FTIR investigation of surface intermediates formed during the ammoxidation of toluene over vanadyl pyrophosphate

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Abstract

The mechanism of formation of surface intermediates, appearing during the interaction of vanadyl pyrophosphate $(VO)_2P_2O_7$ with feed components of the toluene ammoxidation was studied by FTIR spectroscopy. The investigation of ammonia adsorption at elevated temperature showed protonated and coordinated ammonia as expected as well as the generation of amido species; all could be so called 'nitrogen insertion species' or a source of these at least. The interaction of toluene and possible reaction intermediates such as benzaldehyde and benzylamine with $(VO)_2P_2O_7$ was studied. The investigations revealed that the ammoxidation of toluene probably proceeds via the formation of a benzaldehyde intermediate. Afterwards, benzylimine surface species were probably formed by a N-insertion, using NH_4^+ surface species followed by the formation of benzonitrile by subsequent oxidative dehydrogenation. However, no benzamide species were observed. The surface species generated upon adsorption of benzaldehyde were similar to those formed from toluene, indicating the role of the former as intermediate in the nitrile formation path. Otherwise, the adsorption of benzylamine in the presence of oxygen did not lead to the formation of benzonitrile. Therefore, an ammoxidation mechanism of toluene via a benzaldehyde intermediate is preferred and reaction pathways via benzamide or benzylamine as intermediates seem to be improbable.

1. Introduction

The ammoxidation of alkylaromatics has been employed for a long time as a commercial process to produce the corresponding nitriles, being bulk chemicals as well as intermediates for the production of dyestuffs, pharmaceuticals, pesticides and many fine chemicals. In the investigation of the ammoxidation reaction emphasis was mostly placed on the development of new catalysts and the examination of reaction mechanism. Although recent studies have thrown some light on the mechanisms of the ammoxidation on different oxide catalysts, the understanding of reaction steps in detail is still under debate. Murakami et al. [1] and Niwa et al. [2] studied the reaction mechanism of toluene ammoxidation on $V_2O_5-Al_2O_3$. They suggested that the reaction may proceed via the reaction of ammonium ions with benzoate ions detected as surface species by infrared spectroscopy. A

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Langmuir–Hinshelwood mechanism was proposed by Cavalli et al. [3,4] for the same reaction over V_2O_5–TiO_2, corresponding to the obtained kinetic data. Benzylamine as well as benzaldehyde were identified as reaction intermediates. The reaction shall undergo two pathways, namely, the partial oxidation of the formed benzylamine via an imine surface species, generating benzonitrile and the reaction of benzaldehyde with coordinatively bound ammonia to benzonitrile, respectively. These pathways were supported by Busca et al. [5,6], observing the corresponding surface intermediates by means of IR spectroscopy. A kinetic study of the ammoxidation of toluene over V_2O_5 was represented by Otamiri and Andersson [7,8]. In the proposed mechanism a vanadium imido species (V=NH) and a vanadium hydroxylamino species (V–NHOH) were established as 'nitrogen insertion sites' on the surface of the catalyst, reacting with adsorbed toluene to an amine (R–CH_2–NH_2) and subsequently to an imine (R–CH=NH) surface species, generating benzonitrile, finally. Furthermore, a scheme of the mechanism of the toluene ammoxidation on V_2O_5–TiO_2 was suggested by Sanati and Andersson [9], including (C_6H_5)CH(NH_2)O– and (C_6H_5)C(NH_2)(O–)$_2$ species as reaction intermediates, but it was not given a clear conception of the N-insertion step. Otherwise, Ramis et al. [10] observed amido groups apart from protonated and coordinated ammonia, appearing after ammonia adsorption at elevated temperatures on similar catalysts. The formation of vanadium imido species (V=NH) and benzylamine surface species were also postulated by Azimov et al. [11], basing on the results of pulse and flow reaction experiments as well as infrared spectroscopic investigations of the ammoxidation of toluene over V–Sb–Bi oxide catalysts.

Vanadyl pyrophosphate $(VO)_2P_2O_7$ is an active and selective catalyst for the oxidation of n-C_4-hydrocarbons to maleic anhydride (e.g., [12,13]). Recently, $(VO)_2P_2O_7$ has been employed as catalyst in the ammoxidation reaction of substituted aromatic hydrocarbons to produce the corresponding nitriles, indicating its potential in this direction [14–17]. The aim of the present work is to get information about the formation of surface species, being potential intermediates of the above mentioned reaction over $(VO)_2P_2O_7$ by means of an in-situ infrared spectroscopic investigation.

