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On the role of monomeric vanadyl species in toluene oxidation over V_2O_5/TiO_2 catalysts: a kinetic study using the TAP reactor

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Abstract

V_2O_5/TiO_2 catalysts with V_2O_5 loadings of 1 wt.% (Eurocat EL10V1) and 8 wt.% (Eurocat EL10V8) as well as the corresponding NH_3-washed samples (EL10V1w, EL10V8w) exhibiting exclusively monomeric vanadyl species were used as model catalysts in order to elucidate the role of different vanadia species in toluene oxidation. The catalysts were characterized by elemental analysis and X-ray photoelectron spectroscopy. The catalytic performance in toluene oxidation over EL10V1 and EL10V1w was investigated using a temporal analysis of products (TAP) reactor system under high-vacuum conditions. When oxidizing toluene over the untreated sample EL10V1 the products benzaldehyde (BA), benzoic acid (BAc), maleic acid anhydride (MA), and CO_x were detected. BA was observed at low temperatures followed by BAc at temperatures higher than about 500 K, and finally CO_x above 600 K indicating a consecutive oxidation mechanism. However, only the products BA and CO_x were observed for the EL10V1w catalyst. Previous DRIFTS and TPR/TPO studies had shown that the monomeric vanadyl species are able to adsorb toluene dissociatively, and that in the absence of gas-phase oxygen the desorption of oxygenated products from these species cannot occur, since the capability of fast oxygen insertion into toluene and desorption of oxygenates is associated with polymeric and crystalline vanadia species. Thus, a concerted mechanism for the selective oxidation of toluene in the presence of gas-phase oxygen over the ammonia-washed catalysts is suggested, i.e., the desorption of BA and the reoxidation of the monomeric vanadyl species are assumed to occur simultaneously.
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Keywords: Temporal analysis of products; V_2O_5/TiO_2 catalysts; Toluene oxidation

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1. Introduction

Vanadia-based materials represent an important class of oxidation catalysts. During the last decades, the properties of titania-supported vanadia have been thoroughly studied and reviewed, especially considering the different reactivities of isolated monomeric vanadyl species, polymeric 2D vanadia species, and V_2O_5 crystallites coexisting on the support [1–4]. V_2O_5/TiO_2 catalysts are industrially applied in the selective oxidation of *o*-xylene to phthalic acid anhydride [5], but the oxidation of related compounds such as toluene over these catalysts has also been described in the literature [6–17]. Selective oxidation reactions of this type are generally assumed to occur according to the Mars–van Krevelen mechanism [18].

Different views exist in the literature as to which vanadia species are involved in dissociative adsorption, oxygen insertion, and catalyst reoxidation. According to Witko and coworkers [19–23], the bridging oxygen atom coordinated to two vanadium atoms (V–O–V) was identified as the active species. On the other hand, several authors [8,24,25] proposed that the vanadyl oxygen (V=O) is the active oxygen species. Wachs and Weckhuysen [26] pointed to the particular role of the oxygen atoms anchoring the vanadium atoms to the support. Grzybowska-Świerkosz [27] claimed that the monomeric vanadyl species is responsible for hydrogen abstraction, whereas the polymeric species act as centers for oxygen insertion. Also Bond and Védrine [28] supposed that the monomeric species have the ability of dehydrogenation. Bulushev et al. [17,29] considered isolated monomeric and polymeric species as active sites. Konietzni et al. [11] studied an amorphous microporous mixed oxide catalyst (AMM) containing isolated vanadium centers in microporous silica (AMM-V_xSi) in toluene oxidation. The authors identified

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isolated (–SiO)$_3$V=O species as active and selective sites [11].

The aim of the present work is to gain further evidence for the role of monomeric vanadyl species in the oxidation of toluene. Therefore, the influence of the various VO$_x$ species on the catalytic activity and selectivity was examined using the temporal analysis of products (TAP) reactor. The TAP system operating under high-vacuum conditions is an effective tool to examine catalytic oxidation reactions because of the absence of mass and heat transfer limitations and the suppression of gas-phase reactions.

2. Experimental

The Eurocat samples used in this study were kindly supplied by J.C. Védrine. The samples were prepared by wet impregnation of TiO$_2$ (anatase, EL10) with vanadyl oxalate solution, followed by drying and calcining for 4 h at 723 K. The method of preparation as well as extensive characterization and reaction studies are described in [30]. Additional samples were prepared by washing EL10V1 and EL10V8 with aqueous solutions of ammonia (0.4 M). This treatment is known to remove polymeric and crystalline vanadia species [31]. The washed samples were recalcined at 673 K in O$_2$ for 1 h. These samples are denoted as EL10V1w and EL10V8w, respectively.

