JOURNAL OF CATALYSIS **106**, 471–482 (1987)

Oxidation and Ammoxidation of Toluene over Vanadium–Titanium Oxide Catalysts: A Fourier Transform Infrared and Flow Reactor Study

GUIDO BUSCA,*[1] FABRIZIO CAVANI,† AND FERRUCCIO TRIFIRÒ†

Istituto di Chimica, Facoltà di Ingegneria, Università di Genova, Fiera del Mare, Pad. D, 16129 Genova, Italy; and †Istituto di Tecnologie Chimiche Speciali, Facoltà di Chimica Industriale, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

Received December 11, 1986; revised February 17, 1987

A Fourier transform infrared (FT-IR) study of the adsorption of toluene, and of some possible intermediates in its oxidation and ammoxidation, has been carried out on a monolayer vanadia–titania catalyst with and without preadsorbed ammonia in the presence and in the absence of gaseous oxygen at temperatures between 300 and 600 K. The results are discussed in relation to those obtained by ammoxidation of toluene and other methylaromatics in a tubular flow reactor. An intermediate, formed on the clean surface at room temperature, is identified as an adsorbed benzyl species probably having a radical character. Its oxidation produces benzaldehyde, adsorbed benzoates, and maleic anhydride. The coadsorption of toluene and ammonia produces adsorbed benzylamine, which is also observed as a by-product in the flow reactor at low oxygen and ammonia partial pressures, and benzonitrile. Based on these data a mechanism for both oxidation and ammoxidation is proposed and discussed. © 1987 Academic Press, Inc.

INTRODUCTION

Vanadium–titanium oxide catalysts are widely used in industry for the production of phthalic anhydride by *o*-xylene oxidation (*1–3*). They have been shown to be useful also for the selective oxidation and ammoxidation of other methylaromatics (*4–9*). Recently their performances in toluene oxidation (*5–7*) and ammoxidation (*6, 8, 9*) have been reported.

The optimal catalyst performance seems to be developed by vanadia monolayers supported on bulk anatase (*2, 3, 5*) and these may constitute the active phase also on catalysts produced by coprecipitation methods (*9*). The nature and chemistry of these monolayers have been the object of our previous investigations (*10, 11*). Mechanisms of the oxidation and ammoxidation of methylbenzenes have been proposed in the literature (*9, 12, 13*), and IR studies have also been published (*14, 15*).

In this paper we report the results of a Fourier transform infrared (IR) study of the adsorption of toluene and its coadsorption with oxygen and ammonia at different temperatures on a monolayer vanadia–titania catalyst. The spectroscopic results are discussed in relation to those obtained in a flow reactor in the ammoxidation of toluene and some substituted toluenes. The aim was to verify the previously proposed mechanisms and to obtain a deeper characterization of the catalytically active phase.

EXPERIMENTAL

Vanadium–titanium oxide monolayer catalysts were prepared by dry impregnation of Degussa P25 TiO_2 (anatase 80%, rutile 20% from XRD, surface area 53 m^2/g from N_2 adsorption) with a boiling water solution of ammonium metavanadate (Carlo Erba, Milano), followed by drying and calcination in air at 720 K for 3 h. The loaded amount was 10% as V_2O_5 by weight, slightly higher than that needed to complete the monolayer. The dispersion of the sup-

---

[1] To whom correspondence should be addressed.

0021-9517/87 $3.00

ported phase was tested by CO adsorption, as reported in Ref. (*16*), and it was confirmed that the support surface still exposed was negligible. X-ray diffraction (XRD) and IR analyses showed that bulk V_2O_5 was present, if at all, in negligible amounts. The resulting surface area of the catalyst was 48 m^2/g.

For the adsorption experiments the catalyst powder was pressed into self-supporting disks and activated by evacuation in the IR cell at 720 K for 2 h. As discussed elsewhere (*10*), such a treatment causes a slight reduction of the vanadia phase together with a complete cleaning of the surface of adsorbed water and impurities.

Toluene, benzaldehyde, and benzyl alcohol (Carlo Erba, Milano) were purified by multiple freeze–pump–thaw cycles before evaporation to carry out adsorption from gas phase. Ammonia was taken from commercial cylinders obtained from Baker (Phillipsburg). The IR spectra were recorded with a Nicolet MX1 Fourier transform instrument, connected to conventional gas-manipulation/evacuation ramps and IR cells operating at variable temperature and with subtraction of the gas-phase spectra.

Catalytic experiments were carried out in a tubular fixed-bed flow reactor (diameter 4.1 mm) at atmospheric pressure under the same conditions as reported in Refs. (*6, 8, 9*). Usual feed concentrations (partial pressures) were aromatics 0.0117 atm; NH_3 0.075 atm; O_2 0.135 atm; He (to total 1 atm); flow rate 1.4 cm^3/s.

