JOURNAL OF CATALYSIS **142,** 70–83 (1993)

Acrylonitrile from Propane on $(VO)_2P_2O_7$ with Preadsorbed Ammonia

1. Role of Competitive Adsorption Phenomena in Determining Selectivity

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Received August 10, 1992; revised January 7, 1993

The dependence on time-on-stream of the catalytic behavior of $(VO)_2P_2O_7$ and α_I-VPO_5 with preadsorbed ammonia in the aerobic and anaerobic interaction with propane is reported. The rate of propane conversion and the selectivity to acrylonitrile depends on the surface coverage with ammonia. Three different limiting surface situations for vanadyl pyrophosphate as a function of the amount of adsorbed ammonia were found: (a) for high surface coverage with adsorbed ammonia, propane is oxidatively dehydrogenated to propylene, but is not further oxidized to acrylonitrile or to carbon oxides; (b) for an intermediate surface coverage with adsorbed ammonia, the selectivity to acrylonitrile is maximum; and (c) for a very low surface coverage with adsorbed ammonia, the rate of propane depletion is higher, but mainly carbon oxides are formed. The dependence of the activity on the surface coverage with ammonia was attributed to a competitive adsorption between ammonia and oxygen on coordinatively unsaturated vanadyl sites. In addition, the comparison of the evolution of the catalytic behavior of both $(VO)_2P_2O_7$ and α_I-VPO_5 in propane conversion in the presence and absence of gaseous oxygen suggests a possible role of adsorbed oxygen species in the mechanism of propane activation and selective transformation to acrylonitrile. © 1993 Academic Press, Inc.

INTRODUCTION

Catalysts based on vanadium–phosphorus oxides, and in particular the vanadyl pyrophosphate active phase (*1*), are well known to be highly active and selective in the oxidation of *n*-butane to maleic anhydride. This is the only commercial process of oxyfunctionalization of an alkane, and vanadyl pyrophosphate has unmatched catalytic properties in this reaction (*1*). The vanadyl pyrophosphate catalyst also shows a selective behavior in the transformation of *n*-pentane to maleic and phthalic anhydrides (*2*). Therefore, the presence of specific selective sites of alkane selective transformation suggests the possibility that this catalyst will also be useful in other reactions of oxyfunctionalization of alkane feedstocks.

Recently, another reaction of selective oxyfunctionalization of an alkane has gained attention, namely, the synthesis of acrylonitrile directly from propane. Due to the considerable difference in the price of hydrocarbon feedstock, this process has an interesting economic outlook for the development of a new process of direct acrylonitrile synthesis from propane in place of the present commercial process starting from propylene (*3, 4*). Both patent and literature data (Refs. (*3, 5, 6*) and references therein) indicate that V–Sb–Al based mixed oxides show better catalytic performances in this reaction, but the selectivities in acrylonitrile obtained are below those obtained from propylene. Further improvement in the catalytic behavior or the development of alternative catalytic systems for this reaction are thus necessary. Due to its particular behavior in the selective oxidation of C_4–C_5 alkanes, vanadyl pyrophosphate is an inter-

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0021-9517/93 $5.00

esting alternative catalytic system to investigate.

The catalytic behavior of vanadyl pyrophosphate in the ammoxidation of propane has been reported (*7*) and this catalyst is patented for this reaction (*8*). The catalytic performances reported are worse than those of V-antimonate based catalysts (*9*), but the data refer to a composition of the feed mixture which is very different from those reported as preferred for V-antimonate catalysts (*3, 5, 9*). On the latter catalysts it has been shown that the selectivity to acrylonitrile depends considerably on the composition of the feedstock (*5*) and thus also on vanadyl pyrophosphate possible improvements may be expected when different feedstock compositions are used. It should be noted that on vanadyl pyrophosphate (i) propane can be oxidatively dehydrogenated with high selectivity to propylene (*10*) using a high alkane-to-oxygen ratio in the feed mixture in order to limit the rate of the consecutive oxidation to carbon oxides of the alkene, (ii) the rate of propane depletion decreases considerably in the presence of ammonia (*10*), and (iii) the selectivity to acrylonitrile passes through a maximum with increasing ammonia concentration (*7*). Therefore, vanadyl pyrophosphate must have active sites for the selective activation of propane to propylene, but the conversion of this intermediate to acrylonitrile or to carbon oxides depends on the competitive rates of these two pathways of reaction. The presence of ammonia influences this ratio, but ammonia also inhibits the rate of alkane depletion as well as, at the higher concentrations, the synthesis of acrylonitrile. The selectivity to acrylonitrile in propane ammoxidation is thus influenced considerably by the surface concentration of adsorbed ammonia.

In a recent study (*11*) the formation of isobutyronitrile and methacrylonitrile was found in the oxidative dehydrogenation of corresponding carboxylic acids in the absence of ammonia in the feed using the ammonium salt of 12-molybdophosphoric acid as a catalyst. The ammonium salt of this heteropoly acid does not decompose thermally at the temperatures of reaction and therefore these data suggest that surface ammonium ions may act as a source for the selective insertion of N in adsorbed hydrocarbons or carboxylic acids. It is known that vanadyl pyrophosphate possesses strong Brønsted and Lewis acid sites that react with ammonia to form surface ammonium ions or coordinated ammonia complexes stable up to relatively high evacuation temperatures (*12*). The preadsorption of ammonia on vanadyl pyrophosphate allows better control of the surface concentration of adsorbed ammonia than cofeeding ammonia in the reactant mixture.

The objective of this work was to study the transient catalytic behavior of vanadyl pyrophosphate with preadsorbed ammonia in the conversion of propane to acrylonitrile in the absence of ammonia in the feed mixture, in order both to analyze the possibility of an improvement in the selectivity to acrylonitrile when working under unsteady-state reaction conditions, and to study the dependence of the catalytic behavior on the surface concentration of adsorbed ammonia. It should also be mentioned that in the *n*-butane oxidation to maleic anhydride on vanadyl pyrophosphate catalysts, the feasibility of industrial operations using separate stages of reactant interaction with the catalyst has been shown (*13*) and that an improvement in the selectivity to maleic anhydride is possible in these conditions.