2. Experimental

$VO(HPO_4) \cdot 1/2H_2O$ was used as catalyst precursor, synthesized as previously reported (e.g., Refs. [18–20]). $(VO)_2P_2O_7$ was obtained by heating the precursor up to 773 K under nitrogen for 3 h. The completion of the transformation was proven by the XRD-pattern. The results of the potentiometric titration [21,22] indicated only a very small amount of V^V in the sample, because the valence state of vanadium was 4.003 on the average [22]. The sample was pretreated at 725 K for 2 h under vacuum prior to each measurement. The infrared spectra were recorded with a Bruker IFS 66 FTIR spectrophotometer using self-supporting discs (11 mg/cm^2) of the sample with 100 scans for each measurement. The adsorption experiments were carried out in an in-situ cell connected with a gas manifold/evacuation system schematically demonstrated in Fig. 1. The aromatic compounds used (toluene, benzaldehyde and benzylamine) had a purity higher than 99% (Merck). The figures show difference spectra obtained by substraction of the spectrum of the parent $(VO)_2P_2O_7$ recorded before and the spectrum of an adsorbate/reactant//$(VO)_2P_2O_7$ complex recorded after or during adsorption or catalytic reaction experiments.

3. Results

3.1. Adsorption of ammonia

The adsorption of ammonia at room temperature (RT) reveals the appearance of protonated

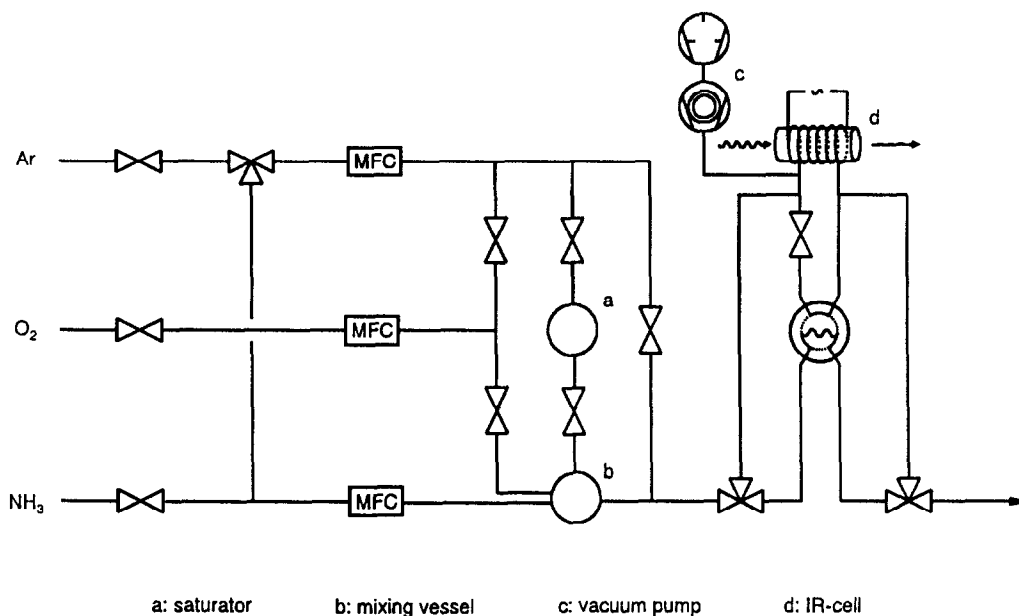a: saturator　　　　b: mixing vessel　　　　c: vacuum pump　　　　d: IR-cell

Fig. 1. Gas manifold/evacuation system used for the in-situ FTIR investigations.

ammonia (NH_4^+ located on Brønsted sites (BS); ca. 1440 cm^{-1}) and coordinated ammonia (NH_3 located on Lewis sites (LS); ca. 1610 cm^{-1}) as expected (e.g., Refs. [10,22-25]). Recently, we have found by IR spectroscopy that ammonia reacts with the pyrophosphate surface, generating additional –OH groups by a break of P–O–P and/or V–O–P links as well as new Lewis sites by an oxygen removal from $V^{IV}=O$ groups [22].

