reaction, a difficult task due to the relative inertness of the alkane and the two–three order of magnitude higher reactivity of possible products or intermediates. The control of the consecutive reactions up to carbon oxides is thus very critical. The selective oxidation of alkanes thus requires the development of novel concepts and catalytic systems to fulfil the strict requirements of controlled surface reactivity necessary for selective behavior. Some aspects of the reactivity of vanadium–phosphorus oxides in the reactions of *n*-butane and *n*-pentane oxidation and of propane ammoxidation are discussed in this paper in order to illustrate some differences and peculiarities of the catalysts for the selective oxidation of alkanes in comparison to catalysts for the selective oxidation of alkenes. Some brief economic considerations are also discussed in order to evidence some key points of the economic comparison of alkane versus alkene or aromatic oxidation.

2. Some economic considerations on alkane oxidation processes

The process for the synthesis of maleic anhydride from *n*-butane was developed around 1974 and today this process is the main route of production of this compound. Older processes based on benzene have been almost completely substituted [2] due to four main reasons: (i) the lower price of *n*-butane as compared to benzene, (ii) the reduced amount of by-products, (iii) the better yield by weight (two carbon atoms are lost as CO_2 in going from benzene to *n*-butane and therefore the yield by weight in the butane process is around 110–115% as compared to 90–95% for benzene, even though the molar yield from the latter (around 74%) is higher than that from butane (around 66%)) and (iv) the reduced environmental problems regarding control of emissions. These advantages compensate the higher capital cost due to (i) the reduced productivity (a plant from *n*-butane is about 15% more expensive than one from benzene for similar production, due to lower catalyst productivity and lower explosion limits of hydrocarbon–oxygen reagent mixture), (ii) the lower production of steam (the heat of reaction for benzene is 1875 kJ/mol against 1260 kJ/mol for benzene) and (iii) the lower selectivity. However, the former advantages largely compensate the higher capital cost and therefore the transfer price for maleic anhydride production from *n*-butane is around 20% lower than that from benzene. It should also be noted that better economics from *n*-butane can be realized by improving the productivity of the process. In fact, a recent development is the realization of a technology for maleic anhydride production from *n*-butane which operates with a fluid bed reactor. The better control of the temperature and of explosion waves in the latter reactor as compared to conventional fixed bed reactors allows operation with a higher initial *n*-butane concentration (around 5% and inside the explosivity region) as compared to fixed bed reactor operations (butane concentration in the 1–2% range) [3]. It should also be noted that the realization of the process of *n*-butane oxidation in a fluid bed reactor has required the development of catalysts with improved mechanical properties while maintaining the level of catalytic performances, a result which is not easy to achieve with the vanadium–phosphorus catalysts used in this process [4].

Therefore, the realization of a successful new oxidation process based on an alkane feedstock involves various economic evaluations, besides the obvious availability of a catalyst able to convert the alkane selectively. The price differential between alkane and alkene is the driving force, but not the only factor which must be considered. In butane oxidation a factor of success in comparison to benzene is the higher yield by weight than that obtained from benzene (loss of two C atoms from benzene) and the reduced environmental problems. In comparison with butene and butadiene, a factor of success in *n*-butane is the reduced number of by-products and related separation costs. These considerations must be taken into account for a correct evaluation of the possibilities of success of other processes of selective oxidation of alkanes, and in particular ethane oxychlorination to vinyl chloride, propane ammoxidation to acrylonitrile and *n*-pentane oxidation to phthalic anhydride. Some economic considerations for the latter process have already been reported [5]. Other interesting possible processes of selective alkane oxidation such as ethane to acetic acid and isobutane to methacrylic acid are at too early a stage of research for any evaluation, because a possible catalyst selective for the reaction has not yet been found.

