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

2. Study of the Mechanism of Ammonia Adsorption and Reaction with C_3 Hydrocarbons

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Infrared data on the time-on-stream changes of the adsorbed species on vanadyl pyrophosphate with preadsorbed ammonia during interaction with propane and oxygen are reported, together with an infrared and thermogravimetric analysis of the ammonia interaction with this catalyst and of the adsorbed species formed in ammonia and propylene coadsorption. Results indicate that (i) ammonia forms mainly ammonium ions at room temperature, but increasing the temperature of interaction up to 400°C results in a progressive increase in the amount of ammonia coordinated to surface Lewis acid sites; (ii) the amount of adsorbed ammonia at 400°C corresponds to about a 1 : 1 NH_3-to-P surface ratio, but is lower for higher reaction temperatures; (iii) in the presence of gaseous oxygen, the amount of coordinated ammonia decreases, with the probable formation of an amido (NH_2) species; (iv) propylene is coordinated as a π-bonded complex with vanadium Lewis acid sites and, in the absence of gaseous oxygen, is slowly transformed to acrylonitrile through the intermediate formation of propylamine; and (v) propane does not form adsorbed intermediates in the absence of gaseous oxygen, but in the presence of gaseous oxygen, acrylate species are detected. It is suggested that two pathways of formation of acrylonitrile from propane are present on vanadyl pyrophosphate, the first in anaerobic conditions involving the intermediate formation of propylamine and the second, when O_2 is present, involving the reaction between surface acrylate species and chemisorbed ammonia species. The second pathway is much more rapid than the first. © 1993 Academic Press, Inc.

INTRODUCTION

In recent years much attention has been directed toward obtaining an understanding of the key factors governing the surface reactivity of vanadyl pyrophosphate (hereinafter called VPO) in alkane selective functionalization in order both to improve its performance in *n*-butane oxidation to maleic anhydride (commercial application of this catalytic active phase) and to design new catalytic systems for alkane oxidation (*1*). In Part 1 of this work (*2*), the role of competitive adsorption phenomena between ammonia and oxygen on the selective behavior of VPO in propane transformation was discussed. A competitive adsorption between hydrocarbon and oxygen was also assumed (i) to explain the kinetics of 1-butene oxidation to maleic anhydride on VPO which shows a self-inhibition of the hydrocarbon on its rate of transformation to maleic anhydride (*3*), (ii) to explain the inhibition effects shown in C_4–C_5 alkane oxidation on VPO when small amounts of the corresponding olefins are cofed with the alkane (*4*, *5*), (iii) to interpret the dependence of the selectivity to propylene on propane on VPO when the propane-to-O_2 ratio in the inlet feed is changed (*1*), and (iv) to discuss some aspects of the deactivation/reactivation phenomena of commercial VPO catalysts for *n*-butane oxidation to maleic anhydride (*5*).

The presence of competitive adsorption phenomena is therefore a more general key for the interpretation of catalytic data for

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the surface reactivity of VPO in alkane oxidation. It should be mentioned that the catalytically active (020) surface of VPO is characterized by the presence of strong Lewis acid sites due to coordinatively unsaturated V^{4+} ions (*6*). The role of these unsaturated vanadium ions in activating oxygen species involved in the mechanism of selective alkane transformation to corresponding adsorbed alkene (Ref. (*1*) and references therein) and in further conversion of reaction intermediates up to maleic anhydride (*7*) has been suggested. On the other hand, the competition of molecules which are basic in nature such as olefins and ammonia for adsorption on these vanadium Lewis acid sites is reasonable. Therefore, a better understanding of the competitive adsorption phenomena during alkane transformation on VPO is fundamental in order to extend our knowledge on the unique surface chemistry and reactivity of VPO in alkane selective transformations.

The aim of the work reported here was to obtain more information on the nature of adsorbed species in ammonia and C_3 hydrocarbon aerobic and anaerobic interaction with VPO in order to gain a better understanding of the mechanism of propane transformation on VPO with preadsorbed ammonia and more generally of the key aspects of the surface chemistry–reactivity of this catalyst in alkane transformation.

EXPERIMENTAL

Catalyst

The VPO catalyst used was the same as that described in Part 1 of this work and was obtained in an organic medium with an activation procedure during the catalytic oxidation of *n*-butane (*2*).

Thermogravimetric Tests

Thermogravimetric tests of ammonia adsorption-desorption were carried out in a computer-controlled Perkin–Elmer 2C instrument in isothermal conditions and using a constant total flow of 6 liter/h. The VPO was ground before the tests; about 10 mg was used. The sample was conditioned in a helium flow up to constant weight at 450°C before each test. A flow containing 1% of anhydrous NH_3 in helium was used for adsorption tests, whereas a helium flow was used for desorption tests. For the latter tests, preadsorption of NH_3 was carried out at 400°C or 450°C with the 1% NH_3/helium flow up to constant weight. Before following the NH_3 desorption, gas phase ammonia was removed.

Infrared Data

Fourier-transform (FT-IR) spectra (resolution 2 cm^{-1}) were recorded with a Perkin–Elmer 1750 instrument in a cell connected to evacuation and gas manipulation grease-free lines. The cell is designed to allow work under vacuum, and static or continuous flow conditions. The self-supporting disk technique was used. Spectra were all recorded at room temperature after temperature equilibration and contribution of gas phase species had been subtracted. The usual pretreatment of the sample was in oxygen at 450°C for 2 h and then under vacuum for a further 4 h in order to clean the surface from adsorbed species. It has already been shown (*5*) that this type of pretreatment does not alter the surface reactivity and does not induce any surface oxidation of VPO. Adsorbate compounds were hyperpure products. Self-supporting disks (about 10–20 mg/cm^2) for infrared examination were prepared by pressing the samples at about 20,000 psi.

