



Structure-reactivity relationships in supported VO_x/TiO_2 catalysts for the oxyhydrative scission of 1-butene to acetic acid: A comprehensive catalytic and in situ-spectroscopic study

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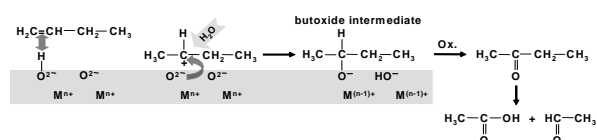
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1. Introduction

Considerable amounts of n-butenes are available as by-products of naphtha cracking for the manufacture of ethene and propene. Actually, these hydrocarbons are not efficiently used. An effective utilization of these cheap hydrocarbons could be realized by a new process based on the oxyhydrative scission of n-butenes and n-butane to acetic acid [1]. Mixed vanadium/titanium oxides appeared to be promising catalysts for this process. However, to make this process economically more attractive, their performance must be further improved. For this reason, additional knowledge about the specific structure of active catalyst components and their role in the reaction mechanism is necessary to develop effective catalysts with better performance.



Scheme 1: Proposed reaction pathway for 1-butene oxidation over oxide catalysts with acidic sites.

According to the oxyhydrative scission mechanism for the butene oxidation proposed by Takita et al. [2], methyl ethyl ketone is initially formed by oxyhydration of the olefin and is consecutively subjected to oxidative C-C bond scission (Scheme 1). As result of this reaction acetic acid and acetaldehyde were obtained, whereas the latter is subsequently oxidized to acetic acid. The first step of this reaction

chain is an acid-catalyzed hydration reaction leading to a butoxide intermediate. Consequently, acidic properties of the catalysts and the presence of water vapor are of inevitable importance.

Other investigations have demonstrated that catalytic activity and selectivity depend on the extent of vanadium loading and the oxidation state of the catalytically active vanadium species [3-5]. Recent own investigations [6, 7] evidenced that catalysts with vanadia contents between 3 and 14 wt.% on TiO_2 (anatase) have almost comparable catalytic performance.

Furthermore, it was shown that only catalysts with vanadia supported on redox active oxides such as TiO_2 act effectively in the selective 1-butene oxidation to acetic acid. Additionally, it was demonstrated [7] that the concerted application of in situ-spectroscopic methods proves to be a useful tool for elucidating structure-reactivity relationships of active sites in VO_x/TiO_2 catalysts during oxyhydrative scission reaction of 1-butene.

The investigations presented in this paper are focused on the influence of various TiO_2 materials with different structures and sulfate contents on the activity of VO_x/TiO_2 catalysts in the selective oxidation of 1-butene to acetic acid. Furthermore, the effects of water vapour and Sb doping in this reaction are described. The catalysts were studied under reaction-like conditions using 1-butene and the intermediate 2-butanol as reactant by spectroscopic in situ-methods (FTIR, EPR, UV-vis-DRS). On the basis of spectroscopic investigations and catalytic tests suggestions for reaction mechanism and catalyst design are made.

2. Experimental

The catalysts (Tab. 1) have been prepared 1) by spray drying (sd) of oxide mixtures V₂O₅/TiO₂ and V₂O₅/Sb₂O₃/TiO₂, 2) by impregnation (i) of the TiO₂ support with vanadyl oxalate, or 3) by hydrolysis of a V, Sb-alkoxide mixture in a TiO₂/CH₂Cl₂ suspension (ao). The TiO₂ materials were commercial products of Millennium Chemicals (Ti-M) and Sachtleben Chemie GmbH (SC3, 5, 7). All catalysts were calcined in air at 400°C for 4 h.

Table 1. Overview of the investigated catalysts.

