Selective oxidation of *p*-substituted toluenes to the corresponding benzaldehydes over $(VO)_2P_2O_7$: an in situ FTIR and EPR study

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Dedicated to Professor Dr. Helmut Knözinger on the occasion of his 65th birthday.

Abstract

The adsorption and oxidation of *p*-chlorotoluene (PCT), *p*-methoxytoluene (PMT), and toluene on vanadyl pyrophosphate catalyst (VPP) were studied by in situ FTIR and EPR spectroscopy. Various amounts of strongly adsorbed benzaldehydes and cyclic anhydride species were observed by FTIR in dependence on the different educts after oxidation experiments. The extent of spin–spin exchange pertubation and, thus, the loss of the EPR signal intensity caused by substrate adsorption and interaction is influenced by the nature of the aromatic compound. The strength of reactant and product adsorption on the catalyst surface was found to be an important selectivity-limiting factor in the aldehyde formation. The benzaldehyde adsorption is enhanced by additional interaction of the carbonyl group with Brønsted acid hydroxyl groups generated during oxidation reaction, which facilitates deeper oxidation. The co-adsorption of pyridine is one possibility to suppress the strong aldehyde adsorption and to improve the selectivities. Yields of benzaldehydes and selectivities at constant conversion increase in the order PMT < toluene < PCT. Strong product adsorption favoured by electron donating *p*-substituents causes total oxidation leading to lower aldehyde selectivities. Both, the acid/basic characters of the reactants and products and their steric properties play an important role for adsorption/desorption processes. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

P-substituted benzaldehydes are important intermediates in the field of specialty and pharmaceutical chemicals, which can be prepared from the corresponding substituted toluenes in a liquid phase oxidation in the presence of transition metal salts in acetic acid medium or by electrochemical methods,

e.g. Refs. [1,2]. Nevertheless, the synthesis can also be carried out in the traditional way of organic chemistry, for example by the hydrolysis of substituted benzal chlorides [3]. However, the efficiencies of these reactions are not satisfactory and, additionally, more wasteful products are produced causing environmental problems. So, there are several advantages for a vapour phase catalytic oxidation process. But, it has to be taken into account that the selective production of aromatic aldehydes in vapour phase processes is much more complicated because the

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aldehydes themselves can be consecutively oxidised very fast to acids and deeper oxidised products. Thus, a main problem is to find promising catalyst compositions to control the selectivity.

Ueshima and Saito [4] and Ueshima et al. [5] used basic metal oxide catalysts based on V_2O_5 for the partial oxidation of *p*-methoxytoluene (PMT) to *p*-methoxybenzaldehyde (*p*-MBA). The best selectivities have been found in the Tl_2O/V_2O_5 system but it has to be considered that the reaction took place at a temperature (703 K) where the catalyst was in a "molten state". Their study further suggested that a well-balanced combination of acid and basic oxide is very effective for this reaction. However, the use of thallium compounds is not applicable. The authors have also investigated the influence of various substituents in the *p*-position on conversion and selectivity and have found that the stronger the electron donating ability the higher the activity and selectivity. Reddy et al. [6,7] have investigated the selective oxidation of PMT over various V_2O_5 based mixed oxide catalysts such as $V_2O_5/TiO_2/SiO_2$, $V_2O_5/TiO_2/Al_2O_3$, $V_2O_5/TiO_2/ZrO_2$, $V_2O_5/TiO_2/Ga_2O_3$, and $V_2O_5/CaO/MgO$. The authors concluded that both acid–base functions and redox properties of the catalysts are essential to obtain good conversion and product selectivity. Yoo [8,9] reported the gas phase oxidation of alkylaromatics over Fe/Mo/borosilicate molecular sieve catalysts prepared by chemical vapour deposition. It was found that *para*-substituents such as OH, OCH_3 and Cl favoured the oxidation of the methyl group to the corresponding aldehydes. Trimm and Irshad [10] described electronic effects on the catalytic oxidation of substituted toluenes over MoO_3. These electronic properties were found to be affected by both the substituents of the aromatic nucleus and the field effects of the catalyst and can be correlated with the catalytic activity.