RESULTS

(*a*) *Toluene Adsorption and Oxidation*

The room temperature (r.t.) adsorption of toluene on the activated sample produces adsorbed species whose spectrum is reported in Fig. 1a. Evacuation at r.t. causes the desorption of weakly held toluene (mainly characterized by several strong bands in the νCH region and by the more intense ring vibrations at 1604 and 1494 cm^{-1} (*17*)) but leaves on the surface strongly adsorbed species responsible for intense bands in the region below 1700 cm^{-1} and very weak ones in the νCH region (Fig. 1b). Further heat treatment even under evacuation causes the transformation of the adsorbed species; the spectrum (Fig. 1c) is now dominated by strong absorptions in the regions 1600–1500 cm^{-1} and 1450–1400 cm^{-1}, typical of carboxylate ions. This indi-

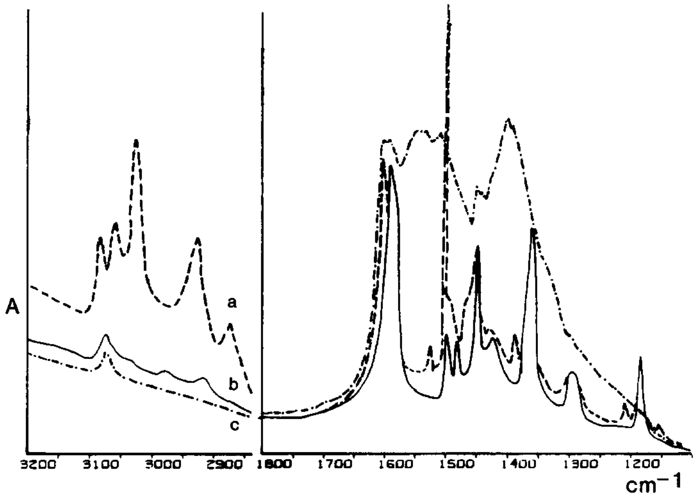


FIG. 1. FT-IR spectra of toluene adsorbed on a vanadia–titania monolayer catalyst (a) at room temperature (r.t.), (b) after evacuation at r.t., and (c) after heating at 570 K *in vacuo*.

cates that toluene adsorption produces an irreversibly adsorbed species that further transforms into carboxylates by oxidation at the expense of the oxidized surface sites of the catalyst. Some typical bands in this spectrum, such as the νCH at 3070 cm^{-1}, the two sharp bands near 1600 cm^{-1} (8a and 8b phenyl ring stretchings), and the weaker band at 1450 cm^{-1} (ν19b), allow us to identify the presence of benzoate ions (*18*), although the complexity of the very strong asymmetric and symmetric stretchings of the carboxylate group suggests that other carboxylates are very probably present.

The observed frequencies of the intermediate species formed at r.t., summarized in Table 1, indicate that this compound retains the intact aromatic ring. The aromatic ring vibrations of the monosubstituted benzenes in the region 1600–1100 cm^{-1} (*19*) are in fact very evident. This indicates that reaction occurred on the methyl group. This is confirmed by the further development into benzoate ions by heating. The detection of bands in the 3000- to 2800-cm^{-1} region (CH stretching), although weak, as well as of additional bands in the region below 1700 cm^{-1} (CH deformation), indicates that decomposition of the methyl group is incomplete. However, the absence of strong bands at appropriate frequencies and the difference with respect to the spectra obtained by adsorption of benzaldehyde and benzyl alcohol (see Fig. 2) seems to exclude the formation of oxygen-containing species.

The strength of the band at 1362 cm^{-1} reminds us of the spectrum obtained by reaction of toluene at room temperature on the surface of iron oxide (*20*), characterized by a strong band at 1390–1369 cm^{-1} and assigned to an adsorbed benzyl species. The general spectrum is in fact consistent with that of metal-benzyl species reported in the literature (*21–23*), as shown in Table 1. The bands at 1428 and 1362 cm^{-1} could be due to scissoring and wagging modes of a perturbed methylene group, whose corresponding stretchings are very reasonably placed at 2980 and 2930 cm^{-1}. The relatively strong band near 1300 cm^{-1} might be assigned to the Ar–C stretching or to the twisting mode of methylene. Thus, the identification of the intermediate species as adsorbed benzyl, suggested on chemical grounds, is also reasonable from the spectroscopic point of view.

The adsorption of toluene at 520 K after

TABLE 1

Observed Wavenumbers (cm^{-1}) of the Intermediate Product of Toluene Adsorption and Comparison with Metal–Benzyl Species

Toluene ads. on V–Ti–O	Bz_2SnCl_2 (Ref. (*19*))	BzHgCl	BzCl	Assignments (Ref. (*20*))
		(Ref. (*20*))		
3075		3082		
		3062		νCH (phenyl)
		3028		
2980		2982		
				νCH (methylene)
2930		2940		
1592,1586	1602,1585	1597,1581	1604,1585	8a, 8b
1497,1485	1498	1493	1497	19a
1452	1454	1454	1456	19b
1428	1411	1416	1445	δCH_2
1362	—	1117	1264	ωCH_2
1298	1210	1212	1209	νAr–C
1187	1185	1182	1183	9a

Note. Bz = benzyl.