Catalyst	V / Sb (wt.%)	preparation	TiO ₂ support
V/Ti-M (sd)	6.1	spray drying	anatase + sulfate
V/Sb/Ti-M (sd)	4.2 / 9.5	spray drying	anatase + sulfate
V/Ti-M (i)	4.8	impregnation *	anatase + sulfate
V/Sb/Ti-M (i)	3.9 / 9.5	impregnation *	anatase + sulfate
V/SC3 (i)	6.0	impregnation *	anatase + sulfate
V/SC5 (i)	9.0	impregnation *	rutile
V/SC7 (i)	4.2	impregnation *	anatase sulfate-free
V/Sb/Ti-M (ao)	4.2 / 9.5	alkoxide route **	anatase + sulfate
V/Sb/SC3 (ao)	4.2 / 9.5	alkoxide route **	anatase + sulfate
V/Sb/SC7 (ao)	4.2 / 9.5	alkoxide route **	anatase + sulfate

* impregnation with vanadyl oxalate, 0.06 wt.% V m⁻²

** TiO₂ suspension + V, Sb-alkoxide + H₂O

FTIR spectra were recorded using a Bruker IFS 66 spectrometer equipped with a heatable and evacuable IR cell with CaF₂ windows, connected to a gas dosing - evacuation system. For the experiments the catalyst powder was pressed into self-supporting discs with a diameter of 20 mm and a weight of 60 mg and activated by heating up to 400°C in air for 30 min followed by cooling to reaction temperature or room temperature, respectively.

The FTIR measurements were performed with 3 vol.% 1-butene/8 vol.% O₂/3 vol.% H₂O / N₂, at 200°C. The adsorption of 2-butanol was carried out by using a saturator. After adsorption of butanol at room temperature and evacuation, the samples were heated in vacuum.

EPR spectra in X-band ($\nu \approx 9.5$ GHz) were recorded by the cw-spectrometer ELEXSYS 500-10/12 (Bruker) using a microwave power of 6.3 mW, a modulation frequency of 100 kHz and a modulation amplitude of 0.5 mT. Measurements were carried out in a home-made flow reactor connected to a gas/liquid-supplying system [8]. This reactor was loaded with 200 mg catalyst particles and directly implemented into the rectangular EPR cavity. The experiments were performed with the same reactant mixture as used for in situ-FTIR.

UV/VIS spectra in diffuse reflectance mode were recorded by a Carry 400 spectrometer (VARIAN) equipped with a diffuse reflectance accessory (type praying mantis, Harrick) and a respective flow cell (Harrick). The reduction/re-oxidation kinetics of the catalysts was studied by following the absorbance at 600 nm as a function of time. This wavelength is in the range for d-d transitions of reduced vanadium species. Samples were pretreated in O₂ flow (5 ml/min) at 200°C for 2 h until a constant value of absorbance at 600 nm was reached.

Catalytic tests were performed in a fixed bed tubular reactor in the temperature range from 160 to 220°C at a total

pressure of 7 bar. The feed composition was 1.9 vol.% 1-butene/9.1 vol.% O₂/24.4 vol.% H₂O / N₂. Product compositions were analyzed by online-GC (GC 17A, Shimadzu) and by non-dispersive IR photometry at normal pressure. Conversion degrees and selectivities were calculated with respect to 1-butene concentrations in the feed and effluent gases.

3. Results and discussion

Even at room temperature, an intense interaction of butene with the catalysts proceeds indicated by a strong increase of the VO²⁺ signal intensity during EPR measurements and the appearance of adsorbed oxidized products (ketone, enolate) detected by FTIR. During reaction at 200°C a continuous increase of the VO²⁺ EPR signal intensity for the Sb-free catalyst V/Ti-M (sd) was observed.