EXPERIMENTAL

Catalyst Preparation and Characterization

The catalyst was prepared in an organic medium according to the procedure already reported (*2, 14*). The final atomic ratio was P : V = 1.03. The vanadyl hydrogen phosphate hemihydrate precursor phase (*14, 15*) obtained using this method was then activated at 400°C in a mixture of 1.5% *n*-butane/air for at least 200 h to form the $(VO)_2P_2O_7$ phase (*14–16*).

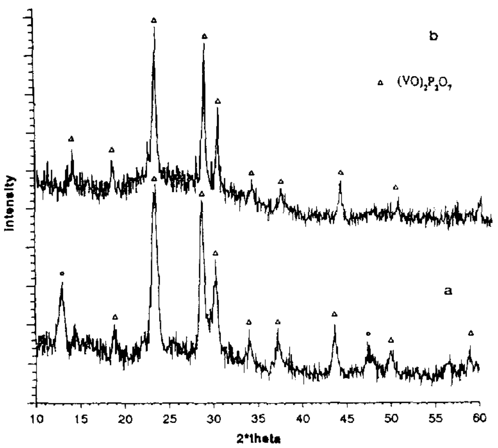

FIG. 1. X-ray diffraction patterns of $(VO)_2P_2O_7$ before (a) and after (b) the interaction with ammonia at 400°C for its preadsorption.

Figure 1 reports the X-ray diffraction (XRD) pattern of this fresh compound and after interaction with a flow containing about 30% ammonia in helium for 30 min. This treatment was used for the preadsorption of NH_3 before the subsequent catalytic tests in transient conditions. It can be seen that only the vanadyl pyrophosphate phase is present after the interaction with ammonia (Fig. 1b). In the fresh catalyst (Fig. 1a), on the contrary, weak additional lines at about $2\theta = 13°$ and 47.5° are observed which indicate the presence in this sample of the $VOPO_4 \cdot H_2O$ phase (*16*) together with $(VO)_2P_2O_7$. The hydrated phase of $VOPO_4$ derives from the reaction of α_I-$VOPO_4$ with the water added during the preparation of the specimens for XRD analysis. This phase disappears after the interaction of ammonia with the catalyst due to the transformation to $(VO)_2P_2O_7$ or possibly to an amorphous phase as may be suggested from a very broad background peak in the 20–30° region of 2θ. No further changes occur after the catalytic tests.

The infrared spectra of these samples before and after the interaction with NH_3 (Figs. 2a and 2b) indicate the presence of only the vanadyl pyrophosphate phase, characterized by the main bands at 1235, 1220, 1140, and 1115 cm^{-1} ($\nu_{as}PO_3$), 1095 cm^{-1} ($\nu_s PO_3$), and 970 cm^{-1} ($\nu V = O$) (*14*, *15*). When α-$VOPO_4$ is present together with $(VO)_2P_2O_7$, the relative intensity of the bands in the 900–1300 cm^{-1} region changes (*14*) (compare spectra (c) and (a) in Fig. 2). Spectra (a) and (b) in Fig. 2, on the contrary, do not give evidence of the presence of α-$VOPO_4$ together with $(VO)_2P_2O_7$. This suggests that the $VOPO_4$ phase evidenced in the XRD pattern (Fig. 1a) of the fresh sample is only a side phase in minor amount. On the other hand, the relative intensity of the diffraction lines at about $2\theta = 13°$ and 47.5° in $VOPO_4 \cdot H_2O$ is much higher than that of equivalent amounts of $(VO)_2P_2O_7$.

Calcination of the fresh sample at 500°C in air for 2 h does not induce any change in the crystalline phases present, in agreement also with thermogravimetric data (*17*). On the contrary, calcination in air for 12 h at 600°C, results in the transformation of vanadyl pyrophosphate to α_I-VPO_5 (*16*, *18*), as indicated by X-ray diffraction and infrared analyses (Fig. 2c). After the interaction with NH_3, however, this sample becomes X-ray amorphous and the chemical analysis indi-

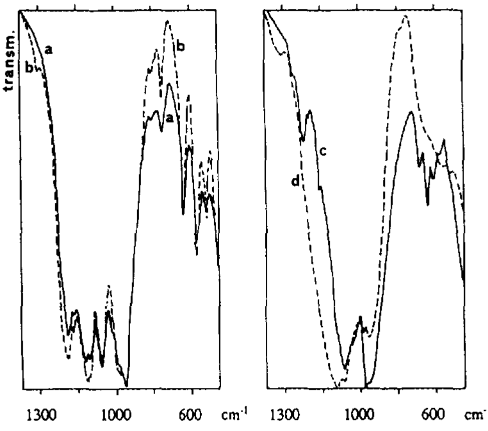

FIG. 2. Infrared spectra of $(VO)_2P_2O_7$ before (a) and after (b) the interaction with NH_3 at 400°C for the preadsorption of ammonia, of sample (a) after oxidation at 600°C (c) and of sample (c) after interaction with NH_3 for the preadsorption of ammonia (d).

cates a reduction of the vanadium from nearly 100% V^{5+} in the fresh α-$VOPO_4$ to about 60% V^{5+} and 40% V^{4+} in the sample after the interaction with NH_3. The infrared analysis (Fig. 2d) also indicates a change in the spectrum in agreement with that previously found for reduced samples of α-$VOPO_4$ (*14*). No further significant changes in the samples after the catalytic tests were observed.

The surface area of these samples is 18.8 m^2/g for vanadyl pyrophosphate and about 1 m^2/g for VPO_5. No changes in the surface area were found after the catalytic tests in propane ammoxidation.

