

Characterization of VO_x-TiO₂ catalysts and their activity in the partial oxidation of methyl ethyl ketone

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Abstract

The present work focuses on the partial oxidation of methyl ethyl ketone to acetic acid over TiO₂ supported vanadia catalysts with V loadings from 1 to 13.5 wt.%. In order to elucidate the relation between catalytic activity and the structure of the catalysts, the catalysts were also characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction with hydrogen (TPR), and temperature programmed desorption of lattice oxygen (TPD-O₂). The investigations show that with increasing V loading the MEK conversion increased whereas the turn-over frequency decreased. At lower V loading (1–4 wt.%) the total oxidation to CO_x was favoured and the selectivities to acetic acid and other oxygenated products were low. The highest selectivities to acetic acid were achieved at V loadings of 4–6 wt.%. Based on literature data and our results, a scheme of the reaction pathways for the partial oxidation of MEK to AcOH and other by-products was developed.

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Keywords: Vanadia-titania catalysts; V loading; Methyl ethyl ketone; Oxidative scission to acetic acid

1. Introduction

After the successful application of the V-Ti-O catalytic system for the production of phthalic anhydride by the selective oxidation of *o*-xylene in the late 1960s, a large number of papers have been published in the following decades concerning the oxidation of organic compounds [1–3]. Among these publications, reports and patents can be found dealing with the selective oxidation of hydrocarbons [4–7] and the oxidative dehydrogenation (ODH) of light alkanes [8–10]. Recently, a new process for the production of C₁ and C₂ acids from Raffinate II (C₄ fraction, a side product of the naphtha cracking process) was developed by the Wacker Company [11–13]. The C₄ fraction (a mixture of *n*-butane/*n*-butenes) is oxidised in the presence of water vapour at low temperature using a VO_x-TiO₂ catalyst. According to [5,14], the formation of acetic acid (AcOH) from C₄ hydrocarbons proceeds via the formation of methyl ethyl ketone (MEK) which further undergoes oxidative scission to AcOH and acetaldehyde (AcH). Moreover, VO_x-TiO₂ catalysts have been found to be

effective for the oxidation of methyl ethyl ketone to AcOH in the presence of water [14–19].

The yield of oxygenated products during the oxidation and ODH of C₄ hydrocarbons depends not only on the reaction conditions and the reactivity of the intermediate products but also on the activity of the VO_x-TiO₂ system [20–24]. The activity of VO_x-TiO₂ catalysts depends besides the preparation method also on the V loading. Isolated monomeric VO_x species on TiO₂ have been detected at a low (≤1 wt.%) content of V₂O₅ [10,20–22]. V oxides condense into two or three-dimensional polyvanadate layers which ultimately crystallize into bulk V₂O₅ (amorphous and/or crystallites) as V loading increases [23,24]. The monomeric and polymeric VO_x species are also known as “monolayer” (ML), which are found to be more active than bulk V₂O₅ in several oxidation reactions [20–24].

Most studies about the structure/activity relationship of VO_x-TiO₂ systems are focused on the ODH of C₂ to C₄ alkanes [8–10,20,21]. Christodoulakis et al. [10] and Khodakov et al. [20] showed that the turn-over frequency (TOF) during the ODH of propane decreased with increasing V surface density. Investigations of the reactivity of VO_x-TiO₂ catalysts in partial oxidation reactions are limited to the oxidation of *n*-butane [22] and methanol [23]. Wachs et al. [22] found that the

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Table 1

Specific surface areas (BET), average pore diameter (D_p), pore volume (V_p), V and V_2O_5 loading (prep. = calculated for preparation, exp. = experimental data by XPS and XFA), and VO_x density and number of theoretical monolayers (ML) of the V/Ti catalysts

Catalyst	BET area ($m^2 g^{-1}$)	D_p (nm)	V_p ($cm^3 g^{-1}$)	V/ V_2O_5 loading (wt.% prep.)	V loading (wt.% exp. (XPS/XFA))	VO_x density $VO_{2.5}$ (nm^{-2}/ML)
1-V/Ti	86	10.5	0.21	1.0/1.8	2.7/0.8	1.8/0.2
4-V/Ti	75	10.5	0.20	4.0/7.2	7.4/4.2	8.5/0.7
6-V/Ti	73	10.3	0.21	6.0/10.7	5.7/5.9	12.9/1.1
8-V/Ti	71	10.3	0.19	8/14.4	7.5/7.8	17.8/1.5
13.5-V/Ti	66	10.0	0.17	13.5/27.9	11.3/12.7	36.4/2.9

oxidation of *n*-butane to maleic anhydride over VO_x - TiO_2 catalysts (V loading between 1 and 5 wt.%) is more efficient with multiple sites, but does not strongly depend on the V surface coverage.

The ODH of alkanes proceeds via two subsequent steps: (i) C–H bond activation and (ii) H abstraction involving one-electron reduction of two V^{5+} cations or two-electron reduction of a single V^{5+} site. In contrary, the selective oxidation of substrates to carboxylic acids proceeds over multiple sequences of parallel and consecutive reaction steps involving C–H activation, H abstraction, O addition, protonation, and C–C bond breaking to shortened activated substrates, which can re-enter the reaction circle [25]. The multiple sequence of oxidation reactions poses the question about the activity, the optimal number of activated H–C centres, and the O transfer substances needed as ingredients for the partial oxidation.

The reasons for different catalytic performance of V_2O_5 - TiO_2 towards partial oxidation are still a matter of controversy. Most of the studies about performance of V/Ti systems involve V loadings in the range from 1 to 5 wt.%. Additional information about the structure/reactivity relationship of VO_x - TiO_2 catalysts can be obtained by the investigation of a broader range of the V content in such catalysts and by the investigation of the oxidation of other substrate molecules. The present work focuses on the partial oxidation of MEK over TiO_2 supported vanadia catalysts with V contents from 1 to 13.5 wt.%. In order to elu-

cidate the relation between catalytic activity and the structure of the catalysts, they were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction with hydrogen (TPR), and temperature programmed desorption of lattice oxygen (TPD- O_2).

