On the role of monomeric vanadyl species in toluene adsorption and oxidation on V_2O_5/TiO_2 catalysts: a Raman and in situ DRIFTS study

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Dedicated to Prof. H. Knözinger on the occasion of his 65th birthday.

Abstract

Supported model catalysts exclusively exposing monomeric vanadyl species were prepared by washing V_2O_5/TiO_2 samples (Eurocat EL10V1 and EL10V8) with aqueous solutions of ammonia. FT-NIR Raman spectroscopy confirmed that V_2O_5 crystallites and polymeric species which had been present on both samples were removed by the washing treatment, leaving behind monomeric vanadyl species. The adsorption of toluene was studied using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in order to elucidate the role of monomeric vanadyl species in hydrocarbon activation and transformation. Oxidative adsorption occurred in all samples, suggesting monomeric vanadyl species to be crucial for this step. Toluene oxidation had proceeded to a lower extent on the washed samples than on the unmodified Eurocat samples which is consistent with the capability of fast oxygen insertion associated with polymeric vanadia species and V_2O_5 crystallites. These species also proved to be essential to make gas-phase oxygen available to adsorbed hydrocarbons. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Anatase-supported vanadia (V_2O_5/TiO_2) is an important oxidation catalyst which finds industrial application in phthalic anhydride production. It has been extensively studied in the literature, a major part of the work being devoted to catalyst characterization. The initial comprehension of an evenly distributed vanadia monolayer has developed into a model involving different vanadia species. By spectroscopic investigations, isolated monomeric vanadyl species, polymeric 2-D vanadia species and V_2O_5 crystallites have been found to coexist on the support, their relative abundance being related to the vanadia content [1–5].

Raman spectroscopy provides an important analytical tool to identify the type of vanadia species present on the catalyst [4–12]. Raman spectroscopy is more suitable for this purpose than IR spectroscopy because of the strong absorption of anatase below $1100 \ cm^{-1}$ in infrared (IR) spectra, which obscures the spectral region where vanadia bands are expected. Only overtone bands of intrinsically weak intensity remain observable which are located in a spectral region where no superposition with hydrocarbon bands is expected, thus allowing to survey the

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state of the catalyst during in situ IR measurements [13].

However, the role of individual vanadia species in hydrocarbon oxidation is not yet fully understood. Due to their substantial difference in vanadia loading, the Eurocat samples [14] represent a suitable system to investigate the influence of different types of vanadia species. Raman spectra of the Eurocat samples have been recently reported in the literature [15]. It is known that crystalline and polymeric vanadia species predominate on the high-loaded sample (EL10V8) whereas monomeric and polymeric species in strong interaction with the support predominate on the low-loaded sample (EL10V1).

Therefore, it appeared interesting to examine the influence of these species on both hydrocarbon activation and transformation. For this purpose, the adsorption of toluene on different V_2O_5/TiO_2 samples has been studied using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). By washing the Eurocat samples with aqueous solutions of ammonia, it was possible to remove selectively polymeric and crystalline vanadia species leaving behind strongly bound monomeric vanadyl species.

In situ spectroscopic investigations of surface species have provided important insights into the reaction pathways. IR spectroscopy is one of a few techniques capable of detecting surface compounds in heterogeneous reaction systems under realistic conditions. Due to its high sensitivity to surface species, DRIFTS is a powerful tool for the investigation of adsorbed species and active sites. IR investigations of toluene adsorption on V_2O_5/TiO_2 [16–23], on Al_2O_3 [24–26], on ZrO_2 [19,23,27], and on various other oxides [28–34] have been reported in the literature. The present work focuses on the influence of catalyst composition and tries to relate differences in reactivity to the presence of different vanadia species as identified by Raman spectroscopy.

2. Experimental

2.1. Samples

The Eurocat samples used in this study have kindly been 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 Ref. [35]. 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 [36]. The washed samples were recalcined at 673 K in O_2 for 1 h. V_2O_5 (purity 99.6%) and TiO_2 (anatase, purity 99.9%) were supplied by Janssen Chimica and by Aldrich, respectively. The samples studied are listed in Table 1.

2.2. FT-NIR Raman and DRIFT spectroscopies

A Nicolet Nexus spectrometer with an FT-NIR Raman attachment equipped with an InGaAs detector was used to obtain Raman spectra. Raman scattering was excited with a Nd–YAG laser operated at a wavelength of 1064 nm with a power output of 90 mW. 1024 scans with a resolution of 4 cm^{-1} were averaged. Since it was not possible to heat the Raman cell, the samples were activated at 673 K in O_2 for 1 h and stored in a sealed glass tube prior to the measurements.

