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Structure–reactivity relationships in VO_x/TiO_2 catalysts for the oxyhydrative scission of 1-butene and *n*-butane to acetic acid as examined by in situ-spectroscopic methods and catalytic tests

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Abstract

Different VO_x/TiO_2 catalyst have been catalytically tested and studied by in situ-spectroscopic methods (FT-IR, UV/vis, EPR) in the oxyhydrative scission (OHS) of 1-butene and *n*-butane to acetic acid (AcOH). While 1-butene OHS follows the sequence butene → butoxide → ketone → AcOH/acetate with a multitude of side products also formed, *n*-butane OHS leads to AcOH, CO_x and H_2O only. Water vapour in the feed improves AcOH selectivity by blocking adsorption sites for acetate. The admixture of Sb_2O_3 was found to improve AcOH selectivity which is due to deeper V reduction under steady state conditions and lowering of surface acidity. VO_x/TiO_2 catalysts with sulfate-containing anatase are the most effective ones. Covalently bonded sulfate at the catalyst surface causes specific bonding of VO_x, stabilizes active V species and ensures their high dispersity.

Keywords: Vanadia–titania catalysts; 1-Butene; *n*-Butane; Oxyhydrative scission; In situ FT-IR; In situ UV/vis-DRS; In situ EPR

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1. Introduction

Butenes and butanes are available as by-products of naphtha cracking for the manufacture of ethene and propene. For utilization of this cheap feedstock Wacker has developed a new cycle process in which a mixture of *n*-butane/*n*-butene (raffinate II) is converted to acetic acid at low temperatures and under elevated pressure using vanadia containing catalysts [1]. The economic efficiency could be more improved, if the butane fraction would be oxidized with comparable conversion rate as butene. For this reason, additional knowledge about both the influence of different reaction conditions and the specific structure of active catalyst components and their role in the reaction mechanism is necessary to develop more effective catalysts with good performance.

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

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 [6–8] evidenced that only catalysts with vanadia supported on redox active oxides such as TiO_2 act effectively in the OHS of 1-butene to acetic acid whereas the vanadia content is of subordinate importance.

The investigations presented in this paper are focused on the influence of various TiO_2 (anatase) materials with different sulfate contents on the activity of VO_x/TiO_2 catalysts in the OHS reaction. Furthermore, the effects of water vapour and Sb admixture in this reaction are described. In addition to catalytic tests, the catalysts were studied under reaction-like conditions by spectroscopic in situ-methods (FT-IR, EPR, UV–vis-DRS) using 1-butene, *n*-butane and the intermediate 2-butanol as reactants.

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2. Experimental

The catalysts have been prepared: (1) by spray drying (sd) of oxide mixtures V_2O_5/TiO_2 and $V_2O_5/Sb_2O_3/TiO_2$ (V/Ti–M, V/Sb/Ti–M); (2) by impregnation (i) of the TiO_2 support with vanadyl oxalate (V/Ti–M, V/Sb/Ti–M, V/SC7) or (3) by hydrolysis of a V, Sb-alkoxide mixture (V/Sb/Ti–M, V/Sb/SC3, V/Sb/SC7) in a TiO_2/CH_2Cl_2 suspension (ao) with 0.06 wt.% V and 0.11 wt.% Sb per m^2 support. Commercial TiO_2 materials of Millennium Chemicals (Ti–M) and Sachtleben Chemie GmbH (SC3, SC7) were used. All catalysts were calcined in air at 400 °C for 4 h.

FT-IR spectra were recorded from self-supporting discs using a Bruker IFS 66 spectrometer equipped with a IR reaction cell [7]. Prior exposing to the reaction mixture (3 vol.% C_4, 8 vol.% O_2, 3 vol.% H_2O/N_2), the samples were activated in air at 400 °C for 30 min.

EPR spectra in X-band ($\nu \approx 9.5$ GHz) were recorded by the cw-spectrometer ELEXSYS 500-10/12 (Bruker). Measurements were carried out in a home-made flow reactor connected to a gas/liquid-supplying system [9].

UV/vis spectra in diffuse reflectance mode were recorded by a Carry 400 spectrometer (VARIAN) equipped with a diffuse reflectance accessory (praying mantis, Harrick) and a respective flow cell (Harrick). Samples were pretreated in O_2 flow (5 ml/min) at 200 °C for 2 h.