The vanadia content of the NH$_3$-washed samples was determined by atomic absorption spectroscopy (AAS) using a graphite furnace. For the AAS measurements, the samples were dissolved in H$_2$SO$_4$ after addition of H$_2$O$_2$ and aqua regia. X-ray photoelectron spectra were measured with a Leybold LH 10/100 spectrometer (multi-channel detector, non-monochromatized Al Kα radiation). Binding energy (BE) data were referenced to Ti 2p $=$ 458.7 eV. Atomic ratios of elements (V/O) were calculated from the V 2p$_{3/2}$/O 1s intensity ratios using the Scofield photoionization cross-section data [32], which is justified for these peaks with almost identical kinetic energies. A refined subtraction procedure to remove the X-ray satellites of the very intense O 1s peak was used based on the software package “MacFit” (author: H.-G. Boyen, University of Basle), which is described in [33].

The general principles as well as the different operating modes of the typical TAP reactor system are given in [34]. The TAP system used in this work (model 1b) is equipped with a high-pressure assembly and has been technically modified in order to handle reactants with low volatility (passivated Silcosteel as well as heated tubing and reservoirs) [35]. Gases were supplied by Messer Griesheim (O$_2$ purity 99.9995%; Ne purity 99.999%; Ar purity 99.999%), and toluene (purity 99.9%) by Merck. *Online* analysis was performed with a calibrated quadrupole mass spectrometer. About 100 mg of the powdered catalyst were placed in the isothermal zone of a passivated catalytic microreactor (length: 40 mm, diameter: 4.5 mm) [35]. The gas flow was in the range of 0.4–0.5 ml min^{-1} (STP). The masses were screened in a range of 1 up to 150 amu. The measured intensities were converted into relative concentrations based on several masses. Prior to each experiment, the sample was pre-oxidized in an O$_2$/neon (1:9) mixture under atmospheric pressure at 673 K for 2 h followed by flushing in Ar down to reaction temperature. Subsequently, temperature-programmed (TP) continuous flow experiments starting at room temperature were carried out. The reaction was monitored while ramping the temperature at 2 K min^{-1} up to 683 K in a toluene/O$_2$/neon (1:12:44.5) flow followed by cooling down to 303 K at the same rate.

3. Results and discussion

The following vanadia contents were obtained by AAS: EL10V8 8.00 wt.%, EL10V8w 0.13 wt.%, EL10V1 1.00 wt.%, and EL10V1w 0.12 wt.%. It is obvious that the washing procedure removed a substantial amount of vanadia in agreement with literature data [31]. Only about one tenth of the theoretical monolayer coverage remained for both EL10V1 and EL10V8.

Fig. 1 shows the V 2p$_{3/2}$ signals of the Eurocat samples in the original state and after washing. The expanded binding-energy region containing the adjacent O 1s, V 2p$_{1/2}$ and V 2p$_{3/2}$ signals is shown in the inset. The V/O atomic ratios are as follows: EL10V8 0.11, EL10V8w 0.016, EL10V1 0.053, and EL10V1w 0.011. Fig. 1 demonstrates that the washing procedure left the titania surface decorated with a small amount of vanadia species. Their V 2p$_{3/2}$ BE seems to be slightly lower than that of the original vanadia species. However, vanadia was observed to be reduced under prolonged X-ray irradiation as known from

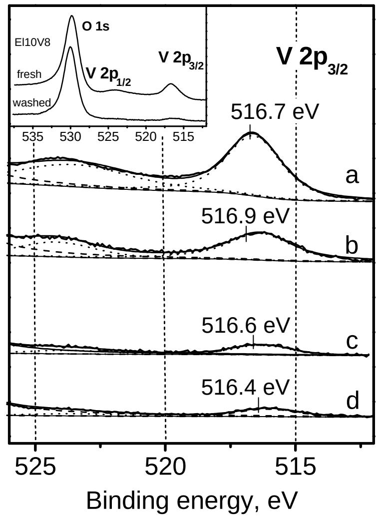

Fig. 1. O 1s and V 2p XP spectra of (a) EL10V8, (b) EL10V1, (c) EL10V8w, and (d) EL10V1w. The specified binding energies originate from XP spectra obtained with significantly shorter acquisition time to minimize X-ray induced reduction.

the literature [36–38], and the binding energies had to be determined from spectra taken with short acquisition time, which affects their accuracy due to the lower signal-to-noise ratio. The traces shown in Fig. 1 were obtained after long acquisition time used for intensity evaluation, where the ongoing reduction compromises the line shapes. The binding energies of vanadia in EL10V8, EL10V1 and EL10V1w are within the range reported by Bulushev et al. [37]. Due to the specific satellite subtraction technique used and the surface enrichment of vanadium, it was possible to reliably detect vanadium in samples containing only ∼0.1 wt.% of this element.