DRIFT spectra were recorded with a Nicolet Protégé FTIR spectrometer equipped with a diffuse reflectance accessory and a Spectra Tech high-temperature chamber. The ceramic sample cup contained about 30 mg of catalyst and was covered by a water-cooled stainless steel dome with ZnS windows. The coolant temperature was maintained at 323 K to minimize the deposition of reaction products on the windows. The temperature was controlled

Table 1
List of investigated samples

Code	Sample
EL10V1	1% V_2O_5/TiO_2, Eurocat
EL10V8	8% V_2O_5/TiO_2, Eurocat
EL10V1w	EL10V1 washed with ammonia
EL10V8w	EL10V8 washed with ammonia
EL10	TiO_2 (anatase), Eurocat
TiO_2	TiO_2 (anatase), purity 99.9% [Aldrich]
V_2O_5	V_2O_5, purity 99.6% [Janssen Chimica]

by a thermocouple in direct contact with the sample. The flow rates passing through the chamber were 20 Nml/min. A four-way valve supplied by Valco allowed fast switching between reactants. Gases were supplied by Messer Griesheim (Ar purity 99.998%; dry and purified synthetic air; H_2 purity 99.999%).

For the adsorption studies, an Ar gas stream was saturated with toluene (HPLC grade, Merck) at 273 K. Prior to adsorption, the samples were pretreated in air at 673 K in order to remove adsorbed water and to fully oxidize the sample. The samples were then cooled down to the adsorption temperature in Ar. At 423 K, after recording a spectrum of the adsorbate-free catalyst, the gas stream of 1% toluene in Ar was passed through the cell for a period of about 6 min until spectral changes were no longer observable.

Subsequently, the chamber was purged with Ar to remove all gas-phase species, and then a spectrum was recorded. The adsorbate-covered samples were submitted to the following treatment in order to study the transformation of the adsorbate:

1. Pretreatment in air at 673 K for 1 h.
2. Adsorption of toluene at 423 K for 6 min.
3. Purging with Ar at 423 K.
4. Heating in Ar with 10 K/min up to 573 K.
5. Heating in air with 10 K/min up to 573 K.
6. Reoxidation in air at 673 K.

Subsequent to steps 3–6, DRIFT spectra were measured at 423 K. The adsorption process as well as the heat treatments were monitored in the "series mode" of the spectrometer allowing a continuous collection of spectra. DRIFT spectra were recorded as single-beam spectra at 423 K using a resolution of 4 cm^{-1} and averaging 2000 (catalyst spectra), 1000 (adsorbate spectra) or 64 ("series mode") scans. All spectra are presented in apparent absorption units as obtained by dividing by background spectra (of KBr in order to obtain catalyst spectra, or of the adsorbate-free catalyst to obtain adsorbate spectra) and taking the negative logarithm. In the range of C−H stretching vibrations (3200–2800 cm^{-1}), a linear baseline correction was carried out.

3. Results

3.1. Spectroscopic characterization of the V_2O_5/TiO_2 samples

3.1.1. Raman spectroscopy

The Raman spectra of the Eurocat samples before and after washing with aqueous ammonia are shown in Fig. 1, which includes spectra of V_2O_5 and EL10 as reference samples. All samples were studied after drying in air at 673 K to avoid the influence of hydration on the Raman bands, which has been studied in detail by Jehng et al. [6]. Relevant Raman shifts reported in the literature are summarized in Table 2. Crystalline vanadia characterized by a Raman band at 995 cm^{-1} is observed for both EL10V8 and EL10V1, although its intensity is weaker for the latter. Raman spectroscopy is a very sensitive technique for the detection of both crystalline and X-ray amorphous V_2O_5, since V_2O_5 is a strong Raman scatterer. The presence of V_2O_5 crystallites on EL10V8 is also known from XRD studies. Based on conductivity measurements, chemical analysis and DTA measurements, it has indirectly been concluded that a large number of very small crystallites must be present on EL10V1 [37,38]. No spectroscopic evidence was found for the presence of polymeric species on the untreated Eurocat samples. It should, however, be kept in mind that the Raman shift varies
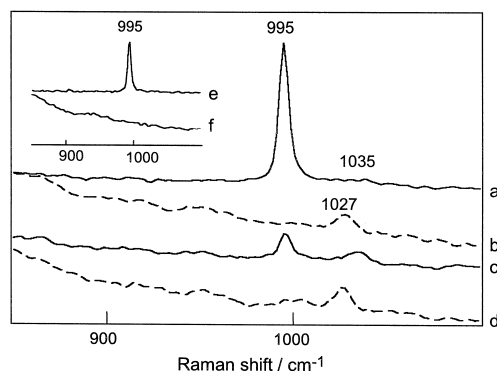

Fig. 1. FT–NIR Raman spectra of dehydrated samples: EL10V8 (a), EL10V8w (b), EL10V1 (c), EL10V1w (d), V_2O_5 (e) and EL10 (f).

Table 2
Raman shifts of vanadyl stretching vibrations on dehydrated V₂O₅/TiO₂ catalysts

Raman shift (cm^{-1})	Assignment	Ref.
1030 (sharp)	isolated monomeric vanadyl species	[4,5,7,10]
1027 (broad)	vanadyl species in close proximity, but still monomeric in nature	[5]
995 (sharp)	terminal V=O groups of bulk V₂O₅	[4,7,11,39]
915 – 990	V=O end groups in 2-D oligomeric vanadate species shifting to higher wavenumbers with increasing level of polymerization	[4,7,12]

with the size of these agglomerates resulting in broad and weak bands which are difficult to detect.