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.% O_2/6.1–24.4 vol.% H_2O/N_2. Product compositions were analyzed by on line-GC (GC 17A, Shimadzu) and by non-dispersive IR photometry at normal pressure. Conversion degrees and selectivities were calculated with respect to C_4 concentrations in the feed.

3. Results and discussion

The FT-IR spectra resulting from reaction of 1-butene/O_2 and n-butane/O_2 on V/Ti–M (sd) at 200 °C are depicted in Fig. 1. As can be seen from the reaction of 1-butene/O_2 (Fig. 1A) already after short contact time a set of bands can be observed. The band at 1653 cm^{-1} is due to the ν(C=O) mode of adsorbed ketone and/or acetic acid (AcOH), whereas the bands at 1542 and 1440 cm^{-1} are attributed to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes of probably acetate species [10]. After 10 min, further bands at 1780/1845 cm^{-1} and around 1628 cm^{-1} appear, the intensities of which increase with reaction time. The latter band is assigned to a ν(C=C) mode while the others are typical for adsorbed cyclic anhydrides [11]. The appearance of adsorbed acetate species may be explained by formation of acetic acid which is partly adsorbed as acetate at the catalyst surface. If the reaction is carried out in the presence of water vapor, the same adsorbed species were detected, however, essentially less anhydride species were formed [7,8]. Obviously, water selectively suppresses the side reaction leading to cyclic anhydride species and blocks adsorption sites.

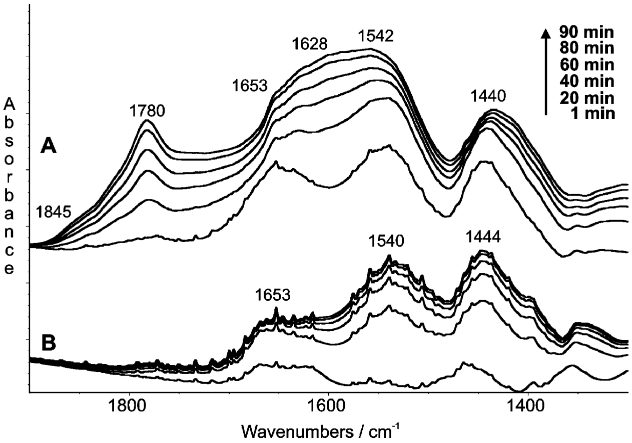

Fig. 1. FT-IR spectra of adsorbates formed on V/Sb/Ti–M (sd) during reaction of (A) 1-butene/O_2 and (B) n-butane/O_2 at 200 °C.

During reaction of n-butane/O_2 (Fig. 1B) the FT-IR spectra are dominated by typical bands of adsorbed ketone/AcOH and acetate species while bands of cyclic anhydride disappear almost completely. This shows clearly that the undesired side reaction plays a negligible role. In the presence of water vapor, only less adsorbed AcOH could be detected. Obviously, water hinders the formation of more stable acetate species.

The influence of water on the oxidation of 1-butene has also been studied by in situ-EPR for the sample V/Ti–M (sd). During reaction at 180 °C the VO^{2+} 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 4 h on stream in the reactant gas flow. Consequently, it must be concluded, that the magnetic interaction between neighbouring VO^{2+} 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 in the catalytic tests with 1-butene that the AcOH selectivities improved from 61 to 74% with increasing water content in the feed, whereas with 24% water content the best selectivity was achieved [8]. When n-butane is used, residence times must be increased by a factor of about 50 to reach conversion degrees comparable to that of the more reactive substrate 1-butene. However, in contrast to the latter, only AcOH, carbon oxides and water are formed during n-butane oxidation. Contrary to the 1-butene oxidation, the mass-related consumtion rate decreases sharply with increasing water concentration reaching a constant level above 10% [8]. This suggests a favoured water adsorption in comparison to butane adsorption at higher water concentrations. The observed slightly decrease of AcOH selectivity might be due to an overcompensation of the selectivity-enhancing AcOH desorption by water vapour.