2. Experimental

2.1. Catalyst preparation

The VO_x - TiO_2 catalysts were prepared by wet impregnation of TiO_2 (anatase, surface area $95 m^2/g$, sulphate content 1.0 wt%, Millenium Chemicals) with an aqueous solution of ammonium vanadate. For that purpose, adequate amounts of NH_4VO_3 were dissolved in heated water and some drops of ammonia under stirring. The solutions were given to the appropriate amounts of TiO_2 and the water was evaporated under stirring. The precursors were dried at 393 K for 15 h. After calcination in air at 720 K, the samples were pressed, sieved into two fractions and used for catalytic investigations and characterization.

2.2. BET surface area, XRD, and XPS

The BET surface area of the samples was measured by N_2 adsorption/desorption isotherms at 77 K using an ASAP 2000 (Micromeritics) apparatus. For the XRD a Siemens D 5000 X-ray diffractometer (Cu $K\alpha$, $\lambda = 154 pm$) was employed. The X-ray tube was operated at 40 kV and 40 mA. The XRD spectra were scanned in an angular range of $8^\circ < 2\theta < 80^\circ$ with an increment of 0.039° . XPS were obtained with a Leybold LHS 10 spectrometer provided with hemispherical electron analyzer and a Mg anode (Mg $K\alpha = 1253.6 eV$). The pressure in the main chamber was about 10^{-9} mbar. The C 1s line was used as an internal standard to calibrate the binding energies. XPS measurements were carried out only with samples after calcination.

2.3. Temperature programmed reduction with hydrogen

The TPR profiles were obtained with an AMI-100 (Altamira Instruments) instrument equipped with a TC detector. The catalysts were pre-treated in nitrogen at 673 K for 30 min and then cooled down to room temperature. The TPR measurement was

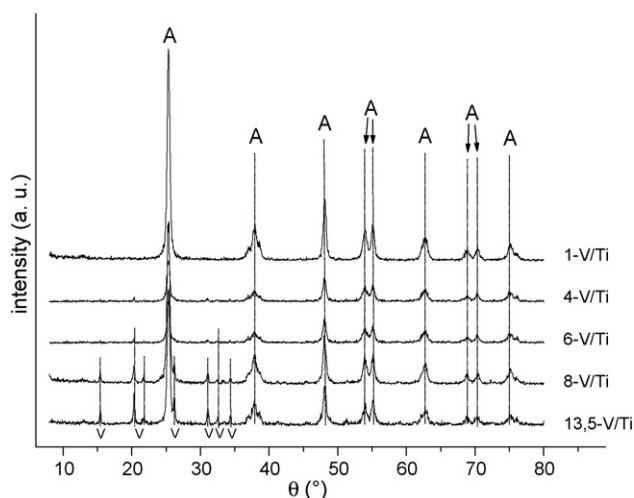


Fig. 1. X ray diffractograms of catalysts supported on titania (A: TiO_2 (anatase); V: V_2O_5).

Table 2
Relative amount of V⁵⁺, V⁴⁺ and V³⁺ ions, and Ti 2p_{3/2} and O 1s atoms determined by XPS analysis and the corresponding binding energies (BE) in electron volts (eV)

Catalyst	Relative amount (at.%)						
	BE of V 2p _{3/2} (eV)			BE of Ti 2p _{3/2} (eV)		BE of O 1s (eV)	
	V ⁵⁺	V ⁴⁺	V ³⁺	459.3	457.2	530.6	528.4
	517.1	515.6	514.3				
TiO ₂ support	0	0	0	100	0	100	0
1-V/Ti	100	0	0	96	4	95	5
4-V/Ti	100	0	0	86	24	82	18
6-V/Ti	82	18	0	78	22	75	25
8-V/Ti	33	30	37	70	30	58	42
13.5-V/Ti	19	43	38	49	51	52	48

started and recorded from 303 to 1173 K in a H₂/Ar flow (8% H₂; flow rate: 50 ml min⁻¹, heating rate: 10 K min⁻¹).

2.4. Temperature programmed desorption of lattice oxygen (TPD-O₂)

The TPD-O₂ measurements were carried out with the Oxylyt analysis system (Sensothec, Magdeburg), using coulometric titration of molecular oxygen which can be desorbed by metal oxides at high temperatures. To remove the physisorbed oxygen from the catalysts, the samples were preheated to 373 K in an argon flow for 1 h. The TPD-O₂ measurements were recorded in an Ar flow from 373 to 1223 K (flow rate: 50 ml min⁻¹; heating rate: 10 K min⁻¹).

2.5. Catalytic activity measurements

The catalysts were tested in a continuous-flow fixed bed reactor (*L*: 30.0 cm; \varnothing : 5 mm) at atmospheric pressure in a temperature range from 393 to 553 K using 200 mg of the catalyst mixed with 200 mg of corundum. The reacting feed consisted of 0.17 vol.% MEK, 3.5 vol.% oxygen and 16.5 vol.% water vapour and helium with a total flow rate of 50 ml min⁻¹. The contact time (τ) was about 0.2 s. Prior to the oxidation reactions, the

catalyst samples were activated at 573 K for 15 h with 3.5 vol.% oxygen and 16.5 vol.% water vapour in helium. After switching on the MEK flow, the reaction system was found to stabilise in about 60 min. Therefore, all data in this work were taken after 60 min of steady state reaction. The oxidation products were analyzed by online mass spectrometry (Omnistar GSD 301C2, QMS 200; Pfeiffer Vacuum) and infrared gas analysis (FTIR gas analyzer 1301; INNOVA). For MS analysis, time depending spectra were recorded for the following *m/e* values: 46 formic acid; 60 acetic acid; 72 methyl ethyl ketone; 29 and 44 acetaldehyde; 86 diacetyl. The MS intensities were converted into concentrations by calibration of standard injections. The concentration of CO₂ was determined by online IR-analysis. A detailed description of the catalytic equipment is given in [26].