The planned commercialization of the propane ammoxidation process in a few years has recently been announced by BP America [6]. The driving force for this process is only the difference in the price between propane and propene; the latter hydrocarbon is quite expensive because of its wide use as a chemical and monomer. The yields reported in the patent or scientific literature ([6,7] and references therein) indicate a yield of acrylonitrile of around 40% (much lower than that from propene which is around 65–70%; the yield by weight from propane is even lower) and the reaction temperatures are about 100°C higher. The fixed investment costs thus are about 15–20% higher. Furthermore, good selectivities may be obtained (i) at propane conversions much lower (in the 40–60% range) than those used in the propene process (95–98% of single-pass conversion) and (ii) using a higher propane concentration. A process from propane may thus reasonably operate with a recycle stream and consequent high costs, or leave unreacted a large amount of propane. Unreacted propane may be used for high pressure steam production because the cost is that of a fuel, but the economic advantage depends on the need for high pressure steam in the plant. BP America [6] claims in addition that, whereas in the propene based process the slight excess of ammonia necessary for good selectivity must be converted to ammonium sulphate, creating a messy recovery problem, the new technology from propane avoids ammonia breakthrough and so offers a cleaner and less expensive process from an environmental control standpoint. Even though present estimations indicate a lower transfer price for acrylonitrile produced from propane, it is evident from the above discussion that the main advantage of the propane process is the difference in price between propane and propene, and thus the process economics are highly dependent on the market. In the former example of butane oxidation, on the contrary, several other additional factors contribute towards making it a winning technology, limiting the sensibility of the process to changes in the price of the alkane.

3. Alkane versus alkene oxidation

In order to discuss a possible reliable strategy in the development of catalysts for alkane oxidation, answers to some basic questions are necessary. The first question is about the first step in alkane oxidation: whether the formation of the corresponding alkene is involved or the activation mechanism proceeds along a different route. For example, in *n*-butane oxidation a mechanism involving a two-H abstraction from the methylenic groups of butane (2,3 positions) with formation of 2-butene on the adsorbed form and further H abstraction to form adsorbed butadiene has been proposed [8,9]. Alternatively, an attack of the lone pairs of electrons of two adjacent bridging oxygens on the LUMO of the butane molecule at carbon atoms 1 and 4 has been suggested [10]. This attack results in the abstraction of H atoms to form surface OH groups and simultaneously render carbon atoms 1 and 4 positive and susceptible to the attack of a third adjacent oxygen. A tetrahydrofuran-like structure thus forms as the first reaction intermediate. A crystallochemical approach [11] for the analysis of the reaction mechanism has resulted in similar conclusions, whereas H–D isotopic exchange experiments [12] are in favour of the first hypothesis for the mechanism.

This problem about the mechanism of alkane activation is important, because it addresses a fundamental question for the design of catalytic systems for alkane oxidation: Is it possible to assemble an efficient catalytic system that combines sites selective for alkane oxidative dehydrogenation with a matrix selective for alkene oxidative conversion or instead does alkane oxidation proceed along a different route as compared to alkene oxidation which implies different active sites and catalysts? Any conclusions for one catalytic system cannot be extended to all systems, but it is instructive to discuss the behavior of vanadyl pyrophosphate (VPO) in alkane oxidation, because this compound is the active phase in the only commercial process of oxyfunctionalization of an alkane (*n*-butane to maleic anhydride). The peculiar reactivity characteristics of VPO are (i) the absence of formation of detectable reaction intermediates (the entire reaction up to maleic anhydride occurs on the surface without gas phase desorption of any intermediate) [8,9], (ii) the high selectivity in *n*-butane and *n*-pentane oxidation, but not in propane oxidation which forms only carbon oxides [8] and (iii) the poorer performances of a VPO catalyst active/selective in butane or pentane oxidation in the oxidation of the corresponding alkenes [13]. For example, compared in table 1 is the behavior of VPO in different C_5 hydrocarbon oxidations on the same catalyst and in the same reaction conditions. Notwithstanding the reasonably easier activation of alkenes as compared to the corresponding alkane, the activity of the catalyst in alkene oxidation is similar and especially mainly carbon oxides are produced. Apparently, these indications on the different reactivity of VPO in the alkane versus alkene oxidation suggest a basic difference in the two mechanisms of transformation. However, when experiments with a high alkane/O_2 feeding ratio are carried out [14], the formation of alkenes can be detected with a typical behavior of reaction intermediates. Reported in fig. 1 are similar experiments on VPO using around 23% propane in the feed and changing the propane to O_2 ratio. Whereas mainly carbon oxides for a O_2/C_3 ratio higher than one are obtained, when oxygen is deficient good selectivities to propene are achieved. This indicates that VPO selectively activates propane through two-H abstraction to form propene, but the latter hydrocarbon can be easily oxidized to carbon oxides and can desorb as such in the gas phase only when oxygen for its further conversion is not available. When more stable products against further oxidation are formed such as anhydrides, on the contrary, higher selectivities are possible. This experiment indicates that the drastic difference in selectivity in the oxidation of C_3 and C_4–C_5 alkanes on VPO cannot be attributed to a difference in the mechanism of activation (for example, a 1,4 oxygen insertion to form a tetrahydrofuran-like intermediate), but rather results from the difference in the intrinsic sensibility to further unselective oxidation of intermediate or reaction product.