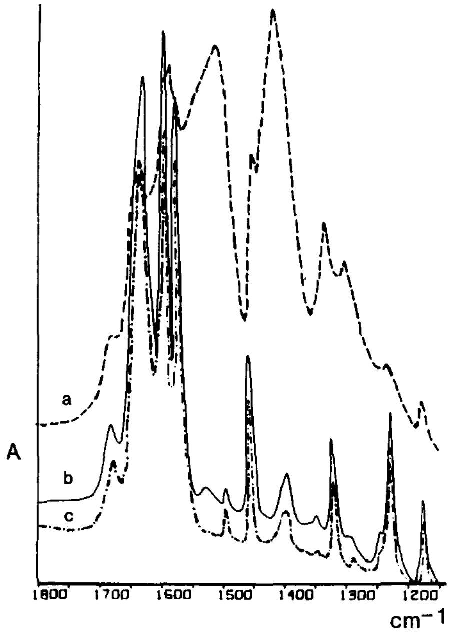


FIG. 2. FT-IR spectra of adsorbed molecules on a vanadia–titania monolayer catalyst: (a) toluene at 520 K, (b) benzaldehyde at r.t., and (c) benzyl alcohol at r.t.

the above-mentioned activation treatment produces species whose spectrum is reported in Fig. 2*a*. Our results are very similar to those reported recently by van Hengstum *et al.* (*15*) in an *in situ* study. The main features are completely consistent with the spectrum of benzoate ion (*14, 18*). Thus at high temperature, complete oxidation of the methyl group is obtained. However, additional bands are also present at 1635 cm^{-1} with shoulders at 1670 and 1330 cm^{-1}. Bands in almost exactly the same position ($\nu C{=}O$ and δCH (*24*)) are observed after adsorption of benzaldehyde at room temperature (Fig. 2b). Under these conditions benzaldehyde is probably coordinated on the Lewis acid sites, without chemical transformation (*11*), although the splitting of $\nu C{=}O$ indicates that it is adsorbed at two different sites or in two different conformations. It is worth noting that almost exactly the same spectrum may also be obtained by adsorption of benzyl alcohol at room temperature (Fig. 2c), showing that at 300 K the alcohol is oxidized quickly to benzaldehyde, while the aldehyde is stable as such. Benzyloxy species might then be intermediates in the oxidation of toluene to benzaldehyde and benzoic acid, but cannot be detected spectroscopically at room temperature.

The above data indicate that both benzaldehyde and benzoate species are formed by high-temperature adsorption of toluene on vanadia–titania in the absence of gaseous oxygen. To determine whether the benzyl intermediate, detected at r.t., may act as an intermediate in the selective oxidation, and if the presence of gaseous oxygen has a detectable effect, we have progressively heated a sample in an oxygen atmosphere where this intermediate was previously produced by toluene adsorption at r.t., followed by evacuation to desorb weakly held toluene. At 420 K (Fig. 3b) the above bands at 1635 and 1670 cm^{-1} are apparent, showing that benzaldehyde is indeed also formed starting from the benzyl intermediate. In these conditions a further

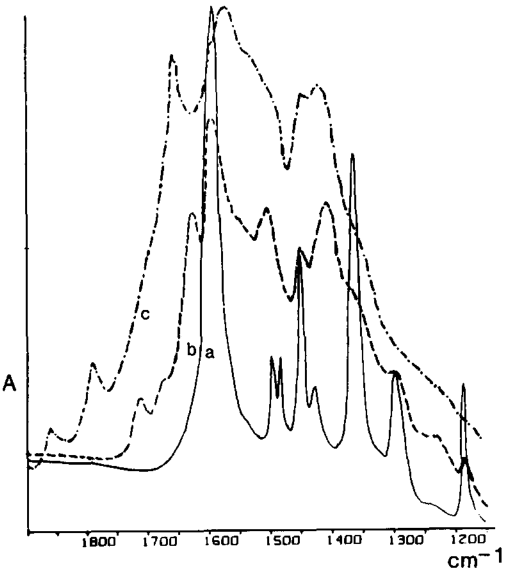


FIG. 3. FT-IR spectra of toluene adsorbed on a vanadia–titania monolayer catalyst: (a) after adsorption at r.t. and evacuation at r.t., and (b) after subsequent heating in O_2 (300 Torr) at 420 K and (c) at 570 K.

νC=O band is observable at 1710 cm^{-1}. Further heating in oxygen (Fig. 3c) causes, together with the appearance of strong bands due to carboxylates, the formation of two bands at 1860 and 1790 cm^{-1}, typical of cyclic anhydrides (*25*) and very probably due to maleic anhydride produced by degradation of the phenyl ring. It is also remarkable that the spectrum obtained by heating the benzyl intermediate (both with and without oxygen in the gas phase) is more complex than that obtained by direct adsorption of small amounts of toluene at high temperature, showing the presence of at least two types of carboxylate ions (as deduced by the complexity of the $\nu_{as}CO_2^-$ and $\nu_sCO_2^-$ bands). According to the formation of maleic anhydride, it is reasonable to propose that C_4 carboxylates may also be formed. This evidence allows us to propose that the reaction of the benzyl species, possibly bonded to vanadium centers through the π-electron cloud or in a η^3 coordination (*21*), may alternatively produce oxidation of the methyl group, giving successively benzaldehyde and benzoate ions, possibly through previous formation of benzyloxy species (reaction predominant at 470 K under our conditions) or of the phenyl ring, producing C_4 carboxylates and, in the presence of oxygen, maleic anhydride.