Vanadium phosphates, especially vanadyl pyrophosphate, are well known as catalysts for selective O- and N-insertion reactions of aliphatics and methyl aromatics [11,12]. Recently, we have studied the partial oxidation of toluene to benzaldehyde on vanadyl pyrophosphate catalysts (VPPs) by means of different spectroscopic in situ methods to elucidate factors limiting the aldehyde selectivity [13–16]. Strongly adsorbed benzaldehyde and adsorbed cyclic

anhydride species were detected by IR spectroscopy at the catalyst surface above 523 K [13,15]. The usually weak adsorption of benzaldehyde becomes stronger in presence of Brønsted acid sites caused by hydrogen bonding between the carbonyl and surface hydroxyl groups. Brønsted acid sites are generated by reaction of the water formed during oxidation reaction with the pyrophosphate by hydrolysis of V−O−P- and/or P−O−P-bonds. This strong interaction facilitates consecutive oxidation and lowers the benzaldehyde selectivity in the partial oxidation of toluene [15]. Furthermore, it has been proved that the co-adsorption of pyridine blocks the acid sites during reaction. Consequently, deeper oxidation was suppressed and a threefold increase of benzaldehyde selectivity at constant conversion rate was observed [14]. In situ EPR investigations [13,16] indicated a temporal decrease of the VO^{2+} signal intensity of the catalyst under working conditions, which arises from a perturbation of the spin–spin exchange between neighbouring VO^{2+} ions. This behaviour results from changes in electron density at the surface VO^{2+} centres, which are caused on the one hand by alternating reduction/oxidation steps and on the other hand by the adsorption of the nucleophilic aromatic system. On switching to inert gas atmosphere, the EPR signal returned only slowly to its initial state indicating a strong adsorption of aromatic products on the surface. However, in presence of pyridine, the signal intensity increase was reversible immediately. These results were in line with the above-described FTIR findings.

In general, it can be stated that the selectivity to benzaldehyde is closely related to the acid–base properties of the catalyst surface during reaction. Another important fact is the strength of the reactant adsorption. The adsorption of toluene on the vanadyl pyrophosphate surface proceeds via the electronic interaction between the aromatic nucleus and Lewis sites [15]. Therefore, *p*-substituents with different electronic properties should influence the adsorption behaviour of reactants and products and consequently, an influence on activity and selectivity has to be expected.

Starting from the knowledge about the partial oxidation of toluene to benzaldehyde, we were interested to study the influence of *p*-substituents with electron donating and withdrawing properties, re-

spectively, on the adsorption behaviour of methyl aromatics on $(VO)_2P_2O_7$ and its catalytic performance. The aim of this work is to compare the selective oxidation reaction of *p*-chlorotoluene (PCT) and PMT to the corresponding aldehydes over vanadyl pyrophosphate with that of toluene. By studying the adsorbate structures of reactants and products on the catalyst surface and the changes of the catalytic active VO^{2+} centres during reaction, a deeper understanding of the specific reactant/product catalyst interaction has to be expected. The combined application of in situ FTIR and EPR spectroscopy and the correlation of the results with that of the catalytic performance should be a suitable way to elucidate the mechanism and the selectivity limiting factors.

2. Experimental

2.1. Vanadyl pyrophosphate catalyst (VPP)

The VPP was prepared by a usual dehydration procedure (4 h, 723 K) under nitrogen using $VOHPO_4 \cdot 1/2\ H_2O$ as precursor material. The obtained sample was characterised by XRD and FTIR. Before adsorption experiments, the catalyst was activated by heating in vacuum at 723 K for 1.5 h.

2.2. FTIR experiments

Spectra were recorded using a Bruker IFS 66 spectrometer equipped with a heatable and evacuable IR cell with CaF_2 windows, connected to a gas dosing–evacuation system. For the experiments, the catalyst powder was pressed into self-supporting discs with a diameter of 20 mm and a weight of 50 mg and activated by heating up to 723 K under vacuum for 1 1/2 h followed by cooling to room temperature.

For the adsorption experiments, toluene, PMT, PCT, water, and *p*-MBA were adsorbed at appropriate temperatures. Toluene, PMT, PCT were fed with argon (4.17, 1.43, 3.07 mmol/h), water with air, and *p*-MBA with argon/air. Additional dosage of air or argon provided a constant gas flow of 11.4 l/h.

For the investigations under reaction-like conditions, the feed composition (molar ratios) was toluene (PCT): air: water = 1:96:1 and PMT: air: water = 1:225:2. Additionally, a solution of 4 wt.% pyridine in water was used in some experiments instead of pure water to realise a permanent dosing of pyridine during reaction. Generally, the adsorption spectra were recorded at room temperature ($2\ cm^{-1}$ resolution, 100 scans) after removing the gas phase by evacuation. The figures show difference spectra obtained by subtraction of the spectrum of the activated catalyst at room temperature.