RESULTS

Thermogravimetric Tests of NH_3 Adsorption/Desorption

The amount of ammonia chemisorbed on $(VO)_2P_2O_7$ was determined at 400 and 450°C in thermogravimetric experiments using a constant flow containing about 1% of NH_3 in helium (Fig. 1a). Due to the reduced amount of the catalyst as compared to the gas flow, the ammonia concentration may be reasonably assumed constant with the time-on-stream. At 400°C, a limiting adsorp-

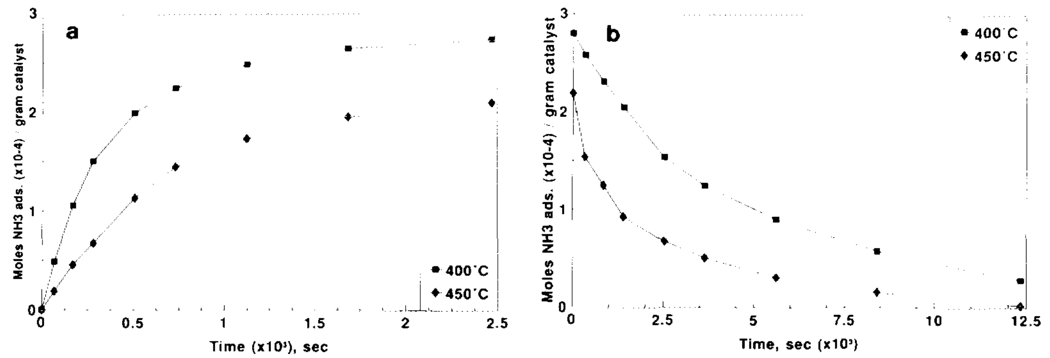


FIG. 1. Thermogravimetric tests of ammonia adsorption at 400 and 450°C in a flow of helium containing 1.1% NH_3 (a) and of consecutive desorption at the same temperature, but using a flow of pure helium (b). Before starting the desorption experiments, gas phase ammonia was removed.

tion value of around 2.7×10^{-4} moles of NH_3 per gram of catalyst is found, whereas at higher temperature (450°C) the limiting value is lower as well as the rate of adsorption. After reaching the limiting value, the flow was switched to a pure helium flow in order to analyze the rate of ammonia desorption from the catalyst. Results are reported in Fig. 1b. At 400°C, the rate of desorption is much lower than that at 450°C. It should also be noted that the rate of adsorption is higher than that of desorption for both reaction temperatures (compare Fig. 1a and Fig. 1b).

Infrared Characterization of Ammonia Adsorption

Figure 2 reports the infrared spectra of the adsorbed ammonia species detected in the 1350–1750 cm^{-1} region after interaction of the catalyst with ammonia for 15 min at different temperatures and subsequent brief removal of gas-phase ammonia by evacuation. The spectrum of the catalyst before ammonia interaction has been subtracted. The VPO catalyst was evacuated at 450°C before the adsorption of ammonia.

At room temperature ammonia interacts with the catalyst forming ammonium ions characterized by the sharp band at 1426 cm^{-1} [δ_{as} $(NH_4)^+$] and by the weaker band at about 1665 cm^{-1} [δ_s $(NH_4)^+$]. No resolved bands due to ν_{NH} vibrations in the 3000–3500 cm^{-1} region were detected. Increasing the temperature of interaction of ammonia with the catalyst up to 400°C increases the rela-

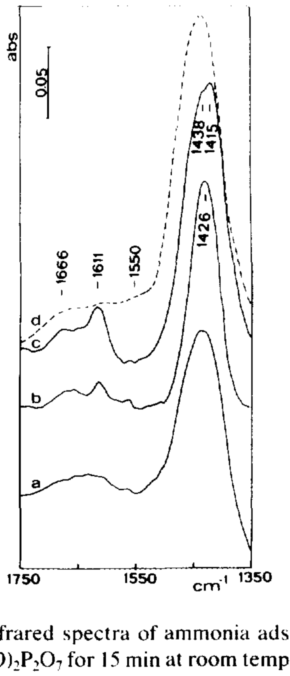


FIG. 2. Infrared spectra of ammonia adsorption (20 Torr) on $(VO)_2P_2O_7$ for 15 min at room temperature (a), at 200°C (b), and at 400°C (c) and subsequent brief evacuation to remove gas-phase ammonia. Spectrum (d) was obtained as for spectrum (c), but after consecutive admission of 20 Torr of O_2 to the IR cell. The background spectrum of the catalyst before adsorption has been subtracted. The spectra were all recorded at r.t.

tive intensity of a band centered at 1611 cm^{-1}, which can be assigned to δ_{as} of coordinated ammonia on vanadium Lewis acid sites (*8*). It should be noted that due to the presence of skeletal vibrations and cut-off of energy, bands below 1350 cm^{-1} cannot be observed and therefore the $\delta_S(NH_3)$ at about 1240 cm^{-1} cannot be detected. In addition, the band centred at 1426 cm^{-1} splits into two components centered at 1438 and 1415 cm^{-1}, due probably to a lowering of the symmetry of the $(NH_4)^+$ group for the bonding of the ammonium ion with an electron-donating centre. The splitting of this band into two or three components has been observed in various cases on transition metal oxides (*8*).