Assuming thus the formation of C_4–C_5 alkenes (in the adsorbed form) as the

Table 1

Comparison of the behavior of vanadyl pyrophosphate in the oxidation of *n*-pentane, 1-pentene and pentadiene. Temperature of 20% conversion (T_{20}) and relative selectivities to main products (MA, maleic anhydride; PA, phthalic anhydride; 2Pe, 2-pentene; Pd, pentadiene; CPd, cyclopentadiene), other than carbon oxides. Experimental conditions: $W/F = 300$ g h/mol C_5, $O_2/C_5 = 20 : 2.2$

Reagent	T_{20} (°C)	Selectivity (%)				
		PA	MA	2Pe	Pd	CPd
n-pentane	318	38	14	–	–	–
1-pentene	303	–	8	33	3	10
1,3-pentadiene	298	2	14	–	–	13

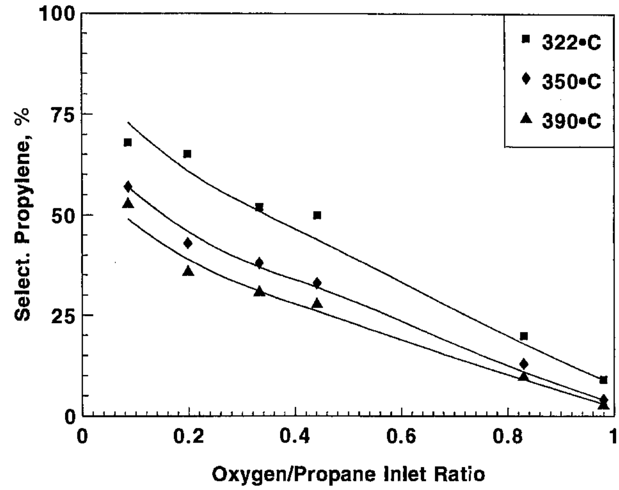

Fig. 1. Effect of the O_2/propane ratio on the selectivity to propylene on vanadyl pyrophosphate. Experimental conditions: 23.1% propane, 5 g catalyst, total flow rate (STP) 40 cm^3/min.

first step in the reaction network, the above discussion evidences that a key factor of selectivity in the mechanism of oxidation of C_4–C_5 alkanes is the necessity for rapid further selective transformation of the alkene intermediates in order to avoid their desorption or surface mobility, because these compounds show a high reactivity towards oxidation to carbon oxides. A kinetic surface model can also be developed to describe these concepts [15] and a maximum in the selectivity can be predicted, in agreement with some experimental indications. The formation of alkenes as reaction intermediates can be evidenced also using high speed transient experiments under vacuum (TAP reactor) [9,16]; the short residence time and the high vacuum favour the desorption of intermediates and the sub-millisecond time-resolution of the instrument makes it possible to note their consecutive transformation.

