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Permanent blockade of *in situ*-generated acid Brønsted sites of vanadyl pyrophosphate catalysts by pyridine during the partial oxidation of toluene

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The permanent blockade of *in situ*-formed Brønsted-acid OH groups and an effective lowering of the catalyst acidity during the partial oxidation of toluene to benzaldehyde is demonstrated by an efficient method using a continuous dosing of pyridine to the feed that leads to drastically increased aldehyde selectivities.

Vanadium phosphates (VPO) are well known as catalysts for selective O- and N-insertion reactions of aliphatics and methylaromatics.[1,2] Recently, we have studied the ammoxidation of toluene on vanadyl pyrophosphate [$(VO)_2P_2O_7$] in detail and obtained knowledge on the formation of benzaldehyde, acting as a reaction intermediate.[3] Therefore, the idea arose to test these catalysts for the partial oxidation of toluene. However, the catalytic performance of these solids is rather poor: benzaldehyde selectivities $>40\%$ could only be reached at toluene conversions $<5\%$ and mainly carbon oxides were identified as by-products in the effluent. A number of further oxidised intermediates (cyclic anhydrides are of prime importance) that remain chemisorbed on the catalyst surface were detected by FTIR spectroscopy.[4] The reason for the rather low aldehyde selectivity can be seen in a very strong adsorption of toluene and/or intermediates on the rather acidic surface of the VPO catalyst as confirmed by *in situ*-EPR measurements carried out recently.[4] Furthermore, it is also supposed that the existence of M–OH sites could be involved in the oxidation of the aromatic nucleus, leading to total oxidation.[5]

Here, we present investigations on the partial oxidation of toluene to benzaldehyde with vanadyl pyrophosphate used as catalyst, especially on the effect of Brønsted-acid OH groups of the catalyst surface using *in situ*-FTIR spectroscopy. A procedure is proposed to block such *in situ*-generated acid OH groups by pyridine. Additionally, an effective increase of the basicity of the catalyst surface can be reached that might enhance the desorption rate of the desired aldehyde.

$(VO)_2P_2O_7$ (VPP) was generated by the usual dehydration of $VOHPO_4 \cdot 0.5H_2O$ used as precursor compound (723 K, 4 h, 10 l h^{-1} N_2). The catalytic properties were determined during the oxidation of toluene to benzaldehyde, using a fixed bed quartz-glass reactor. The catalyst (0.5 g) was applied as sieve fraction (1–1.25 mm) and mixed with an equal portion of quartz glass (1 mm) to avoid local overheating. The effluent was analysed by GC and the formation of CO/CO_2 was permanently followed by non-dispersive IR photometry. 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 an heated IR cell.

Fig. 1 depicts FTIR spectra of adsorbates of the partial oxidation of toluene (air– toluene = 100 : 1, 573 K) on VPP [*(a)* fresh VPP, *(b)* VPP pretreated with water vapour (4.2 mmol h^{-1} H_2O in air, 30 min) at 573 K prior to feed exposure). Beside the bands of the aromatic ring vibration (1605, 1500 cm^{-1}) and that of the adsorbed benzaldehyde (1678 cm^{-1}), the bands of cyclic anhydrides (1858, 1783 cm^{-1}) always appeared. These cyclic anhydrides can be considered as total oxidation precursors.[6] Additionally, Fig. 1 also shows FTIR spectra of air–benzaldehyde mixtures (air–benzaldehyde = 91 : 1) adsorbed at 573 K on the parent VPP sample *(c)* and on a VPP specimen pretreated with water vapour as mentioned above *(d)*. Normally, the benzaldehyde adsorption is characterised by the appearance of two vibration bands at *ca.* 1720 and 1705 cm^{-1} assigned as carbonyl stretching vibrations. In the spectrum of the water vapour pretreated sample a further carbonyl stretching band at 1685 cm^{-1} has been observed. The shift of the carbonyl band to lower wavenumbers points to a weakening of the C=O bond. This effect can be explained by a strengthening of the adsorption of the aldehyde[7] by interaction of neighbouring OH groups with the carbonyl groups probably *via* hydrogen bonding. This can also be seen in the case of the toluene–air adsorption under working conditions [Fig. 1, spectra *(a)* and *(b)*]: The carbonyl band is obviously shifted to lower wavenumbers, independent of the catalyst pretreatment, *i.e.* the water produced during the catalytic reaction causes the same effect as has been found for the water vapour pretreatment of the catalyst. This behaviour explains the findings of the recent *in situ*-EPR measurements[4] and provides a reason for the strong chemisorption of aldehyde intermediates and therefore, their subsequent oxidation in consecutive reactions.