3. Results and discussion

3.1. Surface area and XRD

The BET surface area, the average pore diameter, and the pore volume are given in Table 1. Table 1 additionally contains the loading of pure vanadium, of V₂O₅ calculated for the catalysts' preparation and the V loading measured by XPS and

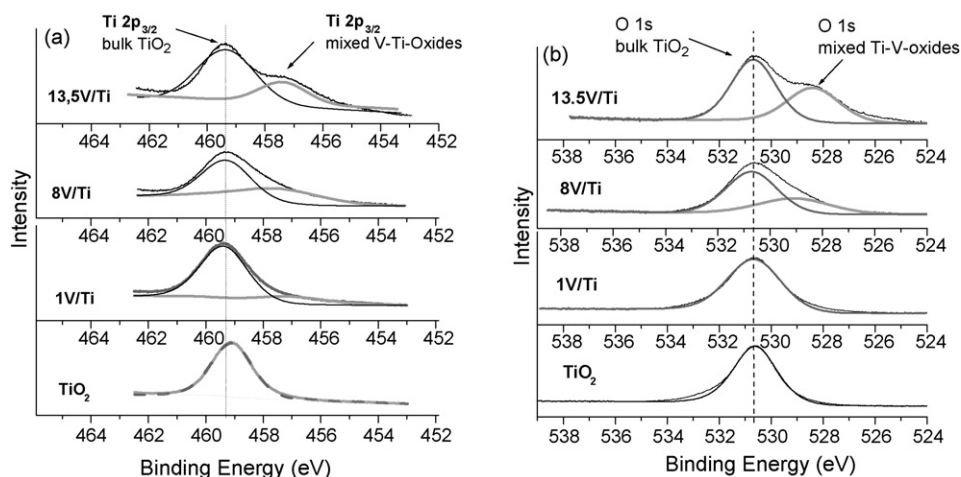


Fig. 2. XPS spectra (smoothed) of the Ti 2p_{3/2} (a) and O 1s (b) regions of pure TiO₂ (anatase) and the catalysts 1-V/Ti, 8-V/Ti, and 13.5-V/Ti.

Table 3

H₂ consumption, O₂ content, and temperatures of the peak maxima of the TPR profiles and the TPD-O₂ curves of the V/Ti catalysts

Catalyst	TPR-H ₂		TPD-O ₂	
	H ₂ consumption (mol H ₂ /mol V ₂ O ₅)	T _{max} (K)	O ₂ content (mol O ₂ /mol V ₂ O ₅)	T _{max} (K)
1-V/Ti	1.99	713; 733	0.50	978
4-V/Ti	1.98	713; 734	0.39	980
6-V/Ti	2.04	713; 734	0.34	984
8-V/Ti	1.65	713; 734; 785; 857	0.31	1038
13.5-V/Ti	1.42	713; 734; 787; 858	0.27	1044

The data of the TPD-O₂ measurements are described and discussed in Section 3.4.

XFA. Moreover, the calculated VO_x density and the number of theoretical monolayers can be found in Table 1.

The average pore diameters of all catalysts were nearly constant at 10.3 ± 0.2 nm. The pore volume of the catalysts was constant up to a V loading of 6 wt.% and then decreased with increasing V loading. The specific surface area decreased with increasing V loading. This effect can be explained by sintering of TiO₂ [21] and/or the formation of a V–Ti–O solid solution and/or mixed oxides which block the pores of the support [27]. Christodoulakis et al. [10] observed the same trend in surface areas for V₂O₅-TiO₂ catalysts calcinated at 873 K. The calculation of the VO_x surface density was based on the TiO₂ support surface area. According to literature, the VO_x density for a monolayer surface coverage is approximately 8–12 VO_x nm⁻² [10,21,24,28].

The XRD spectra of the catalysts after calcinations are presented in Fig. 1. All samples contain only TiO₂ anatase as support phase. Therefore, no transformation of anatase to rutile took place during the calcination of the catalysts at 723 K. XRD lines of V₂O₅ crystallites could only be detected in the spectra of 6-V/Ti, 8-V/Ti, and 13.5-V/Ti. The intensities and the number of peaks for V₂O₅ crystallites increased with increasing V loading. It can be concluded that the number and/or the size of V₂O₅ crystallites increased with increasing vanadium loading [21]. The XRD spectra of 1-V/Ti and 4-V/Ti showed no lines of V₂O₅ crystallites. Obviously the vanadium oxide is only present as monomeric, polymeric and/or X-ray amorphous VO_x species in these catalysts.

3.2. X-ray photoelectron spectroscopy (XPS)

According to XPS measurements, the V loading of 6-V/Ti, 8-V/Ti, and 13.5-V/Ti corresponds to that calculated for preparation whereas the V loading of 1-V/Ti and 4-V/Ti is higher than that calculated for preparation. For comparison the total content of V in all catalysts was determined by XFA and the XFA values correspond nearly to the values calculated for preparation. Therefore, the V loading of 1-V/Ti and 4-V/Ti on the surface is higher than that in the sub-layer (deeper than 10 nm). Consequently, the distribution of VO_x species on the surface and in the sub-layer of the catalyst is different for these two catalysts compared to the catalysts with V loadings ≥ 6 wt.%. Obviously at low V loading (≤ 4 wt.%) the vanadium oxides form monomeric

and polymeric VO_x species which mainly spread on the catalyst surface [10].

Additionally to analysis of total V contents (Table 1), from the XPS data the relative content of V⁵⁺, V⁴⁺ and V³⁺ ions and Ti and O atoms was determined cf. Table 2. The content of V ions was calculated via deconvolution of the V 2p_{3/2} levels of the catalysts using Gaussian-shaped curves. In the catalysts 1-V/Ti and 4-V/Ti only V⁵⁺ could be detected. The binding energy of V 2p_{3/2} in 1-V/Ti and 4-V/Ti was 517.1 ± 0.1 eV and corresponds to that of V⁵⁺ [29]. With increasing V loading the relative amount of V⁴⁺ and V³⁺ increased while the relative amount of V⁵⁺ decreased (Table 2) indicating that isolated monomeric VO_x species can be easier oxidised than polymeric VO_x species and/or amorphous and crystalline V₂O₅.