2.3. EPR experiments

EPR spectra were recorded with the cw-spectrometer ELEXSYS 500-10/12 (Bruker) in X-band. In situ-investigations under reaction conditions were performed using a home-made flow reactor [17,18], which was placed into the cavity of the spectrometer and filled with a mixture of 70 mg catalyst particles and 70 mg quartz particles (0.25–0.50 mm). The experiments were performed at 658 K using a feed composition of air/toluene (air/PMT, air/PCT, respectively) = 100 and a reciprocal space time of $W/F = 0.77\ g_{cat}\ h\ mol^{-1}$.

3. Results and discussion

3.1. FTIR spectroscopic investigations

3.1.1. Adsorption of p-substituted toluenes

The spectra observed after adsorption of toluene, PCT, and PMT on the activated VPP catalyst at room temperature are presented in Fig. 1. For comparison, the spectra of liquid toluene, PCT, and PMT are also shown. The strong increase and broadening of the typical aromatic vibrations around $1600\ cm^{-1}$ and the decrease of the bands at about $1500\ cm^{-1}$ indicate an interaction of the aromatic ring with obviously Lewis acid sites. From investigations of the pyridine adsorption at VPP, it is known that mainly Lewis acid sites and only few Brønsted acid sites are present on the surface [15]. No indication has been found for the formation of benzyl species,
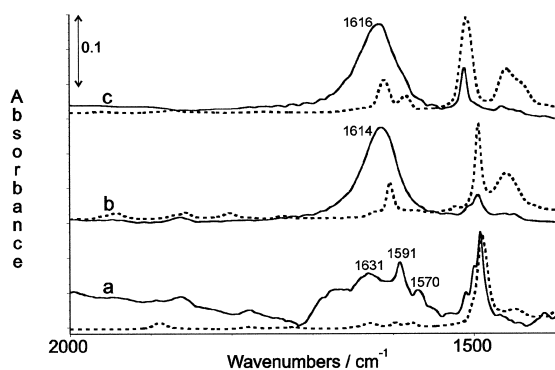
Fig. 1. FTIR spectra of (a) PCT, (b) toluene, and (c) PMT adsorbed on VPP at room temperature for 1 h after evacuation (dotted lines: spectra of liquid methyl aromatics, respectively).

which should be formed after H-abstraction in the first reaction step. The characteristic $\delta(CH_2)$ band at 1428 cm^{-1} reported in the literature [19,20] does not appear in the spectra. Whereas toluene and PCT are adsorbed in comparable quantities, about the three-fold amount of PMT was found adsorbed on the surface despite of a lower dosing in comparison to toluene. Obviously, the electron-donating ability of the methoxy group increases the electron density in the aromatic ring and favours the stronger adsorption.

The adsorption of toluene, PCT, and PMT on the VPP catalysts at 573 K for 1 h in presence of air yields the spectra, which are depicted in Fig. 2. Besides the aromatic ring vibrations at about 1600 and 1500 cm^{-1} bands in the range 1673–1683, 1745–1783 and about 1860 cm^{-1} were observed. The bands at 1683, 1673, 1677 cm^{-1} for toluene, PMT, and PCT, respectively, are most likely due to the C=O group of adsorbed coordinately bonded benzaldehydes whereas the bands at 1745–1783 and about 1860 cm^{-1} are caused by cyclic anhydride species physically adsorbed on the surface [15,21]. Such anhydrides may be generated by an oxidative attack on the aromatic nucleus and have to be considered as intermediates on the way to total oxidation. The appearance of adsorbed benzaldehyde is always accompanied by that of adsorbed cyclic anhydride. By comparing the quantities of both adsorbed species estimated by the integral absorbance, it is obvious that in the case of PCT the amount of adsorbed species is much lower than in the case of

toluene and PMT. But, whereas the sum of adsorbed aldehyde and anhydride is nearly equal in the case of toluene and PMT, the proportion of benzaldehyde to anhydride is different, namely, 1:5 (toluene) and 1:11 (PMT). For PCT, a proportion of 1:5 was estimated. The markedly higher ratio of cyclic anhydrids in the case of PMT reflects the consecutive oxidation, which leads to lower aldehyde selectivities. These findings suggest that the differences in the reactivity of the *p*-substituted toluenes are caused by their different adsorption on the catalyst surface. Obviously, the higher the electron density of the aromatic ring induced by the *p*-substituents, the better and stronger the methyl aromatics are adsorbed on the catalyst surface. This was also found for the adsorption of the aromatics at room temperature. Another aspect, which has to be considered, is the adsorption behaviour of the corresponding benzaldehydes. A similar result has to be expected, and consequently, a stronger aldehyde adsorption should lead to deeper oxidation by formation of cyclic anhydrides being precursors for total oxidation products.

