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Catalytic performance of vanadyl pyrophosphate in the partial oxidation of toluene to benzaldehyde

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Dedicated to Professor Dr. Manfred Baerns on the occasion of his 65th birthday

Vanadyl pyrophosphate catalysts were generated by dehydrating $VOHPO_4\cdot(1/2)H_2O$ at different temperatures and duration of the dehydration procedure. The as-synthesised materials were characterised by X-ray diffractometry, FTIR spectroscopy and temperature-programmed reduction. The prolongation of the formation period at higher temperatures led to improved crystallinity and lower BET surface areas of the vanadyl pyrophosphate specimens and, additionally, a significantly impeded reducibility of the vanadyl sites was observed. The catalytic performance of the samples was tested in the partial oxidation of toluene to benzaldehyde. The obtained results revealed an increasing benzaldehyde selectivity with improved crystallinity. *In situ* FTIR and ESR spectroscopy were used to throw more light on the interaction of the toluene–air feed with the surface of the catalyst.

Keywords: vanadyl pyrophosphate, partial oxidation of toluene, *in situ* spectroscopy, reactant–catalyst interaction

1. Introduction

Benzaldehyde is the simplest and industrially the most important aromatic aldehyde. In general, it is produced by the hydrolysis of benzal chloride or the partial oxidation of toluene [1]. Due to the industrial demand and the obligation to reduce chlorine-dependent chemical production a growing importance must be attached to the partial oxidation in the liquid as well as in the gas phase. In the latter case, the oxidation is usually carried out by passing a vaporised toluene–air mixture through a catalyst bed at short residence times (0.1–1.0 s) at a temperature of ca. 573–873 K. Mainly vanadium(V) oxide and transition metal oxides of the elements of groups V and VI, sometimes mixed with other oxides, doped with alkali metals and on carriers are used as catalysts [1]. In general, low conversion rates of 10–25% are favoured to avoid deeper oxidation, however, selectivities of only 40–60% are reached [1]. Therefore, this reaction has been studied by many researchers to improve its performance [2–6]. The reason for the rather low selectivities can be seen in the fact that benzaldehyde itself is easily further oxidised to benzoic acid and it is also supposed that Me–OH sites are responsible for the oxidation of the aromatic nucleus [7]. Thus, various O-containing by-products are observed apart from benzoic acid, for example, maleic as well as phthalic anhydride, quinones and others [8,9]. Many of these compounds may act as precursor structures of coke-like intermediates which are, in turn, converted to CO_x.

Vanadium phosphates (VPO) are well known as catalysts for selective O- and N-insertion reactions of aliphatics and methyl aromatics [10–12]. This class of catalysts has been intensively investigated in the last decade because of its immense significance in the n-butane oxidation reaction to maleic anhydride. Vanadyl pyrophosphate $(VO)_2P_2O_7$ is the outstanding specimen of these materials [10].

Recent investigations on the mechanism of the ammoxidation of toluene revealed that benzaldehyde appears as first oxygen-containing intermediate during the reaction cycle [13,14], however, benzaldehyde is never found in the product stream since it reacts very fast with surface ammonium groups to benzonitrile. Therefore, the idea arose to investigate the catalytic performance of $(VO)_2P_2O_7$ in a partial oxidation carried out in the absence of ammonia. It was the aim of the present work to study the partial oxidation of toluene to benzaldehyde and to elucidate the aldehyde selectivity limiting factors by the help of *in situ* methods.

2. Experimental

2.1. Catalysts

Different $(VO)_2P_2O_7$ (VPP) catalysts were prepared by a usual dehydration procedure under nitrogen (10 l/h) using $VOHPO_4\cdot(1/2)H_2O$ as the starting material [10]. The obtained samples were characterised by X-ray diffractometry (XRD; Stoe automatic transmission powder diffractometer equipped with a Ge monochromator and a linear position-sensitive detector using Cu Kα_1 radiation), FTIR spectroscopy (Mattson Galaxy 5020) using the KBr technique and temperature-programmed reduction (TPR; AMI-1, Altamira Instruments) using 5% H_2 in Ar as the reduction gas (50 ml/min, heating rate $\beta = 10$ K/min). The surface

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Table 1
Preparation of $(VO)_2P_2O_7$ catalysts by dehydration of $VOHPO_4\cdot(1/2)H_2O$ and some characterisation data.