The oxidation state of vanadium in VO_x-TiO₂ catalysts is the subject of many discussions in the literature. Some authors propose that monomeric and polymeric VO_x species only contain V⁵⁺ ions [30,31] whereas others could show that even in samples after calcination in air the oxidation state of vanadium is lower than five [32–36]. According to Gasior et al. [32], the amount of lower valent vanadium decreased with increasing V loading in the presence of V₂O₅ crystallites. Rusiecka et al. detected V⁴⁺ ions in VO_x-TiO₂ catalysts by EPR at high V loadings [33]. The presence of V³⁺ ions in VO_x-TiO₂ catalysts after calcination in air was proposed by Grzybowska-Świerkosz [21].

Additional information about the structure of the VO_x-TiO₂ catalysts can be obtained by the analysis of the Ti and O XPS signals (Fig. 2). XP spectra were recorded for all V/Ti catalysts. Only the spectra of the TiO₂ support, 1-V/Ti, 8-V/Ti, and 13.5-V/Ti are shown in Fig. 2 for reasons of brevity. The binding energies of Ti 2p_{3/2} and O 1s of the support are 459.3 and 530.6 eV, respectively [37]. Additional peaks as shoulders were observed for the catalysts at about 457.2 and 528.4 eV (Fig. 2). These additional peaks can be assigned to the formation of mixed binary oxides of the types V₃Ti₆O₁₇ and/or TiV₂O₆. The reason for the formation of these complex oxides may be the preparation method. During the wet impregnation the aqueous solution of NH₃VO₄ may react with the surface of TiO₂ combined with a partial dissolution of V and Ti oxides [38], which then leads to the formation of the mixed crystallised phases of V–Ti oxides after calcination. For catalysts with lower V loading these shoulders were only small.

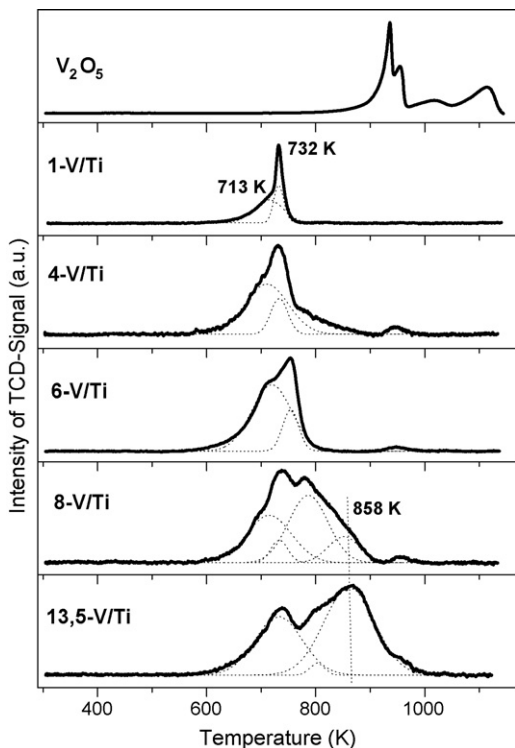


Fig. 3. TPR profiles (solid lines) of calcined V_2O_5 and of the V/Ti catalysts; the dotted lines show the deconvoluted peaks of overlapping TPR curves. Sample weight: 50 mg; total flow rate of the 8.0 vol.% H_2 in Ar mixture: 50 ml min^{-1} ; heating rate: 10 K min^{-1} .

3.3. Temperature programmed reduction with hydrogen

To investigate the different surface forms of vanadia with respect to their reducibility, the catalysts were investigated by temperature programmed reduction with H_2 after calcination. The TPR profiles of pure V_2O_5 and of the V/Ti catalysts are shown in Fig. 3. Pure V_2O_5 is reduced by hydrogen in four characteristic steps [39]. According to Bosch et al. [39], the four steps of the reduction process can be described as follows:



The reduction of pure V_2O_5 was observed only at temperatures above 950 K (Fig. 3). Compared to pure V_2O_5 , the TPR profiles of the V/Ti catalysts show peaks which are generally shifted to lower temperatures (720–780 K). The higher reducibility of the V/Ti catalysts compared to bulk V_2O_5 can be explained by the formation of monomeric and polymeric VO_x species on the TiO_2 surface and their interaction with the support (formation of binary Ti–V oxides). By comparison of the TPR curves and data of the catalysts in Fig. 3 and Table 3 it can be concluded that the increase in V loading has an effect on the shape, the number of peaks, the consumption of hydrogen, and the temperature of the peak maximum (T_{max}).

From investigations by Raman spectroscopy [40] it can be concluded that in the VO_x - TiO_2 system monomeric, polymeric, amorphous, and crystalline VO_x species can coexist. Bulushev et al. [24] reported that T_{max} at 770–780 K can be assigned to the reduction of monomeric species and $T_{max} > 810 \text{ K}$ can