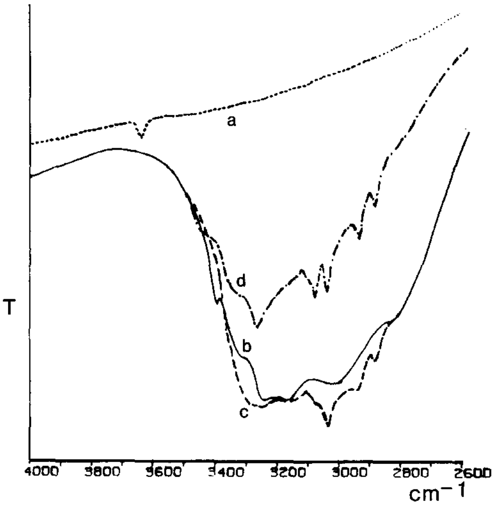


FIG. 4. FT-IR spectra of a vanadia–titania monolayer catalyst (a) after activation, (b) after heating in an ammonia atmosphere (100 Torr) at 570 K for 1 h, and subsequent evacuation at r.t., (c) after successive contact with toluene vapor ($P < 1$ Torr) at r.t., and (d) after contact with toluene vapor ($P = 5$ Torr) at 470 K.

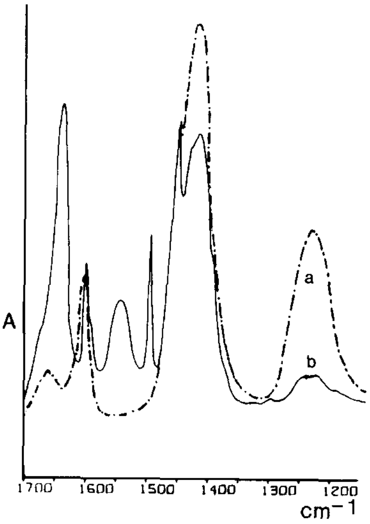


FIG. 5. FT-IR spectra of (a) ammonia adsorbed on a vanadia–titania monolayer catalyst at 570 K and (b) after successive contact with toluene vapor ($P = 5$ Torr) at 470 K.

(*b*) *Toluene-Ammonia Coadsorption*

The adsorption of ammonia at room temperature on vanadia–titania monolayer catalysts has been the object of a previous study (*11*). According to investigations from other laboratories (*26, 27*), it was found that ammonia is adsorbed both as such, coordinated to Lewis acid sites, and as ammonium cations by reaction with acidic νOH groups, and its presence causes a perturbation of surface vanadyl groups (*11*). In the present study we have also investigated the adsorption of ammonia at higher temperatures, up to 670 K, without any substantial change in the spectra of the surface species (Figs. 4b, 5a, and 6a). In particular we do not observe any evidence of the formation of amido or of the M=NH imido surface species, hypothesized as an

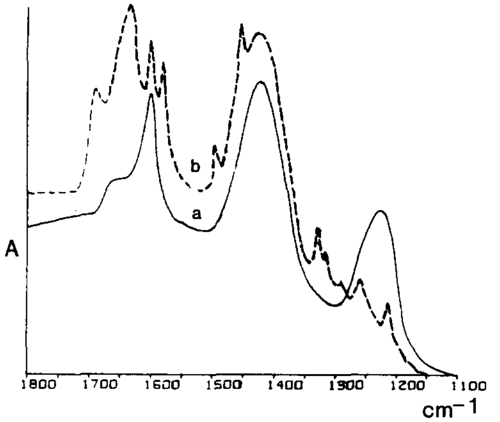


FIG. 6. FT-IR spectra of (a) ammonia adsorbed on a vanadia–titania monolayer catalyst at 570 K and (b) after successive contact with benzaldehyde (P = 1 Torr) at r.t.

active species in ammoxidation reactions (*28*).

Adsorption of toluene at room temperature on an ammonia-covered surface results in the appearance of the bands typical of toluene adsorbed as such in the 3100- to 2800-cm^{-1} region (νCH's; Fig. 4c) as well as in the ring-stretching region (1650–1300 cm^{-1}). Simultaneously a perturbation is observed of the νNH bands of chemisorbed ammonia (that at 3390 cm^{-1} is clearly displaced; Fig. 4c) and, surprisingly, an inverse change of the intensities of the deformation bands of ammonium cation (1420 cm^{-1}), which increases slightly, and chemisorbed ammonia (1235 cm^{-1}), which decreases slightly. Contact of such an ammonia-covered surface with toluene vapor at 470 K causes almost the complete disappearance of the bands due to chemisorbed ammonia (the symmetric deformation band at 1230 cm^{-1} is completely suppressed; Fig. 5b) and the partial decrease of that of ammonium cations, together with the appearance of the spectrum of a new compound, stable to evacuation. Such a compound is characterized by strong bands at 3340 (shoulder), 3260, and 1642 cm^{-1}, which may be due to the stretchings and deformation of an NH_2 group. Further bands at 3060, 3040, 1602, 1592, 1496, and 1452 cm^{-1} show that this compound again retains the aromatic ring, while further absorptions at 2930, 2865, 1438, and 1385 cm^{-1} would also indicate the presence of an aliphatic methylene group. The overall spectrum is consistent with that of adsorbed benzylamine (*29–31*). Under such conditions a very weak band is also observed at 2270 cm^{-1}, which is very probably due to adsorbed benzonitrile (νCN at 2240 cm^{-1} (*32*), further enhanced by adsorption on electron-withdrawing centers) present in small amounts due to its almost complete desorption at 470 K, while the further broad band near 1540 cm^{-1} could be due to small amounts of carboxylates or to a protonated form of benzylamine.