Sample	$T_{\text{dehydration}}$ (K)	$t_{\text{dehydration}}$ (h)	$T_{\max}$ (TPR) (K)	BET ($m^2\,g^{-1}$)
VPP-1	723	4	1070	6.6
VPP-2	873	4	–[a]	6.4
VPP-3	1023	4	1076	6.0
VPP-4	1023	72	1094	4.7

[a] Not determined.

areas of the solids were determined, using the BET method (Gemini III, Micromeritics). Table 1 shows a survey on the sample preparation and some data of the physico-chemical characterisation.

2.2. Catalytic measurements

The catalytic properties of the solids were determined during the oxidation of toluene to benzaldehyde, using a fixed bed U-tube quartz-glass reactor (i.d. 8 mm, 0.5 mm thermocouple inside, ca. 3 ml effective volume). The catalysts (0.5 ml each, corresponding to ca. 0.5 g) were used as sieve fractions (1–1.25 mm) and mixed with the equal portion of quartz glass (1 mm) to avoid local overheating. The following reaction conditions were applied: toluene : air molar ratio $= (0.5, 1, 2):100$, atmospheric pressure, W/F (total flow) $\approx 1\ \text{g}\,\text{h}\,\text{mol}^{-1}$. Additionally, the oxygen content of the feed was varied (toluene : O_2 molar ratio $= 1:(22, 16, 6)$; N_2 was added to keep a constant W/F). The catalytic runs were performed at ca. 623, 648 and 673 K for 30 min each. The product stream was trapped in ethanol and analysed by off-line capillary GC using a FID as detector. The formation of carbon oxides was permanently followed by non-dispersive IR photometry.

2.3. In situ catalyst characterisation

The *in situ* FTIR investigations were carried out on a Bruker IFS 66 FTIR spectrometer using self-supporting discs with a diameter of 20 mm and a weight of 50 mg mounted in a heated IR cell. The samples were pretreated by heating up to 723 K ($\beta = 10$ K/min) under vacuum for 1.5 h. The adsorption spectra were recorded, adopting the following procedure: a sample was heated up to 473, 523, 573 and 623 K each under a toluene–air stream (molar ratio $= 1:100$), using a saturator, then kept under the feed stream at the chosen temperature for 1 h, cooled down to room temperature followed by evacuation and recording the spectra.

In situ ESR measurements were performed with the cw spectrometer ELEXSYS 500-10/12 (Bruker) equipped with a flow reactor and a gas–liquid supplying system, consisting of mass flow controllers and saturators [15,16]. 0.14 g of the solids (0.5–1 mm fraction) each were applied as the catalyst. The samples were tested under similar toluene oxidation conditions as described above.

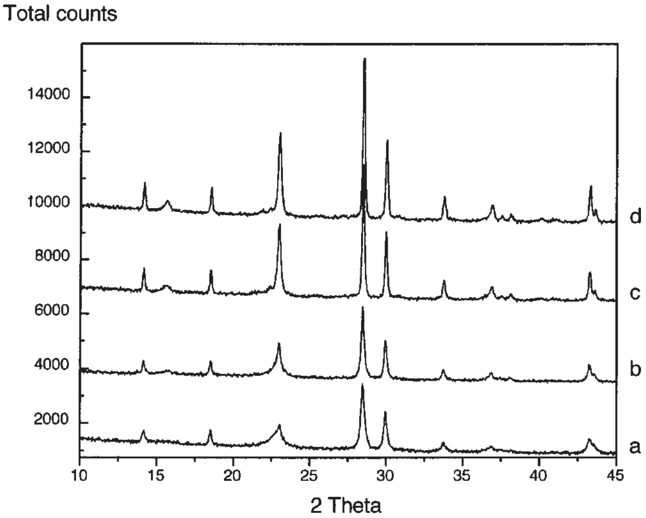

Figure 1. XRD pattern of the parent vanadyl pyrophosphate specimens generated by dehydration of $VOHPO_4\cdot(1/2)H_2O$ in dependence on temperature and time. (a) VPP-1: 723 K, 4 h; (b) VPP-2: 873 K, 4 h; (c) VPP-3: 1023 K, 4 h; (d) VPP-4: 1023 K, 72 h.