The selective oxidation of toluene with oxygen to benzaldehyde (BA) and benzoic acid (BAc) was used to study the catalytic performance of the samples EL10V1 and EL10V1w under vacuum conditions in the TAP reactor in the temperature range from 303 to 683 K ramping the temperature up and down. All these TP continuous flow experiments were found to be reproducible. The comparison of the results of the TP-continuous flow experiments with isothermal flow experiments in an ongoing study has shown that the transient mode is an effective method to study the activity and selectivity more rapidly [39]. For the untreated Eurocat samples, an essentially equal activity was observed. However, the EL10V8 catalyst was found to be more selective than the EL10V1 catalyst with lower vanadia loading. The catalytic properties of the ammonia-washed samples EL10V1w and EL10V8w were rather similar.

Fig. 2 summarizes the yields of toluene oxidation over EL10V1. The detected products were BA, BAc, CO_x, and maleic acid anhydride (MA). Traces of benzene and *p*-quinone were also detected (not shown). The product spectrum observed in the TAP experiment is similar to results obtained in conventional flow apparatuses operating at ambient pressure [8,39]. The formation of the selective products (BA, BAc) started at lower temperatures and passed through a maximum ($Y_{\mathrm{BA}} = 5\%$, $Y_{\mathrm{BAc}} = 3\%$). BA was observed first followed by BAc at higher temperature indicating a consecutive oxidation mechanism [6,8]. As shown by the corresponding DRIFT spectra, BA is formed at even lower temperatures on the catalyst, but the desorption requires higher temperatures leading to the first maximum during the ascending branch already at 440 K [12]. The formation of the non-selective oxidation products (CO_x and MA) started at about 560 K: CO_x increased up to 683 K ($Y_{\mathrm{CO}} = 22\%$, $Y_{\mathrm{CO_2}} = 56\%$), whereas MA passed through a maximum at 628 K ($Y_{\mathrm{MA}} = 14\%$). The observed hysteresis between the experiments with rising and falling temperature was caused by adsorption phenomena as shown by solving the carbon mass balance [39].

For the ammonia-washed sample EL10V1w the conversion of toluene at 683 K was about 30% lower amounting to roughly 55%. The yields obtained with EL10V1w are shown in Fig. 3. Surprisingly, only the products BA and CO_x were detected, implying that the monomeric vandyl species is able to insert one oxygen atom in the presence of gas-phase oxygen, but not two oxygen atoms as required to form BAc. In contrast to EL10V1, the yield of CO_x at 683 K is lower ($Y_{\mathrm{CO}} = 16\%$, $Y_{\mathrm{CO_2}} = 50\%$), and the onset of the formation of CO_x is shifted by about 20 K to higher temperatures, although the maximum yield of BA is equal. For EL10V1w, the first maximum in the yield of BA is shifted to lower temperatures while ramping up, and the yield of BA decreased just slightly above 650 K, presumably because of the missing consecutive oxidation to BAc. These results demonstrate that the washed sample is significantly more selective to BA than the unwashed sample.

The AAS and XPS results clearly indicate that the washing procedure removed the major part of the vanadia content. This quantitative observation is in good agreement with previous qualitative FT-NIR Raman results which showed that the washed samples exhibit only monomeric vanadyl species [12]. Thus, a suitable model system was generated to study the behavior of such species. Correspondingly, the same reaction products were obtained as in the literature with the isolated $(\text{–SiO})_3\text{V=O}$ species [11]. We reported recently the results of an in situ DRIFTS study of the adsorption of toluene on the Eurocat catalysts as well

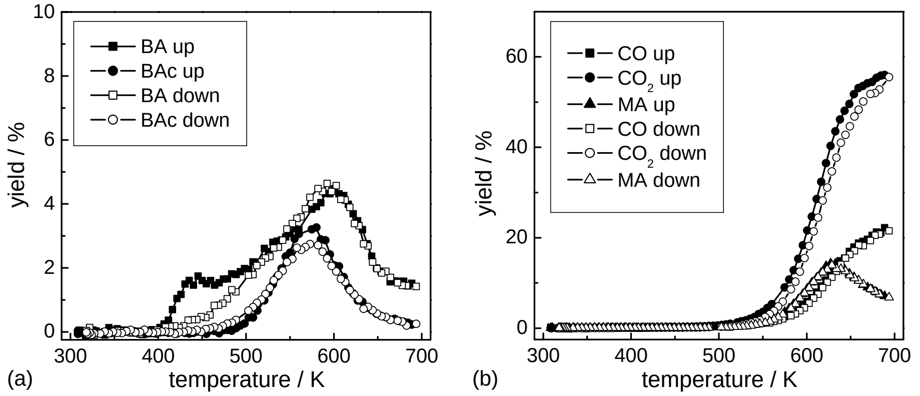

Fig. 2. Yields of detected products as a function of temperature for EL10V1: (a) benzaldehyde (BA) and benzoic acid (BAc); (b) CO_x and maleic anhydride (MA).