Fig. 2 shows the spectra of surface species obtained upon ammonia (spectrum a) and ammonia/oxygen adsorption (spectrum b) at elevated temperatures, revealing both bands mentioned and additionally a band at ca. 1550 cm^{-1}, indicating the formation of some amido surface species, probably (e.g., Refs. [10,11,24,26]). Additionally, the ammonium ion band is shifted a little towards lower frequencies (ca. 1420 cm^{-1}), probably due to an interaction of the ammonium ions with adjacent V=O groups by hydrogen bonding discussed below in detail. The spectrum obtained after ammonia adsorption in the presence of oxygen is quite analogous to that obtained in the absence of oxygen except a slight decrease in the band intensity of

coordinated ammonia due to a recoverage of O-vacancies at coordinatively unsaturated vanadyl groups. The ammonium ion band is increased again due to the formation of further
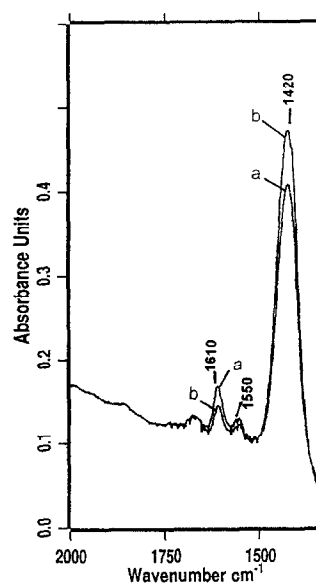

Fig. 2. Infrared spectra of surface species of ammonia adsorbed on $(VO)_2P_2O_7$: (a) after adsorption at 673 K for 30 min and (b) after adsorption at 673 K in the presence of oxygen for 30 min; the spectra were recorded at RT after evacuation.

ammonium ions by combustion of ammonia to nitrogen and water, the latter generates additional OH-groups.

No evidence for the formation of V=NH imido surface species was obtained in the present work. The stretching vibration of V=NH surface species should be expected in the range of the V=O stretches $(1000-950\ cm^{-1})$ but the spectrum has in this range $(< 1300\ cm^{-1})$ a 100% total absorption. Thus, it should be difficult to observe V=NH groups in the presence of V=O by means of IR spectroscopy, generally.

3.2. Adsorption of toluene, benzaldehyde and benzylamine

The adsorption of toluene, benzaldehyde and benzylamine on $(VO)_2P_2O_7$ has been studied in order to identify the adsorbed species that could arise on the surface of $(VO)_2P_2O_7$ during the ammoxidation of toluene. Fig. 3 shows the infrared spectra of the compounds adsorbed at RT on $(VO)_2P_2O_7$. Details of the attribution of the surface species observed after adsorption are given in Table 1.
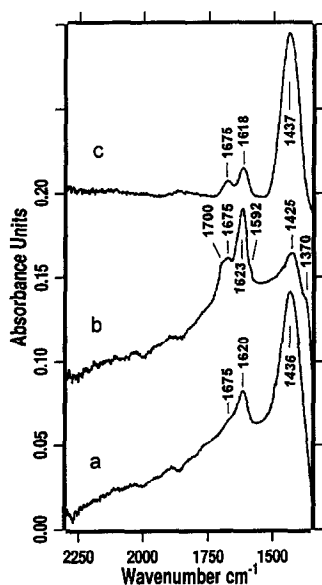
Fig. 3. Infrared spectra of: (a) toluene; (b) benzaldehyde and (c) benzylamine on $(VO)_2P_2O_7$ at RT for 60 min each after evacuation.

Table 1
Wavenumbers (cm^{-1}) of characteristic bands of FTIR spectra of toluene, benzaldehyde and benzylamine adsorbed on $(VO)_2P_2O_7$ at RT

Toluene	Benzaldehyde	Benzylamine	Assignment
	1700(sh)		ν(C=O)
1675(sh)	1675(m)		ν(C=O)
		1675(w)	ν(CH=NH)
1620(m)	1623(s)	1618(m)	ν(C=C)$_{aromatic}$
	1592(sh)		ν(C=C)$_{aromatic}$
1436(vs)		1437(vs)	ν(CH$_2$)
	1425(m)		ν_s(COO$^-$)
	1370(sh)		δ(CH)

vs = very strong, s = strong, m = middle, w = weak, sh = shoulder.