When O_2 is admitted to the catalyst after the interaction with ammonia at 400°C, the relative intensity of the band at 1611 cm^{-1} decreases, whereas a further not well resolved band may be observed at around 1550 cm^{-1}. This band may be assigned to an amido-like species $[(NH_2)^-]$ (*9*, *10*) which tentatively may derive from the abstraction of an H^+ from chemisorbed ammonia due to the presence of activated oxygen species such as $(O_2)^-$. Dissociative chemisorption of the ammonia, forming NH_2 and OH, on an acid–base pair of the $M^{n+}O^{2-}$ type such as occurs on MgO or on other oxides (*8*, *9*) may be ruled out, because the band at 1550 cm^{-1} appears only when O_2 is admitted to the catalyst. On the contrary, oxygen interaction with the catalyst after adsorption of ammonia at room temperature does not induce any change in the spectrum (Fig. 2a).

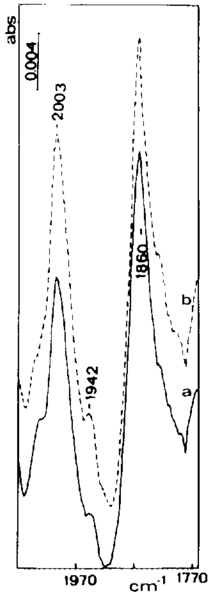


FIG. 3. Infrared spectra of the region of overtone bands of skeletal vibrations of vanadyl pyrophosphate before (a) and after (b) interaction with ammonia at 400°C for 15 min.

Reported in Fig. 3 are the infrared spectra of $(VO)_2P_2O_7$ in the 1760–2140 cm^{-1} region before and after contact at 400°C with ammonia. The bands present in this region correspond to the overtones of the skeletal vibrations of vanadyl pyrophosphate. In particular, the two stronger bands at 2003 and 1860 cm^{-1} may be assigned to combination bands of phosphate groups [$(\nu_{as}PO_3 + \nu_sPOP)$ and $(\nu_sPO_3 + \nu POP)$, respectively], whereas the weak, but well resolved band at 1942 cm^{-1} is assigned to $2\nu_{V=O}$ (*18*). Any change in these bands is observed upon interaction with ammonia, indicating that ammonia does not induce structural changes of vanadyl pyrophosphate.

Ammonia and Propylene Coadsorption

Two types of experiments were carried out, the first involved preadsorbing propylene and following the changes of the adsorbed species in contact with ammonia and the second, preadsorbing ammonia and following the changes of the adsorbed species in contact with propylene.

Figure 4 shows the changes of the adsorbed species in the first case. Propylene (100 torr) was adsorbed at room temperature (r.t.) for 3 h and after evacuation was put in contact with 20 Torr of NH_3 at different temperatures and times of contact. Spectrum (a) of Fig. 4 is the spectrum in the 1350–1800 cm^{-1} region of propylene adsorbed at r.t. for 3 h and subsequent evacuation, spectra (b)–(f) are for the adsorbed species after subsequent contact with NH_3

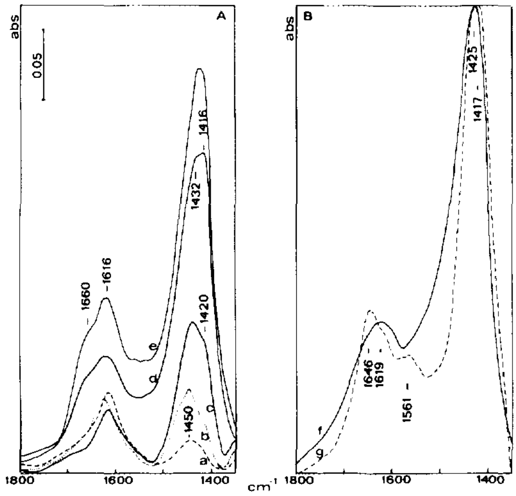


FIG. 4. Infrared spectra of the adsorbed species formed on vanadyl pyrophosphate after interaction of propylene (100 Torr) at r.t. for 3 h and subsequent removal of gas-phase species by brief evacuation (a) and after consecutive contact with ammonia (20 Torr) at r.t. (b), at 200°C for 15 min (c), at 400°C for 15 min (d), at 400°C for 40 min (e) and at 400°C for 80 min (f) and consecutive brief evacuation to remove gas-phase ammonia. Spectrum (g) was obtained as for spectrum (f), but after subsequent evacuation at 100°C for 15 min. The background spectrum of the catalyst before adsorption has been subtracted. The spectra were all recorded at r.t.

at r.t. (b), 200°C for 15 min (c), 400°C for 15 min (d), 40 min (e), and 80 min (f). The spectra were registered after a brief evacuation at r.t. to remove gas-phase species. Spectrum (g) of Fig. 4B, on the contrary, refers to the situation as in spectrum (f), but after evacuation at 100°C for 30 min. Figure 5 shows the spectra in the 1800–4000 cm^{-1} region for $(VO)_2P_2O_7$ after adsorption of propylene (a), and after subsequent contact with NH_3 at 400°C for 15 min (b), and for 80 min (c). The spectra of Fig. 5 are as recorded, whereas in those of Fig. 4 the contribution of the $(VO)_2P_2O_7$ sample before propylene adsorption has been subtracted.