The catalyst performance can also be improved by varying the catalyst composition. The admixture of Sb_2O_3 causes enhanced selectivities for AcOH and acetaldehyde which is

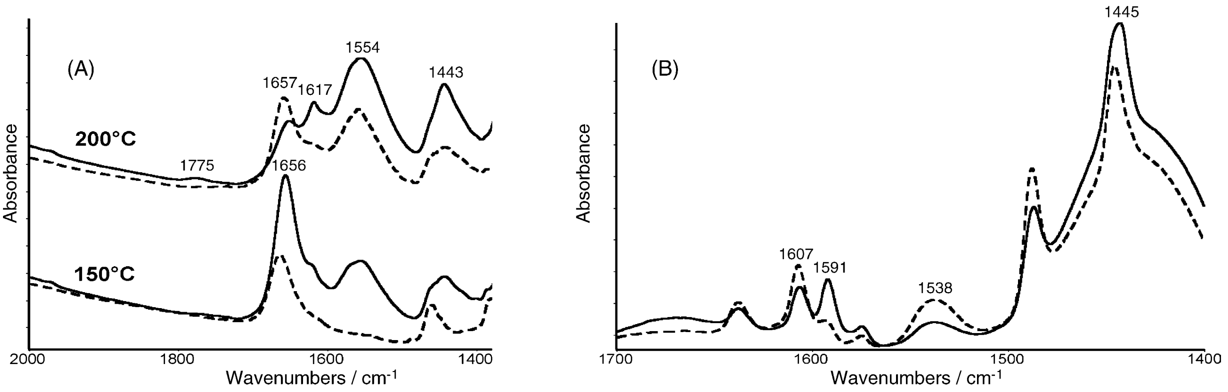

Fig. 2. FT-IR spectra of (A) 2-butanol and (B) pyridine adsorbed on V/Ti–M (sd), dashed line and V/Sb/Ti–M (sd), solid line.

mainly attributed to a lower formation of the total oxidation product CO_2 [7].

It was found by in situ-EPR experiments that the Sb-containing catalysts were deeper reduced under reaction conditions than catalysts without Sb. 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 [7,8]. This effect is also known from other reactions in which reducing agents like propane or ammonia are present [12]. The modified redox behavior can also be seen by studying the oxidation of the pre-adsorbed intermediate 2-butanol at higher temperatures (Fig. 2A). The formation of the ketone indicated by the carbonyl band at 1656 cm^{-1} is delayed in the case of the Sb-containing catalyst. Additionally, no cyclic anhydride species (bands at 1617 and 1775 cm^{-1}) were observed at 200 °C which points to a suppressing of undesired side reactions. As can be seen from pyridine adsorption (Fig. 2B), the admixture of Sb_2O_3 moderates the acidity. The Brønsted-acid sites (band at 1538 cm^{-1}) are diminished in the Sb-containing catalyst. The Lewis-acid sites (band at 1445 cm^{-1}) remain constant whereas the ratio of stronger (band at 1607 cm^{-1}) and medium strong (band at 1591 cm^{-1}) Lewis sites varies [7,13]. Obviously, both, the modified redox activity and the moderate acidity change the adsorption properties and oxidation power of the Sb-containing catalyst and thus enhance AcOH selectivity.

As could be shown by recent investigations [6], only catalysts with vanadia supported on redox active oxides such as TiO_2 act effectively in the OHS of 1-butene. To elucidate the influence of different anatase supports, VO_x catalysts with 2.2% sulfate-containing and sulfate-free anatase materials of different manufacturers were prepared. The V-content related to the specific surface area was 0.06 wt.% m^{-2} for all catalysts.

More information about the redox behaviour was achieved by studying the redox kinetics using 3% 1-butene/N_2 as reducing and 9% O_2/N_2 as oxidizing agent. UV–vis measurements have been applied to observe changes in the range for d–d transitions of reduced vanadium species in dependence on time. Two pseudo-first-order processes had to be assumed for both reduction and re-oxidation [7,8]. Probably, 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 bulk of the VO_x particles. For comparison the rate constants for these two processes are listed for the catalysts V/Ti–M (sd) and V/SC7 (i) in Table 1.