The appearance of a vague shoulder around $1675\ cm^{-1}$ points to a small amount of benzaldehyde surface species formed by adsorption of toluene on $(VO)_2P_2O_7$ even at ambient temperature (spectrum a). The strong band at $1436\ cm^{-1}$ is probably due to methylene surface groups, indicating a toluene dehydrogenation on the electrophilic catalyst surface.

The adsorption of benzaldehyde on $(VO)_2P_2O_7$ (spectrum b) leads to the formation of benzoate ions $(C_6H_5COO^-)$ revealed by the weak band at $1425\ cm^{-1}$ apart from the bands caused by the benzaldehyde itself (see also Table 1).

Adsorbed benzylamine (spectrum c) also shows a band at $1675\ cm^{-1}$ caused by the stretching vibration of the CH=NH double bond, suggesting a dehydrogenation of benzylamine on $(VO)_2P_2O_7$ even under these mild conditions.

3.3. Oxidation and ammoxidation of toluene

Fig. 4 depicts the spectra of surface species observed on $(VO)_2P_2O_7$, appearing upon adsorption of toluene at 673 K in the presence of oxygen as well as oxygen and ammonia. The assignment of the surface species, appearing in the oxidation and ammoxidation of toluene are given in the Tables 2 and 3.

The oxidation of toluene results in a complex spectrum (spectrum a). The strong band at 1436

Table 2
Wavenumbers (cm^{-1}) of characteristic bands of FTIR spectra of the surface species on $(VO)_2P_2O_7$ occurring during the oxidation of toluene, benzaldehyde and benzylamine

Toluene	Benzaldehyde	Benzylamine	Assignment
1855(w), 1780(m), 1725(w)	1855(w), 1780(w), 1724(w)		cyclic anhydride
1703(w), 1675(w)	1675(w)		$\nu(C=O)_{aldehyde}$
		1673(w)	$\nu(CH=NH)$ or $\nu(C=O)_{aldehyde}$
1605(m), 1495(w), 1450(w)	1610(w)		$\nu(C=C)_{aromatic}$
1560(sh)	1550(sh)		$\nu_{as}(COO^-)$
1425(w)	1425(w)	1425(s)	$\nu_s(COO^-)$

vs = very strong, s = strong, m = middle, w = weak, sh = shoulder.

cm^{-1} caused by surface methylene groups almost disappears due to the oxidation of this groups. The appearance of bands at 1675 and 1703 cm^{-1} suggests the formation of benzaldehyde. The bands observed at 1855, 1780 and 1725 cm^{-1} can be reasonably attributed to the formation of cyclic anhydride species, indicating the oxidation of the aromatic ring which leads to carbon oxides as total oxidation products, finally. A very weak band at 1425 cm^{-1} and a vague shoulder at 1560 cm^{-1} are observed, pointing to the presence of some benzoate ions on the surface of $(VO)_2P_2O_7$.
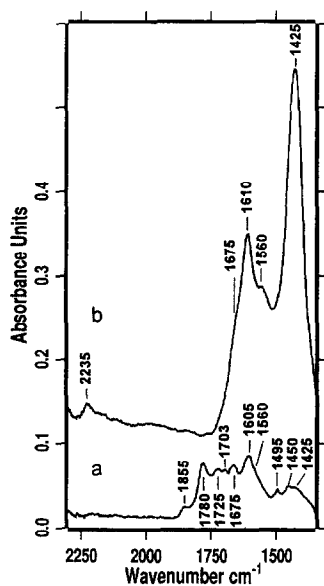

Fig. 4. Infrared spectra of surface species on $(VO)_2P_2O_7$ after adsorption of toluene $(30 \times 10^{-3}$ atm) at 673 K for 30 min: (a) in the presence of oxygen (0.250 atm); (b) in the presence of oxygen and ammonia (0.125 atm each); the spectra were recorded at RT after evacuation.

The unselective oxidation of toluene was obviously suppressed if ammonia was mixed to the feed gas (spectrum b). A vague shoulder near 1675 cm^{-1} can be detected instead of the bands at 1855, 1780 and 1725 cm^{-1}, pointing to some R–CH=NH imine surface species, still remaining under these conditions. Moreover, a significant absorption band is observed at 2235 cm^{-1} ($\nu C\equiv N$), revealing the formation of benzonitrile. In addition, the band at 1560 cm^{-1}, assigned to the asymmetric stretching vibration of the carboxylate group COO^-, is more in evidence due to a suppression of the decarboxylation by formation of more stable ammonium benzoate structures, probably.