Additionally, the findings described in Refs. [14,15] suggest that stronger adsorption of benzaldehyde is also caused by hydrogen bonding between the carbonyl group and acid surface hydroxyl groups, which were generated by reaction of the vanadyl pyrophosphate with water formed during oxidation. It has to be considered that water is a product of the
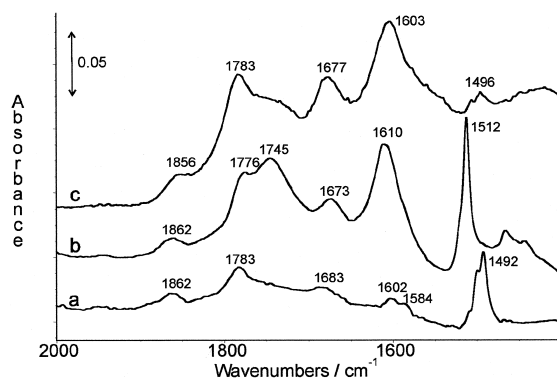

Fig. 2. FTIR spectra of adsorbed species on VPP after oxidation of methyl aromatics in presence of air for 1 h at 573 K, cooling and evacuation at room temperature: (a) PCT, (b) PMT, (c) toluene.
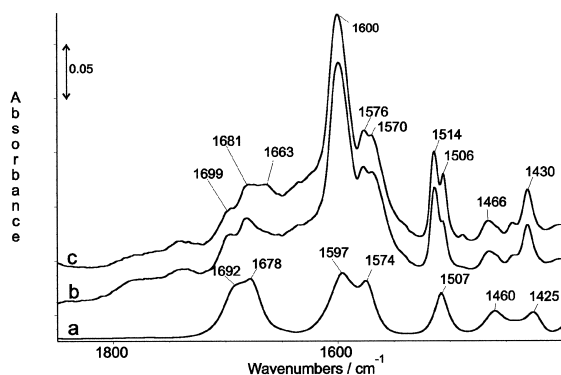
Fig. 3. FTIR spectra of (a) liquid *p*-MBA, (b) and (c) adsorbed *p*-MBA on VPP after reaction at 573 K for 30 min in presence of air, cooling and evacuation at room temperature: (b) without pre-treatment of the catalyst and (c) after pre-treatment of the catalyst with water vapour for 30 min at 573 K.

oxidation reaction and is formed in situ at the catalytic active centres of the surface and therefore it is able to influence the product adsorption. The formation of Brønsted acid sites through hydrolysis of V—O—P- and/or P—O—P-bonds by water vapour pre-treatment was proved by adsorption of pyridine [15]. Furthermore, it was shown that the co-adsorption of pyridine causes a blockade of the acid sites and therefore a suppression of deeper oxidation reactions. From this point of view, the adsorption of *p*-substituted aldehydes especially *p*-MBA and also the oxidation of *p*-substituted toluenes in presence of pyridine were investigated.

3.1.2. Adsorption of p-MBA

The simultaneous appearance of aldehyde and cyclic anhydride gives rise to the assumption that the sorption behaviour of the benzaldehydes also plays an important role for the reaction pathway and consequently for the selectivity of the oxidation reaction. The adsorption of *p*-MBA on VPP was investigated at the reaction temperature of 573 K without and with pre-treatment of the catalyst with water vapour. The spectra are represented in Fig. 3, the spectrum of liquid *p*-MBA is also included (spectrum a). By comparing spectra a and b (Fig. 3), it can be seen that the interaction of the aldehyde with Lewis acid sites at the catalyst surface particularly proceeds via the aromatic ring. The typical aromatic vibrations at

1597, 1574, 1507 cm^{-1} are split, shifted, or the intensities are changed. The bands at 1681 and 1699 cm^{-1} have to be assigned as carbonyl stretchings and are less affected.

The pre-treatment with water vapour at 573 K prior to the aldehyde adsorption was carried out to generate Brønsted hydroxyl groups and to study a possibly changed adsorption of *p*-MBA. Comparing spectra b and c (Fig. 3), it is obvious that they are alike in principle but, an additional band at 1663 cm^{-1} was observed. This band can also be assigned to the carbonyl stretching vibration. A lowering of the carbonyl stretch leads to a weakening of the C=O bond, which is caused by the interaction of the carbonyl group with the catalyst surface. Taking into account that the pre-treatment with water vapour leads to the formation of Brønsted sites at the catalyst surface, the carbonyl groups can interact with surface hydroxyl groups via hydrogen bonding. Therefore, the creation of Brønsted sites by the reaction with water promotes a stronger adsorption of *p*-MBA. This is the same effect as described in Ref. [15].