The FTIR spectra resulting from reaction of 1-butene/O₂ and 1-butene/O₂/H₂O on V/Ti-M (sd) at 200°C are depicted in Fig. 1. As can be seen from the reaction of 1-butene/O₂ (Fig. 1A) already after short contact time a set of bands can be observed. The band at 1655 cm⁻¹ is due to the $\nu(\text{C}=\text{O})$ mode of adsorbed ketone, whereas the bands at 1540 and 1441 cm⁻¹ are attributed to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ modes of carboxylate, probably acetate species [9]. After 10 min, further bands at 1780 cm⁻¹ and around 1620 cm⁻¹ appear, the intensities of which increase with reaction time. The band at 1620 cm⁻¹ is assigned to a $\nu(\text{C}=\text{C})$ mode while the band at 1780 cm⁻¹ is typical for adsorbed cyclic anhydrides [10]. The appearance of adsorbed carboxylate species may be explained by formation of acetic acid which is partly adsorbed as acetate at the catalyst surface. Cyclic anhydrides are formed by oxidation of butadiene [11]. This points to the fact that oxidative dehydrogenation of 1-butene proceeds as a side reaction.

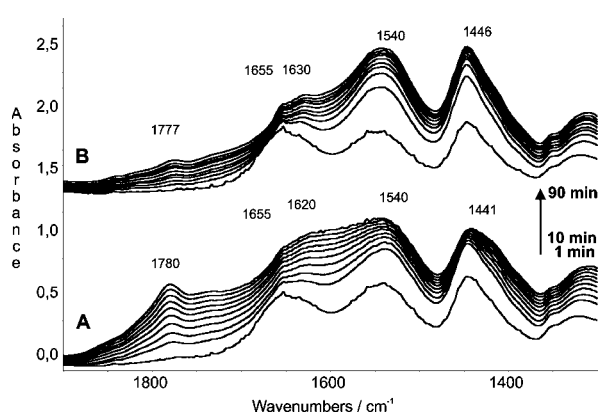


Figure 1: FTIR spectra of adsorbates formed on V/Ti-M (sd) during reaction of 1-butene/O₂ (A) and 1-butene/O₂/H₂O (B) at 200°C.

Table 2: 1-Butene conversion (%) at 180°C and selectivities (%) of different products at 20% butene conversion.

Catalyst	X _{1-butene}	S _{AcOH}	S _{AcH}	S _{HCOOH}	S _{CO}	S _{CO₂}
V/Ti-M (sd)	36	51	6	6	20	17
V/Sb/Ti-M (sd)	40	61	10	4	17	8

If the reaction is carried out in the presence of water vapor, the same adsorbed species as observed during butene/O₂ reaction without water were detected (Fig. 1B). However, the crucial difference is that essentially less anhydride species are observable. Obviously, water selectively suppresses the side reaction leading to cyclic anhydride species and blocks adsorption sites.

The influence of water has also been studied by in situ-EPR for the same sample. During heating under feed up to 180°C, the EPR spectra do not differ much in dependence on the water content. However, well visible differences appear with increasing time on stream at 180°C. The VO²⁺ EPR signal broadens with increasing water content in the feed. Thus, the line width derived by spectra simulation increases from 35.5 mT (without water) to 38.7 mT (with 5.1% water) and 46.5 mT (with 24.4% water) after 4h time on stream in the reactant gas flow. Consequently, it must be concluded, that the magnetic interaction between neighbouring VO²⁺ sites is weakened by increasing amounts of water in the feed. This suggests that water favours spreading of large VO_x clusters, and thus, enhances dispersion.

In good agreement with these spectroscopic results, it was found during catalytic tests that the selectivities for acetic acid improve from 61 to 74 % with increasing water content in the feed, whereas with 24% water content the best selectivity was achieved.

Besides water admixture, also the doping with Sb causes enhanced selectivities for acetic acid (AcOH) and acetaldehyde (AcH) which is mainly attributed to a lower formation of CO₂ (Tab. 2).