Propylene adsorbed at r.t. on $(VO)_2P_2O_7$ is characterized by two main bands centered at 1616 and 1450 cm^{-1} with a shoulder at 1420 cm^{-1} (Fig. 4a) which may be attributed to $\nu_{C=C}$, δ_{CH_3}, and δ_{CH_2}, respectively. Very weak bands in the 2900–3100 cm^{-1} region were detected (Fig. 5a) due to $\nu{=}CH_2$, $\nu{=}CH$, and νCH_3 modes. The shift of about 34 cm^{-1} in $\nu_{C=C}$ as compared to gaseous propylene (1650 cm^{-1}) indicates the formation of a π-complex with a coordinatively unsaturated cation, reasonably V^{4+} (*8*).

After the $(VO)_2P_2O_7$ with preadsorbed propylene has been in contact with NH_3 (Fig. 4(b)–(e)), the band centered near 1450 cm^{-1} increases and shifts progressively to 1416 cm^{-1} due to the stronger contribution of δ_{as} of ammonium ions (see Fig. 2). The band centered at 1616 cm^{-1} also increases in intensity and a shoulder at 1665 cm^{-1} becomes progressively evident. The changes in the spectra can be reasonably interpreted as a progressive increase in the amount of ammonium ions (bands at 1416 and 1665 cm^{-1}) together with the presence of the π-bonded propylene. Due to the coincidence of the bands of coordinated ammonia and $\nu_{C=C}$ (1616 cm^{-1}) it is not possible to indicate clearly the presence of NH_3 coordinated to Lewis acid sites, but the increase in intensity of this band as compared to that of chemisorbed propylene (spectrum (a) of Fig. 4) is in agreement with this suggestion.

Evacuation at 100°C led to a considerable modification in the spectrum of the sample after interaction at 400°C of ammonia with the vanadyl pyrophosphate with preadsorbed propylene (Fig. 4B). In particular, the higher frequency asymmetric tail of the band at around 1420 cm^{-1} disappears and a clear new band appears at 1561 cm^{-1}. This band (δ_{NH_2}) may be assigned to a NH_2-type species and is found in various alkylamine complexes (*10*) or amines adsorbed on various oxides (*11*). In the absence of O_2, a similar evacuation procedure does not induce the appearance of this band in vanadyl pyrophosphate with only ammonia adsorbed, neither does this band appear when ammonia is put in contact at only 200°C with the catalyst with preadsorbed ammonia.

In the 2800–3600 cm^{-1} region (Fig. 5A) a series of new bands appears after the inter-

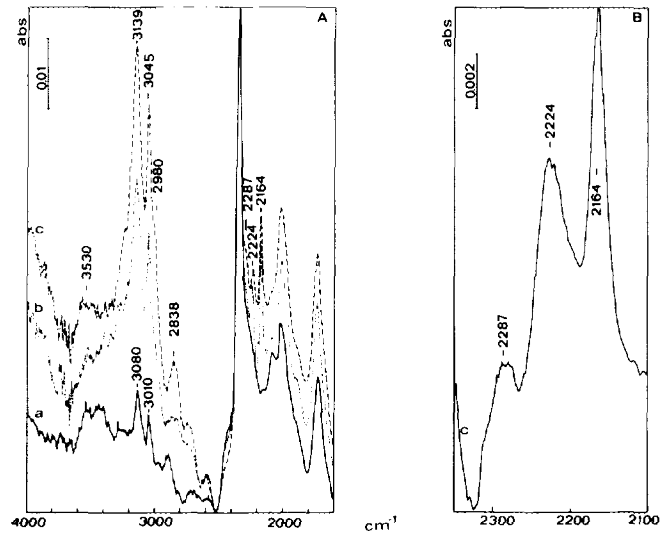


FIG. 5. (A) Infrared spectrum of the 1800–4000 cm^{-1} region of vanadyl pyrophosphate after evacuation and propylene preadsorption (a) and after consecutive contact with ammonia at 400°C for 15 min (b) or for 80 min (c) and subsequent brief evacuation to remove gas-phase ammonia. (B) Expansion of the adsorbed species detected in the 2100–2400 cm^{-1} region after propylene preadsorption and subsequent interaction of NH_3 at 400°C for 80 min. In this case, but not for the spectra of Fig. 5A, the background spectrum of the catalyst before adsorption has been subtracted. The spectra were all recorded at r.t.

action of NH_3 at 400°C with vanadyl pyrophosphate carrying preadsorbed propylene. In particular, a relatively intense band is found at 3139 and 3045 cm^{-1} with a possible shoulder at 2980 cm^{-1} and a weak band centered at 2838 cm^{-1}. The bands below 3050 cm^{-1} may be assigned to ν=CH$_2$, ν=CH, and νCH$_3$ vibration modes, whereas the stronger band at 3139 cm^{-1} falls at too high a frequency for an assignment to C–H vibrations. A reasonable interpretation for this band, however, is the ν_{as} mode of nearly free $(NH_4)^+$ and therefore the 3045 cm^{-1} band may also be assigned to the ν_s mode of ammonium ions which become IR active due to interaction with the surface. These bands become evident, however, only when NH_3 interacts at higher temperature (400°C) with $(VO)_2P_2O_7$, and therefore suggest an activated process of formation of the ammonium ions responsible for the bands in the 3000–3200 cm^{-1} region, notwithstanding the fact that the formation of ammonium ions also is detected after interaction at r.t. (Fig. 2). This interpretation is in agreement with the splitting of the band of ammonium ions near 1420 cm^{-1} after high-temperature interaction (Fig. 4). It should also be noted that these bands near 3000 cm^{-1} were not detected in the case of only ammonia interaction with the catalyst (Fig. 2), indicating a role of the coadsorbed propylene in the formation of the species of ammonium ion responsible for these bands.