Catalytic Tests

Catalytic tests were carried out in a quartz flow microreactor with on-line gas-chromatographic analysis of the reaction products. The procedure usually employed for the study of the evolution of the catalytic behavior of the catalyst with preadsorbed ammonia was as follows: The catalyst (2 g) was pretreated at the same temperature as the reaction temperature (in the 400–500°C range) for about 30 min with a flow (6 liter/h) containing about 30% ammonia in helium. Then, the flow was switched to a pure helium flow (6 liter/h) in order to remove gas-phase ammonia or weakly adsorbed surface ammonia. After 15 min of the helium flow, the reacting mixture (about 7% propane in helium with or without around 7% oxygen) was fed into the reactor maintained at the same temperature as that used for the ammonia preadsorption. The analysis of the evolution of the catalytic behavior as a function of the time-on-stream started at the inlet of the propane/O_2 feedstocks, but analyses were also made during the preadsorption of ammonia in order to follow the conversion of NH_3 to N_2 and NO.

Two on-line gas-chromatographs (GC) were used for the analysis of the reaction products. The first GC was equipped with a flame ionization detector and a Porapak QS column for the analysis of propane, propylene, acetonitrile, and acrylonitrile and the second GC was equipped with a thermoconductivity detector and a Carbosieve-II column for the analysis of O_2, N_2, CO, CO_2, and NO. Detailed further information on the reactor apparatus and on the method of analysis has been reported elsewhere (*5*). The same apparatus was also used for the steady-state catalytic tests.

RESULTS

Catalytic Behavior of Vanadyl Pyrophosphate with Preadsorbed Ammonia

Reported in Fig. 3 is the evolution of the catalytic behavior of vanadyl pyrophosphate with preadsorbed ammonia in the conversion of propane in the presence of gaseous oxygen (around a 1 : 1 propane to oxygen ratio) but absence of NH_3 in the gaseous phase. The data are reported for two reaction temperatures, namely, 403 and 451°C (Figs. 3a and 3b, respectively). The preadsorption of ammonia was made at the same temperature as the reaction temperature according to the method described in the Experimental section.

For the lower reaction temperature (Fig. 3a) the starting selectivity to acrylonitrile is about 15–20%, but rapidly increases and passes through a maximum in selectivity (about 40–50%) after around 80 min of time on stream. For higher values of the time-on-stream the selectivity to acrylonitrile decreases and is nearly zero after 200 min. In parallel with this, development of the conversion of propane is observed which, apart from a slightly initial decrease, increases from about 12 to 23%. The selectivity to propylene instead decreases continuously and the selectivity to carbon oxides, initially very low, increases considerably after the time corresponding to the maximum in the selectivity to acrylonitrile. At the higher reaction temperature (Fig. 3b) the catalytic behavior is relatively similar to that at the lower temperature, but the development is much more rapid probably because of the lower amount of preadsorbed ammonia and only the final part of the evolution of the catalytic behavior can be observed. In addition, at the higher

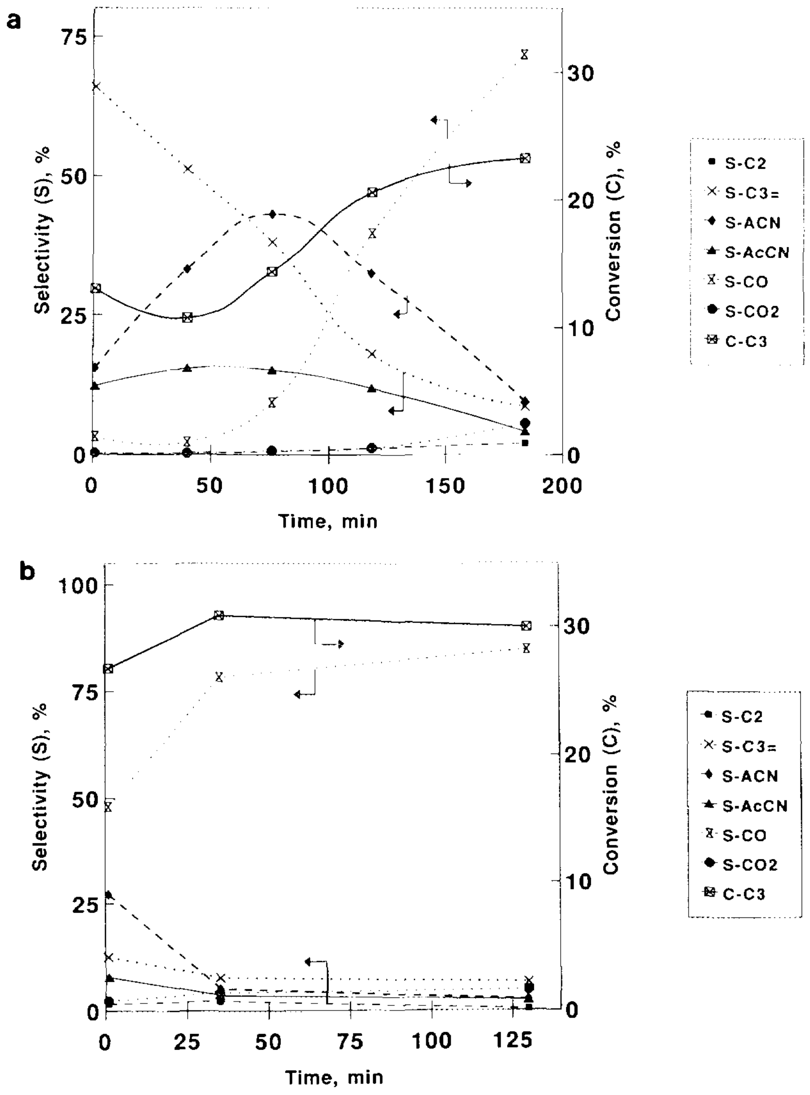

FIG. 3. Development of the aerobic catalytic behavior of $(VO)_2P_2O_7$ with preadsorbed ammonia as a function of the time on stream. Feed mixture composition: 6.6% propane and 7.6% oxygen in helium. Reaction temperature: (a) 403°C and (b) 451°C. Preadsorption of ammonia for 30 min (flow containing 30% NH_3 in helium) at the same temperature as the reaction temperature. Total flow (STP conditions): 5.8 L/h; 2 g of catalyst. Symbols: (*S*) selectivity, (*C*) conversion, (C2) C_2 hydrocarbons, (C3=) propylene, (ACN) acrylonitrile, (AcCN) acetonitrile, and (C3) propane.

reaction temperature the selectivity to acrylonitrile and propylene is much lower, but the conversion of propane is higher.