Isolated monomeric vanadyl species giving rise to the Raman bands at 1035 and 1027 cm^{-1} are observed for EL10V1 and for the washed samples, respectively. The lower wavenumber is attributed to isolated species in close proximity. It can be safely concluded from the Raman spectra that the treatment with aqueous ammonia has succeeded in removing

V₂O₅ crystallites efficiently leaving behind monomeric vanadyl species on both samples.

3.1.2. DRIFT spectroscopy

The DRIFT spectra of the samples in the region of overtone vibrations of vanadia species are shown in Fig. 2a. The most prominent feature in the case of the modified samples EL10V1w and EL10V8w is the band at 2047 cm^{-1}, which is also detected for EL10V1. It is assigned to an overtone vibration of monomeric vanadyl species in agreement with the Raman results. As reported in the literature [15], EL10V8 exhibits vanadyl overtone vibrations at 2018 and 1972 cm^{-1} as observed for unsupported vanadia. They also appear as very weak absorption bands on EL10V1 indicating the presence of crystallites on this sample, too.

The reactivity of these samples may depend on the presence of OH groups acting as acid sites. The DRIFT spectra indeed reveal the presence of OH vibration bands (Fig. 2b). The most prominent OH band of the support EL10 is centered at 3667 cm^{-1}. Such a band has also been reported in the literature for very pure anatase with low surface area and was assigned to a weak acid site [40]. A similar band is observed for the modified samples as well as for EL10V1. Due to the large width of the band, it
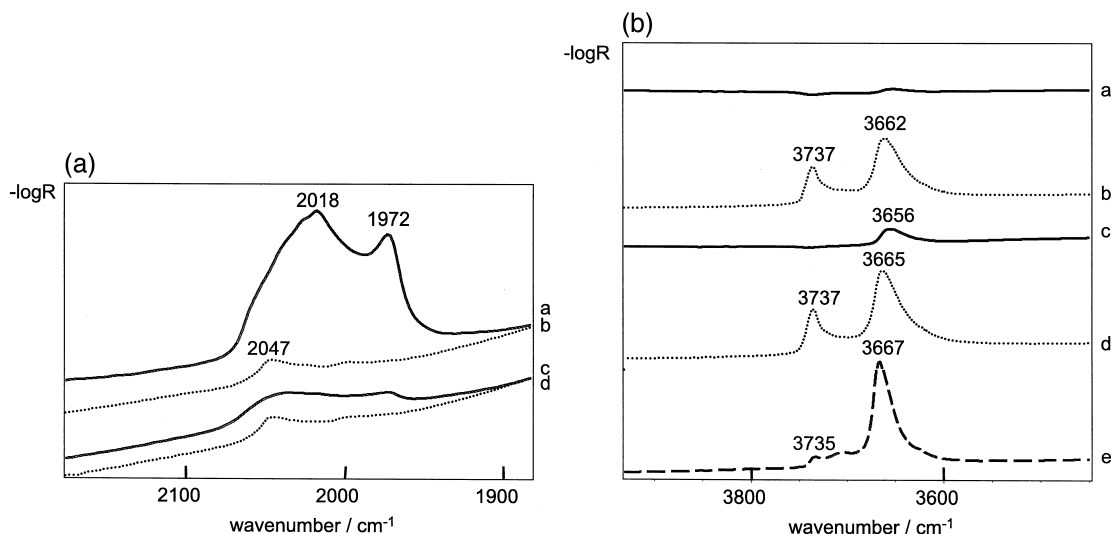

Fig. 2. a. DRIFT spectra of dehydrated and fully oxidized samples in the region of overtone vibrations of vanadyl groups (background: KBr): EL10V8 (a), EL10V8w (b), EL10V1 (c) and EL10V1w (d). b. DRIFT spectra of dehydrated and fully oxidized samples in the region of OH stretching vibrations (background: KBr): EL10V8 (a), EL10V8w (b), EL10V1 (c), EL10V1w (d) and EL10 (e).

cannot clearly be decided whether it is the TiOH band of exposed support sites, probably affected by a modified coordination of Ti, or rather a newly formed VOH band. VOH bands, though not observable on unsupported, low-surface V_2O_5, have been reported for V_2O_5/TiO_2 catalysts in the literature [3,41]. A superposition of both phenomena appears to be likely in this case. The washed Eurocat samples and the support exhibit an additional OH band at 3737 cm^{-1}, which is not observed for the unmodified samples. It is ascribed to SiOH groups originating from SiO_2 impurities which are known to be present on the calcined support [35].