Therefore, various experimental evidence agrees in indicating the formation of alkenes (in the adsorbed form) as the first step of the reaction network on VPO. If so, however, why do the alkane and alkene behave in a different fashion on VPO? The alkene is less selective, has a lower reactivity and gives rise to the formation of a wider spectrum of products. There is also a basic difference in their kinetic behavior. For butane oxidation on VPO, the order with respect to hydrocarbon and oxygen is one or lower, depending on the catalytic system; for 1-butene or butadiene oxidation on VPO the order with respect to oxygen is higher than one and a self-inhibition on the rate of maleic anhydride formation which increases the hydrocarbon partial pressure is observed ([9] and references therein). The inhibition suggests a competition between alkene and oxygen adsorption on the same site. In addition, even small amounts of co-feed alkenes together with the alkane lead to a complete inhibition of the reactivity of VPO in alkane oxidation [13,17], but a treatment with O_2 (at temperatures higher than those of reaction) or with SO_2 can restore the original activity [17].

Infrared spectroscopy shows that the effect of O_2 or SO_2 is to oxidize or enhance the desorption of strongly held organic species formed during the catalytic reaction and characterized by a broad adsorption band in the 1500–1720 cm^{-1} region (fig. 2). These adsorbed species can be attributed to strongly coordinated alkenes and alkadienes and to partially oxidized intermediates such as furan [17]. No changes, on the contrary, occur to the bands in the 1850–2150 cm^{-1} region that are due to overtones of the fundamental skeletal vibrations of vanadyl pyrophosphate. Therefore, structural changes in the catalyst after the high temperature treatment with O_2 do not occur. These adspecies reform feeding again the hydrocarbon/O_2 mixture [17], but their amount is lower in the case of alkane oxidation than in alkene oxidation. Part of these strongly held adspecies (they do not desorb

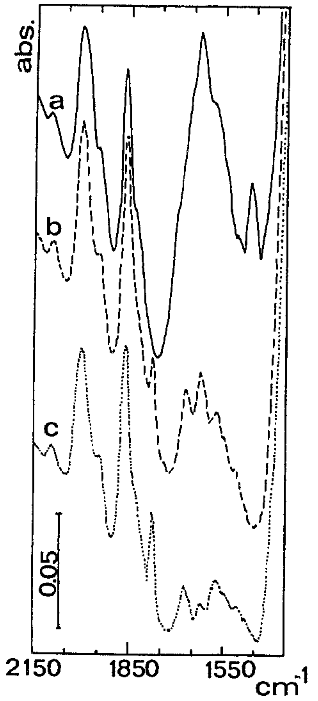

Fig. 2. Fourier-transform infrared spectra of VPO after catalytic tests in *n*-butane oxidation and (a) evacuation in the IR cell at 400°C, (b) consecutive heating at 400°C for 2 h in the presence of O_2 and (c) further consecutive heating for an additional 2 h in the presence of O_2, but at a higher reaction temperature (480°C).

at the reaction temperature of around 300°C) can desorb in a not-reactive flow (helium) at temperatures higher than those of reaction. Compared in table 2 are the quantitative data of the analysis of the products of thermal desorption of VPO after steady-state oxidation of butane and butadiene [18] and removal of weakly bonded adspecies with a helium flow at the reaction temperature (300°C). It is evident from the comparison that a larger amount of strongly held adspecies is present on the surface during alkene oxidation. Similar conclusions can be derived from the titration of these species with pulses of oxygen and monitoring CO_2 formation [17,19]. Remarkable evidence from the latter experiments is that a decrease of about one order of magnitude may be estimated for the specific rate of alkane selective oxidation in going from the initial clean to the steady-state surface situation of VPO characterized by the presence of a large fraction of adsorbed species with a reduced rate of surface transformation or desorption. The decrease is more drastic in alkene oxidation; in agreement, a rapid initial decrease in the activity of VPO during 1-butene oxidation is observed [20].