Reported in Fig. 4 is the evolution of the catalytic behavior of vanadyl pyrophosphate with preadsorbed ammonia in propane conversion in the absence of both oxygen and ammonia from the gas. The data refer to three reaction temperatures, namely, 410°C (Fig. 4a), 460°C (Fig. 4b), and 510°C (Fig. 4c). In all cases the conversion of propane is very low (lower than 5%) and mainly propylene is formed, with traces (selectivities lower than 5%) of acrylonitrile (ACN) and acetonitrile

(AcCN). Therefore, with the vanadyl pyrophosphate catalyst, the presence of gaseous oxygen is necessary to activate and convert propane to acrylonitrile.

In order to verify the influence on the propane conversion of a preliminary oxidizing treatment of the catalyst, the test as above was repeated after a preliminary pretreatment of the vanadyl pyrophosphate with oxygen at 500°C (2 h) before the adsorption of ammonia at 400°C. Reported in Fig. 5 are the results obtained with only the propane/helium mixture as the feed. The results do not differ significantly from those discussed before (Fig. 4a). Also in this case the propane conversion is low and mainly propylene forms. The high-temperature pretreatment of vanadyl pyrophosphate thus does not lead to an increase in the selective conversion of propane to acrylonitrile.

Catalytic Behavior of VPO_5 with Preadsorbed Ammonia

In order to determine if the low rate of anaerobic propane conversion of vanadyl pyrophosphate with preadsorbed ammonia may be attributed to a too limited number of oxidizing surface sites on this V(IV)-phosphate sample, catalytic tests were carried out with the corresponding oxidized phase (VPO_5).

Reported in Fig. 6 is the evolution of the catalytic behavior of VPO_5 with preadsorbed ammonia in propane conversion with a propane-oxygen reacting mixture as the feed, the composition of which was similar to that used in the tests with the vanadyl pyrophosphate (Fig. 3). The data refer to two reaction temperatures, namely 411°C (Fig. 6a) and 460°C (Fig. 6b). It should be noted that, using this catalyst, the formation of significant amounts of N_2 and NO was observed during the preadsorption of ammonia, indicating that ammonia is oxidized by the interaction with the catalyst. In line with this, a reduction of the catalyst was observed in thermogravimetric tests. This phenomenon of surface reduction of VPO_5 by interaction with the ammonia flow can explain why the catalyst becomes X-ray

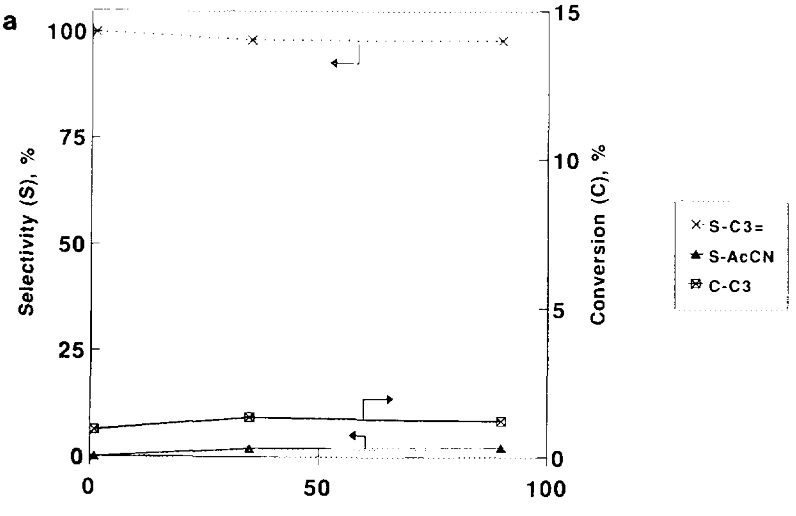

FIG. 4. Development of the anaerobic catalytic behavior of $(VO)_2P_2O_7$ with preadsorbed ammonia as a function of the time-on-stream. Feed mixture composition: 6.6% propane in helium. Reaction temperature: (a) 410°C, (b) 460°C, and (c) 510°C. Preadsorption of ammonia for 30 min (flow containing 30% NH_3 in helium) at the same temperature as the reaction temperature. Total flow (STP conditions): 6.1 liter/h; 2 g of catalyst. Symbols as in Fig. 3.