In addition to the bands near 3000 cm^{-1}, three new bands centred at 2287 (weak and not well resolved), 2224, and 2164 cm^{-1} are overlapped by the stronger vibrations due to overtones of skeletal vibrations of vanadyl pyrophosphate (Fig. 5A). Figure 5B shows these bands after subtraction of the contribution of skeletal vibrations of the catalyst. It should be pointed out that apparently the relative intensity of these bands changes with the time in contact with ammonia, but since they are localized on the tail of a more intense band, clear conclusions cannot be derived. Certain assignment is not possible, but without doubt these bands must be associated with a product deriving from the coadsorption of propylene and ammonia because these bands were not observed after similar treatment, but without one of the two reagents, and can be removed after evacuation at 100°C. Acrylonitrile shows a main sharp band at 2230 cm^{-1} (fundamental ν_{CN}), a weaker band at 2283 cm^{-1} (Fermi resonance between fundamental and ν_{CC} + δ_{CH_2} combination vibrations), and an additional poorly resolved band at 2180 cm^{-1} presumably due to the overtone band of the in-plane CH_2 rocking mode (*12*). Coordination of acrylonitrile to the surface may shift or increase the relative intensity of these bands (*12*). In nitrile-to-metal bonding through the nitrogen lone-pair, the shift of ν_{CN} to higher frequencies is well known and may be used to study the Lewis acid strength (*13*). However, acrylonitrile may also be coordinated as a σ- or π-complex through the C=C double bond or through the C≡N triple bond (*12*). In the latter case, a shift toward lower frequencies as compared to the ν_{CN} frequency in not-adsorbed acrylonitrile (2230 cm^{-1}) may be expected, whereas, when acrylonitrile is coordinated as a π-complex through the C=C double bond, a slight shift to higher frequencies is expected (*12*). It should also be mentioned that two or three quite intense bands in this region have been observed for acetonitrile adsorbed in zeolites (*13*) in conditions where probably an adduct species may form. In conclusion, the two stronger bands observed in the 2100–2300 cm^{-1} region may be tentatively attributed to the ν_{CN} of weakly bonded acrylonitrile through C atoms of the C=C bond and of acrylonitrile coordinated through the C≡N triple bond, respectively, or to the formation of an adduct between two acrylonitrile molecules which gives rise to the appearence of two or three bands in the region examined (*12*, *13*). On the contrary, the formation of surface-bonded azides (three to five bands in the 2000–2300 cm^{-1} region) as suggested for high-temperature ammonia and methylamine interaction with copper/alumina samples (*14*, *15*) seems not to be reasonable in our case because the species disappear by evacuation at 100°C and form only when both propylene and ammonia are coadsorbed. The attribution of the band at 2164 cm^{-1} to coordinated CO also seems not to be reasonable, because other oxygenated products of surface complexes were not detected.

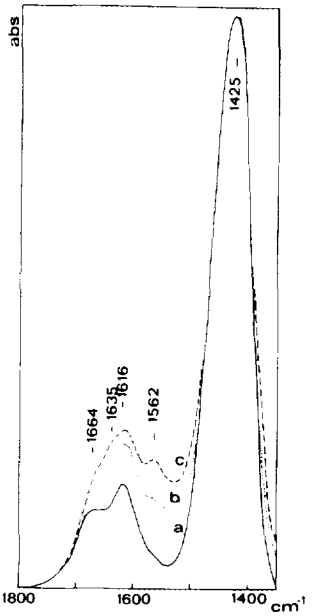


FIG. 6. Infrared spectra of the adsorbed species formed on vanadyl pyrophosphate after interaction of ammonia (20 Torr) at 400°C for 1 h and subsequent removal of gas-phase species by brief evacuation (a) and after consecutive contact with propylene (100 Torr) at 200°C for 30 min (b) and at 400°C for 200 min (c) and subsequent brief evacuation to remove gas-phase species. The background spectrum of the catalyst before adsorption has been subtracted. The spectra were all recorded at r.t.

Figure 6 shows the results obtained after preliminary adsorption of NH_3 (20 Torr) at 400°C and, after removal of gas-phase ammonia, contact with propylene (100 Torr) at r.t. (a), at 200°C for 30 min (b), and at 400°C for 200 min (c). The results are nearly the same as those obtained from preliminary propylene adsorption followed by ammonia interaction at various temperatures (see Fig.

4). The main difference is that in this case the growth of the band at 1562 cm^{-1} with increasing time and temperature of interaction of propylene with the vanadyl pyrophosphate with preadsorbed ammonia is more clearly evident. In addition, also in this case the bands near 3000 and near 2200 cm^{-1} discussed above also are present.

Changes in the Adsorbed Species Following Propane Interaction with $(VO)_2P_2O_7$ Carrying Preadsorbed Ammonia

The changes in the species formed in the interaction of propane in an infrared cell with $(VO)_2P_2O_7$ with preadsorbed ammonia was followed at 400°C as a function of the time in contact of the sample with a flow of helium containing about 6% propane and 7% oxygen. This composition is nearly equivalent to that used in flow reactor catalytic tests to analyze the development of the catalytic behavior of vanadyl pyrophosphate with preadsorbed ammonia in aerobic interaction with propane (*2*).