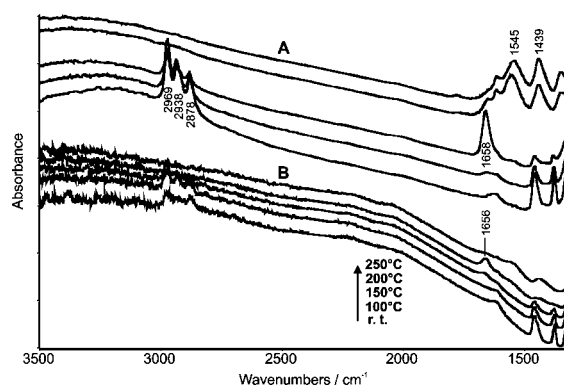
It was found by in situ-EPR experiments that the Sb-containing catalysts were deeper reduced under reaction conditions than catalysts without Sb. This leads to an increased concentration of EPR-silent V³⁺ which is re-oxidized to V⁴⁺ upon contact with air at room temperature. This effect may be caused by the formation of an amorphous non-stoichiometric antimony vanadate-like component which lowers the oxidation potential of VO_x species and leads to lower activity but higher selectivity in comparison to the Sb-free catalysts [7].

As could be shown by recent investigations [6], only catalysts with vanadia supported on redox active oxides such as TiO₂ act effectively in the selective 1-butene oxidation to acetic acid, whereas surprisingly the preparation method proved to be of lower importance. For comparative investigations concerning the influence of different TiO₂ supports, VO_x catalysts with various TiO₂ materials were prepared. These materials comprised rutile, sulfate-containing anatase of different manufacturers and sulfate-

free anatase. The V-content corresponding to the specific surface area was 0.06 wt.% m⁻² for all catalysts (*cf.* Tab. 1).

The number of redox active surface sites for bulk metal oxides can be estimated by means of isopropanol as a chemical probe molecule [12]. Therefore, we have adapted this method for characterizing VO_x/TiO₂ catalysts with different TiO₂ supports using 2-butanol as reactant [13], in view of the fact that butoxide species are important intermediates in the oxyhydrative scission reaction (*cf.* Scheme 1). The formation of butoxide, its oxidation to butanone and subsequent formation of acetate at higher temperatures was followed by means of in situ FTIR spectroscopy. The temperature of butanone formation indicated by appearance of the typical ν(C=O) mode of the adsorbed ketone is a measure for the oxidation power of the catalyst.

The spectra obtained during adsorption of 2-butanol on V/Ti-M (sulfate-containing anatase) and V/SC7 (sulfate-free anatase) at ambient temperature and subsequent heating up to 250°C are depicted in Fig. 2.

**Figure 2:** FTIR spectra of 2-butanol adsorbed on V/Ti-M (i) (A) and V/SC7 (i) (B) at different temperatures.

On both catalysts, 2-butanol is adsorbed as butoxide species on Lewis sites indicated by the ν(C–H) modes at 2969, 2938, 2878 cm⁻¹ and ν(C–O) modes around 1120 and 1090 cm⁻¹ (not shown in the Figure) whereas the amounts of adsorbed butanol are different. It is clearly seen that in the case of V/Ti-M (Fig. 2A) butanone is formed at 150°C indicated by the strong carbonyl band at 1658 cm⁻¹. At 200°C new bands at 1545/1439 cm⁻¹ appear which are assigned to ν_{as} and ν_s modes of adsorbed acetate. At the catalyst with the sulfate-free support (Fig. 2B), only marginal formation of butanone was observed and practically no acetate.