A suitable method to block permanently the hydroxyl groups which are generated during reaction, is the co-adsorption of pyridine [14]. Fig. 4 depicts the spectra of adsorbed *p*-MBA obtained after 30 min pre-treatment of the catalyst with water vapour at 573 K and following adsorption of aldehyde–air (a)
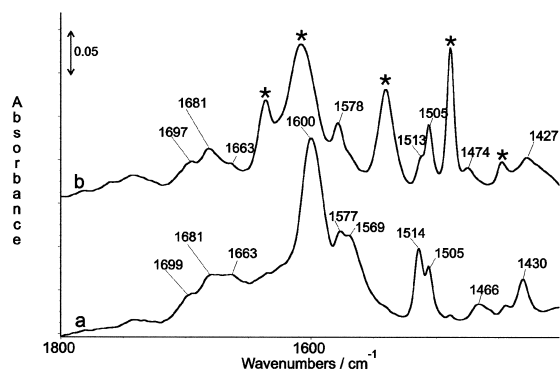

Fig. 4. FTIR spectra of *p*-MBA adsorbed on VPP in presence of air at 573 K for 30 min cooling and evacuation at room temperature: (a) after 30 min pre-treatment of the catalyst with water vapour at 573 K, (b) after 30 min pre-treatment of the catalyst with water vapour containing 4 wt.% pyridine at 573 K.

and after pre-treatment of the catalyst with a 4 wt.% solution of pyridine in water and following adsorption of aldehyde–air at 573 K (b).

The bands marked with asterisks at 1636, 1609, 1539, 1488, and 1447 cm^{-1} are typical for pyridine adsorbed at Brønsted and Lewis acid sites (Fig. 4b). It is obvious that pyridine occupies the generated hydroxyl groups (bands of pyridinium cations at 1539 and 1636 cm^{-1}). Otherwise, the known *p*-MBA bands at 1699, 1681, and 1663 cm^{-1} are also observed. The band at 1663 cm^{-1} typical for additional interaction of the carbonyl group with acid hydroxyl groups is only slightly decreased in intensity, which means that the total blockade of these acid hydroxyl groups by pyridine is hindered. In the case of benzaldehyde, it was found [15] that the strong adsorption is suppressed because pyridine blocks a predominant part of adsorption sites, especially Brønsted acidic hydroxyl groups. Obviously, this effect is less pronounced in the case of *p*-MBA. The intensities of the Brønsted and Lewis bands observed after pretreatment of the catalyst with water–pyridine vapour are diminished by subsequent *p*-MBA adsorption. This result points to a competition between pyridine and *p*-MBA adsorption. When benzaldehyde is adsorbed under comparable conditions, no intensity changes of the Brønsted and Lewis bands were observed, only the quantity of adsorbed aldehyde was diminished indicating the effective suppression of the strong aldehyde adsorption [15]. It is also seen from Fig. 4 that in consequence of the pre-treatment with water–pyridine, a modification of the typical aromatic bands of *p*-MBA (1578, 1513/1505 and 1474 cm^{-1}) in position and intensity takes place, which points to changed adsorption conditions. A possible explanation could be the additional interaction of the methoxy group with acid hydroxyl groups. Unfortunately, changes in position and splitting of the typical methoxy bands are not detectable because these bands lie in the optical opaque area of the spectrum.

The stronger adsorption of *p*-MBA on the catalyst surface via hydrogen bonding of the carbonyl group and additional interaction of the methoxy group with acid hydroxyl groups is obviously the reason for the preferred deeper oxidation of *p*-MBA forming cyclic anhydrides as intermediates for total oxidation products. The adsorption of the less basic

benzaldehyde is rather weak and can be successfully suppressed by co-adsorption of pyridine [15].