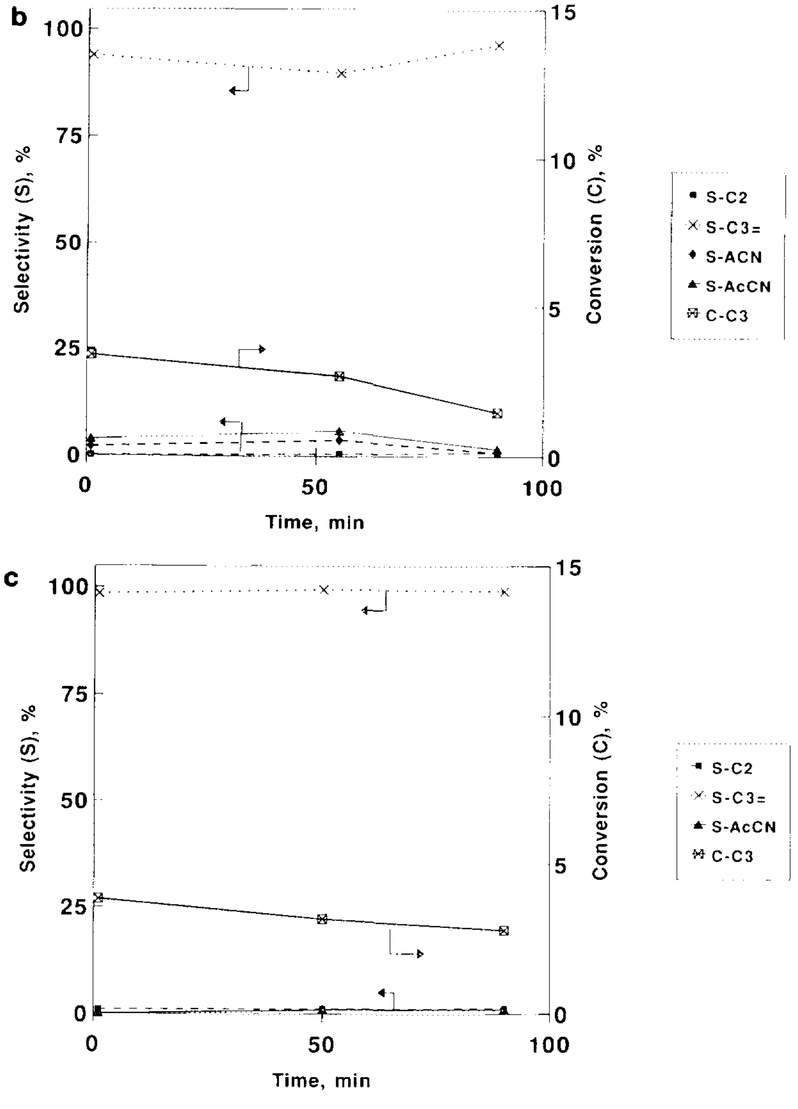

FIG. 4—*Continued*

amorphous after these catalytic tests (see Experimental section).

In the aerobic interaction of propane with this catalyst after the pretreatment with ammonia at the lower reaction temperature (Fig. 6a) the formation of acrylonitrile with an initial selectivity of around 20% is observed, but the selectivity decreases rapidly to nearly zero. The conversion of propane is lower than in the case of vanadyl pyrophosphate, due possibly to the lower surface area. Furthermore, as compared to vanadyl pyrophosphate, the selectivity is lower due to the enhanced formation of carbon oxides, particularly CO. At the higher reaction temperature (Fig. 6b) the selectivity to acrylonitrile and propylene decreases further.

Reported in Fig. 7 is the catalytic behavior of VPO_5 with preadsorbed ammonia in the anaerobic interaction with propane. The behavior is summarized by reporting the initial activity (after 1–3 min of time-on-stream)

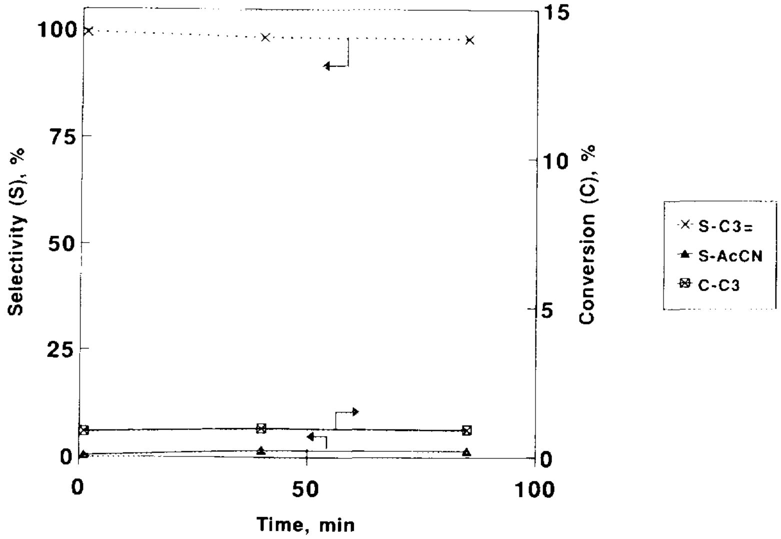

FIG. 5. Development of the aerobic catalytic behavior of $(VO)_2P_2O_7$ with preadsorbed ammonia as a function of the time-on-stream. Experimental conditions as in Fig. 4. Reaction temperature: 408°C. The $(VO)_2P_2O_7$ before the preadsorption of ammonia made at 408°C, was treated with a flow of pure oxygen at 500°C for 2 h. Symbols as in Fig. 3.

for each of the temperatures investigated. Ammonia was preadsorbed for 30 min before each test at the different reaction temperatures. The behavior is very similar to that observed for vanadyl pyrophosphate (Fig. 4): very low activity in propane conversion and mainly propylene formation, with only traces of acetonitrile and acrylonitrile formation.

Steady-State Catalytic Behavior of Vanadyl Pyrophosphate

In order to obtain a better understanding of the catalytic performances of vanadyl pyrophosphate in propane ammoxidation, the steady-state catalytic behavior was also studied using a feed mixture with a composition analogous to that reported in the patent literature for propane ammoxidation on V-antimonate catalysts (Ref. (5) and references therein) and similar to that used in the transient experiments with preadsorbed ammonia. Figure 8 summarizes the dependence of the catalytic behavior on the reaction temperature. The data refer to the steady-state behavior usually after 1 h of time-on-stream. It can be seen that in these tests using a cofeed of all reactants, the selectivity to acrylonitrile is generally low and below the maximum selectivity observed in unsteady-state conditions. It can be noted, furthermore, that the data obtained are similar to those found at time zero in the analysis of the transient evolution of the catalytic behavior of vanadyl pyrophosphate with preadsorbed ammonia (see Figs. 3 and 4).