Table 1
Pseudo-first-order rate constants for reduction of V^{5+} in a flow of 5% 1-butene/N_2 and re-oxidation in O_2

	k_1 (10^{-3} min^{-1})		k_2 (10^{-3} min^{-1})	
	Reduction	Re-oxidation	Reduction	Re-oxidation
V/Ti–M (sd)	172	187	11	15
V/SC7 (i)	449	76	19	11

The rate constants k_2 of V-sites in the bulk differ only moderately. Contrarily, it is clearly seen from the rate constants k_1 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. 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 by UV–vis spectra that on sulfate-free V/SC7 (i) a distinct formation of VO_x clusters can be observed whereas on sulfate-containing V/Ti–M (sd) the VO_x species are markedly higher dispersed [14]. EPR and FT-IR spectroscopic measurements revealed the formation of two types of VO^{2+} sites on sulphated instead of only one on sulphate-free anatase and pointed to a direct bonding of a part of VO_x species to the surface sulfate groups [14].

The catalytic tests confirm these spectroscopic findings. The 1-butene conversion and AcOH selectivity in dependence on the catalyst temperature for different Sb-containing VO_x/TiO_2 catalysts prepared via the alkoxide method are shown in Fig. 3. The catalysts V/Sb/Ti–M (ao) and V/Sb/SC3 (ao) with sulfate-containing supports act very similar. 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 AcOH

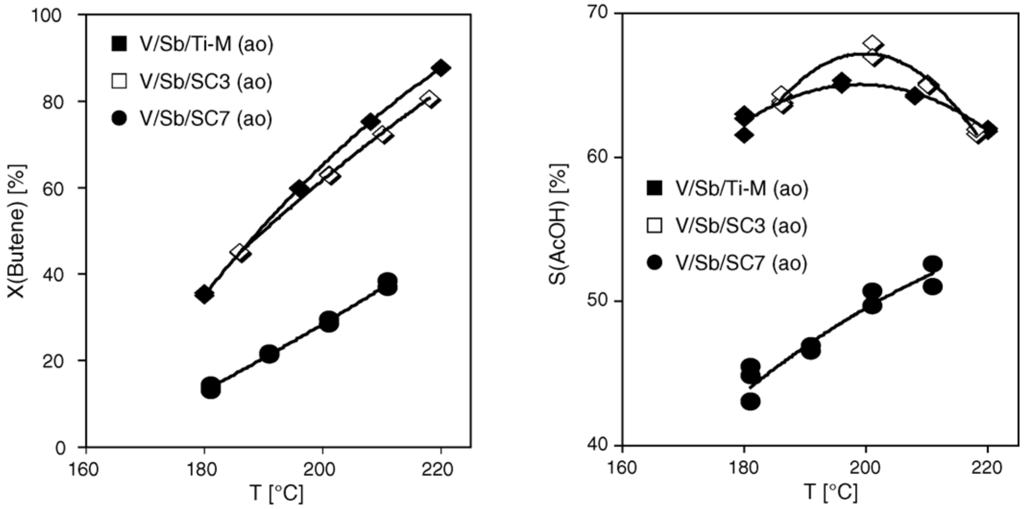

Fig. 3. Conversion of 1-butene (left) and acetic acid (AcOH) selectivity (right) as function of the catalyst temperature (feed: 1.9% 1-butene, 9.1% O_2, 24.4% H_2O/N_2, $p = 7$ bar).

selectivity is proved to be much lower than that of the sulfate-containing catalyst.

4. Conclusions

In principle, 1-butene and *n*-butane react in the same way on VO_x/TiO_2 catalysts. However, the essential lower reactivity of *n*-butane is not markedly influenceable by varying the reaction conditions and therefore requires the separation of butane and butane OHS processes.

In situ FT-IR studies revealed that the reaction proceeds via the sequence $C_4 \rightarrow$ butoxide $\rightarrow$ ketone $\rightarrow$ AcOH/acetate. Cyclic anhydride as a precursor of CO_x is formed in a side reaction. The admixture of water vapour suppresses its formation distinctly and additionally favours the desorption of acetic acid by blocking the adsorption sites for acetate. Furthermore, water vapour supports spreading of vanadia on the TiO_2 surface.

The admixture of Sb_2O_3 moderates the acidity and enhances the reduction to V^{3+} and, thus, influences the redox behaviour of the catalysts. Both effects improve the AcOH selectivity.

The performance of VO_x/TiO_2 catalysts is markedly influenced by the nature of the support, whereas the preparation method plays a negligible role. The existence of covalently bonded sulfate at the catalyst surface is indispensable for the effective bonding of VO_x species. It stabilizes active VO_x species at the surface and ensures their high dispersity.

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