3.1.3. Oxidation of p-substituted toluenes in presence of pyridine

The spectra presented in Fig. 5 were obtained after the reaction of PMT (PCT)–air–water feed (spectra a1, b1), and PMT (PCT)–air–water–pyridine feed (spectra a2, b2) with VPP at 573 K for 1 h. Admixture of water to the feed did not influence the adsorbate spectrum of PMT (spectrum a1, Fig. 5) despite the additional band of adsorbed water around 1620 cm^{-1}, compared with that depicted in Fig. 2b. In the case of PCT, only traces of cyclic anhydride besides the band of adsorbed water could be detected. If the reaction was carried out by using a 4 wt.% pyridine water vapour mixture instead of pure water vapour, spectra a2 and b2 (Fig. 5) were obtained, which reveal the existence of pyridinium ions (Brønsted sites) at 1540 cm^{-1} as well as coordinately bonded pyridine (Lewis sites) at 1448 cm^{-1}. In the case of toluene oxidation in presence of pyridine, the typical band for adsorbed aldehyde disappears and the bands of cyclic anhydride have only a low intensity [14]. This effect is negligible in the case of PMT. The characteristic bands of adsorbed *p*-MBA (1675 cm^{-1}) and cyclic anhydride (1737, 1781 cm^{-1}) were observed also in presence of pyridine (spectrum a2, Fig. 5). For PCT, no effect
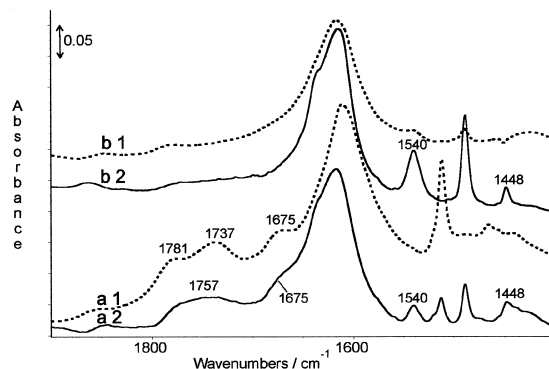

Fig. 5. FTIR spectra of adsorbates on VPP after reaction of (a1) PMT–air–water flow (molar ratio = 1:225:2), (a2) PMT–air–water flow containing 4 wt.% pyridine, (b1) PCT–air–water flow (molar ratio = 1:96:1), and (b2) PCT–air–water flow containing 4 wt.% pyridine at 573 K for 1 h cooling and evacuation at room temperature.

Table 1
Catalytic data of oxidation of PMT, toluene, and PCT obtained at conversion of 12%

	PMT	Toluene	PCT
Yield$_{aldehyde}$ (%)	0.5	1.5	4.7
Selectivity$_{aldehyde}$ (%)	4.0	13.0	40.0

with reference to the aldehyde/anhydride adsorption was found, only the bands at 1540 and 1448 cm^{-1} indicate Brønsted and Lewis sites. The intensity of the typical pyridinium band at 1540 cm^{-1} is greater for PCT than for PMT, which means that in the case of PCT more Brønsted sites are blocked by pyridine. Obviously, the more basic PMT and/or *p*-MBA are able to compete with pyridine for possible adsorption places. This is in good agreement with the results of *p*-MBA adsorption described in Section 3.1.2.

The results of the catalytic tests using PMT (PCT)–air–water feed are presented in Table 1. At constant conversion rate of 12%, the yield and selectivity follow the order PCT > toluene > PMT. This order corresponds with the increasing nucleophilic character of the aromatic ring in the methyl aromat-ics and the aldehydes leading to an increasing strength of adsorption at the catalyst surface in the same order. Especially, strong aldehyde adsorption favours deeper oxidation and, thus, consequently lower alde-hyde selectivities are observed.

Additionally, co-adsorption of pyridine can influ-ence the sorption properties, especially in the case of benzaldehyde formation. The influence on the sorp-tion properties of substituted methyl aromatics seems to be more complicate. Co-adsorption as well as steric properties could be involved, probably.