3.4. Oxidation and ammoxidation of benzaldehyde

The oxidation and ammoxidation of benzaldehyde (Fig. 5) were also investigated under the same conditions as applied in the case of toluene

Table 3
Wavenumbers (cm^{-1}) of characteristic bands of FTIR spectra of the surface species on $(VO)_2P_2O_7$ occurring during the ammoxidation of toluene, benzaldehyde and benzylamine

Toluene	Benzaldehyde	Benzylamine	Assignment
2235(w)	2235(w)		$\nu(C\equiv N)$
1675(sh)	1675(sh)	1675(w)	$\nu(CH=NH)$
1610(s)	1610(s)	1610(m)	$\delta(NH_3) + \nu(C=C)$
1560(sh)	1560(sh)	1560(w)	$\nu_{as}(COO^-)$
1425(vs)	1425(vs)	1425(vs)	$\delta(NH_4^+) + \nu_s(COO^-)$

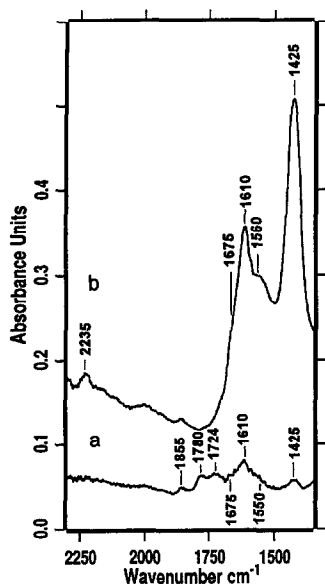vs = very strong, s = strong, m = middle, w = weak, sh = shoulder.

Fig. 5. Infrared spectra of surface species on $(VO)_2P_2O_7$ after adsorption of benzaldehyde $(1.3 \times 10^{-3}$ atm) at 673 K for 30 min: (a) in the presence of oxygen (0.250 atm); (b) in the presence of oxygen and ammonia (0.125 atm each); the spectra were recorded at RT after evacuation.

(for band assignment see also Tables 2 and 3). It is clearly demonstrated that similar surface species are found upon oxidative treatment of benzaldehyde (spectrum a) as by oxidation of toluene (compare with Fig. 4, spectrum a). Otherwise, benzonitrile is formed upon ammoxidation of benzaldehyde, which is evident by the appearance of the characteristic band at 2235 cm^{-1} (spectrum b).

3.5. Oxidation and ammoxidation of benzylamine

Benzylamine has been often proposed as one of the reaction intermediates of the ammoxidation of toluene over vanadia-containing catalysts (e.g., Refs. [4,7]). According to these ideas, benzonitrile should be also formed over $(VO)_2P_2O_7$ upon oxidation of benzylamine via oxidative dehydrogenation. Therefore, the oxidation and ammoxidation of benzylamine were studied.

Fig. 6 depicts the spectra of surface species

formed in the oxidation and ammoxidation of benzylamine (for band assignment see also Tables 2 and 3, respectively). A complete oxidation of benzylamine at 673 K mainly to CO_x was observed in the presence of oxygen apart from the band at 1425 cm^{-1} which is probably due to $\nu_s(COO^-)$ (spectrum a). In the presence of oxygen and ammonia the bands at 1675, 1610 and 1560 cm^{-1} are preserved, indicating the suppression of unselective oxidation of benzylamine. There is no evidence for the formation of benzonitrile because a band near 2235 cm^{-1} was absent in both experiments.

3.6. Successive ammonia and toluene / oxygen adsorption

Fig. 7 shows the appearance of the bands at 1420 cm^{-1} and 1610 cm^{-1} after adsorption of ammonia at 673 K for 20 min followed by Ar flushing for 30 min (spectrum a) and the change of these bands after interaction of the as-treated sample with a toluene/oxygen flow for 60 min
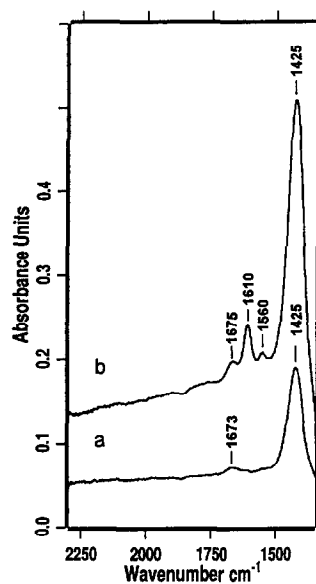