DISCUSSION

Dependence of Catalytic Behavior on Surface Coverage with Adsorbed Ammonia

The development of the catalytic behavior of vanadyl pyrophosphate with preadsorbed ammonia in the interaction with a propane/O_2 flow (Fig. 3) shows some interesting aspects of the surface chemistry of this catalyst in propane ammoxidation:

(i) On the surface of $(VO)_2P_2O_7$ com-

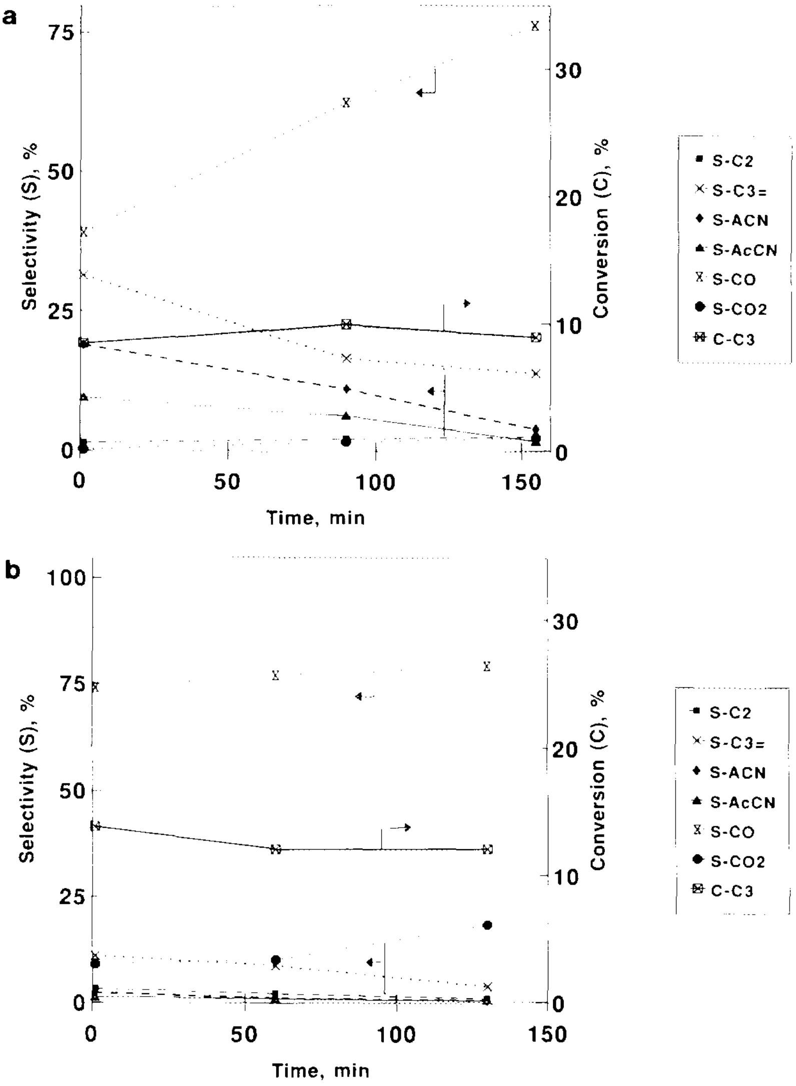

FIG. 6. Development of the aerobic catalytic behavior of VPO_x with preadsorbed ammonia as a function of the time-on-stream. Feed mixture composition: 6.6% propane and 5.1% oxygen in helium. Reaction temperature: (a) 411°C and (b) 460°C. Preadsorption of ammonia for 30 min (flow containing 30% NH_3 in helium) at the same temperature as the reaction temperature; the formation of NO and N_2 as reaction products is observed during the interaction with ammonia. Total flow (STP conditions): 6.1 liter/h; 2 g of catalyst. Symbols as in Fig. 3.

pletely covered with chemisorbed ammonia (time zero in Fig. 3a) propane can be selectively activated and oxidatively dehydrogenated to propylene, but a limited amount of acrylonitrile is also formed. In these conditions, however, the formation of carbon oxides is very limited and thus the selectivity to the sum of the products of selective oxidation (propylene, acrylonitrile and acetonitrile) is very high (about 98%).

(ii) As time-on-stream increases, the surface coverage with adsorbed ammonia decreases due to the reaction with hydrocarbon to form acrylonitrile, acetonitrile and

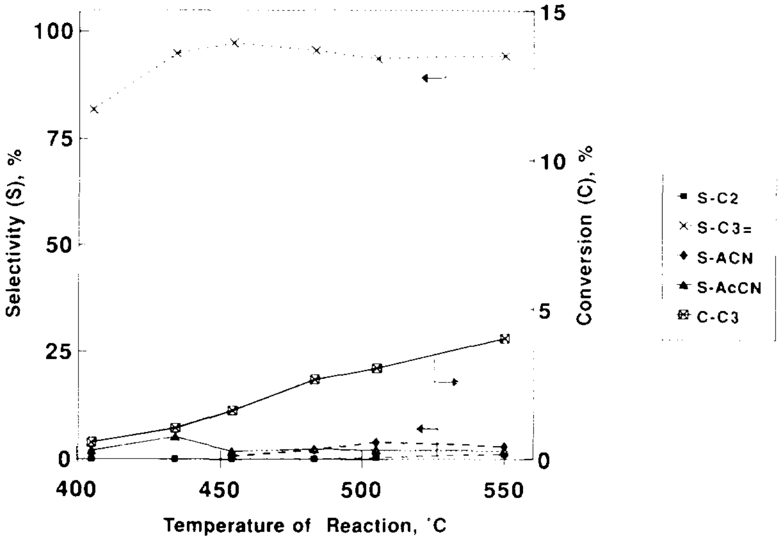

FIG. 7. Initial anaerobic catalytic behavior (after about 1–3 min of time-on-stream) of VPO_5 with preadsorbed ammonia as a function of the reaction temperature. Feed mixture composition: 6.1% propane in helium. Preadsorption of ammonia for 30 min (flow containing 30% NH_3 in helium) at the same temperature as the reaction temperature before each of the reaction temperatures tested. Total flow (STP conditions): 6.1 liter/h; 2 g of catalyst. Symbols as in Fig. 3.