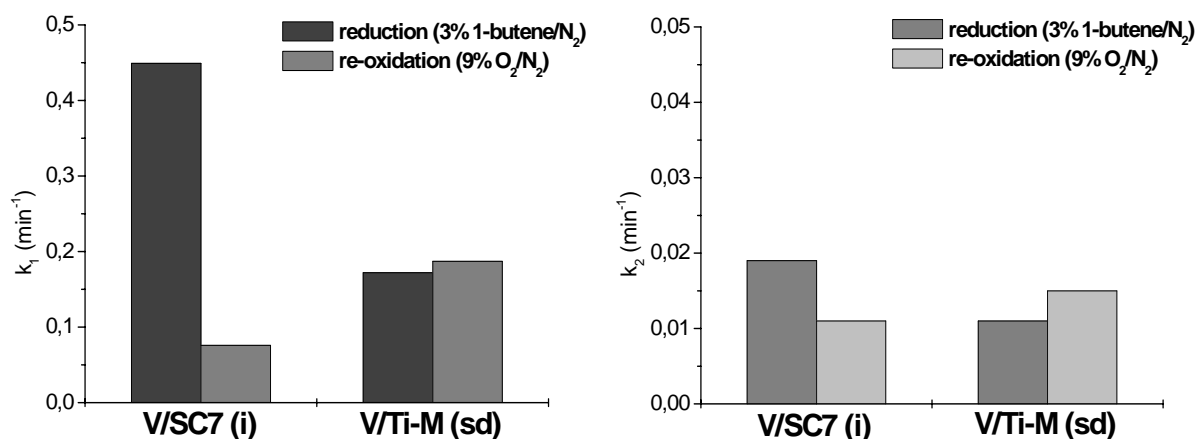


Figure 3: Rate constants k_1 (left) and k_2 (right) derived for reduction and re-oxidation of V-sites in the catalysts by UV-vis spectroscopy.

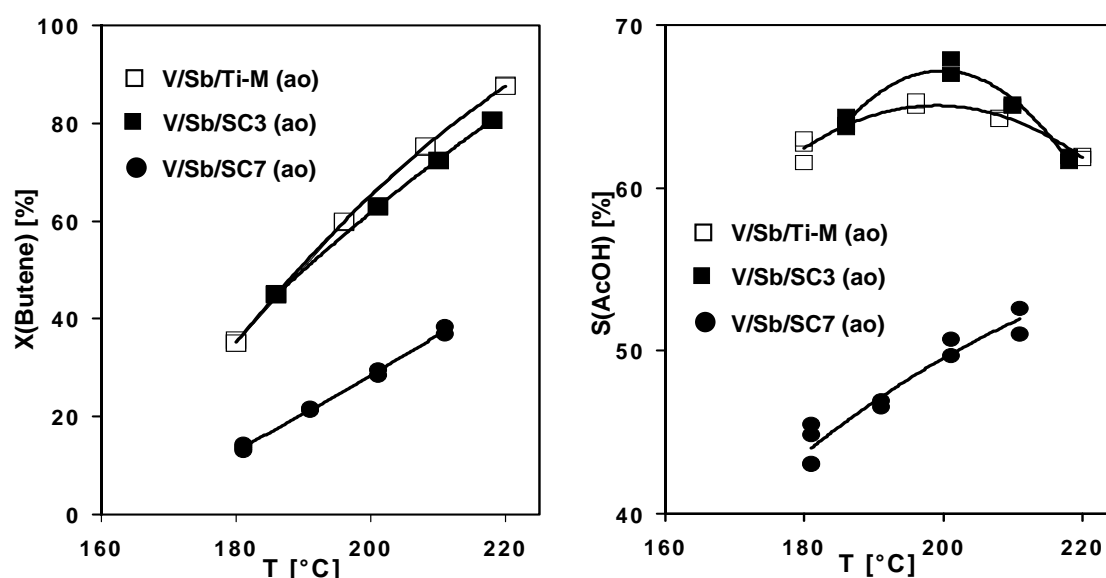


Figure 4: 1-butene conversion (left) and acetic acid (AcOH) selectivity (right) as function of the catalyst temperature (feed: 1.9% 1-butene, 9.1% O₂, 24.4% H₂O/N₂, p=7 bar).

Catalysts with different sulfate-containing anatase supports showed the same principle behaviour. In detail however, the amount and stability of adsorbed butanone was different as well as the extent of acetate formation. The catalyst with rutile support is also redox active, however, two different carbonyl bands were observed in the spectra that point to the formation of probably two butanone species (possibly methyl ethyl and methyl vinyl ketone) at 150°C. This suggests a slightly modified reaction pathway on this catalyst.