In conclusion, due to the strong adsorption of alkenes and especially alkadienes on VPO and the reduced rate of transformation of these surface adspecies, the number of free active sites in the steady-state conditions is much lower in comparison with the clean VPO surface. The effect is limited in alkane oxidation, since the surface concentration of alkenes is controlled by the rate of alkane activation and the rate of alkene further oxidation. In the direct oxidation of alkenes, on the contrary, almost all active sites are blocked, and therefore an inhibition of oxygen adsorption is present. This influences the availability of selective sites for the selective transformation of adspecies to anhydrides and favours the unselective reaction of adspecies with gaseous oxygen to form carbon oxides. The higher surface concentration of adspecies also favours the desorption of some intermediates in the gas phase and the occurrence of other reaction pathways to form other reaction products (for example, methyl vinyl ketone from 1-butene [9]). The difference between alkane and alkene selective oxidation on VPO can thus be more reasonably discussed in terms of difference in the surface concentration of adspecies and related effects more than on the basis of differences in the reaction mechanism.

Table 2
Products of thermal desorption in a helium flow after catalytic tests in *n*-butane and butadiene oxidation at 300°C (1 : 20 hydrocarbon to oxygen inlet ratio) and removal of gas phase species with a helium flow for 15 min at 300°C. Legend: C4, C_4 hydrocarbons (mainly butadiene); AC, acetic acid and acetaldehyde; MA, maleic anhydride; PA, phthalic anhydride; FU, furan

Reagent	Products of thermal desorption (mol ($\times 10^{-7}$) / g catalyst)					
	C4	AC	FU	CR	PA	MA
n-butane	1.6	0.5	–	4.3	1.7	5.6
butadiene	25.8	0.6	2.4	27.8	8.3	11.2

4. Surface isolation of the active intermediates

From the comparison with alkene oxidation, the peculiarities of the VPO catalyst in the selective transformation of C_4–C_5 alkanes can be summarized as follows: (i) the presence of balanced rates of alkane activation to form the corresponding alkene and of further oxidation of the latter to anhydride (controlled concentration of adspecies), (ii) the relative inertness of VPO towards the further oxidation of anhydrides to carbon oxides due to a limited number of oxidation sites, and (iii) the strong adsorption properties towards the reaction intermediates which limit their gas phase desorption or surface mobility and at the same time, by limiting the number of free active sites, provide a mechanism of geometrical surface isolation of the active intermediate due to the presence of too high a number of near-lying oxidizing sites that enhance the formation of carbon oxides. When all near-lying sites are blocked, however, the rate of surface transformation of the intermediate (turnover frequency) is too low and other unselective reactions may occur as in the case of alkene oxidation. The alkane oxidation on VPO is therefore characterized by a delicate equilibrium of the relative reactivities of the various active elements in the cluster-type multinuclear actives site and the reactivities of adspecies. Few isolated, but highly reactive, sites are required for a selective transformation.