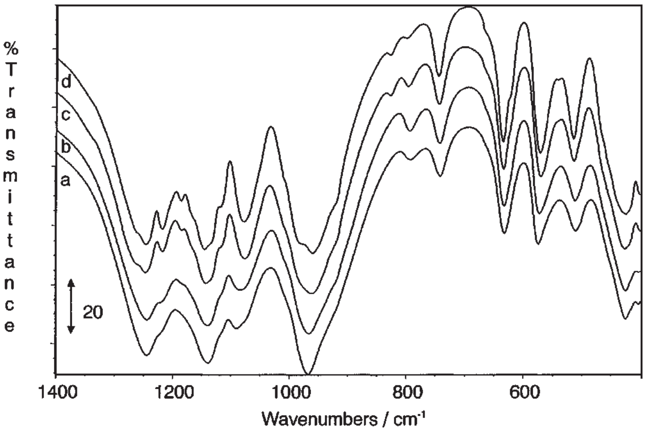

Figure 2. FTIR spectra of the parent vanadyl pyrophosphate samples obtained by different $VOHPO_4\cdot(1/2)H_2O$ dehydration procedures. (a) VPP-1: 723 K, 4 h; (b) VPP-2: 873 K, 4 h; (c) VPP-3: 1023 K, 4 h; (d) VPP-4: 1023 K, 72 h.

3. Results and discussion

3.1. Catalytic investigations

Figure 1 depicts the recorded XRD patterns that reveal an improved crystallinity of the VPP specimens with increasing dehydration temperature and prolonged treatment. The intensity of the main reflections is significantly enhanced. The amorphous background is suppressed and the characteristic reflections are markedly narrowed. Recently, similar observations were made by Delichère et al. [17], showing also a number of VPP powder patterns.

An improved crystallinity could also be seen by recording the structure vibration bands of the solids by FTIR spectroscopy (figure 2). In comparison to VPP-4 (spectrum (d)), having been calcined under more severe conditions, the IR bands of VPP-1 (spectrum (a)) are broader and less resolved, pointing to lower crystallinity of the lat-

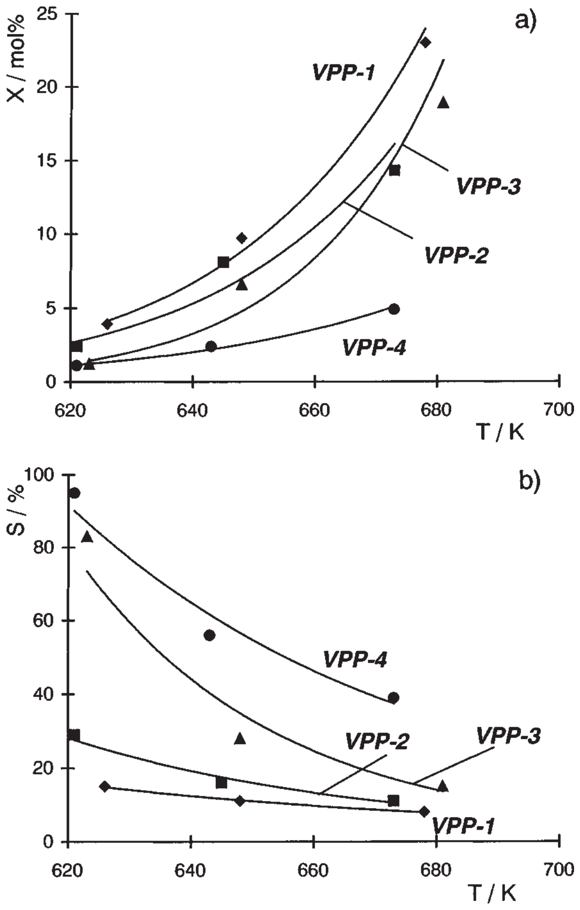

Figure 3. Toluene conversion (a) and benzaldehyde selectivity (b) vs. reaction temperature, respectively, during the oxidation of toluene on differently generated $(VO)_2P_2O_7$ catalysts (0.5 g catalyst, toluene : air molar ratio $= 1:100$, $W/F = 0.9$ g h mol^{-1}).

ter. In addition to diverse PO_3 (ν_s, ν_{as}) bands in the 1030–1230 cm^{-1} region, the intensity of the characteristic pyrophosphate P–O–P (ν_s) band at ca. 745 cm^{-1} is increased. A strong band at ca. 975–980 cm^{-1} can be assigned to $V^{IV}{=}O$ groups. The improvement of the crystallinity is also supported by the TPR data (see table 1), showing a shift of the peak maximum of the first reduction peak to higher temperatures.