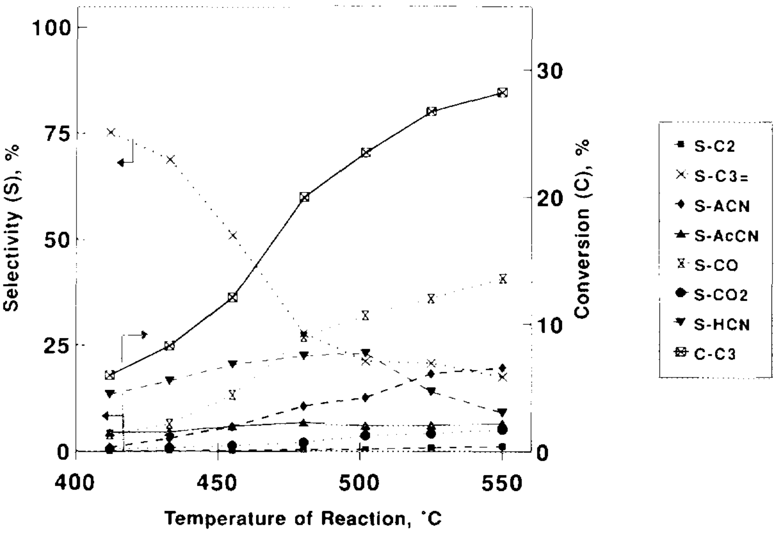

FIG. 8. Steady-state catalytic behavior of $(VO)_2P_2O_7$ in propane ammoxidation (cofeeding of the three reactants) as a function of the reaction temperature. Feed mixture composition: 7.2% propane, 10.2% oxygen, and 4.6% ammonia in helium. Total flow (STP conditions): 5.8 liter/h; 2 g of catalyst. Symbols as in Fig. 3.

HCN. When the adsorbed ammonia on vanadyl pyrophosphate decreases, the rate of formation of acrylonitrile from the intermediate propylene increases (Fig. 3a), and at the same time the rate of propane conversion increases. The formation of carbon oxides remains very low and the selectivity to acetonitrile is nearly constant.

(iii) With further increases in time-on-stream, the selectivity to acrylonitrile decreases with a parallel drastic increase in carbon monoxide formation and propane conversion. It should be noted also that the formation of N_2, due to the side reaction of oxidation of NH_3, becomes noticeable after the maximum in the selectivity to acrylonitrile, and its formation parallels that of CO formation.

The quantification of the change of the catalytic behavior of vanadyl pyrophosphate as a function of the amount of ammonia chemisorbed on the catalyst is difficult. In fact, this amount can be calculated from the amount of ammonia involved for the synthesis of the various products of reaction assuming that the desorption of ammonia as such does not occur. Chemisorbed ammonia is involved in the synthesis of acrylonitrile and acetonitrile and can be estimated from the integral amount of these products as a function of the time-on-stream. However, side reactions of ammonia consumption due to (i) its oxidation to N_2 and NO in the presence of gaseous oxygen and (ii) its reaction with the hydrocarbon to form HCN are also possible. In the present tests in transient conditions it was not possible to analyze the amount of these products and thus to quantify the relative importance of these side reactions. In addition, the limited number of experimental points do not allow an exact integration of the amount of the various products formed. Therefore, only a rough estimation of the change of the amount of chemisorbed ammonia as a function of the time-on-stream can be calculated and based on the assumption that the side reactions mentioned above are negligible. Figure 9 shows the indicative relationship between depletion in ammonia and activity change that can be estimated assuming the hypotheses discussed above.

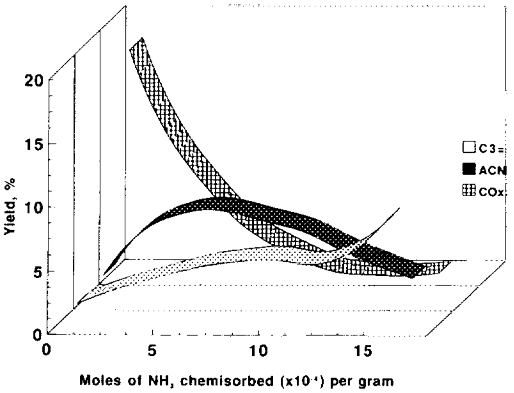

FIG. 9. Relationship between the amount of chemisorbed ammonia and the changes in the yield of products in the tests of Fig. 3. The amount of chemisorbed NH_3 is estimated on the basis of the integral amounts of formed acrylonitrile and acetonitrile, but do not take into account the possible side reactions of ammonia conversion to N_2 and NO and NH_3 reaction with the hydrocarbon to form HCN.

At higher reaction temperatures (Fig. 3b), due to the lower amount of adsorbed ammonia, only the end part of the above evolution with time-on-stream can be observed.

Therefore, three different surface situations for vanadyl pyrophosphate occur, depending on the amount of adsorbed ammonia: (a) for the higher surface coverage with adsorbed ammonia, propane is oxidatively dehydrogenated to propylene, but is not further oxidized to acrylonitrile or to carbon oxides; (b) for an intermediate surface coverage with adsorbed ammonia, the selectivity to acrylonitrile is maximum; and (c) for a very low surface coverage with adsorbed ammonia, the rate of propane depletion is higher, but with formation of mainly carbon oxides. The surface reactivity and selectivity of vanadyl pyrophosphate thus depends considerably on the surface coverage with ammonia. On the contrary, spectroscopic evidence does not indicate the formation of defined ammonium–oxovanadium phosphates by reaction of NH_3 with $(VO)_2P_2O_7$

or α-$VOPO_4$, as found in the case of ammoxidation of halogen-substituted toluenes but not of picoline (Ref. (*19*) and reference therein).

It is interesting to note that the behavior of vanadyl pyrophosphate when all three reactants (propane, oxygen and ammonia) are cofed (Fig. 8) is very similar to the catalytic behavior at time zero in the tests with preadsorbed ammonia (Fig. 3). This suggests that in steady-state conditions the catalytic behavior is dominated by the influence of adsorbed ammonia on the surface reactivity. The relatively poorer catalytic performance of vanadyl pyrophosphate in propane ammoxidation depends mainly on the strong adsorption of ammonia which inhibits the surface reactivity, more than on the absence of specific sites of selective transformation of propane to acrylonitrile. These data clearly demonstrate that the catalytic behavior of a surface does not depend only on the presence of a particular surface configuration or structure, but also depends on the nature of the changes in the surface reactivity induced by the adsorption of the reactants.