Scheme 1 illustrates these ideas. The VPP catalyst surface consists of vanadyl dioctahedra units linked *via* V–O–P bridges with the phosphate tetrahedra of the pyrophosphate chains. A toluene molecule is chemisorbed on the Lewis sites *via* its π-electron system. An electrophilic attack on the methyl group leads to a methylene-like species, water is probably eliminated by the collaboration of bulk oxygen, which is in turn replaced by gas-phase oxygen. Thus, benzaldehyde is formed that is able to desorb, but simultaneously, the liberated water molecule can attack the neighbouring V–O–P bond, generating OH groups (V–OH and P–OH) which interact with benzaldehyde *via* hydrogen bonding and its fast desorption is markedly hindered.

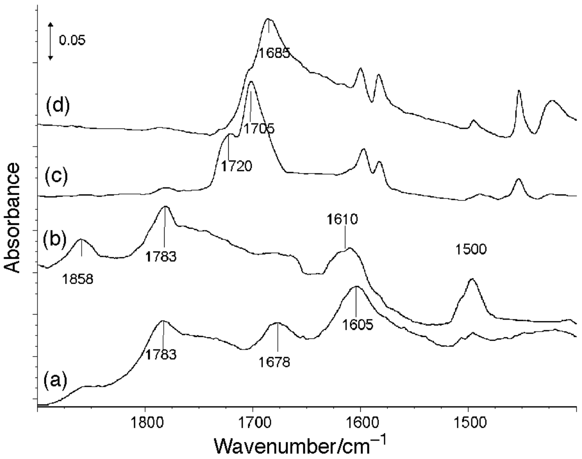
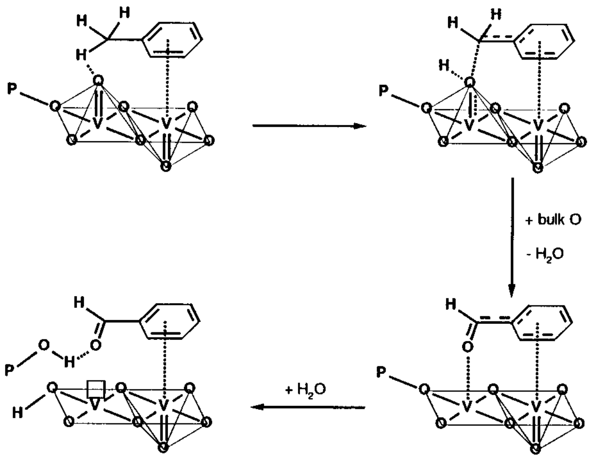


Fig. 1 FTIR spectra of adsorbates on a $(VO)_2P_2O_7$ catalyst at 673 K: (a) air–toluene flow (molar ratio = 100 : 1, 4.2 mmol toluene h^{-1}, 60 min), (b) the same air–toluene flow after water vapour pretreatment (4.2 mmol H_2O h^{-1} in air, 30 min), (c) air–benzaldehyde flow (molar ratio = 91 : 1, 2.3 mmol benzaldehyde h^{-1}, 60 min) and (d) the same air-benzaldehyde flow after water vapour pretreatment (4.2 mmol H_2O h^{-1} in air, 30 min).



Scheme 1

The blockade or poisoning of OH groups by alkali metal cations[8] or tertiary amines[9] prior to use is already known but also *in situ*-poisoning experiments have been described. Nag *et al.*[10] observed a benzaldehyde selectivity increasing effect on MoO_x/TiO_2 catalysts at 633 K by introduction of pyridine pulses to a toluene-containing feed. This selectivity increase was accompanied by a sudden drop in the toluene conversion; acid sites (Brønsted as well as Lewis sites being necessary for toluene chemisorption) were immediately blocked. The authors concluded that the total oxidation is connected with relatively strong acid sites.

However, the idea arose to block the OH groups generated under VPP catalyst working conditions permanently. Thus, the task was to find a blocking agent that meets diverse requirements; (i) the blocking agent can be continuously dosed, (ii) it should not be involved in the catalytic reaction and (iii) sites of catalytic activity should not be covered.