3.2. EPR spectroscopic investigations

The EPR spectrum of VPP is characterized by a slightly anisotropic singlet with a peak-to-peak line width of about 8 mT (Fig. 6). The rather small line width is caused by exchange-narrowing, which arises from effective interactions between the spins of neighbouring VO^{2+} centres within the ladder-like double chains of VO$_6$ octahedra in the crystal struc-ture of (VO)$_2$P$_2$O$_7$ [22]. This interaction averages out the hyperfine splitting from the coupling of the
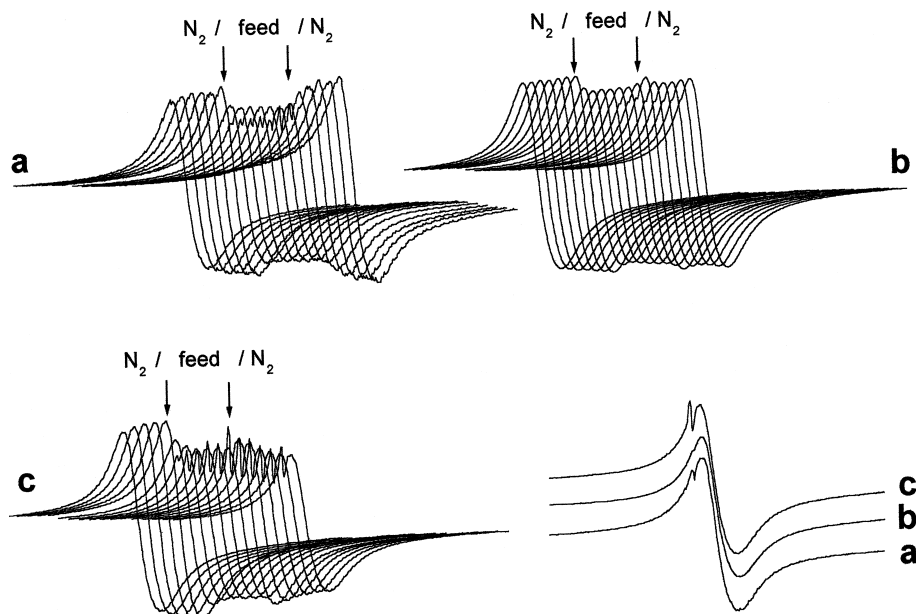

Fig. 6. In situ EPR spectra of VPP at 658 K (300 < B$_0$/mT < 400) during subsequent periods under flow of N$_2$, (a) toluene–air, (b) PCT–air, (c) PMT–air, respectively, and again N$_2$ (time interval between spectra: 10 min). Additionally, the spectra after 60 min under feed are shown separately.

unpaired electron with the nuclear spin of the vanadium ($I = 7/2$), which is characteristic of EPR spectra of isolated tetravalent vanadium ions. The line width of the exchange-narrowed EPR signal depends sensitively on the strength of the exchange interaction: The stronger the exchange interaction the smaller the line width. Accordingly, the signal amplitude follows the reverse trend.

In the in situ-EPR experiments presented in Fig. 6, the VPP catalyst was heated under nitrogen flow at 658 K for 1 h. Then, nitrogen was replaced by the reactant/air mixture and the reaction was run for 1 h before switching back to nitrogen again and keeping at 658 K for another hour. During the whole period, EPR spectra were recorded after every 10 min. For all substrates, a sudden decrease of the EPR signal intensity was observed on switching from nitrogen to feed. The effect is most pronounced for PMT (Fig. 6c) and only weakly visible for PCT (Fig. 6b). It is caused by a perturbation of the spin–spin exchange interaction, which arises since the electron density of vanadyl sites on the surface is altered due to the adsorption of the basic aromatic ring system and alternating reduction and re-oxidation according to a Mars-van-Krevelen mechanism [23].

The extent of spin–spin exchange perturbation and, thus, the loss of the EPR signal intensity depends on the nature of the aromatic substrate. It is strongest for PMT in which the electron donating p-OCH$_3$ substituent enhances the nucleophilic properties of the aromatic system in comparison to toluene and, accordingly, the adsorption strength of the aromatic ring. A similar behaviour of substituted toluenes has been observed, too, in their ammoxidation to the corresponding benzonitriles over catalysts based on $(NH_4)_2(VO)_3(P_2O_7)_2$ [23]. The adsorption of PMT is obviously so strong that, in contrast to toluene (Fig. 6a) and PCT (Fig. 6b), it cannot be removed on switching back from feed to nitrogen flow. This observation agrees with the in situ FTIR results. Moreover, a narrow singlet is superimposed on the exchange narrowed EPR signal of VPP that arise from carbon radicals, which are formed as intermediates in the course of oxidative educt degradation to CO$_x$. The radical signal is most pronounced for PMT for which catalytic tests revealed lowest selectivity and virtually not visible for PCT (Fig. 6). By comparing the results for the three different

substrates, it is obvious that strong product adsorption favoured by electron donating second substituents (p-OCH$_3$) facilitates total oxidation and leads to lower selectivities. The opposite effect is observed for substrates with electron withdrawing second substituents (p-Cl).