The catalytic results (figure 3 (a) and (b)) reveal a decreasing toluene conversion with an increasing crystallinity of the samples that is caused by more severe calcination conditions. Simultaneously, a significantly increased benzaldehyde selectivity is found. This is not only due to the real conversion–selectivity relationship. The reason for the dropped activity and the over-proportionally enhanced selectivity can be rather seen in the more perfect generation of the crystals, i.e., the improvement of the solid crystallinity. This has been proven by the calculation of area-specific toluene conversion rates that results in the same ranking of the activity drop instead of the expected equal activity data that would be found if only the surface area is reduced but the number of active sites per surface area unit remains constant. It is supposed that with the progressive improvement of the crystallinity the number of sites involved in unselective pathways is reduced (e.g., acid OH groups [7]), i.e., the benzaldehyde selectivity is over-proportionally increased. Table 2 lists some benzaldehyde selectivity data at constant conversion as well as area-specific toluene conversion rates to support these ideas. On the other hand, a higher amount of water is formed by the proceeding oxidation reaction with increasing reaction temperature which might create new OH groups and, thus, favour the unselective reaction pathway as well. Catalytic tests with a decreasing oxygen proportion (toluene : O_2 molar ratio $= 1:(22, 16, 6)$) in the feed reveal an additional drop of the toluene conversion and the aldehyde selectivity could be further increased by ca. 10%.

Table 2
Area-specific toluene conversion rates (R_{tol} (μmol h^{-1} m^{-2})) at different reaction temperatures and benzaldehyde selectivity data (S_{ba}) at a constant toluene conversion (X_{tol}) in dependence on the sample crystallinity.

Sample	R_{tol} (μmol h^{-1} m^{-2})			S_{ba} at $X_{tol} = 5$ mol%
	ca. 623 K	ca. 648 K	ca. 673 K	(%)
VPP-1	73.7	183.2	434.4	15
VPP-2	45.7	154.2	272.2	20
VPP-3	20.6	113.4	324.7	35
VPP-4	25.1	54.7	111.8	47

As expected, the toluene concentration dependent investigations carried out on VPP-2 at several temperatures show the lowest toluene conversion at its highest concentration in the feed (figure 4(a)). Otherwise, the benzaldehyde selectivities (figure 4(b)) approach an average value with increasing toluene proportion in the feed. It can be seen that the highest aldehyde selectivity is reached at low reaction temperatures (623 K) and low toluene : air ratio. No significant influence of the toluene concentration in the feed is observed at 648 K but, interestingly, the selectivity still increases at 673 K. At this high reaction temperature (673 K) the normal relation of increasing selectivity with decreasing conversion is observed. Surprisingly, this behaviour tends to be inverted as the reaction temperature drops; despite a decreasing toluene conversion at 623 K the benzaldehyde selectivity drops as well with increasing toluene : air ratio. The reason may be that in the latter case benzaldehyde is stronger adsorbed on the catalyst surface and, thus, can be further oxidised to by-products and/or CO_x.

3.2. In situ FTIR spectroscopy

Figure 5 depicts the FTIR spectra recorded after passing a toluene–air feed over the VPP-1 catalyst at temperatures up to 623 K. It can be clearly seen that the bands at 1678, 1783 and 1852 cm^{-1} increase with higher reaction temperatures. The first band is typical for adsorbed benzaldehyde, the others can be assigned to adsorbed cyclic anhydride [18]. Such anhydrides can be generated by an oxidative attack on the aromatic nucleus of the chemisorbed toluene and/or the formed benzaldehyde that is rather likely and, consequently, are considered as total oxidation intermediates by a deeper oxidation as mentioned [9]. It can be stated that with higher amounts of formed benzaldehyde also the proportion of the produced cyclic anhydride is increased. Its formation is more pronounced at higher reaction temperatures, leading in turn to lower benzaldehyde amounts, as also found during the catalytic tests. Thus, these *in situ* measurements have shown that the formation of by-products is always present and governs the reaction pathway with increasing reaction temperature. Furthermore, it seems very likely that the generated benzaldehyde cannot desorb fast enough from the catalyst surface and will be deeper oxidised.