The self-control of the site distribution on the active surface of VPO due to the formation of strongly held adspecies is thus one of the key features of vanadyl pyrophosphate for the surface isolation of the active intermediates. However, recent structural data have suggested a further mechanism [21]. Single crystal data for vanadyl pyrophosphate indicate the presence of disorder in the directional orientation of vanadyl columns running perpendicular to the active (1, 0, 0) surface [21]. A good correlation is generally found between selective behavior of $(VO)_2P_2O_7$ and the preferential surface exposure of this crystalline plane ([22] and references therein). However, this active surface cannot be simply considered as that resulting from the truncation of the bulk vanadyl pyrophosphate; uncoordinated surface vanadium atoms can be saturated by dangling pyrophosphate groups [21]. In agreement, X-ray photoelectron spectroscopy determinations indicate a P : V surface ratio higher (around 2.0) than the stoichiometric value of 1.0 for vanadyl pyrophosphate ([22] and references therein). On the (1, 0, 0) surface fully terminated as pyrophosphate, vanadium centres are isolated on the bottom of the clefts or cavities created from these dangling surface pyrophosphate groups. Furthermore, the dimensions and form of the cavities depend on the disorder in the structure of the vanadyl pyrophosphate [21]. The accessibility to the reactants of the active vanadium centres on the bottom of these cavities and the surface motion of activated species would certainly be limited and controlled by the *architecture* of these phosphate groups covering the active vanadyl pyrophosphate surface. This effect combines with that previously described for an efficient surface isolation of the active intermediates. In alkene oxidation, on the contrary, the easier adsorption of the hydrocarbon due, for example, to the possible formation of an allylic intermediate makes much less critical the problem of the surface isolation of the active intermediates.

A key feature of a catalyst for alkane selective oxidation is the presence of an efficient mechanism of surface isolation of active sites, due to a controlled "architecture" of the active surface and/or to the self-induced restructuring of the active surface during the catalytic reaction.

5. Surface concentration of adspecies and catalytic behavior

One question addressed from the previous considerations is the relationship between adsorption phenomena, site isolation and catalyst characteristics. The necessity of having few isolated, but highly reactive, vanadium active centres for a selective oxidation of *n*-butane has already been discussed. Due to the limited number of active centres, butane oxidation is highly dependent on the presence of competitive adsorption phenomena and it has been previously pointed out that small amounts of cofed alkenes may completely inhibit the reactivity of VPO in alkane conversion [13]. However, the concept of the relationship between surface concentration of adspecies and catalytic behavior can be better understood from the analysis of the catalytic behavior of VPO in propane ammoxidation. The data of fig. 1 have shown that VPO is able to form propene selectively from propane, but when sufficient oxygen is available, the former is quickly converted to carbon oxides.

In the presence of ammonia, the propene intermediate may be transformed to acrylonitrile and therefore it is interesting to analyze if, in the presence of NH_3, it is possible to stabilize the reaction intermediates and thus decrease the formation of carbon oxides. The interest in developing catalysts for the direct propane ammoxidation to acrylonitrile has already been pointed out. Reported in fig. 3 is the behavior of vanadyl pyrophosphate in propane ammoxidation using a composition of reagents similar to those reported in the patents for V-antimonate based catalysts ([17] and references therein). The presence of ammonia effectively decreases the formation of carbon oxides with an increase in the formation of propene and acrylonitrile, but the selectivity to products of partial oxidation (especially acrylonitrile) remains relatively low. It should be observed that VPO is able to activate propane to propene selectively (see fig. 1; at low conversion, a selective formation of propene is observed also in propane ammoxidation – see fig. 3), is highly active in allylic H abstraction (for example, in forming butadiene from 1-butene [9]), and is highly selective in butane oxidation. Therefore, the low selectivity in propane ammoxidation can be interpreted as a low rate of allylic N insertion on activated propene intermediate and thus the rate of acrylonitrile formation is slow as compared to competitive pathways to CO_x and/or to a high rate of both acrylonitrile and propene conversion to CO_x. The better selectivity in propane ammoxidation