To have more data, the adsorption of benzaldehyde on ammonia-covered surfaces has also been investigated (Fig. 6). Under such conditions, as expected, the spectrum of the intermediate compound benzylamine is not observed. However, also in this case coordinated ammonia (bands at 1610 and 1230 cm^{-1}) substantially disappears, while bands due to coordinated benzaldehyde are formed (in such a case the band at 1670 cm^{-1} is shifted at 1690 cm^{-1}, and is relatively increased in intensity). Coordinated benzonitrile is also present in very small amounts (νCN band at 2270 cm^{-1}).

(*c*) *Flow Reactor Studies*

Figure 7 reports typical toluene conversions, benzonitrile yields, and selectivities of carbon products obtained on the vanadia–titania catalyst in the ammoxidation as a function of reaction temperature. Toluene conversion reaches 100% at 610 K, a slightly higher temperature than that obtained for 100% conversion in the absence of ammonia (about 570 K (*5, 6*)). This is evidence for the inhibiting effect of ammonia with respect to toluene oxidation (*6*). The yield of benzonitrile reaches a maximum at the same temperature (610 K). However, the trend of the selectivities of

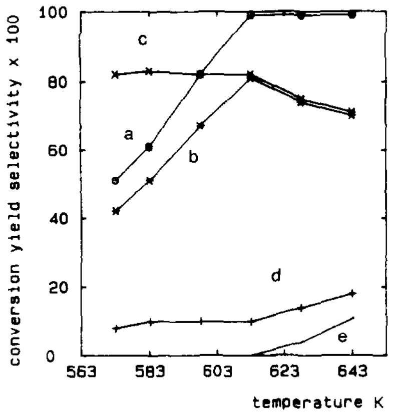


FIG. 7. (a) Toluene conversions, (b) benzonitrile yields, and (c–e) selectivities of the carbon products, benzonitrile (c), CO_2 (d), and CO (e).

the main carbon products, almost constant in the temperature range where conversion increases from 50 to 100%, indicates that the increase of the benzonitrile yield up to 610 K is due to the increase in conversion. In this temperature range, the constant benzonitrile selectivity (about 82%) is then a measure of the relative rates of the competitive oxidation and ammoxidation pathways. At higher temperatures, selectivity and yield of benzonitrile decrease due to the unavailability of ammonia, whose oxidation to N_2 and N_2O becomes significant.

The controlling effect of the availability of ammonia on the benzonitrile yield is evident from Fig. 8, where productivities in benzonitrile and carbon dioxide are reported as a function of ammonia partial pressure. The increase of ammonia concentration decreases the overall reactant depletion in the whole range, according to the inhibiting effect cited above on toluene conversion. Moreover, the selectivity in benzonitrile strongly increases with a corresponding decrease of CO_2 formation. Thus, the selective ammoxidative route becomes prevailing over the nonselective oxidative route. The benzonitrile productivity shows a maximum at a concentration slightly higher than that of the stoichiometric requirement. As expected, at very low ammonia concentrations the oxidation products, including benzaldehyde, are observed.

To detect intermediates in the ammoxidation pathway, experiments were also carried out at reduced oxygen pressure. Under these conditions nonnegligible amounts of benzylamine were detected. To obtain further data on the reaction mechanism, possible intermediates of the ammoxidation reaction, such as benzaldehyde, benzoic acid, and benzylamine, were fed together with the usual ammonia/oxygen mixture, and their conversion and the resulting benzonitrile selectivities were measured (Table 2). At 593 K all of the cited compounds exhibited 100% conversion, but, although selectivities of benzonitrile starting from benzaldehyde and benzylamine were similar or higher than those obtained from toluene, that obtained starting from benzoic acid was definitely smaller. These results indicate that all of these compounds may act as intermediates in benzonitrile synthesis, but that the pathway involving benzoic acid would be secondary.

The relative rate of ammoxidation of different substituted toluenes was also mea-

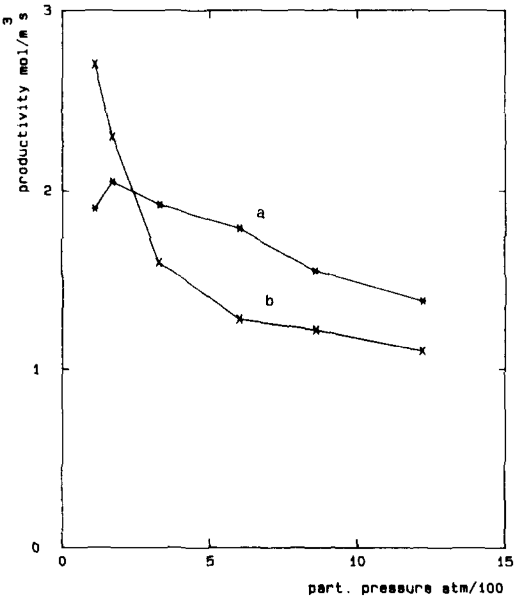


FIG. 8. Dependence of the productivities of benzonitrile (a) and CO_2 (b) on the ammonia partial pressure.