Fig. 6. Infrared spectra of surface species on $(VO)_2P_2O_7$ after adsorption of benzylamine $(1.3 \times 10^{-3}$ atm) at 673 K for 30 min: (a) in the presence of oxygen (0.250 atm); (b) in the presence of oxygen and ammonia (0.125 atm each); the spectra were recorded at RT after evacuation.
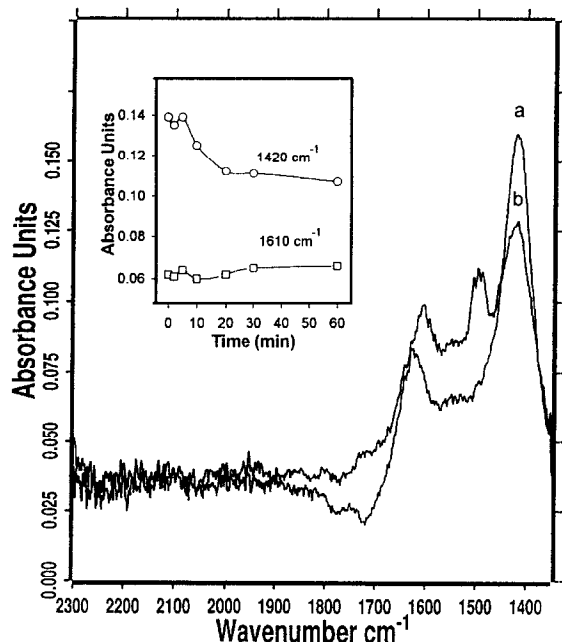
Fig. 7. Infrared spectra of ammonia species on $(VO)_2P_2O_7$ after adsorption of ammonia at 673 K for 20 min (a) and after subsequent interaction of a toluene/oxygen flow for 60 min (The picture inside shows the base line corrected band heights depending on flushing period for NH_4^+ and NH_3 band).

again (spectrum b). The intensity of the ammonium ion band is significantly decreased due to interaction of the toluene/oxygen with the ammonium ions despite the appearance of bands attributed to vibrations of the aromatic ring of toluene, intermediates as well as products that could superimpose the ammonium ion band. The picture inside demonstrates the baseline corrected band heights of the 1420 cm^{-1} and 1610 cm^{-1} bands in dependence on the interaction period of the toluene/oxygen flow. The figures indicate that ammonium ions were consumed whereas the band of the coordinatively bound ammonia remains constant. The decrease of the ammonium ion band by interaction of a toluene/oxygen flow is also clearly shown by an experiment using ND_3, demonstrating a significant intensity decrease in the N–D stretching vibration at ca. 2450 cm^{-1} [27], being not influenced by other bands.

4. Discussion

A proposal of a reaction mechanism of the toluene ammoxidation to benzonitrile on the surface of a $(VO)_2P_2O_7$ catalyst, basing on the observed surface intermediates is shown in Scheme 1. The scheme also considers the interaction of surface vanadyl groups with oxygen and ammonia. All the species or structures mentioned are denoted by symbols (A–H) for the sake of simplicity in the following discussion.

The IR-spectroscopic investigation of the ammonia adsorption on $(VO)_2P_2O_7$ (A) revealed that there are three forms of nitrogen-containing surface species: coordinatively adsorbed NH_3, NH_4^+ ions and NH_2 groups. Their concentrations increased by interaction of ammonia with the pyrophosphate surface at elevated temperatures as shown in [22]. Recently, it was already found that the ammonia adsorption is accompanied by a redox interaction with the $(VO)_2P_2O_7$, resulting in a partial reduction of $V^{IV} \Rightarrow V^{III}$ and generation of –OH groups by hydrolysis or ammonolysis of P–O–V bonds, forming ammonium ions and amido species (B1, B2) [22]. Furthermore, coordinatively unsaturated vanadyl sites were generated by removal of oxygen from V=O groups (A $\Rightarrow$ G). These sites should be responsible for the increase of coordinatively bound ammonia.

Now we have found that in the presence of oxygen the amount of coordinatively bound ammonia decreased slightly in comparison with that in the absence of oxygen. Obviously, this decrease is caused by a competitive oxygen adsorption or a reoxidation (G $\Rightarrow$ A).