More specific information about the redox behaviour was achieved by studying the redox kinetics. UV-vis measurements have been applied to observe changes in the range for d-d transitions of reduced vanadium species in dependence on time.

To fit experimental curves properly, two pseudo-first-order processes had to be assumed for both reduction and re-oxidation. It is probable, that the fast process (rate constant k_1) comprises VO_x species on the surface that are

readily exposed to reactants while the slow process (rate constant k_2) might be related to VO_x sites in deeper layers, e.g., in the volume of the VO_x particles. The rate constants for these two processes are compared for the catalysts V/Ti-M (sd) and V/SC7 (i) in Fig. 3.

The rate constants for reduction and re-oxidation of V-sites in the volume differ only moderately (Fig. 3, right). Contrarily, it is clearly seen that the V-sites at the surface on V/SC7 (i) with sulfate-free support are faster reduced than on V/Ti-M (sd) with the sulfate-containing support (Fig. 3, left).

However, not only the rate of re-oxidation but also the percentage of re-oxidable V sites in V/SC7 (i) are much lower (only 24% of the V-sites can be re-oxidized) than that of V/Ti-M (sd), which is fully re-oxidized. This finding suggests an inhibition of deeper reduction of V-sites in the equilibrium by sulfate present at the surface. Moreover, it could be shown from UV-vis spectra that on sulfate-free V/SC7 (i) a distinct formation of VO_x clusters can be ob-

served whereas on sulfate-containing V/Ti-M (sd) the VO_x species are markedly higher dispersed.

The catalytic tests confirm the spectroscopic findings. The 1-butene conversion and acetic acid selectivity in dependence on the catalyst temperature for different Sb-containing VO_x/TiO₂ catalysts prepared via the alkoxide method are shown in Fig. 4.

The catalysts V/Sb/Ti-M (ao) and V/Sb/SC3 (ao) with sulfate-containing supports act very similar. They show comparable 1-butene conversions and selectivities within the temperature range 180 - 220°C. In contrast, the catalyst V/Sb/SC7 (ao) with the sulfate-free support was essentially less active. For reaching comparable conversions the residence time has to be strongly increased. However, the estimated acetic acid selectivity is much lower than that of the sulfate-containing catalyst.

Comparing the catalytic performance of catalysts with sulfate-containing supports with that of the V/SC5 catalyst with rutile support, comparable selectivities were found, however lower 1-butene conversions were obtained for the latter.

4. Conclusions

1-Butene reacts very quickly with the investigated VO_x/TiO₂ catalysts. Already at ambient temperature, the V-sites at the surface are easily reduced and re-oxidized, whereas this redox process proceeds slowly at V sites in the volume.

Cyclic anhydride as one precursor for CO_x is formed in a side reaction. The admixture of water vapour suppresses its formation markedly and favours the formation and/or desorption of acetic acid by blocking the adsorption

sites for acetate. Additionally, water vapour supports spreading of vanadia on the TiO₂ surface.

The admixture of Sb enhances the reduction to V³⁺ and, thus, influences the redox behaviour of the catalysts resulting in improved selectivities for acetic acid.

The intermediate 2-butanol is adsorbed as butoxide at the catalyst surface. It is oxidized at active catalysts to butanone and finally transformed to acetic acid by oxyhydrative scission of the C–C bond indicated by formation of acetate species at the catalyst surface. Thus, the proposed reaction mechanism [2] could be confirmed.

The performance of VO_x/TiO₂ catalysts is markedly influenced by the nature of the support, whereas the preparation method plays a negligible role. Sulfate-containing anatase materials are the most suitable supports. The existence of covalently bonded sulfate at the catalyst surface is inevitable for the effective bonding of VO_x species. It stabilizes active VO_x species at the surface and ensures their high dispersity.

The results of catalytic tests and in situ spectroscopic investigations are in good agreement.

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