be assigned to the reduction of polymeric VO_x species. The reduction of amorphous V_2O_5 takes place at temperatures about 70–80 K above that of polymeric species. It is however difficult to differentiate the peaks in the TPR profiles of the catalysts as reduction of only one type of VO_x species. The reduction profiles could be also considered as interferences of different reduction steps of vanadium ($V^{5+} \rightarrow V^{4+} \rightarrow V^{3+}$) and of different VO_x species. Table 3 summarizes the measured molar H_2 consumption and T_{max} during the TPR measurements. The calculated amount of consumed H_2 is based on the following equation: $V_2O_5 + 2H_2 \rightarrow V_2O_3 + 2H_2O$. To determine the consumed amount of hydrogen, the total TPR profile areas were integrated. The TPR apparatus was calibrated by the reduction of CuO to Cu. The amount of consumed H_2 was nearly constant for V loadings from 1 to 6 wt.% (1-V/Ti, 4-V/Ti, and 6-V/Ti). With a further increase in V loading above 6 wt.% the H_2 consumption decreased with increasing V loading (8-V/Ti; 13.5-V/Ti). The calculated molar H_2 consumption is about 2.0 mol H_2 per mol V_2O_5 . The measured H_2 consumptions for 1-V/Ti, 4-V/Ti, and 6-V/Ti are in good agreement with the calculated amount. Hence, it can be assumed that the vanadium in these catalysts is mainly in the oxidation state +5 and the reduction to the state +3 was complete. The measured H_2 consumptions of 8-V/Ti and 13.5-V/Ti are lower than the calculated ones. Taking the results of the XPS measurements into account, the lower H_2 consumption of the catalysts with high V loading can be explained by a lower average oxidation state of vanadium in the catalysts with higher V loading ($>6 \text{ wt.}\%$) compared to the catalysts with low V loading ($\leq 4 \text{ wt.}\%$). Moreover, the catalysts with V loadings $>6 \text{ wt.}\%$ contain additional and/or different V species (monomeric, polymeric VO_x , amorphous and crystalline

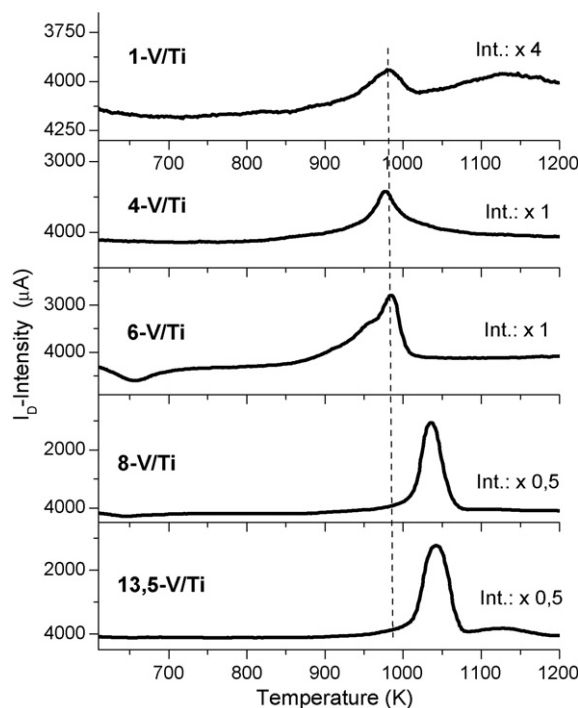


Fig. 4. Desorption profiles of oxygen of the V/Ti catalysts. Sample weight: 50 mg; total flow rate of helium: 50 ml min^{-1} ; heating rate: 10 K min^{-1} .

V_2O_5) and mixed V–Ti oxides which are less easily reducible than the VO_x species in the catalysts with V loadings <6 wt.%.

3.4. Temperature programmed desorption of lattice oxygen

The TPD- O_2 investigations were carried out to obtain information about the thermal stability of the catalysts and the amount of active lattice oxygen which can be desorbed from the catalysts at higher temperatures. The TRD- O_2 curves of the catalysts are shown in Fig. 4. The desorption of oxygen from pure V_2O_5 took place in the temperature range from 980 to 1050 K (not shown in Fig. 4). The desorption of oxygen from 8-V/Ti and 13.5-V/Ti took place at about 70–80 K above that from the catalysts with V loadings ≤ 6 wt.% (Fig. 4). In Table 3 the molar amount of desorbed oxygen from the catalysts after calcination in air and the temperature of the maximum of desorption (T_{max}) are listed. The determination of the amount of desorbed O_2 is based on the equation: $V_2O_5 \rightarrow V_2O_3 + O_2$. The amount of desorbed O_2 decreased with increasing V loading and can be explained by an increase of VO_x species that contain V cations with oxidation states lower than +5. The results of the TPD- O_2 measurements are in good agreement with the results from the TPR investigations in which the molar H_2 consumption per moles of V_2O_5 decreased with increasing V loading. Therefore, the additional and/or different VO_x species at high V loading do not only hinder the reduction of V^{5+} and V^{4+} ions but also suppress the re-oxidation of polymeric V_2O_5 species and/or mixed Ti–V oxides.

3.5. Catalytic oxidation of MEK

3.5.1. Oxidation products of MEK

The conversion and the product distribution as a function of reaction temperature are depicted in Fig. 5 for the most selective catalyst 6-V/Ti. The main oxidation products were acetic acid (AcOH), formic acid (FA) and CO_x at a conversion range from 35 to 75%. At lower conversions (temperature <413 K) significant amounts of diacetyl ($S = 8$ –17%), acetaldehyde ($S = 5$ –6%), and propionaldehyde ($S = 4$ –5%) could be observed. The selectivity to these products decreased with increasing reaction temperature and conversion of MEK. This indicates that these