The observed shift of $\delta_{as}(NH_4^+)$ to lower frequencies could be due to the formation of additional hydrogen bonding by interaction of NH_4^+ ions with adjacent V^{IV}=O on the (100) plane of the $(VO)_2P_2O_7$.

In addition, some V^{IV} sites should be oxidized to V^V by adsorption of oxygen on the coordinatively unsaturated top of the dimers of vanadyl octahedra, forming V^V-containing sites
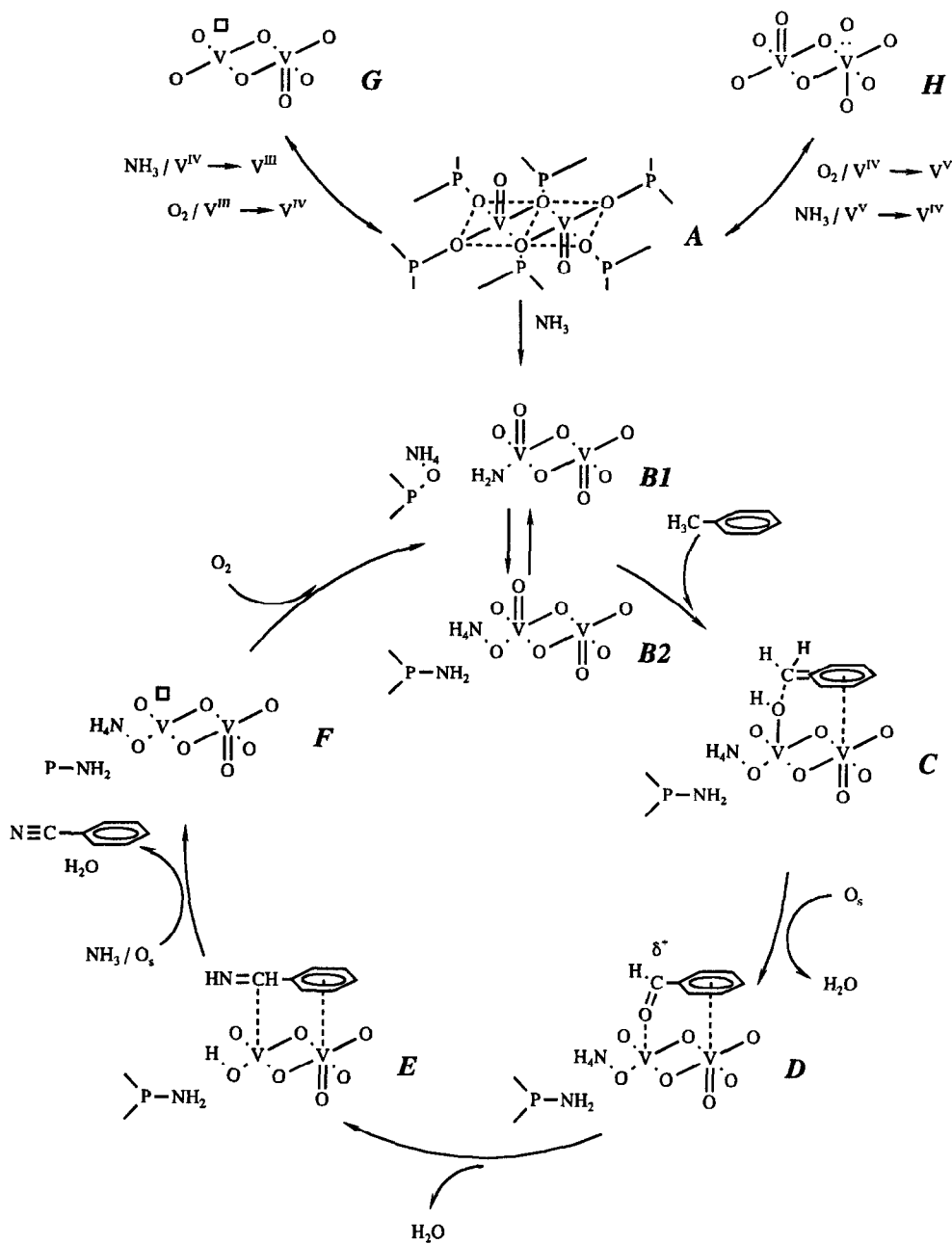
Scheme 1.

(A ⇒ H). This oxygen species was designed as O_s in Scheme 1.