TABLE 2

Conversions and Selectivities Obtained by Feeding Possible Reaction Intermediates in the Reactant Mixture (NH_3 + O_2) at 593 K

Reactant	Conversion	Selectivity to benzonitrile
Benzaldehyde	100	95
Benzoic acid	100	50
Benzylamine	100	75
Toluene	60	82

sured, in order to obtain data on the mode of activation of the hydrocarbon compound. The results are reported in Table 3. It is evident that all of the substituted toluenes, both with electron-withdrawing and electron-donating substituents, are more active than unsubstituted toluene, although the observed differences are low. This result seems to be sufficient to rule out an ionic mechanism of hydrocarbon activation. In the case of an ionic mechanism, in fact, strong differences are expected between the reactivity of toluenes substituted with electron-withdrawing and with electron-donating substituents, which are instead both slightly activated with respect to toluene in our case (*33*). According also to recent data of Grasselli and co-workers (*34*) as well as in the opinion of Germain and Laugier (*13*) concerning toluene oxidation, a radical-like mechanism is very probably operating, for which an activation effect is expected both from electron-withdrawing and electron-donating substituents (*35*).

DISCUSSION

(*a*) *Mechanism of Toluene Oxidation and Ammoxidation*

As reported previously, the selective oxidation of toluene may be carried out on vanadia–titania catalysts at 500–700 K. Almost complete toluene conversion may be obtained at near 570 K, the maximum selectivity in benzoic acid being near 540 K (*5, 6*) with benzaldehyde and maleic anhydride as the main by-products, although a great number of other by-products have also been observed (*5, 12*). At higher temperatures, total combustion becomes predominant.

The behavior of toluene ammoxidation, producing benzonitrile and CO_2 as the main carbon-containing products, although benzylamine and benzaldehyde may also be observed as predominant by-products at very low conversions, is shown in Fig. 7. The surface chemical reactions we observed spectroscopically under our conditions take place at a temperature lower than, or similar to, that of the catalytic reactions. The spectra recorded at high temperature are very similar to those reported recently in a FT-IR *in situ* study (*15*), although the milder conditions of our study may be more appropriate to simplify the situation and provide evidence for possible labile intermediates. Accordingly, the adsorbed species we observed spectroscopically (benzaldehyde, benzoates, maleic anhydride, and C_4 carboxylates, as well as benzyl species on the clean oxidized surface, benzylamine, and benzonitrile in the presence of ammonia) appear to be well correlated with the main products of the catalytic reactions. We may then suppose that the conditions of our spectroscopic study are sufficiently comparable to those of the flow reactor experiments to be taken as significant for a mechanistic study of the main reaction pathway. The spectroscopic

TABLE 3

Relative Rates of the Overall Reactant Depletion in the Ammoxidation of Different Methylaromatics at 573 K

Reactant	Relative rate
Toluene	1.00
m-Xylene	1.115
p-Methoxytoluene	1.27
p-Chlorotoluene	1.42
p-Xylene	1.45

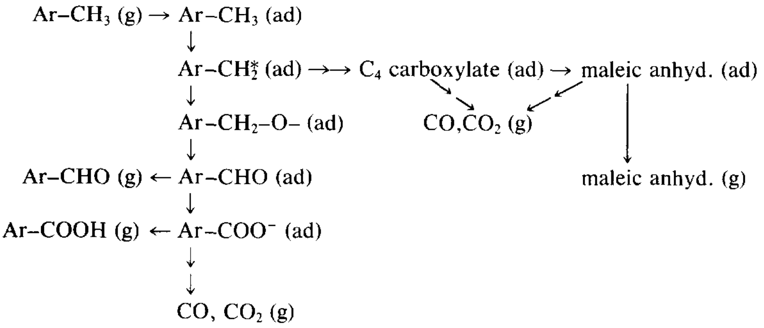
study of toluene adsorption at room temperature shows clearly the formation of an intermediate that may be identified, on spectroscopic grounds, as a benzyl species. This identification, strongly supported by its change into benzaldehyde and benzoate species by heating, is also confirmed by detection, both during spectroscopic experiments and in the flow reactor experiments operating at low oxygen concentration in the presence of ammonia, of benzylamine. It seems confirmed then that hydrogen abstraction from toluene to produce a stable benzyl species represents the first step in both the oxidation and ammoxidation reactions.

The comparison of the relative rates of ammoxidation of differently substituted toluenes, as presented in the results section, strongly supports the idea that the mechanism proceeds via a radical-like intermediate. The present results may then be taken as a confirmation of the idea of Germain and Laugier (*13*), mainly based on the detection of the radical-coupling products anthraquinone and *o*-methyldiphenyl methane during toluene oxidation on vanadium oxide, that a benzyl radical is the first intermediate species.

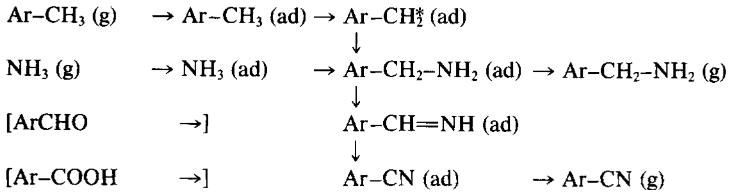
Based on our spectroscopic data, we propose for the selective oxidation of toluene the mechanism illustrated in Scheme **I**. There are two differences between this mechanism and those of Germain and Laugier (*13*) and Andersson (*12*) proposed previously. The first concerns the benzyl radical. Based on the observed very fast oxidation of benzyloxy species (undetectable at r.t.) to benzaldehyde, and the presumed high reactivity of the benzyl species, we propose their reaction with surface oxidized vanadium centers to produce benzyloxy species and, subsequently and very rapidly, benzaldehyde. This is also why we have no evidence for the formation of the benzylidene diradical, proposed previously (*13*). Another difference with respect to the main route advanced by Andersson (*12*) from kinetic experiments is that the phenyl-ring degradation products are thought to be formed not only through a consecutive reaction with respect to the pathway producing benzaldehyde and benzoic acid, but also via a side reaction.