According to the Raman and DRIFTS results discussed above it can be concluded that the nature of the washed sample does not depend on the initial vanadia content. The chosen samples are considered suitable model systems to study the role of the different vanadia species. On the one hand, V_2O_5 crystallites should influence the properties of EL10V8. The reactivity of the ammonia-treated catalysts, on the other hand, should be governed by monomeric vanadyl species. Additionally, as expected for sub-monolayer coverages, exposed support sites might also play a role for the low-loading samples. Unfortunately, no significant spectroscopic hints have been found for the presence of polymeric vanadia species.

3.2. The adsorption and oxidation of toluene

Toluene adsorption was studied on EL10V8, EL10V1 and EL10V1w. Only one modified sample was chosen because the state of the modified samples did not depend on the initial vanadia content in agreement with the Eurocat study [42]. In the following, DRIFT spectra of the adsorbate-covered sample obtained by using the catalyst spectrum as background are discussed which are referred to as adsorbate spectra. In addition to the evolution of bands due to adsorption products, changes of the catalyst state are displayed. For instance, an intensity decrease of a catalyst band appears as a negative band in the adsorbate spectrum. However, such phenomena may be superimposed by a variation of the penetration depth of the IR beam and should therefore be discussed only qualitatively.

3.2.1. Changes of the state of the catalyst

The adsorbate spectra of toluene-covered samples recorded after purging with Ar at 423 K are shown in Fig. 3. Despite the different vanadia content, similar adsorption products were found on all samples as discussed in detail below, but substantial differences exist with regard to the baseline, vanadyl bands, and OH bands. These features are related to changes of the catalyst. Negative bands at 2020 and 1972 cm^{-1} are ascribed to the reduction of vanadia crystallites. They are prominent in the case of EL10V8, very weak for EL10V1 and, as expected, absent for EL10V1w. The interaction of monomeric vanadyl species with toluene can be inferred from the negative band at 2048 cm^{-1}, which is observed for EL10V1 and EL10V1w.

A further indication of catalyst reduction is the change of the baseline which occurs strongly in the case of EL10V8, but only slightly in the case of the low-loading samples. It is known that, upon reduction, the optical properties of V_2O_5/TiO_2 samples are modified resulting in color changes [15,43]. When reducing the samples with hydrogen, the same phenomena occur. This is shown in Fig. 4, which displays the DRIFT spectra of EL10V1 in the partly reduced and in the oxidized state.

Furthermore, OH groups intervene in the adsorption process resulting in weak negative bands at 3737 and at 3656 cm^{-1} (unmodified samples) or at 3664 cm^{-1} (modified sample). A broad band around
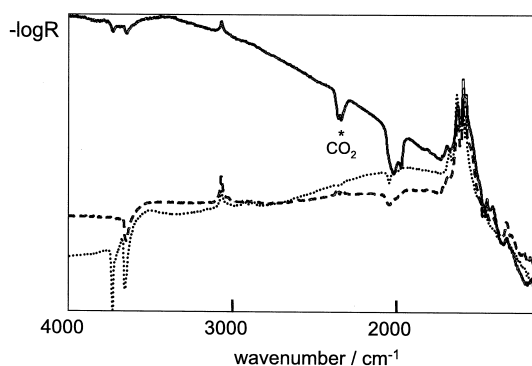
Fig. 3. DRIFT spectra of V_2O_5/TiO_2 samples after adsorption of toluene at 423 K and purging with Ar (background: catalyst spectrum): EL10V8 (solid line), EL10V1 (dashed line) and EL10V1w (dotted line).
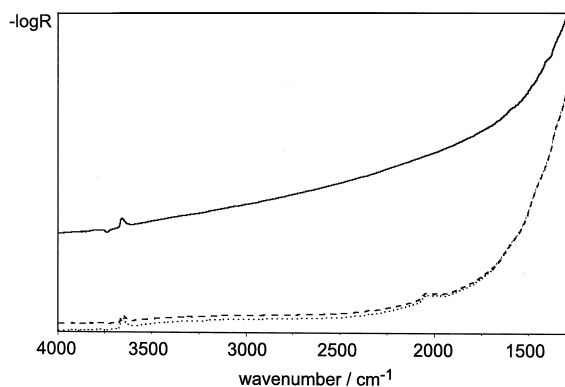
Fig. 4. DRIFT spectra of EL10V1: fully oxidized sample (dashed line), partially reduced sample by exposure to H_2 at 673 K (solid line) and reoxidized sample (dotted line).

3500 cm^{-1} indicates hydrogen bonding, which may be assigned to surface oxygen species interacting with the hydrogen atoms of the methyl group. TiO$_2$ was contacted with toluene under the same experimental conditions in order to evaluate the influence of exposed support sites. Pure TiO$_2$ did not form any adsorbates, but on the Eurocat TiO$_2$ sample (EL10) very weak, broad bands centered at 1685 and 1616

cm^{-1} were observed. Thus, they are ascribed to the influence of impurities known to be present in the support [35]. Generally, exposed support sites are considered negligible for the formation of adsorption products on high-loaded V$_2$O$_5$/TiO$_2$ catalysts.