3.3. *In situ* ESR spectroscopy

The *in situ* ESR investigations are performed with the VPP-1 catalyst at similar reaction conditions as applied in the catalytic tests. Figure 6 (a)–(c) demonstrates three series of *in situ* spectra recorded at different reaction temperatures and gas flows. The following procedure is adopted: the catalyst is heated under nitrogen up to the chosen temperature (608, 658 and 673 K) and kept for 1 h at this temperature before the gas flow is switched to the toluene–air feed (denoted as point A), after 1 h of reaction the gas flow is changed back to nitrogen (denoted as point B) and some

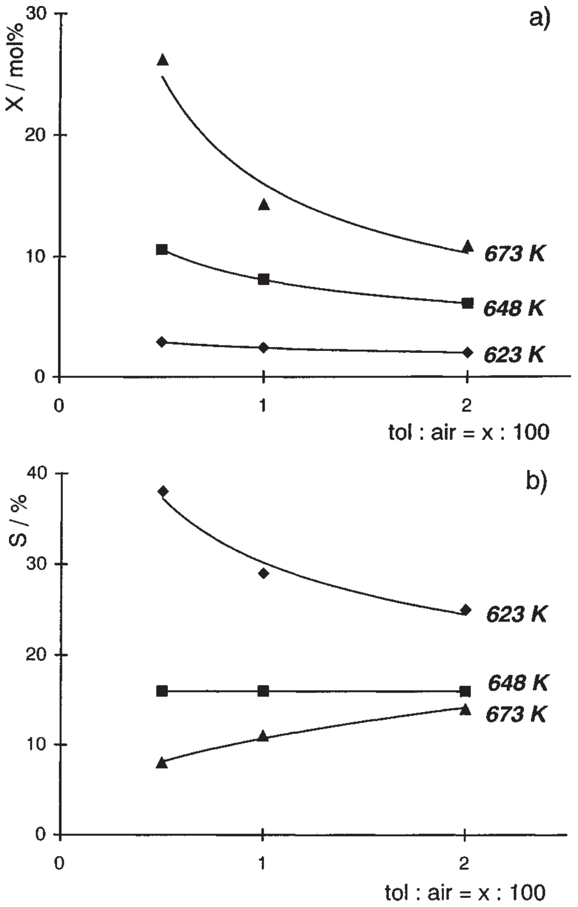

Figure 4. Toluene conversion (a) and benzaldehyde selectivity (b) vs. toluene : air molar ratio, respectively, during the partial oxidation of toluene on VPP-2 (0.5 g catalyst, $W/F = 0.9$ g h mol^{-1}).

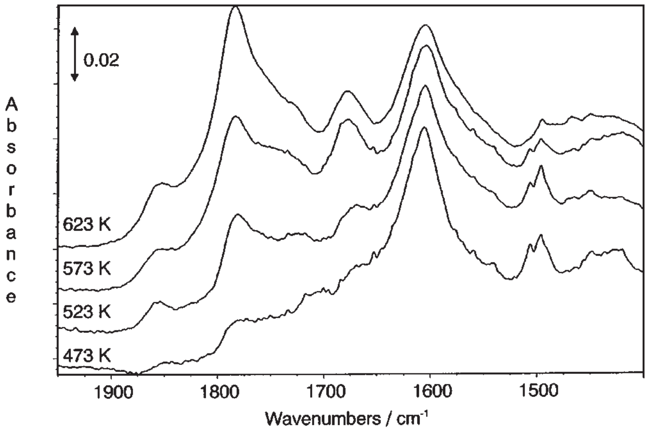

Figure 5. FTIR spectra (catalyst spectra recorded after pretreatment were subtracted) of adsorbed species on VPP-1 after oxidation of toluene in the presence of air at different reaction temperatures.