Our data suggest also that in the case of ammoxidation, the benzyl intermediate may play a key role, reacting with ammonia (probably coordinated on Lewis sites, whose N–H bonds are weakened), to produce benzylamine, which is further oxidized to nitrile (necessarily via the imine intermediate). The selectivity to benzonitrile during ammoxidation is constant in the conversion range 50–100%. This would indicate that selectivity is governed by the relative rate of the competitive reactions of the benzyl intermediate with surface oxygen and adsorbed ammonia.

Our results show that the nitrile may also be produced starting from benzaldehyde



SCHEME I



SCHEME II

and, although in smaller amounts, from benzoic acid; thus, parallel routes may be due also to the reaction of the products of oxidation, with ammonia. Hence the mechanism we observe, parallel to the above one due to oxidation, may be represented as in Scheme **II**.

Based on both IR and kinetic data, Niwa *et al.* (*14, 36*) recently proposed a mechanism for the ammoxidation of toluene and xylenes on vanadia–alumina catalysts consisting of the reaction of the surface carboxylates produced by oxidation with ammonium cations as the active ammonia species. In our spectroscopic experiments we certainly observed both carboxylates and ammonium cations. However, we do not have evidence of such a reaction, thought to be a secondary pathway on our catalysts on the basis of flow reactor experiments starting from benzoic acid as the reactant. We have no evidence of the formation of benzamide.

Our data seem to suggest that the activation of ammonia consists of its coordination on Lewis acid sites, with a consequent lowering of the strength of the NH bonds, thereby activating it toward homolytic breaking.

(*b*) *Characterization of the Active Sites*

The above data showing the formation of benzyl intermediates indicate that the first step in both the oxidation and ammoxidation of toluene is abstraction of a hydrogen atom from the methyl group.

It has been previously emphasized that vanadia–titania catalysts are active, although not selective, in the oxidation of *n*-butane under conditions similar (570–670 K) to those at which the selective vanadium–phosphorus mixed-oxide catalysts operate (*37*). The first step of such a reaction has also been identified as a hydrogen abstraction involving very strong Lewis acid sites, present in both catalysts (*11, 38*). This would indicate that these catalysts are able to abstract a hydrogen atom also from the very unreactive butane molecule under relatively mild conditions. The hydrogen abstraction from the much more active benzylic position already observed by us at room temperature, as well as the activity of the same catalysts at an even lower temperature (520–570 K) in the oxidation of toluene (*4, 6*) with respect to *n*-butane, then, are not surprising from this point of view.

Following such observations, it seems reasonable to identify the active sites for hydrogen abstraction as very strongly acidic vanadium centers, which, according to the possibility of one-electron transitions, may also behave as radical centers. The same sites would also be responsible for the activation of ammonia, according to the observed competition of ammonia and toluene on the same adsorption sites as well as with the inhibiting effect of ammonia on the toluene oxidation.

Recently Jonson *et al.* (*39*) related the catalytic activity of pure oxides in the oxidation of toluene to their bulk metal–oxygen vibrational frequencies. These authors suggest that to have an active catalyst a specific energy transfer must take place from a vibrational mode of the catalyst to the methyl rocking mode of toluene (1040 cm^{-1}), through a vibrational resonance. As support to this suggestive, although very tentative, idea, we note that the νVO stretching of surface vanadyls on our catalysts is detected at a very similar frequency (1035 cm^{-1} (*10, 11*)).

It is appropriate to remark upon the poor selectivity of benzaldehyde obtained using vanadia–titania catalysts with respect to that obtained using other catalysts such as metal molybdates (*7, 40*). This difference may be due to a chemical factor, such as the presence on vanadia–titania catalyst surfaces of stronger although moderately nucleophilic sites which are responsible for the conversion of adsorbed aldehydes into carboxylates. However, the higher surface area of such catalysts may also have an effect favoring the consecutive reaction which produces the carboxylic acid. In any case, the surface nucleophilic sites are certainly not so strong as to react with the much weaker electrophilic carbon atom of the nitrile group. This allows the desorption of benzonitrile without further transformation.

According to our data and to the mechanism which we have proposed, the following features of the surface of vanadia–titania monolayer catalyst are relevant with respect to its behavior as an oxidation and ammoxidation catalyst: (i) the presence of strong Lewis sites also having a radical-like nature able to activate hydrocarbons by hydrogen abstraction; (ii) the activity of a surface phase able to undergo redox cycles at sufficiently low temperatures to avoid deeper transformation of the adsorbed species; and (iii) the presence of surface nucleophilic sites of medium strength, which favor the formation of carboxylates in the case of the oxidation reaction.

CONCLUSIONS

The FT-IR study of the adsorption of toluene on clean and ammonia-covered surfaces of a vanadium–titanium oxide monolayer catalyst at different temperatures both in the presence and in the absence of gaseous oxygen, taken together with results obtained from a flow reactor study of the ammoxidation of substituted toluenes, has allowed us to propose a Mars–van Krevelen (*41*) type of mechanism for both the oxidation and the ammoxidation of methylaromatics. The mechanism involves the formation of radical-like benzyl species as the first step.