Therefore, we attempted to use pyridine as an unoxidizable 'co-feed' and the FTIR spectra of Fig. 2 demonstrate the effect. Spectrum (a) shows the known spectrum if toluene and air are dosed. A continuous admixture of water vapour to such a feed causes no significant change of adsorbed species, additionally, a broad band of adsorbed water (1618 cm^{-1}) is observed as demonstrated in spectrum *(b)*. However, if a 4 wt% aqueous pyridine solution is used instead of pure water, spectrum *(c)* is obtained. This spectrum reveals the existence of pyridinium ions (Brønsted-acid sites) at 1540 cm^{-1} as well as coordinatively bound pyridine (Lewis-acid sites) at 1448 cm^{-1} but surprisingly, only low intensity bands of cyclic anhydrides and no band of adsorbed benzaldehyde are observed. One could suppose that no reaction occurred but the catalytic investigations prove the opposite. The beneficial effect of pyridine on the product desorption has also been demonstrated by *in situ*-EPR measurements. Changes of the EPR signal shape due to strong adsorption were found to be reversible by adding a 4 wt% aqueous pyridine solution to the feed, while no such effect was observed by adding water only. Fig. 3 depicts the selectivity data using a similar VPP catalyst during catalytic runs at 663 K; the toluene conversion amounts to *ca.* 12 mol%. It is clearly shown that the admixture of water vapour does not influence the selectivity but the addition of pyridine reveals a nearly threefold improvement of selectivity to benzaldehyde at constant conversion rates. Thus, pyridine is able to block the Brønsted-acid sites generated during the reaction and also to increase the surface basicity of the catalyst; otherwise, it seems unlikely that the chemisorption of toluene, occurring *via* the Lewis sites is markedly influenced.

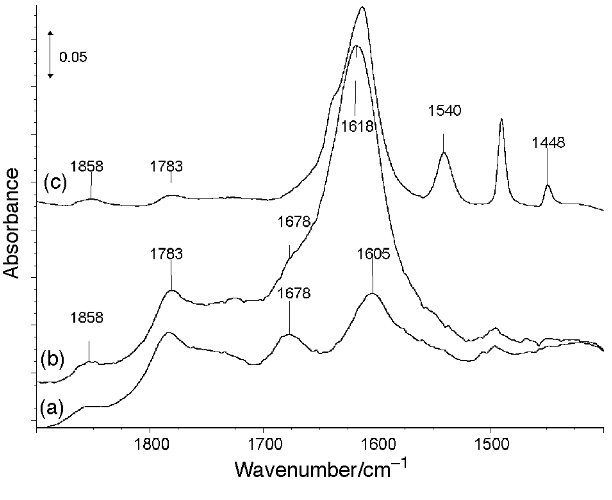


Fig. 2 FTIR spectra of intermediates of the partial oxidation of toluene on a $(VO)_2P_2O_7$ catalyst at 573 K: (a) air-toluene flow (molar ratio = 100 : 1, 4.2 mmol toluene h^{-1}, 60 min), (b) air–toluene–water vapour flow (molar ratio = 100 : 1 : 1, 4.2 mmol toluene h^{-1}, 60 min) and (c) air–toluene–water vapour (containing 4 wt% pyridine) flow (molar ratio = 100 : 1 : 1, 4.2 mmol toluene h^{-1}, 60 min).

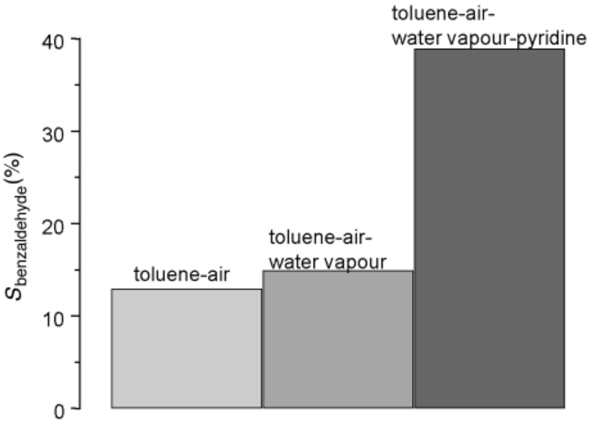


Fig. 3 Benzaldehyde selectivity of the partial oxidation of toluene over a $(VO)_2P_2O_7$ catalyst at 663 K and a *W*/*F* (total flow) = *ca.* 1 g h mol^{-1} using the following feed compositions: (a) air–toluene flow (molar ratio = 100 : 1), (b) air–toluene–water vapour flow (molar ratio = 100 : 1 : 1) and (c) air–toluene–water vapour (containing 4 wt% pyridine) flow (molar ratio = 100 : 1 : 1). Toluene conversion: 12 mmol in each case.

The demonstrated continuous tuning of the acid–base properties of the catalyst surface by a permanent blockade of *in situ*-generated OH groups, accompanied by the increase of the surface basicity of the surface results in drastically increased partial oxidation product selectivities.

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