Infrared tests were made in order to analyze the changes in the adsorbed species by interaction of propane at 400°C in the absence of gaseous oxygen, but neither new bands nor changes in the spectrum of preadsorbed ammonia were observed. On the contrary, a clear change is observed when oxygen is cofed with propane (Fig. 7). In particular, in addition to the appearance of a not well resolved band near 1560–1580 cm^{-1} when oxygen is admitted to the catalyst after interaction with ammonia at 400°C (see Fig. 2), the intensity of which remains approximately constant as a function of the time in contact, the following changes are observed (Fig. 7): (i) the absorption band centred at 1650 cm^{-1} initially increases in intensity, but later decreases, (ii) the absorption band at 1425 cm^{-1} decreases continuously in intensity, and (iii) new bands appear at 1513, 1462, and 1370 cm^{-1}. The latter bands agree well with those found after acrylic acid adsorption on SnO_2 doped with Pd (*16*) and assigned to an acrylate species with the C=C double bond interacting with surface Lewis acidic sites.

The bands at 1513, 1462, and about 1370 cm^{-1} may thus be assigned to $\nu_{as}(COO)$, $\nu_s(COO)$, and $\delta(C\text{–}H)$ modes, respectively, whereas the absorption band centred at 1650 cm^{-1} is assigned to $\nu(C{=}C)$ in coordinated propylene or acrylic acid. As previously discussed, the bands at about 1560–1580 cm^{-1} may be assigned to the $\delta(NH_2)$ mode of an amido-like species and the stronger band centred at 1425 cm^{-1} to the δ_s mode of ammonium ions. The presence of other species such as surface acetate cannot be excluded on the basis of infrared spectra, because the relative bands are expected in the same region; however, the presence of acrylate is more consistent with the nature of the products of catalytic transformation (*2*). On the contrary, for adsorbed acrolein a band in the 1650–1720 cm^{-1} region is expected ($\nu_{C=O}$) and therefore the presence of acrolein may be excluded, at least as the predominating species.

DISCUSSION

Nature of the Ammonia Chemisorbed Species

Infrared data (Fig. 2) provide evidence that ammonia is chemisorbed on $(VO)_2P_2O_7$ both on Brønsted and Lewis acid sites, in agreement with previous data (*6*). However, the analysis of the change of the relative intensities of the bands of ammonium ions and coordinated ammonia as a function of the temperature of interaction with the catalyst shows that the relative amount of these species depends on this factor. Increasing the temperature of interaction increases the relative amount of ammonia coordinated on Lewis sites (unsaturated vanadyl ions) indicating that this is an activated process.

The coadsorption of other molecules also changes the nature of ammonia chemisorbed species. In fact, it should be observed that, notwithstanding the previous observation in $(VO)_2P_2O_7$ of a weak, but sharp band at 3660 cm^{-1} assigned to ν_{OH} of free P–OH groups (*6*), in this sample after

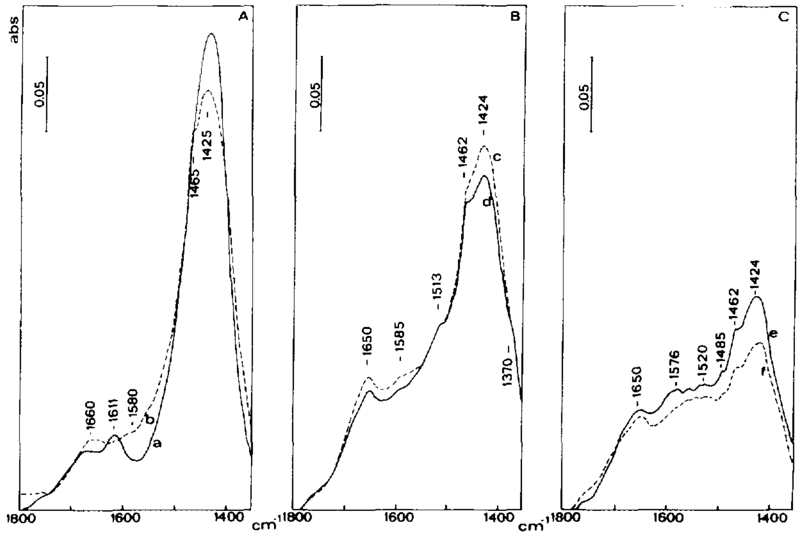


FIG. 7. Infrared spectra of the adsorbed species formed on vanadyl pyrophosphate after interaction of ammonia (200 Torr) at 400°C for 1 h and subsequent removal of gas-phase species by brief evacuation (a) and after consecutive contact at 400°C for different times with a flow of helium containing about 6% propane and 7% of oxygen: after 5 min (b), 10 min (c), 15 min (d), 60 min (e), and 80 min (f). The background spectrum of the catalyst before adsorption has been subtracted. The spectra were all recorded at r.t after brief evacuation to remove gas-phase species.

long-term catalytic tests no clear band in the 2600–4000 cm^{-1} region due to free OH groups is observed even after extended evacuation, but rather only a broad absorption band. Possibly because of the presence of residual strongly adsorbed hydrocarbon species (*1*, *5*) on the surface of the $(VO)_2P_2O_7$ sample used in these experiments (a sample activated in a flow of *n*-butane/air), no localized M–OH vibrations are detected. The hydrocarbon adsorbed species reasonably induce H bonding or enhance the mobility of the protons preventing the detection of free M–OH vibrations. For the same reason, no localized NH vibrations are detected in the 3300–3500 cm^{-1} region upon ammonia adsorption. However, when propylene is coadsorbed (Fig. 5A) with ammonia, new sharp bands are detected at 3139 and 3045 cm^{-1} assigned to the ν modes of nearly free $(NH_4)^+$. In parallel with this, a splitting of the band of ammonium ions near 1420 cm^{-1} is noted (Fig. 4). These observations indicate that the coadsorption of propylene modifies the localization or surface configuration of the chemisorbed ammonium ions.