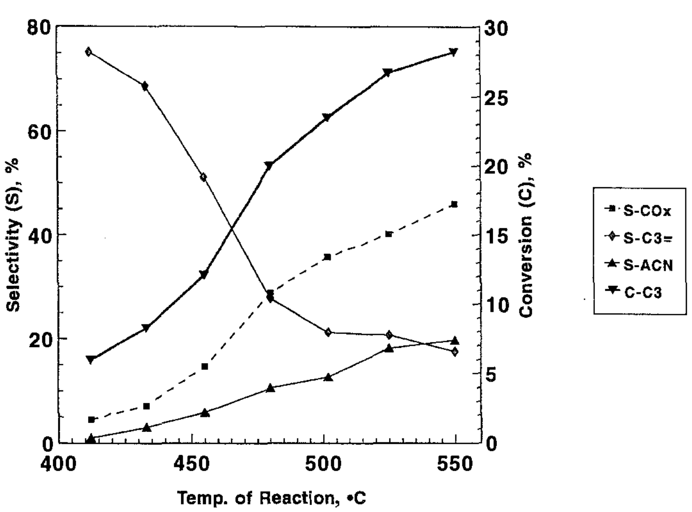

Fig. 3. Propane ammoxidation (steady-state conditions) on vanadyl pyrophosphate. Experimental conditions: propane, 7.2%, O_2, 10.2%, NH_3, 4.6%, 2 g of catalyst, total flow (STP) 95 cm^3/min. Legend: C3=, propene; ACN, acrylonitrile; C3 propane conversion; CO_x, carbon oxides.

with respect to propane oxidation, however, suggests that acrylonitrile is slightly more stable against oxidation to CO_x as compared to propene intermediate and/or that the competitive partial oxidation of co-reactant ammonia to N_2 (N_2 forms in significant amounts, indicating thus the occurrence of this reaction) limits the surface availability of oxidizing sites for unselective oxidation to CO_x as compared to the case of propane oxidation. From these considerations, a positive dependence of the selectivity on the surface coverage with ammonia can be expected. However, transient analysis of the catalytic behavior of VPO in propane ammoxidation instead reveals a more complex dependence. The tests were carried out preadsorbing ammonia on VPO at 400°C, then removing gas phase ammonia with a helium flow and finally analyzing the catalytic behavior of VPO with preadsorbed ammonia at the same temperature (400°C) as a function of time-on-stream, feeding a propane–oxygen (1 : 1 molar ratio) reagent mixture. Reported in fig. 4 are the results of these tests. The surface concentration of adsorbed ammonia (NH_{3ads}) decreases with time-on-stream, due to the reaction with both propane to form acrylonitrile and with oxygen to give N_2. As the NH_{3ads} decreases, the propane conversion increases. Ammonia, besides interacting with surface Brønsted P–OH sites, is strongly coordinatively adsorbed on the vanadium strong Lewis acid sites of vanadyl pyrophosphate [23] that have been suggested to be responsible for the selective activation of the alkane molecule [8,9]. The surface complex is stable up to relatively high evacuation temperatures and therefore a competitive adsorption between ammonia and propane may be expected. In fact, the activity of VPO in pro-

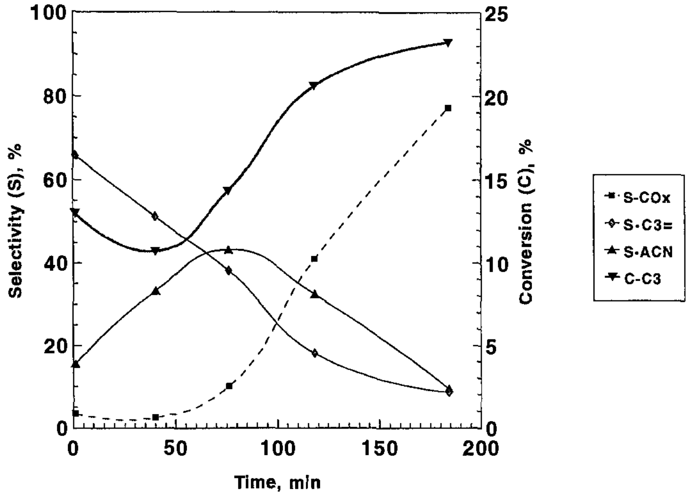

Fig. 4. Transient catalytic behavior in propane conversion of vanadyl pyrophosphate with preadsorbed ammonia. Experimental conditions: reaction temperature, 403°C; NH_3 preadsorbed for 30 min at 403°C and then gas phase ammonia was removed with a helium flow (15 min) at the same temperature; reagent flow: 6.6% propane and 7.6% oxygen; 2 g of catalyst; total flow rate (STP) 95 cm^3/min. Legend as in fig. 3.