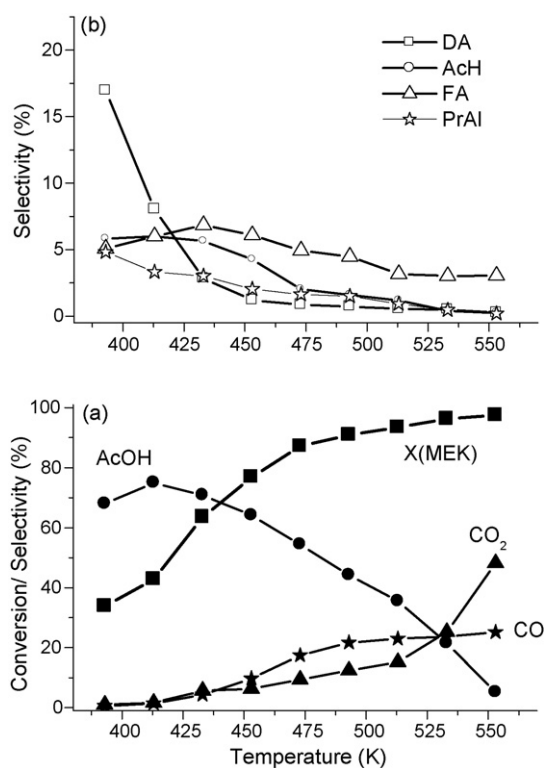
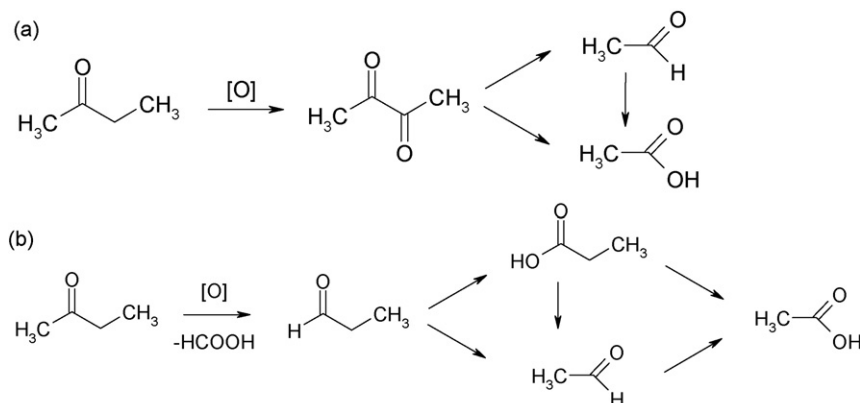


Fig. 5. Conversion of methyl ethyl ketone and selectivities to CO, CO₂, acetic acid (AcOH), acetaldehyde (AcH), formic acid (FA), diacetyl (DA), and propionaldehyde (PrAl) as a function of reaction temperature during the oxidation of MEK on catalyst 6-V/Ti. GHSV: 10,000 h⁻¹; $c_0(O_2)$: 3.5 vol.%; $c_0(MEK)$: 0.17 vol.%; $c_0(H_2O)$: 16.5 vol.%; He: rest.

compounds are intermediate products. The selectivities to all oxygenates depended on the reaction temperature (Fig. 5). The maximum selectivity to AcOH (70–75%) was observed at temperatures between 383 and 433 K. At 550 K the AcOH selectivity decreased below 5% and the selectivities to total oxidation products CO and CO₂ increased. Other side products were propionic acid, methyl vinyl ketone and acetoin. The total selectivity to these products was about 5–7% at 393–413 K and decreased to nearly zero at 553 K. Based on [17–19] and our results, a simple reaction scheme for the partial oxidation of MEK to AcOH and other by-products were developed (Scheme 1). These reaction



Scheme 1. Possible reaction pathways for the formation of AcOH during the oxidation of MEK on vanadium oxide containing catalysts. (a) via oxidative scission of diacetyl; (b) via oxidative scission of propionaldehyde and propionic acid.

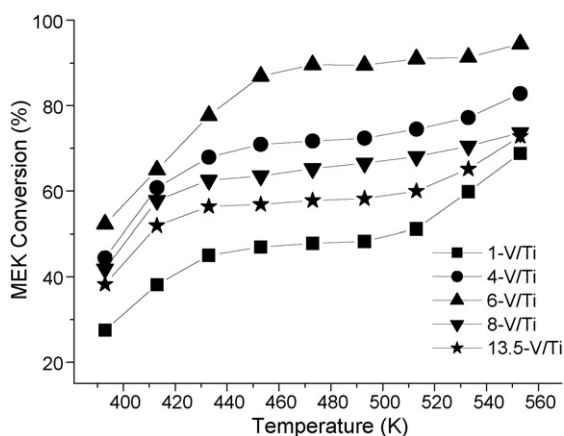


Fig. 6. Conversions of MEK as a function of temperature. GHSV: 10,000 h⁻¹; c₀(O₂): 3.5 vol.%; c₀(MEK): 0.17 vol.%; c₀(H₂O): 16.5 vol.%; He: rest.

pathways include primary selective oxidation of MEK to DA, which undergoes further oxidative scission to AcH and AcOH. AcOH can also be formed from PrAl, which is initially formed by an oxidative C–C scission of MEK. AcH and PrAl are precursors for the formation of C₂ and C₃ acids. Propionic acid is more reactive than AcOH and can be also oxidised to AcOH, FA and CO_x. The observed change in selectivities with increasing temperature implies different apparent energies of the activation of DA, AcH and PrAl to form AcOH at lower temperature and the total oxidation preferred at higher temperatures. CO_x and FA can be formed by non-selective oxidation of MEK, DA, AcH, PrAl and propionic acid.

3.5.2. The effect of the V loading on the conversion of MEK

All catalysts were measured over a temperature range of 393–553 K at constant feed and GHSV values. The conversions of MEK in dependence on temperature are depicted in Fig. 6. For all catalysts the conversions of MEK increased with increasing temperature. Catalyst 6-V/Ti showed about 20–25% higher conversions at temperatures above 423 K compared to the other catalysts. Contrary, catalyst 1-V/Ti showed the lowest conversion.

For the estimation of textural effects on the catalytic activity, the so-called specific reaction rates r_s (mol m⁻² h⁻¹) were calculated by Eq. (1):

$$r_s = \frac{nX}{m_{\text{Kat}}s(\text{BET})} \quad (1)$$

with n : flow rate of MEK (mol h⁻¹); X : conversion of MEK (%); m_{Kat} : catalyst weight (g); $s(\text{BET})$: BET surface area (m² g⁻¹). The r_s and TOF values are plotted against the number of theoretical monolayers (ML) and the surface density of VO_x in Fig. 7 for three different temperatures (393, 413, and 473 K) to account for the different V loadings of the catalysts at representative reaction temperatures. The TOF values were calculated as moles of MEK per moles of V per hour. A theoretical ML is assumed to be 10 V atoms nm⁻², or 0.1 wt.% V₂O₅/m² of the specific surface area of TiO₂ [21,28]. The amount of V₂O₅ which is necessary for the formation of a monolayer was calculated from the BET area and the surface coverage of a VO_{2.5} unit (0.105 nm²) [41,42].