According to a recent structural hypothesis of the surface structure of vanadyl pyrophosphate (*17*), probably the active surface of the catalyst is not flat, but rather active vanadium centers are localized on the bottom of cavities created from pendent pyrophosphate groups. Hydrocarbon or ammonia molecules coordinated on these vanadium sites are thus localized in the restricted environment deriving from these cavities and have the possibility of multiple bonds with the phosphate groups on the walls. This model can explain some of the anomalies observed in the spectra and discussed above, but present knowledge does not allow any more precise discussion.

The coadsorption of O_2 also modifies the nature of the ammonia chemisorbed species. In fact, when O_2 is admitted to the catalyst after interaction with ammonia at 400°C, the relative intensity of the band of ammonia coordinated on Lewis sites decreases and a new band is observed at around 1550 cm^{-1} attributed to an amido-like species $[(NH_2)^-]$. This species can derive from the abstraction of an H^+ from coordinated ammonia due to the presence of activated oxygen species or alternatively from the abstraction of 2 H^+ from ammonium ions and competition between oxygen and ammonia coordination on the Lewis sites. Gaseous oxygen may also induce a local oxidation of vanadium ions forming V^{5+} which is then responsible for H-abstraction from chemisorbed ammonia. It is not possible to clearly discriminate between these hypotheses, but it should be observed that when O_2 interacts with the catalyst with ammonia preadsorbed at room temperature (mainly ammonium ions) the band at 1550 cm^{-1} does not form.

Amount of Chemisorbed Ammonia Species

Thermogravimetric data (Fig. 1) show that the amount of NH_3 adsorbed at 400°C is about 2.7×10^{-4} moles. Assuming that the surface of the $(VO)_2P_2O_7$ is constituted preferentially by the (100) plane in agreement with various pieces of evidence (*18*), an ideal surface concentration of about 1.6×10^{-4} moles of P atoms per gram of catalyst may be estimated, on the basis of the 2-dimensional unit cell measurement (about 160 Å) and the surface area of the catalyst. However, in the real catalysts the pyrophosphate orientation is not ordered as in the ideal crystallographic model (*17*) and probably full pyrophosphate groups exist pending at the surface that may give $P–O–P(O)(OH)_2$ structure with double number of acid sites, in agreement with a mean P : V surface ratio of about 1.5 found using XPS measurements. These pyrophosphate groups pending at the surface can condense between them or not depending on various factors like the type of pretreatment. An estimation of the number of surface Brønsted sites is thus difficult. Experiments of selective K doping of the Brønsted acid sites of $(VO)_2P_2O_7$ have shown that the number of surface OH groups is about 1.5–2.0 times higher than the calculated value of P–OH groups based on a simple structural model of cutting the crystal unit at the (100) plane (*19*). Therefore, thermogravimetric data are in rough agreement with the possible estimated number of P–OH surface groups taking into account of the limits of this estimation discussed above and suggest that at 400°C almost all sites are occupied by adsorbed ammonia.

The adsorption of ammonia is completely reversible (Fig. 1B), but the rate of desorption is lower than that of adsorption. The complete reversibility in helium suggests that NH_3 does not react with surface sites to form irreversible species as expected when vanadyl groups (V=O) form imido groups (V=NH). In agreement with these data, no changes in the overtone of V=O vibrations are observed (Fig. 3). The amount of surface V=O groups with respect to the bulk is about 3–5% for a specimen with about 20 m^2/g of surface area, but overtone modes are more sensitive to alterations in the surface structure. The detection of possible changes is thus rather difficult, but the absence of modifications is in agreement with the thermogravimetric data indicating the absence of irreversible surface changes. In addition, the analysis of the IR overtone region (Fig. 3) indicates the absence of bulk modification after ammonia adsorption.

Mechanism of Acrylonitrile Synthesis in the Absence of Gaseous Oxygen

Propylene is adsorbed on $(VO)_2P_2O_7$ as a π-complex with a coordinatively unsaturated cation, reasonably V^{4+} (Fig. 4a). There is no evidence of formation from anaerobic propylene interaction with $(VO)_2P_2O_7$, of isopropoxy, acetate, carboxylate, acetone, or other O-containing surface species. These species are detected after anaerobic interaction of propylene at room temperature with various V-containing catalysts (*8*) such as V-TiO_2 (*20*) or V-SnO_2 (*21*). This indicates the very limited ability of the vanadyl pyrophosphate in O-insertion reactions in comparison with other

V-based oxidation catalysts and implies possible differences in the reaction mechanism on $(VO)_2P_2O_7$ as well as being one of the reasons for the particular selectivity of vanadyl pyrophosphate in alkane oxidation.

When ammonia and propylene are coadsorbed at high temperature (Figs. 4 and 6) a new band is observed at 1562 cm^{-1} attributed to the δ_{NH_2} mode in propylamine and three bands near to 2200 cm^{-1} attributed to differently coordinated acrylonitrile species. At room temperature, on the contrary, these bands are not present. Furthermore, no significant differences are noted when ammonia is adsorbed on a catalyst with preadsorbed propylene or the contrary. This indicates that a reaction between both adsorbed species occurs and that this is a process activated by the temperature. It may therefore be tentatively suggested that at high temperature chemisorbed ammonia is dehydrogenated and reacts with π-bonded propylene to form propylamine. Further dehydrogenation of this species leads to the final formation of acrylonitrile. Therefore, the reaction mechanism suggested from IR data of acrylonitrile formation on $(VO)_2P_2O_7$ in the absence of gaseous oxygen involves only H-abstraction steps and not steps of O-insertion in the hydrocarbon molecule.