3.2.2. Characterization of adsorption products

Fig. 5 is an expanded view from Fig. 3 showing the spectral regions where bands due to adsorption products of toluene are expected. The band assignment is summarized in Table 3. The spectral regions are located between 1800 and 1200 cm^{-1} (CO stretching vibrations, vibrations of the aromatic ring and deformation modes of C−H) as well as around 3000 cm^{-1} (C−H stretching vibrations). The spectrum does not correspond to those of liquid- or gas-phase toluene, since reaction has already occurred at 423 K in agreement with literature results [18,21,22]. The aromatic system has remained intact as can be concluded from the presence of the ring vibrations at 1596 (8a), 1577 (8b), 1501 (19a) and 1457 cm^{-1} (19b). The band due to a phenylic C−H stretching vibration at 3030 cm^{-1}, which is the most intense in the spectrum of liquid- or gas-phase toluene
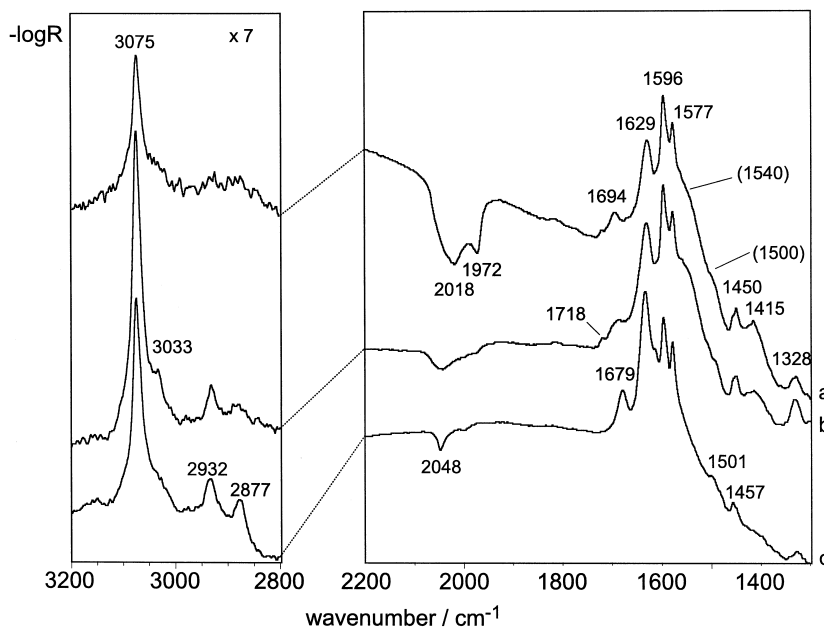

Fig. 5. Adsorbate spectra of toluene on V$_2$O$_5$/TiO$_2$ samples: EL10V8 (a), EL10V1 (b) and EL10V1w (c). All spectra have been recorded at 423 K.

Table 3
Assignment of IR bands appearing after the adsorption and reaction of toluene on V_2O_5/TiO_2 catalysts at 423 K

Position/cm^{-1}	Assignment	characteristic of
3075, 3033	phenylic C—H stretching vibration	aromatic ring
2932	symmetric C—H stretching vibration of CH$_2$ group	benzyl species
2877	antisymmetric C—H stretching vibration of CH$_2$ group	benzyl species
1718	C=O stretching vibration	physisorbed benzaldehyde
1694–1629	C=O stretching vibration	aldehydic adsorbate
1596	skeletal C—C stretching vibration (8a)	aromatic ring
1577	skeletal C—C stretching vibration (8b)	aromatic ring
1540 (sh)	antisymmetric C—O stretching vibration	benzoate
1500 (sh)	antisymmetric C—O stretching vibration	benzoate
1501	skeletal C—C stretching vibration (19a)	aromatic ring
Around 1450	skeletal C—C stretching vibration (19b)	aromatic ring
1415	symmetric C—O stretching vibration	benzoate
1328	skeletal C—C stretching vibration (14)	benzaldehyde

is reduced to a very weak shoulder near the band at 3075 cm^{-1}. This observation points to the transformation of the methyl group as the stretching vibrations of aromatic C—H bands are known to be substituent-sensitive and have been related to the Hammett parameter of the substituent [44].

It is known that the oxidation of the side chain proceeds in consecutive steps via a benzylic, aldehydic and benzoate species (e.g., Ref. [22] and references therein). The aldehydic species gives rise to carbonyl bands in the region 1630–1720 cm^{-1} while carboxylate bands are typically situated at 1610–1550 cm^{-1} (antisymmetric vibration) and 1400–1300 cm^{-1} (symmetric vibration). A detailed analysis of the adsorbate spectra reveals that the oxidation has progressed to a different extent for the individual samples. The C—H stretching vibrations of the alkyl group are observed as weak bands at 2932 and 2877 cm^{-1} for EL10V1 and EL10V1w. They can be

assigned to the antisymmetric/symmetric stretching vibration of a methylene group which is characteristic of a benzyl species. Such bands are no longer detected for EL10V8 indicating that all hydrogen atoms of the methyl group have been abstracted.