Role of Competitive Adsorption Phenomena in Propane Ammoxidation

Figure 3a shows that the selectivity to acrylonitrile increases initially as the amount of adsorbed ammonia decreases. In the anaerobic interaction of propane with vanadyl pyrophosphate with preadsorbed ammonia the rate of propane depletion is very low and only propylene forms (Fig. 4). Similar results are also obtained in the propane interaction with α_I-VPO_5 in the absence of gaseous oxygen (Fig. 7). This suggests that the presence of gaseous oxygen is required for the synthesis of acrylonitrile.

A possible interpretation of the presence of a maximum in the selectivity to acrylonitrile as a function of the time on stream in propane/O_2 interaction with $(VO)_2P_2O_7$ with preadsorbed ammonia (Fig. 3a) is thus as follows. Ammonia and oxygen compete for adsorption on the same site and their contemporaneous presence is required for the selective formation of acrylonitrile from the intermediate propylene. Initially, when the surface sites are occupied by adsorbed ammonia, oxygen adsorption and activation is inhibited. In the presence of a limited number of activated oxygen sites, propane can be oxidatively dehydrogenated to propylene, but not further oxidized. As the number of sites occupied by adsorbed ammonia decreases and the number of sites of activated oxygen simultaneously increases, the rate of acrylonitrile formation increases. When the number of activated oxygen sites is too high, however, the consecutive oxidation to carbon oxides predominates as well as the side reaction of ammonia conversion to N_2 which further accelerates the phenomenon. According to this interpretation, the catalytic reactivity of vanadyl pyrophosphate in propane ammoxidation thus depends on the presence of competitive adsorption phenomena between ammonia and oxygen and on the relative distribution and amount of these adsorbed species during the catalytic reaction. It should also be noted that the strong adsorption of ammonia blocks some surface sites self-inducing a site isolation of the oxidizing sites and this effect induces a considerable increase in the selectivity to products of partial oxidation.

Various alternative interpretations of the observed effects are possible, such as the hypothesis that ammonia could hinder the adsorption of the hydrocarbon in the state necessary for its reaction with oxygen (adsorbed or not). Present data do not allow an undoubted discrimination between these alternative hypotheses, but the relatively limited change in the rate of hydrocarbon conversion in comparison to the more relevant change in the selectivity to acrylonitrile (Fig. 3, first 60 min of time-on-stream) suggests that ammonia does not hinder the adsorption of hydrocarbon, but specifically the synthesis of acrylonitrile. However, more experiments will be necessary to clarify this aspect.

An alternative interpretation to explain the presence of the maximum is also that ammonia interacts with surface vanadyl groups to form an inactive surface species, which in the interaction with gaseous oxygen can be transformed first to a species selective in acrylonitrile synthesis and then to an unselective surface species able only to give rise to carbon oxide formation. Even though present data cannot discriminate between these two interpretations, it should be mentioned that infrared data show no evidence of any type of modification in the overtone stretching frequency of vanadyl or phosphate groups due to the interaction with ammonia and/or oxygen. It is known that overtones of the skeletal vibrations are much more sensitive probes than fundamentals for the study of the possible surface changes (*20*) and in fact their perturbation from the adsorption of suitable probe molecules can be shown. This suggests that the interpretation based on the presence of competitive adsorption phenomena is more likely than the interpretation based on structural or surface changes. However, also in this case more detailed data are necessary.

The surface reactivity of vanadyl pyrophosphate and its selective behavior can thus be tentatively interpreted in terms of surface population of adsorbed reactants and presence of competitive adsorption phenomena. It is interesting to note that the kinetic analysis of propane ammoxidation on V-antimonate based catalysts (*5*) has also indicated the presence of a competitive adsorption between ammonia and oxygen, even though less accentuated than in the case of vanadyl pyrophosphate which, however, is more reactive in propane conversion than V-antimonate. This suggests a possible tentative correlation between the nature of the sites required for an efficient activation of the alkane and their strong properties of adsorption of ammonia. In agreement, as clearly shown in Fig. 3a, adsorbed ammonia inhibits propane conversion and in the absence of gaseous oxygen only a very limited amount of propane is converted. Furthermore, the role of strong Lewis acid sites in the mechanism of *n*-butane oxidation on vanadyl pyrophosphate has been suggested (*1, 12, 21*), in agreement with the observed effect of inhibition of adsorbed ammonia on the rate of alkane depletion.

Role of Gaseous Oxygen in Propane Transformation

The comparison of the behavior of vanadyl pyrophosphate in aerobic (Fig. 3) and anaerobic (Fig. 4) interaction with propane suggests a role of gaseous oxygen both in propane oxidative dehydrogenation to propylene and in the conversion of this intermediate to acrylonitrile. Similar results are obtained after a preliminary oxidation of vanadyl pyrophosphate at 500°C (Fig. 5) and after the oxidation of $(VO)_2P_2O_7$ to α_I-VPO_5 (Figs. 6 and 7). In addition, it should be noted that the $(VO)_2P_2O_7$ sample used in these tests [a catalyst equilibrated for a long time in the reaction of *n*-butane oxidation (*1, 21*)] is stable against oxidation up to temperatures of about 500°C, as shown in thermogravimetric tests (*17*). All these data suggest that, even taking into consideration that α_I-VPO_5 is reduced during the preadsorption of ammonia, as shown from the detection of N_2 as a product of reaction, the considerable difference in the catalytic behavior in the presence and absence of gaseous oxygen cannot be associated with a role of gaseous oxygen only in the reoxidation of reduced sites according to a classical redox mechanism of selective ammoxidation of propylene to acrylonitrile (*22*). It should be noted, in fact, that in this case, a rapid decline in the activity and selectivity with time-on-stream is expected in the absence of gaseous oxygen, especially for the oxidized catalyst (α_I-VPO_5). On the contrary, the catalytic results do not provide evidence on this aspect and therefore are indicative of, even though they do not undoubtedly demonstrate, a direct role of adsorbed oxygen in the mechanism of propane activation and selective transformation to acrylonitrile. It should also be mentioned that the role of gaseous oxygen in the mechanism of *n*-butane activation and selective transformation to maleic anhydride on vanadyl pyrophosphate has already been proposed (*23*).

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