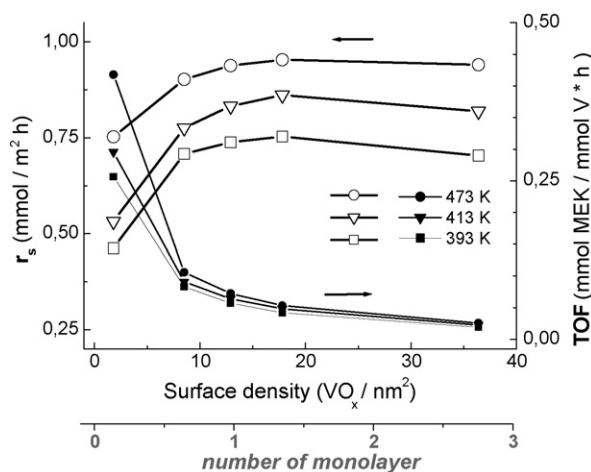


Fig. 7. Specific reaction rates of MEK conversion (left axis) and turn-over frequency (TOF, right axis) as a function of the VO_x surface density and number of monolayers at three different temperatures.

Table 1 shows that the V loading of 1-V/Ti is far below the theoretical ML covering. Therefore, mainly monomeric VO_x species are present on the surface. Fig. 7 shows that these monomeric VO_x species possess only low catalytic activity compared to the polymeric VO_x species. The catalyst samples with V loadings ≥ 6 wt.% ($n_s \sim 18 \text{ VO}_x \text{ nm}^{-2}$) exhibit the highest activity.

Fig. 7 also shows a moderate decrease of TOF with increasing surface density of VO_x (n_s values). The observed decrease of the TOF with increasing n_s values (or ML) was stronger for lower temperatures 393–413 K. As shown in the previous section, the catalysts with V loadings from 1 to 6 wt.% possess a higher reducibility and the desorption of lattice oxygen proceeds at lower temperatures compared to the catalysts with 8 and 13.5 wt.% V. Therefore, it seems that the reactivity of the catalysts correlates with the reducibility [43] and the thermal stability of the active lattice oxygen. Thus it is confirmed that the local structure of VO_x active sites at lower V loading ($n_s = 8\text{--}12 \text{ VO}_x \text{ nm}^{-2}$) significantly affects the ability of a fast activation of a C–H bond of the MEK molecule during partial oxidation. On the other hand, it can be concluded that VO_x sites at sub-monolayer surface coverage are less effective for the oxidation of MEK. High surface density of VO_x ($n_s > 15\text{--}20 \text{ V nm}^{-2}$) leads to the formation of polymeric VO_x species and/or crystalline V₂O₅ with lower catalytic activity [38]. Moreover, the formation of mixed V–Ti–O solid solutions in catalysts with V loadings ≥ 6 wt.% prepared by different methods (flash drying, wet impregnation, grafting) was reported by [44–46]. The observed effect of the V loading on the conversion of MEK in the present work is similar to the reports of Khodakov et al. [20], Christodoulakis et al. [10], and Gao et al. [47] who investigated the oxidative dehydrogenation (ODH) of propane in the presence of VO_x-TiO₂ catalysts and observed an initial increase of the reaction rate (for small n_s values) and then a moderate decrease with a further increasing surface density of V.

The observed decrease of the TOF with increasing VO_x surface density is similar to the results of Christodoulakis et al. [10]. It indicates that the individual sites for the activation of

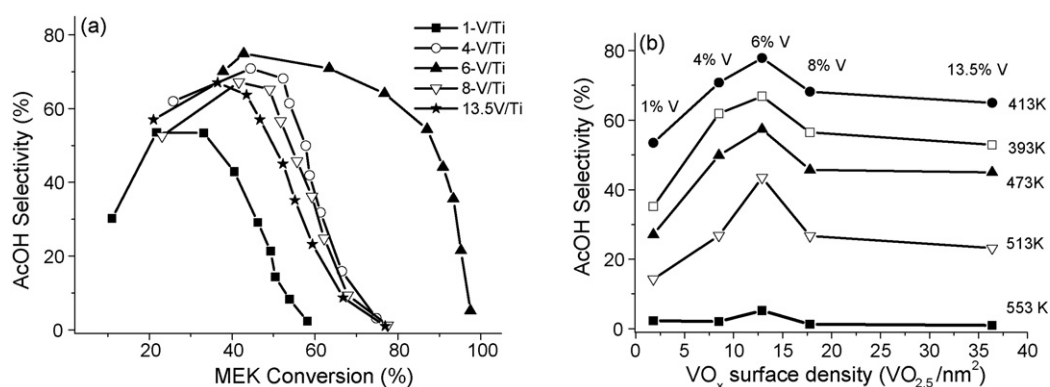


Fig. 8. Selectivity to acetic acid as a function of the MEK conversion (a), and of surface VO_x density (b) at the temperature range of 383–553 K. GHSV: 10,000 h⁻¹; c₀(O₂): 3.5 vol.%; c₀(MEK): 0.17 vol.%; c₀(H₂O): 16.5 vol.%; He: rest.

MEK become less effective with increasing V loading. Wachs et al. concluded the importance of the bridging V–O–support bonds in ODH reactions [43] and selective oxidation reactions [22,23]. In these studies it was pointed out that the decrease of the TOF for catalysts with V loadings above 6 wt.% could be correlated to a decreasing number of V–O–Ti bonds. According to [22], the strong influence of the used oxide support (Al₂O₃, CeO₂, SiO₂, TiO₂ and ZrO₂) on catalysis suggests that the bridging V–O–support bonds are involved in the rate determining step, associated with the oxidation of hydrocarbons. On the other hand, the high TOF values for catalyst 1-V/Ti in which vanadium predominantly exists in the pentavalent state, indicates that V⁵⁺ is responsible for H–C bond activation and H-abstraction in the MEK molecule [48]. However, other authors concluded that V⁵⁺ ions are “parasitical species” responsible for the consecutive over-oxidation of substrates to CO_x [49].