Absorption bands in the C=O region were observed for all samples, with slightly varying wavenumbers: 1694 and 1629 cm^{-1} for unmodified samples, 1679 and 1633 cm^{-1} for EL10V1w. They are assigned to aldehydic species, since similar bands at 1685 and 1635 cm^{-1} were observed for unmodified Eurocat samples when benzaldehyde was adsorbed as reference measurement in agreement with Refs. [16–18]. The appearance of a high- and a low-wavenumber band is attributed to different coordination complexes. Various structures have been proposed by van Hengstum et al. [16] who assigned the bands at 1691 and 1672 cm^{-1} to aldehyde molecules coordinated via the carbonyl oxygen atom. The difference in wavenumber is due to different degrees of interaction. Such a difference is also observed here, the 1679 cm^{-1} band obtained with the modified sample reflecting a weaker C=O bond and consequently a stronger interaction with the catalyst in comparison to the unmodified samples where the band is found at 1694 cm^{-1}. The weak band at 1328 cm^{-1} is also associated with an aldehydic species and results from a ring vibration. The bands due to free aldehyde expected at 1710 (CO) and 2820 cm^{-1}, as well as 2720 cm^{-1} (C—H stretching, 1st overtone of CHO deformation, doublet due to Fermi resonance) are not detected, but a very weak band at 1718 cm^{-1} appears on sample EL10V8. It may be ascribed to physisorbed benzaldehyde, probably resulting from readsorption. This would imply that benzaldehyde is able to desorb from the unmodified samples under the given conditions.

Furthermore, weak bands at 1415 and around 1540 cm^{-1}, which are characteristic of a carboxylate group, indicate the formation of benzoate already at 423 K. Such bands are observed for unmodified samples, but not for the washed sample. Considering the consecutive reaction path of selective toluene oxidation, the entire series of transformations has occurred on the unmodified samples whereas, under the imposed experimental conditions, it stopped at the aldehydic intermediate in the case of EL10V1w, the initial benzyl species being still detectable.

The transformations upon heating of the adsorbate-covered samples up to 573 K are shown in Fig. 6 (EL10V8) and Fig. 7 (EL10V1w). The heat treatment has been conducted first in the absence and then in the presence of gas-phase oxygen. Results obtained for EL10V8 will be discussed first and then compared to EL10V1w in order to evaluate the influence of crystalline vanadia. In the case of EL10V8, the catalyst is reduced further when heating in Ar as concluded from the steeper slope of the baseline and the more intense negative vanadyl bands (overtone vibrations, 1972 and 2018 cm^{-1}). Simultaneously, the adsorbate is oxidized further. Bands due to the carboxylate group have become the most prominent features (bands at 1540 [broad] and 1413 cm^{-1}). The ring vibrations persist, though slightly shifted to higher wavenumbers. Furthermore, carbonyl bands at 1694 and 1629 cm^{-1} are replaced by a new band at 1681 cm^{-1}. Such a band has also been reported for an intermediate in the production of maleic anhydride from *n*-butane [45]. Thus, it is possible that the aromatic ring of a certain fraction of adsorbed molecules is no longer intact.

When repeating the heat treatment in air, the vanadyl bands regain part of their initial intensity, and the change of the baseline is partly reversed. This indicates a partial reoxidation of the catalyst. At the same time, a decrease in intensity of adsorbate bands is observed which results from transformation and desorption. The benzoate bands, though less intense, are still present. New bands evolved at 1866 and 1783 cm^{-1}, whereas the band at 1681 cm^{-1} has remained. This indicates the formation of a cyclic anhydride, most probably maleic anhydride. Thus, heating in air leads to the degradation of the aromatic ring. The same observation has been made by Busca [22] who concludes that the reaction with gas-phase oxygen is the main route for the formation of maleic anhydride. The same adsorption products were obtained with both unmodified Eurocat samples.

In the case of the ammonia-washed sample, the heat treatment in Ar also produced benzoate as major species (Fig. 7b). The band of the symmetric carboxylate stretching vibrations appears at the same wavenumber (1414 cm^{-1}), but several bands can be
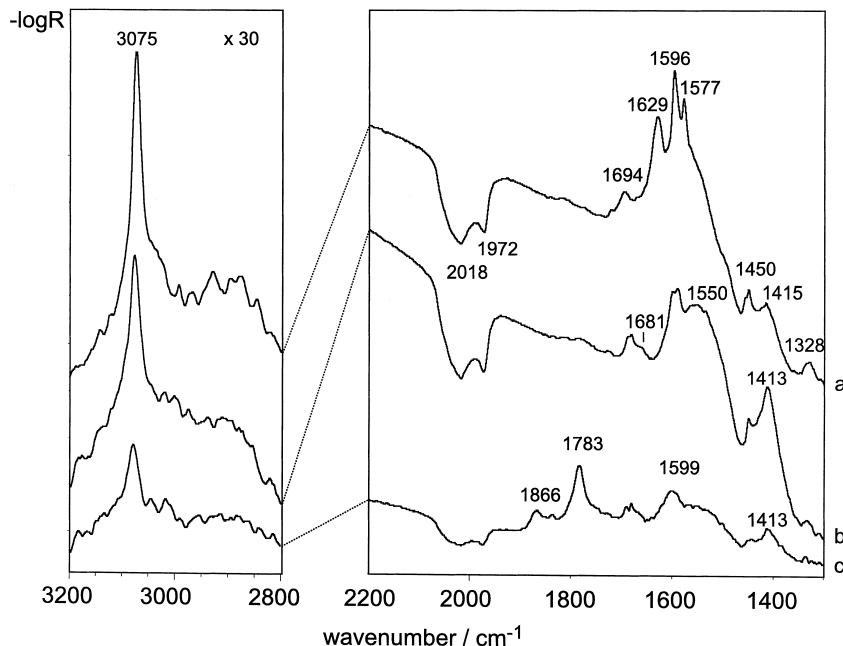