REFERENCES

1. Wainwright, M. S., and Foster, N. R., *Catal. Rev.* **19,** 211 (1979).

2. Bond, G. C., and Bruckman, K., *Faraday Discuss. Chem. Soc.* **72,** 235 (1982).

3. Wachs, I. E., Saleh, R. Y., Chan, S. S., and Chersich, C. C., *Appl. Catal.* **15,** 339 (1985).

4. Andersson, A., and Lundin, S. T., *J. Catal.* **65,** 9 (1980).

5. van Hengstum, A. J., van Ommen, J. G., Bosch, H., and Gellings, P. J., *Appl. Catal.* **8,** 369 (1983).

6. Cavalli, P., Cavani, F., Manenti, I., and Trifirò, F., Symposium on "New Developments in Partial Oxidation (Louvain-la-Neuve, 1986)," *Catalysis Today* **1,** 245 (1987).

7. Grzybowska, B., Czerwenka, M., and Sloczynski, J., Symposium on "New Developments in Partial Oxidation (Louvain-la-Neuve, 1986)," *Catalysis Today* **1,** 157 (1987).

8. Cavani, F., Foresti, E., Trifirò, F., and Busca, G., *J. Catal.*, in press.

9. Cavalli, P., Cavani, F., Manenti, I., Trifirò, F., and El-Sawi, M., *Ind. Eng. Chem. Res.* **26,** 804 (1987).

10. Busca, G., Centi, G., Marchetti, L., and Trifirò, F., *Langmuir* **2,** 568 (1986).

11. Busca, G., *Langmuir* **2,** 577 (1986).

12. Andersson, S. L. T., *J. Catal.* **98,** 138 (1986).

13. Germain, J. E., and Laugier, R., *Bull. Soc. Chim. France*, p. 650 (1971).

14. Niwa, M., Ando, H., and Murakami, Y., *J. Catal.* **49,** 92 (1977).

15. Van Hengstum, A. J., Pranger, J., van Hengstum-Nijhuis, S. M., van Ommen, J. G., and Gellings, P. J., *J. Catal.* **101,** 323 (1986).

16. Ramis, G., Busca, G., and Lorenzelli, V., *Z. Phys. Chem. Neue Folge,* in press.

17. La Lau, C., and Snyder, R. G., *Spectrochim. Acta A* **27,** 2073 (1971).

18. Machida, K., Kuwae, A., Saito, Y., and Uno, T., *Spectrochim. Acta A* **34,** 793 (1978).

19. Katritzky, A. R., and Lagowski, J. M., *J. Chem. Soc.*, p. 4155 (1958).

20. Busca, G., Zerlia, T., Lorenzelli, V., and Girelli, A., *React. Kinet. Catal. Lett.* **27,** 429 (1985).

21. Cattanach, C. J., and Mooney, E. F., *Spectrochim. Acta A* **24,** 407 (1968).

22. Green, J. H. S., *Spectrochim. Acta A* **24,** 863 (1968).
23. Roberts, J. S., and Klabunde, K. J., *J. Amer. Chem. Soc.* **99,** 2509 (1977).
24. Green, J. H. S., *Spectrochim. Acta A* **32,** 1265 (1976).
25. Bellamy, L. J., Connelly, B. R., Philpotts, A. R., and Williams, R. L., *Z. Electrochem.* **64,** 563 (1960).
26. Inomata, M., Mori, K., Miyamoto, A., Ui, T., and Murakami, Y., *J. Phys. Chem.* **87,** 754 (1983).
27. Miyata, H., Nakagawa, Y., Ono, T., and Kubokawa, Y., *Chem. Lett.,* p. 1141 (1983).
28. Grasselli, R. K., and Burrington, J. D., *in* "Advances in Catalysis," Vol. 30, p. 133. Academic Press, New York, 1981.
29. Leysen, R., and van Rysselberge, J., *Spectrochim. Acta* **19,** 243 (1963).
30. Joeckle, R., Schmid, E. D., and Mecke, R., *Z. Naturforsch. A* **21,** 1906 (1966).
31. Chattopadyay, S., *Ind. J. Phys.* **41,** 759 (1967).
32. Green, J. H. S., *Spectrochim. Acta A* **32,** 1279 (1976).
33. Ingold, C. K., "Structure and Mechanism in Organic Chemistry." Bell, London, 1953.
34. Burrington, J. D., Kartisek, C. T., and Grasselli, R. K., *J. Catal.* **69,** 495 (1981).
35. Shelton, J. R., and Uzelmeier, C. W., *J. Amer. Chem. Soc.* **88,** 5222 (1966).
36. Niwa, M., Ando, H., and Murakami, Y., *J. Catal.* **70,** 1 (1981).
37. Busca, G., Centi, G., and Trifirò, F., *Appl. Catal.* **25,** 265 (1986).
38. Busca, G., Centi, G., and Trifirò, F., *J. Amer. Chem. Soc.* **107,** 7757 (1985).
39. Jonson, B., Larsson, R., and Rebenstorf, B., *J. Catal.* **102,** 29 (1986).
40. Nag, N. K., Fransen, T., and Mars, P., *J. Catal.* **68,** 77 (1981).
41. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci. Suppl.* **3,** 41 (1954).