3.5.3. The effect of the V loading on the selectivity to AcOH and on product distribution

In order to examine the effect of the V loading on the selectivity to oxidation products of MEK, a series of catalytic test reactions were conducted at constant reaction conditions in a temperature range from 383 to 553 K. The selectivities to AcOH of the catalysts were plotted against the MEK conversion (Fig. 8a). In all cases, the initial selectivity to AcOH was rather high but decreased rapidly with increasing conversion and reaction temperatures. From the selectivity/conversion plot (Fig. 8a) and the selectivity/V-surface density plot (Fig. 8b) it can be concluded that the catalyst 6-V/Ti possessed the highest selectivity to the formation of AcOH over the whole MEK conversion and temperature range.

The temperature dependency of the selectivity to diacetyl (primary product) and FA and CO₂ for all investigated catalysts are shown in Fig. 9. Catalyst 1-V/Ti exhibited the lowest selectivity to DA, FA and AcOH in the whole temperature range and consequently was most effective in the total oxidation, especially at temperatures above 473 K. The catalysts 4-V/Ti, 6-V/Ti, and 8-V/Ti showed the highest selectivities to the primary product DA (7–10%) and low selectivities to the total oxidation product CO₂ at temperatures between 393 and 413 K. The high selec-

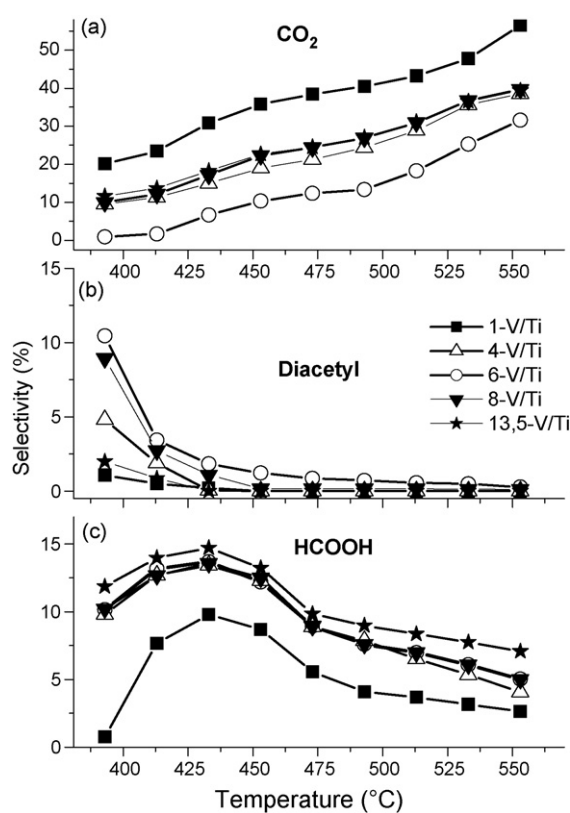


Fig. 9. Dependency of the selectivity to (a) CO₂, (b) diacetyl and (c) formic acid on reaction temperature for the V/Ti catalysts. GHSV: 10 000 h⁻¹; c₀(O₂): 3.5 vol.%; c₀(MEK): 0.17 vol.%; c₀(H₂O): 16.5 vol.%; He: rest.

tivity to CO₂ and the low selectivity to carboxylic acids in the presence of 1-V/Ti indicate that monomeric VO_x species are less selective than polymeric VO_x species and/or mixed V–Ti oxides [21,38]. The decrease of the activity of the V/Ti catalysts with higher V loading and therefore higher VO_x surface density ($n_s \sim 15\text{--}25 \text{ VO}_x \text{ nm}^{-2}$) can be mainly explained by (i) the formation of a vanadia phase on the catalyst’s surface (detected by XRD). In this case an increasing number of active V centres are not accessible to reacting molecules due to an increasing coverage of the surface by the vanadia phase.

4. Conclusions

The activity of supported V-Ti-O catalysts with V loadings from 1 to 13.5 wt.% in the selective oxidation of methyl ethyl ketone was investigated. The oxidation state of vanadium in the pre-oxidised catalysts with V loadings lower than 4 wt.% was mainly pentavalent as shown by XPS. The relative amount of V⁵⁺ decreased with increasing V loading. The TPR-H₂ investigations of the V/Ti catalysts showed that with increasing V loading the number of different VO_x species increases. These VO_x species possess different activity of reduction and therefore the catalytic performance changes with changing V loading. This phenomenon can be explained by an agglomeration of VO_x species to form bulk V₂O₅ at the catalyst surface in catalysts with high V loading (>6 wt.%). Moreover, a partial migration of V into the bulk of the TiO₂ support and the formation of binary V-Ti oxides cannot be excluded. In contrast to the selective oxidation of *n*-butenes to maleic anhydride over V/Ti catalysts (V loading: 1–5 wt.%) in absence of water, the general observation of this study (V content from 1 to 13.5 wt.%) is that the turn-over frequency of methyl ethyl ketone during its selective oxidation in the presence of water depends on the surface vanadia coverage (exponentially decreasing TOF values with increasing surface V density from 1.8 to 36 VO_x nm⁻²). The last finding is in good agreement with the observation of the catalytic activity by ODH of propane.

At V loadings far below monolayer covering (1–4 wt.%), mainly isolated, monomeric VO_x species are present on the catalyst surface. These VO_x species possess a low catalytic activity and low selectivity to the formation of diacetyl, formic acid and acetic acid and favour the total oxidation. The higher selectivity to AcOH at V loadings of about 4–6 wt.% suggests that adjacent surface V sites are more effective in selective oxidation than the isolated V sites at low V loading (<4 wt.%) or agglomerated VO_x species at high V loading (>6 wt.%). However, the nature of such mixed V-Ti oxides associated with supported V₂O₅ species needs further Raman spectroscopic investigations and a clarification of their properties and their role in the selective oxidation.

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