Fig. 6. Adsorbate spectra of toluene on EL10V8 after purging with Ar (a), after heating to 573 K in Ar (b) and after heating to 573 K in air (c). All spectra have been recorded at 423 K.
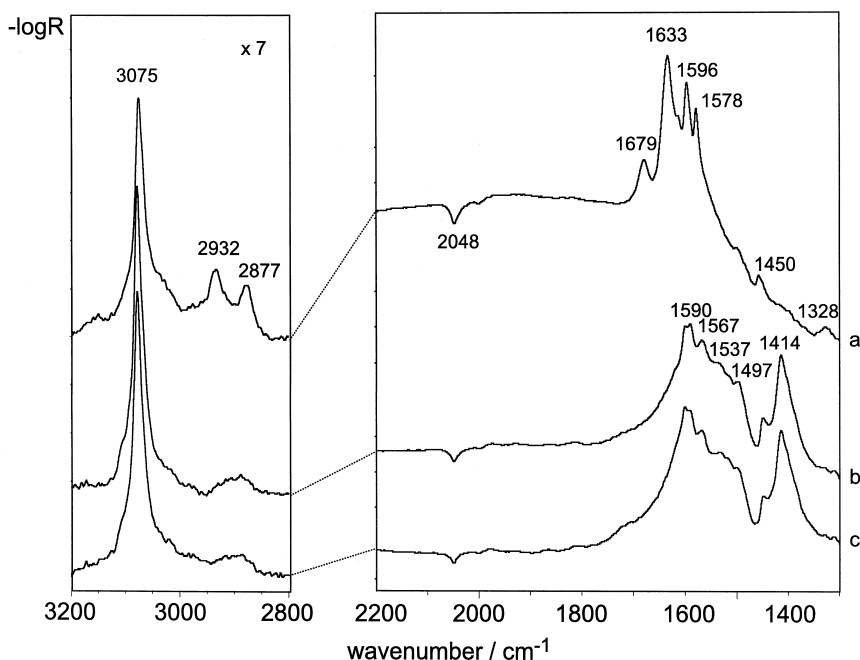
Fig. 7. Adsorbate spectra of toluene on EL10V1w after purging with Ar (a), after heating to 573 K in Ar (b) and after heating to 573 K in air (c). All spectra have been recorded at 423 K.

distinguished in the 1495–1565 cm^{-1} region, which has been covered by a broad band (1540 cm^{-1}) in the case of EL10V8. In addition to the bond strength, carboxylate frequencies are influenced by the angle between both C—O bonds, a wide bond angle resulting in a high frequency splitting [44]. The presence of benzoate species having different geometries might therefore explain the spectral features described above. Different O—C—O angles for EL10V8 and EL10V1w might be related to the different distances between neighboring adsorption sites in agreement with van Hengstum et al. [16] who proposed bidentate (1500/1410 cm^{-1}) and bridging (1545/1410 cm^{-1}) benzoate complexes. Furthermore, alkyl C—H bands are no longer detectable. Again the ring vibrations persist combined with the same small shift of the bands to higher wavenumbers. However, the carbonyl band at 1681 cm^{-1}, possibly due to a precursor of maleic anhydride, is not observed for EL10V1w.

The subsequent oxidation in air at temperatures up to 573 K (Fig. 7c) influenced the baseline of the toluene-covered sample EL10V1w which changed back to a straight line indicating a partial reoxidation of the catalyst. However, it did not induce any further transformation of the adsorbate in strong contrast to toluene-covered EL10V8. Thus, the presence of polymeric and crystalline vanadia species appears to be essential to make gas-phase oxygen available to the adsorbate. Furthermore, heating to temperatures higher than 573 K in air did not lead to the formation of maleic anhydride, and a higher reoxidation temperature was necessary to restore the initial state of the catalyst. These observations imply that the lack of available lattice oxygen is not simply compensated by an excess of gas-phase oxygen.