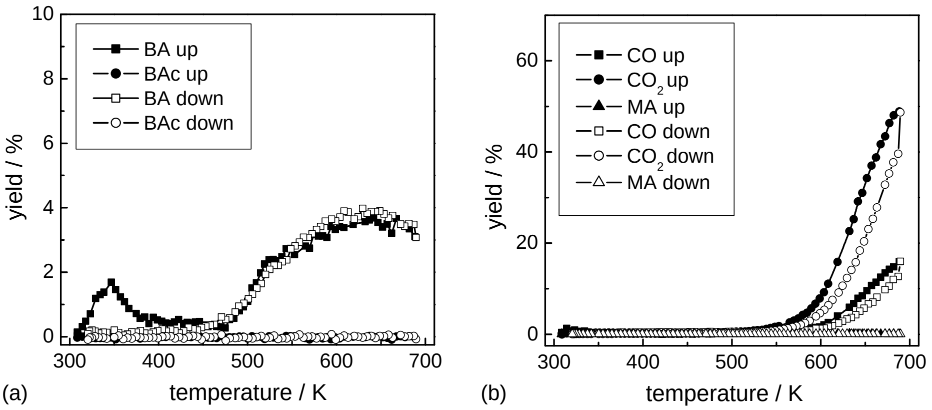

Fig. 3. Yields of detected products as a function of temperature for EL10V1w: (a) benzaldehyde (BA) and benzoic acid (BAc); (b) CO_x and maleic anhydride (MA).

as on the corresponding NH_3-washed samples [12]. It was found that oxidative adsorption occurred on all samples indicating monomeric vanadyl species to be crucial for this step (Eq. (1)). However, the oxidation of adsorbed toluene had proceeded to a lower extent on the washed samples at 423 K yielding adsorbed benzylic and aldehydic species compared to the unmodified Eurocat samples on which also adsorbed benzoate species were detected. By heating up to 573 K, the benzylic and aldehydic species on EL10V1w were transformed into adsorbed benzoate which was not removed in air at 573 K. In contrast, the capability of fast oxygen insertion and desorption of oxygenated products was found to be associated with polymeric vanadia species and V_2O_5 crystallites [12]. The results of the in situ DRIFTS study were supported by the results of the TP oxidation of toluene-covered samples, leading to the conclusion that in the absence of gas-phase oxygen desorption of oxygenated products from the monomeric species cannot occur [40].

In the present TAP reactor study it was shown that the monomeric species is active in toluene oxidation when cofeeding toluene and oxygen. However, only BA was formed over EL10V1w as selective oxidation product, whereas BAc was not detected. Therefore, we suggest a concerted mechanism for the oxidation to BA requiring the insertion of one oxygen atom, i.e., the desorption of BA and the reoxidation of the monomeric vanadyl species by oxygen (Eq. (2)) are assumed to occur simultaneously

$$C_6H_5\text{–}CH_3 + O{=}V(OTi\text{–})_3 \rightarrow C_6H_5\text{–}CHO\text{–}V(OTi\text{–})_2 \times (\square Ti\text{–}) + H_2O \tag{1}$$

$$C_6H_5\text{–}CHO\text{–}V(OTi\text{–})_2(\square Ti\text{–}) + O_2 \rightarrow C_6H_5\text{–}CHO + O{=}V(OTi\text{–})_3 \tag{2}$$

This hypothesis is in agreement with recent isotopic exchange experiments over the AMM-V_xSi catalyst containing isolated VO_x centers which showed in addition that the vanadium-bound lattice oxygen is indeed inserted into the product BA, and that oxygen adsorbed from the gas phase acts as reoxidizing agent for the reduced vanadium site [11].

4. Conclusions

A suitable model system was generated by washing a V_2O_5/TiO_2 catalyst with ammonia to study the behavior of the monomeric vanadyl species. The obtained TP reaction results applying the TAP reactor in high-vacuum support a consecutive mechanism for the oxidation of toluene. Only the products BA and CO_x were observed for the ammonia-washed catalyst. Previous DRIFTS and TPO studies had shown that the monomeric species is responsible for the oxidative adsorption and that in the absence of gas-phase oxygen the desorption of oxygenated products from the monomeric species cannot occur. Therefore, a concerted mechanism for the selective oxidation of toluene in the presence of gas-phase oxygen over the ammonia-washed catalysts is suggested, i.e., the desorption of benzaldehyde and the reoxidation of the monomeric vanadyl species are assumed to occur simultaneously.

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