4. Conclusions

The FTIR and EPR investigations of the adsorption and oxidation reactions of p-substituted toluenes on VPP improved the knowledge about the nature and quantities of the adsorbed species and their interaction with the active vanadyl sites of the catalyst surface. In dependence on the substrate, different amounts of strongly adsorbed benzaldehyde and adsorbed cyclic anhydride species have been detected by FTIR. The extent of spin–spin exchange pertubation and, thus, the loss of the EPR signal intensity caused by substrate adsorption and interaction are influenced by the nature of the aromatic compound. Taking into consideration that adsorption proceeds via the aromatic ring on Lewis acid sites of the rather acid catalyst surface, the strong adsorption of PMT in contrast to toluene and PCT is caused by the electron-donating ability of the methoxy group, which increases the electron density of the aromatic nucleus. The strong reactant adsorption on the one hand and the strong adsorption of the products especially benzaldehydes on the other hand are important factors, which influence the benzaldehyde selectivity markedly. The carbonyl groups, normally unaffected by adsorption of the benzaldehydes, participate in the adsorbate complex when Brønsted acid hydroxyl groups are present at the surface formed during oxidation reaction. Additional hydrogen bonding between the carbonyl and hydroxyl groups leads to a strengthening of the aldehyde adsorption. Whereas this strong adsorption could be successfully suppressed by the co-adsorption of pyridine in the case of the lower basic substrates p-chlorobenzaldehyde and benzaldehyde, this effect was not pronounced in the case of p-MBA because this more nucleophilic compound is able to compete with pyridine for the adsorption sites. But, the selectivity enhancing effect of pyridine was only found for benzaldehyde, not for

p-chlorobenzaldehyde. This suggests that, besides the acid/basic character of the reactants, their steric properties also seem to play an important role for adsorption. By comparing the results for the three different substrates, it is obvious that strong product adsorption favoured by electron donating second substituents facilitates total oxidation leading to lower aldehyde selectivities. The catalytic tests confirmed this observations. So, enhanced yields and selectivities at constant conversion in the order PMT < toluene < PCT were found.

To improve the aldehyde selectivities, also the modification of the surface by basic sites, seem to be recommendable.

Acknowledgements

References

[1] T. Tzedakis, A.J. Savall, Ind. Eng. Chem. Res. 31 (1992) 2475.
[2] R.A. Sheldon, N. de Heij, Stud. Org. Chem. 33 (1988) 234.
[3] F. Brühne, E. Wright, in: Ullmann (Ed.), Electronic Release, 6th edn.,1998, (benzaldehyde entry).
[4] M. Ueshima, N. Saito, Chem. Lett. (1992) 1341.
[5] M. Ueshima, N. Saito, N. Shimizu, Stud. Surf. Sci. Catal. 90 (1994) .
[6] B.M. Reddy, I. Ganesh, B. Chowdhury, Chem. Lett. (1997) 1145.
[7] B.M. Reddy, M.V. Kumar, K.J. Ratnam, Appl. Catal., A 181 (1999) 77.
[8] J.S. Yoo, Appl. Catal., A 135 (1996) 261.
[9] J.S. Yoo, Appl. Catal., A 143 (1996) 29.
[10] D.L. Trimm, M. Irshad, J. Catal. 18 (1970) 142.
[11] G. Centi (Ed.), Vanadylpyrophosphate catalysts, Catal. Today vol. 16 1993.
[12] A. Martin, H. Berndt, B. Lücke, M. Meisel, Top. Catal. 3 (1996) 377.
[13] A. Martin, U. Bentrup, A. Brückner, B. Lücke, Catal. Lett. 59 (1999) 61.
[14] A. Martin, U. Bentrup, B. Lücke, A. Brückner, Chem. Commun. (1999) 1169.
[15] U. Bentrup, A. Martin, B. Lücke,Topics Catal. in press.
[16] A. Brückner, U. Bentrup, A. Martin, J. Radnik, L. Wilde, G.-U. Wolf, Stud. Surf. Sci. Catal., Topics Catal. 11/12 (2000) 139.
[17] A. Brückner, B. Kubias, B. Lücke, R. Stößer, Colloids and Surfaces 115 (1996) 179.
[18] H.G. Karge, J.P. Lange, A. Gutze, M. Laniecki, J. Catal. 114 (1988) 144.
[19] G. Busca, J. Chem. Soc., Faraday Trans. 89 (1993) 753.
[20] Y. Zhang, A. Martin, H. Berndt, B. Lücke, M. Meisel, J. Mol. Catal. A 118 (1997) 205.
[21] A.J. van Hengstum, J. Pranger, S.M. van Hengstum-Nijhuis, J.G. van Ommen, P.J. Gellings, J. Catal. 101 (1986) 323.
[22] A. Brückner, G.-U. Wolf, M. Meisel, R. Stößer, Eur. J. Solid State Inorg. Chem. 30 (1993) 801.
[23] A. Brückner, A. Martin, B. Lücke, F.K. Hannour, Stud. Surf. Sci. Catal. 110 (1997) 919.