A flow reactor study of Eurocat samples involving temperature-programmed reduction (TPR), catalyst reduction in a hydrocarbon atmosphere and subsequent temperature-programmed oxidation (TPO) is in progress to provide further evidence that the presence of polymeric and crystalline vanadia species (EL10V8) may be associated with the ability of fast oxygen insertion whereas monomeric vanadyl species (EL10V1) exhibit a capacity only for oxidative adsorption [46]. V_2O_5 crystallites were found to be the most difficult to reduce but easiest to reoxidize signaling an easy uptake of gas-phase oxygen.

4. Discussion

In summary, DRIFT spectroscopy has been applied to study the adsorption of toluene on different V_2O_5/TiO_2 catalysts. Eurocat samples exhibiting different vanadia loadings (EL10V8, EL10V1) as well as a modified sample (EL10V1w) from which crystalline and polymeric vanadia have been removed by washing with an aqueous solution of ammonia were used to obtain information on the role of the different vanadia species. The presence of both crystalline and monomeric vanadia species on EL10V8 and EL10V1, and of only monomeric vanadia species on EL10V8w and EL10V1w was confirmed by Raman spectroscopy.

The exposure to toluene at 423 K resulted in similar adsorption products on all three samples which did not correspond to molecularly adsorbed toluene. Thus, oxidative adsorption has occurred in which monomeric vanadyl species are involved. On the other hand, spectral changes resulting from catalyst reduction were pronounced when polymeric and crystalline vanadia species were present, and were nearly not detectable for the washed catalyst. The oxidation products of toluene are therefore able to desorb only when the catalyst contains polymeric and crystalline vanadia species leading to the observed reduction of the catalyst. Thus, the capability of fast oxygen insertion can be assigned to polymeric and crystalline vanadia species.

This hypothesis is supported by the observation that the oxidation has proceeded further when crystalline and polymeric vanadia species are present. Under conditions when a benzyl species is still detectable on the catalyst exhibiting only monomeric vanadyl species, benzoate has already formed on the unmodified catalysts. Benzoate species are also observed for the washed catalyst when the temperature is raised, indicating that the insertion of oxygen has a higher activation energy in the case of monomeric vanadyl species.

In general, polymeric and crystalline vanadia species appear to be essential for the formation of oxidized aromatic products which are able to desorb from the catalyst. Several observations lead to this conclusion:

• In addition to the effect on catalyst reduction described above, the adsorbate is readily transformed in the presence of gas-phase oxygen when polymeric and crystalline vanadia species are available. If only monomeric vanadyl species are present, no further reaction occurs.

• Desorption of oxidized aromatic species can be monitored by the decrease in intensity of the phenylic C−H stretching band which may be used qualitatively to estimate the coverage. Its intensity remains constant in the case of the washed sample EL10V1w.

• High temperatures (723 K) are required to remove the adsorbate from EL10V1w, and no hints for the formation of maleic anhydride were obtained. It can be assumed that the adsorbate is burned off yielding CO_x and water. A Eurocat catalyst modified by treatment with ammonia has been reported in the literature to possess mainly total oxidation activity [38].

Hence, toluene can be adsorbed oxidatively on monomeric vanadyl species, but the formation and desorption of oxidized aromatic products such as benzoic acid or maleic anhydride is only possible when polymeric and crystalline vanadia species are present.

Polymeric and crystalline vanadia species were also found essential to make gas-phase oxygen available, since the lack of lattice oxygen in the case of the sample having only monomeric vanadyl species was not compensated by gas-phase oxygen. The size of the crystallites did not appear to be important as the same adsorption products were observed for both the low- and high-loaded Eurocat catalyst. While crystallites observable in XRD are present on EL10V8, a large number of very small crystallites is present on EL10V1 according to the literature [38]. Thus, crystalline and polymeric vanadia species are able to adsorb oxygen from the gas phase and to insert it easily into the adsorbates according to the Mars−van Krevelen type reduction–reoxidation mechanism whereas monomeric vanadyl species seem to function mainly as sites for the oxidative adsorption of aromatic hydrocarbons.

5. Conclusions

1. The combined application of DRIFT and FT-NIR Raman spectroscopy was found to be a valuable

tool to identify the presence of monomeric and crystalline vanadia species. Supported model catalysts exclusively exposing monomeric vanadyl species were prepared by washing V_2O_5/TiO_2 samples (Eurocat EL10V8, EL10V1) with aqueous solutions of ammonia (EL10V8w, EL10V1w).

2. Oxidative adsorption occurred on all samples suggesting monomeric vanadyl species to be crucial for this step. The oxidation of the side chain was found to proceed in consecutive steps via a benzylic, aldehydic and benzoate species. Toluene oxidation had proceeded to a lower extent at 423 K on the washed sample than on the unmodified Eurocat samples which is consistent with the capability of fast oxygen insertion associated with polymeric vanadia species and V_2O_5 crystallites.

3. These species also appear essential to make gas-phase oxygen available to adsorbed hydrocarbons, since no further reaction of adsorbed benzoate occurred on EL10V1w in the presence of air at 573 K. Thus, polymeric and crystalline vanadia species are essential for the Mars–van Krevelen mechanism to occur on V_2O_5/TiO_2 catalysts.

Acknowledgements

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