pane conversion decreases in the presence of co-feed ammonia [24]. The selectivity to acrylonitrile, however, passes through a maximum with time-on-stream. The decrease at the higher times-on-stream is reasonably related to the consumption of preadsorbed ammonia for the formation of acrylonitrile. Due to the different rates of consecutive oxidation to CO_x of propene and acrylonitrile, the lower rate of formation of acrylonitrile leads to a decrease in the global selectivity and higher formation of carbon oxides. The initial increase in the selectivity to acrylonitrile, however, reveals that when NH_{3ads} is too high, acrylonitrile does not form, and only propene is found. If oxygen is not co-fed together with propane, the rate of conversion decreases considerably and propene is the only product formed. In addition, infrared characterization of the overtones region of VPO before and after ammonia adsorption and as a function of time-on-stream with a propane–oxygen feed does not provide any indication of the formation of V=NH surface species. It may be concluded, therefore, that ammonia and oxygen competitively interact on the same site, but adsorbed oxygen is necessary for the synthesis of acrylonitrile on VPO. When surface sites (probably, coordinatively unsaturated vanadium sites) are fully covered with preadsorbed ammonia, O_2 is not adsorbed and propane can be dehydrogenated to propene, but at a low rate and without further conversion to acrylonitrile. When the occupance of surface sites with adsorbed ammonia is decreased, oxygen can be activated leading to an increase in both the rate of propane conversion and the rate of acrylonitrile formation. However, when the surface concentration of activated oxygen is too high, the unselective oxidation to carbon oxides becomes the principal reaction.

The discussion of the transient behavior of vanadyl pyrophosphate in propane ammoxidation thus reveals two important concepts for the understanding of the catalytic chemistry of alkane oxyfunctionalization: (i) the role of the relative surface concentration of adspecies and of the competitive adsorption phenomena and (ii) the role of oxygen adsorbed species in the mechanism of selective oxidation. It should be mentioned that activated oxygen adspecies have been proposed as also being involved in the mechanism of maleic anhydride formation from butane ([8,22] and references therein).

6. Conclusions

Vanadyl pyrophosphate is the active phase of the only commercial process of alkane oxyfunctionalization and has an unmatched ability in the selective conversion of *n*-butane and *n*-pentane. Therefore it is a useful reference model for the analysis of the peculiar characteristics of reactivity necessary in a catalyst to be selective in the conversion of alkanes, even though obviously conclusions cannot necessarily be extended to all systems. Some aspects regard the interrelationship between surface characteristics of VPO, changes induced during the reaction from the formation of strongly held adspecies, competitive phenomena of reactants adsorption and surface concentration of adspecies, competitive pathways of surface transformation and turnover rate of intermediates transformation have been discussed. These aspects, however, are not exhaustive of the catalytic chemistry of VPO in C_3–C_5 alkane oxidation. Even so, these considerations illustrate the different nature of the problems in alkane oxidation as compared to those of traditional catalysts for alkene or aromatics oxidation [25]. For the design of catalysts selective in alkane oxidation it therefore must be considered that sites of alkane oxidative dehydrogenation cannot be simply ideally inserted in a matrix active for the oxidation of the corresponding alkene, because the surface population of adsorbed species and the sensibility of the adsorbed intermediates to the coordination environment (concentration and distribution of oxidizing sites) in the oxidation of the two hydrocarbons are different. All the surface catalytic chemistry of the single steps must be tuned in order to control the competitive pathways and the distribution and surface mobility of adspecies. A possible interesting approach is the design of catalytic active surfaces with steric limitations on the accessible sites, i.e. surface microcavities where the restricted environment allows control of competitive pathways. This concept must be further explored and its true feasibility demonstrated, but probably represents a key possibility for the design of new catalysts and reactions of alkane oxyfunctionalization.

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