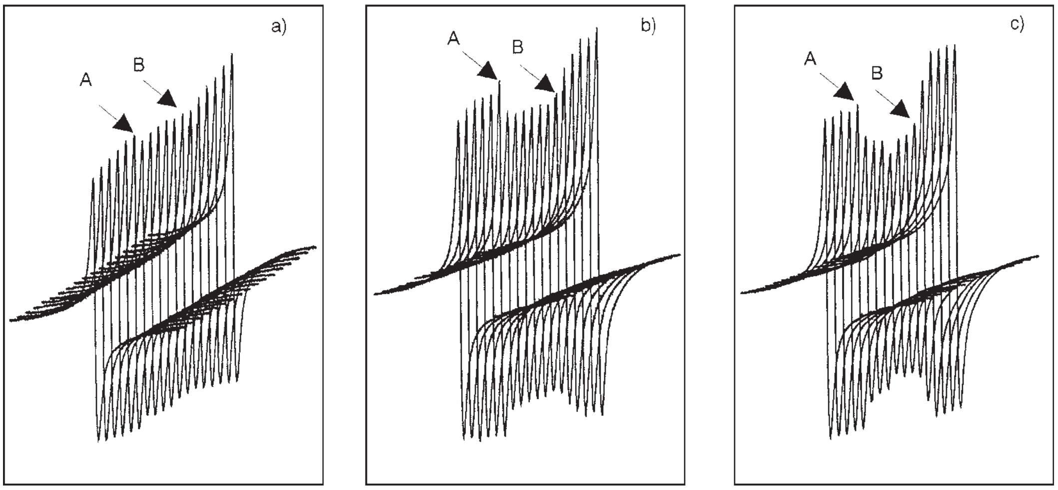

Figure 6. *In situ* ESR spectra of VPP-1 during the oxidation of toluene at (a) $T = 608$ K, (b) $T = 658$ K and (c) $T = 673$ K under the following gas flow sequence: N_2, gas switch A, toluene : air = 1 : 100, gas switch B, N_2.

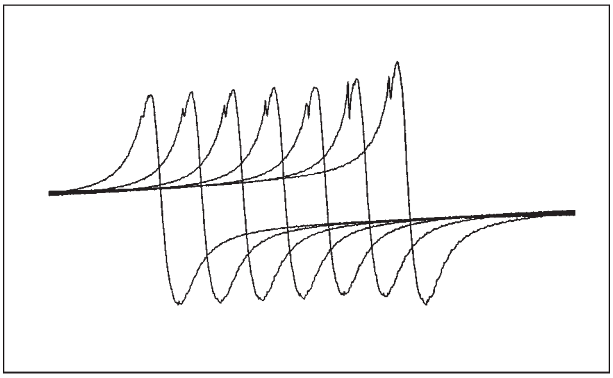

Figure 7. Detail of *in situ* ESR spectra of VPP-1 during the oxidation of toluene at $T = 658$ K showing the superposition of the vanadyl signal by the narrow signal of radicalic carbon species.

further spectra are taken under nitrogen. The ESR spectra are recorded in time intervals of 10 min each.

The spectra of series (a) show no significant change during the contact with the toluene–air feed, i.e., no remarkable interaction of the reactants with the catalyst surface occurs and, as expected, no toluene conversion is observed. The *in situ* spectra alter by increasing the reaction temperature (series (b)). The reversible intensity decrease under feed is due to line broadening and reflects the distortion of the spin–spin exchange interaction between coupled vanadyl sites of the catalyst by reduction/reoxidation cycles of the latter [15]. Simultaneously, a sharp increase of the toluene conversion was determined gas-chromatographically. Furthermore, the spectra increasingly reveal the superposition of a very narrow signal with time-on-stream, indicating the formation of radicalic carbon species, as shown in detail in figure 7. Since deactivation by coking of the catalyst surface seems not to play an important role because no coke deposition after catalytic runs is observed, it is very likely that carbon radicals are intermediates of the CO_x formation and, thus, responsible for low benzaldehyde selectivities. Interestingly, the original signal shape and height is not restored immediately after changing back to nitrogen. This process takes roughly 1 h. It can be concluded that such a behaviour points to a strong interaction of benzaldehyde and deeper oxidation products with the catalyst surface, i.e., significant higher benzaldehyde selectivities that would require a faster desorption cannot be reached. At even higher reaction temperature the observed effect (series (c)) is more marked but the carbon radical derived peak is reduced. This could be due to the higher reaction temperature, leading to a faster burn-off of coke-like surface compounds.

4. Conclusion

The investigations have shown that vanadyl pyrophosphates are able to catalyse the partial oxidation of toluene to benzaldehyde. The aldehyde selectivity can be significantly increased at low conversions with an improved solid crystallinity. The applied *in situ* methods have allowed first insights into chemisorption processes and reaction pathways. They have demonstrated that the generated benzaldehyde is strongly adsorbed on the catalyst surface and, therefore, consecutive reaction products such as cyclic anhydrides and radicalic degradation products of the aromatic ring can be formed easily. Higher reaction temperatures promote the total oxidation. The sorption behaviour of the investigated solids may be mainly determined by their acid–base properties on-stream, being still under study.

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