The formation of methylene-like species (C) formed upon the adsorption of toluene on the surface proceeds probably via oxidative H-abstraction from the methyl group of toluene ad-

sorbed through π-complex of the aromatic ring with the adjacent $V^{IV}=O$ group (B1,2 ⇒ C). Similar conclusions were drawn by Miyata et al. [28], observing such benzyl species as well as benzaldehyde by interaction of the toluene methyl group and surface V=O species of vana-

dium oxide layered on ZrO_2 and TiO_2. The comparison of the adsorption of toluene with that of potential reaction intermediates of the ammoxidation reaction (benzaldehyde, benzylamine) suggest that the oxidation and oxidative dehydrogenation can take place to a slight extent at the surface of $(VO)_2P_2O_7$ even at RT, forming R–CH=O, R–CH=NH and R–COO⁻ surface species. Very active O_s species formed in the complex redox processes described above may be responsible for these actions.

Although in the course of oxidation and ammoxidation of toluene benzoate ions were formed, in the present work no signal could be identified as evidence for the formation of benzamide. The latter should be a reaction intermediate of the so called 'benzoate–ammonium ions mechanism' (e.g., Refs. [1,2]) of the ammoxidation of toluene whereby benzonitrile should be formed by dehydration of benzamide.

According to the 'amine mechanism', benzylamine surface species should be formed by the reaction of benzylmethylene surface species with adsorbed ammonia [7,8] or by reaction of adsorbed toluene with surface vanadyl imido species (V=NH), alternatively [11,29]. Afterwards, an oxidative dehydrogenation should generate benzylimine surface species and benzonitrile, finally. In similar way, the adsorption of benzylamine in the presence of oxygen should result in the formation of benzonitrile. However, we did not find any indication for the formation of benzonitrile from benzylamine, even under mild oxidation conditions, i.e., at competitive adsorption of oxygen and ammonia.

From the similarity of the spectra of the observed surface species, it is suggested that the ammoxidation of toluene analogously occurred to the one of benzaldehyde. Hence, it seems reasonable to consider a benzaldehyde surface species (D) as intermediate of the ammoxidation of toluene, being probably converted to benzylimine species (E) by nitrogen insertion from adjacent NH_4^+ ions as revealed by successive adsorption experiments. Finally, benzonitrile is formed by a subsequent oxidative dehydrogena-

tion step (E ⇒ F). Otherwise, a portion of benzaldehyde species should be oxidized to benzoate ions and consecutively to 'products of the total oxidation', being the main side reaction products of the ammoxidation.

The reaction steps of the nitrile formation were reasonably attributed to one edge-sharing VO_6 octahedra-unit of the pyrophosphate surface. It seems possible that the steric properties enable a simultaneous interaction of the aromatic ring as well as the methyl group with adjacent vanadium sites. The coordinatively unsaturated part (Lewis-acidic site) of the VO_6 dimer could bind the aromatic substrate via π-complex formation whereas the reaction sequence of the partial oxidation could run on the other site according to a V $\cdots$ V distance of the vanadyl groups of ca. 3.3–3.4 Å [30] and C–C_{ring} and C–CH_3 distances of the toluene molecule of 1.4 Å and 1.52 Å [31], respectively, i.e., the distance of π-complex center to the carbon atom of the methyl group amounts to ca. 3 Å.

This proposal of the reaction mechanism could be supported by further studies, applying the temporal-analysis-of-products (TAP) technique. Only benzaldehyde was detected as short-lived reaction intermediate, desorbing from the catalyst surface upon interaction of ammoxidation feed pulses with the $(VO)_2P_2O_7$ [32]. Another experiment, using an [14]NH_4^+-containing VPO catalyst (α-$(NH_4)_2[(VO)_3(P_2O_7)_2]$) and pulses of [15]$NH_3$-containing ammoxidation feed revealed that ammonium ions should be the source of the N-insertion species in the ammoxidation because ^{14}N-benzonitrile was the main product during the first pulse series [33].

5. Conclusions

The ammoxidation of toluene over $(VO)_2P_2O_7$ proceeds through a mechanism, which involves the dehydrogenation of adsorbed toluene and formation of a benzaldehyde surface species as intermediate of the reaction. A

benzylimine surface species seems to be generated by nitrogen insertion provided by ammonium ions, followed by the formation of the nitrile by a further dehydrogenation step. Benzoate ions, occurring in the reaction may be the precursor of the products of total oxidation.

Acknowledgements

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