Role of O_2 in the Formation of Acrylonitrile from Propane

When gaseous oxygen is present, analysis of the adsorbed species in the adsorption or coadsorption of ammonia and C_3 hydrocarbons suggests that a different mechanism of acrylonitrile synthesis occurs on vanadyl pyrophosphate. In anaerobic conditions only H-abstraction steps are involved with the formation of propylamine as a reaction intermediate, whereas in the presence of O_2 a reaction between a surface acrylate and chemisorbed ammonia probably occurs. The second mechanism appears to be much more efficient, according also to the catalytic results (*2*).

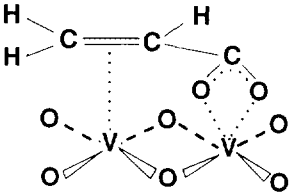
The changes which occur in the adsorbed species on vanadyl pyrophosphate with preadsorbed ammonia in contact with the flow containing propane and oxygen (Fig. 7) may be interpreted as follows: (i) oxygen interacts with coordinated ammonia forming a partially dehydrogenated species (NH_2) which, however, reacts more slowly as compared to ammonium ions, and (ii) oxygen induces the oxidative dehydrogenation of propane to propylene and its further transformation to a surface acrylate species. Since there is a parallel decrease in the intensity of the bands due to ammonium ions and acrylate species, it is reasonable to assume that the formation of acrylonitrile on this catalyst involves the surface reaction between acrylate and ammonium ions to form acrylonitrile and two molecules of water. This mechanism is consistent with the observation that a carboxylic acid such as methacrylic acid may form the corresponding nitriles by reaction with the ammonium salt of 12-molybdophosphoric acid (*22*).

An alternative hypothesis for the mechanism is that adsorbed oxygen species react with NH_4^+ to give NH_2 groups able to react with acrylate, so that when such NH_2 species are accumulated in enough quantity the latter reaction dominates and acrylonitrile begins to decrease. NH_2 would behave as a reaction intermediate with its concentration remaining stationary or slowly decreasing and therefore also this mechanism is in agreement with the experimental results. It should be observed that the reaction of an electron-deficient N atom such as in the ammonium ion with the electron-deficient C atom in the acrylate is not likely and the involvement of the electron-rich N atom in an amide-like species is more reasonable. On the other hand, an equilibrium exists at 400°C between ammonia coordinated on Lewis and Brønsted sites and therefore it is not possible to discriminate between the two hypotheses for the reaction mechanism.

It should also be noted that no new oxygen-containing species is observed in the infrared spectra also for the longer times in contact (Fig. 7f). This suggests that acrylates are reaction intermediates to acrylonitrile, but also to carbon oxides, when ammonium ions are no longer available.

When anaerobic experiments of coadsorption of propane and ammonia are performed, no new species such as chemisorbed propylene or acrylate are detected. The presence of gaseous oxygen thus has two main roles in enhancing the selective transformation of propane to acrylonitrile. It induces the oxidative dehydrogenation of propane to propylene and the transformation of this species to a surface acrylate. The latter species may quickly react with chemisorbed ammonia species to form acrylonitrile, but, when ammonium ions are no longer present, may be further transformed to carbon oxides. This double effect and the possible competition of ammonia and oxygen adsorption on the same sites may explain the observed dependence of the surface reactivity as a function of the amount of chemisorbed ammonia (*2*). However, it is not possible to discriminate in these experiments between a direct role of gaseous oxygen species in the steps discussed above and an indirect role in the oxidation of some V sites which are then involved in the reaction mechanism. Experiments using a V^{5+}-phosphate phase (*2*) are in favor of the first hypothesis, but they are not conclusive because the pretreatment with ammonia may have induced a complete reduction of the surface V^{5+} sites. Further experiments using labeled O_2 molecules may clarify this aspect.

A further aspect is that acrylate species were detected, but adsorbed acrolein was not. In flow reactor tests, Te-doped vanadyl pyrophosphate shows some selectivity in propane transformation to acrylic acid (*23*), but also in this case the formation of acrolein was not detected. These observations, even though not conclusive, suggest that acrylate species form directly from the π-bonded propylene without apparent intermediate formation of acrolein. The proposed model of surface acrylate formed on vanadyl pyrophosphate consistent with IR data is shown in Scheme 1. Tentatively, a propylene intermediate is chemisorbed on coordinatively unsaturated vanadyl ions forming a π-complex. The nearby V=O group abstracts 2 H from the methyl group forming water. The remaining H is abstracted from the adjacent oxygen of phosphate groups, whereas gaseous oxygen reacts with the reduced vanadium to form an η-peroxo species (*7*). The latter reacts with the C atom of the methyl group of propylene giving the adsorbed acrylate species shown in Scheme 1. This tentative mechanism is rather speculative and deserves much more experimental data for its demonstration, but is in agreement with the various experimental observations. In particular, it can explain the difference between a mechanism of only H-abstraction in the absence of gaseous oxygen and of formation of acrylate when gaseous O_2 is present.



Scheme 1. Model of acrylate species formed on vanadyl pyrophosphate.

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