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Effect of water on oxidative scission of 1-butene to acetic acid over V₂O₅-TiO₂ catalyst. Transient isotopic and kinetic study

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ABSTRACT

The role of water in the oxidation of 1-butene to AcOH over VOx-TiO₂ was investigated using spectroscopic and transient isotopic exchange methods. It was shown that the influence of water strongly depended on the temperature of reaction. In particular, DRIFTS and NH₃-TPD studies confirmed the temperature influence on the acidity and the amount of adsorbed water. XPS investigations suggested that not only oxygen from vanadia, but also from the lattice of titania was involved in the oxygen transfer during the reaction. Formation of oxidation products proceeded over two types of active vanadium oxide centers, i.e., VOH and VO. Hydrated vanadium species exhibited high selectivity towards AcOH formation. On the other hand, VO centers favored total oxidation. Kinetic model was developed for an unambiguous interpretation of the experimental results. Modelled reaction constants of the formation of AcOH over VOH centers were ca. 3.5 times higher than over VO centers. At the same time, the reaction rate constant of total oxidation in the presence of water was ca. 3.2 times lower than in dry flow. Estimated values suggested that in the presence of water the number of VOH centers was substantially lower than VO sites; however their contribution to the rate of AcOH formation was much higher.

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1. Introduction

Acetic acid (AcOH) is an important intermediate product for the production of many value added chemicals like vinyl acetate. Currently it is mainly produced by carbonylation of methanol and oxidation of ethylene according to the Wacker process [1]. Some attempts were made in the last decades to develop a process for the production of AcOH by catalytic gas phase oxidation of light hydrocarbons on MeO_x supported catalysts [2-7]. Various redox catalysts were proposed for the selective oxidation of C_4 -hydrocarbons mostly on the basis of vanadium oxide [3,4]. Especially VO_x containing catalysts supported on TiO₂ (anatase) have shown promising results in the C₄ oxidation [7]. Only a few older articles [2-4] were devoted to the mechanism of the catalytic oxidation of C₄ hydrocarbons to AcOH. However, none of these publications explained unambiguously the oxidative cleavage of 1-butene to AcOH and, hence, the mechanism is still a matter of discussion [8,9]. Seiyama et al. [4] proposed an oxidative cleavage mechanism, which involves water as one of the reactants and 2butanol as the primary intermediate product. In contrast, Kaneko

et al. [3] suggested a reaction mechanism without the participation of water. Other authors [10,11] studied the influence of water vapor on the oxidative dehydrogenation of hydrocarbons (HC) on VO_x catalysts and observed different effects of water on the formation of the reaction products. For example, in the oxidation of HCs at low temperatures, the formation of carboxylic acid was promoted by addition of water [8]. On the contrary, water was found to suppress the rate of oxidative dehydrogenation reaction at high temperatures [10,12]. D. Linke et al. studied catalytic partial oxidation of ethane over VOx-containing catalyst to AcOH at 200–350 °C and found that at higher temperatures above 300 °C higher water partial pressures are necessary to suppress the formation of ethylene and CO₂ and thereby increase the selectivity to AcOH [13].

It was shown in the literature that water is essential additive during catalytic gas phase oxidation and oxidative dehydrogenation for higher conversion of hydrocarbon and higher selectivities towards oxygenated products [13–25]. The water is generally believed to influence the reaction in several ways, (i) it increases the desorption rate of polar products and/or alters the adsorption – desorption equilibria of educts, products and oxygen [14–18], (ii) it depresses the coke formation by clearing the surface of the catalyst [2,7,19], (iii) it modifies the catalyst surface, i.e., participates in the reoxidation of catalytically active centers and facilitates the transformation of surface-oxygenated complex to products [20–26], (iv)

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Nomenclature						
L_V	the total number of surface sites (mol) per mole					
θ _i	the concentration (mol/mol)					
Cj	the concentration (molar fraction)					
τ	the residence time (s)					
r _i	the rate of the elementary step <i>i</i> ;					
α_{ij}	the matrix of stoichiometric coefficients.					
α_i	relative concentrations of isotopic fractions in the					
	gaseous phase					
α_{j}	relative concentrations of adsorbed species					
x_i^{exp}	experimental concentration value in gaseous phase					
ı	or isotopic fraction					
x_i^{calc}	calculated concentration value					
Ėа	activation energy (kJ/mol)					
j	number of experimental points					
k	kinetic constant					
Κ	equilibrium constant					
n, m	reaction orders in kinetic equation concentration of					
	active sites					

it improves the heat exchange by dissipation of hot-spots [2,5,7].

All these effects contribute to the complexity of the investigated catalytic process and therefore, the combination of several analytical techniques is required to fully explain, both surface and catalytic properties of VOx-TiO₂ in the oxidation of hydrocarbons.

Transient isotopic experiments are particularly suitable to elucidate the role of water in the catalytic oxidation and oxidative dehydration of hydrocarbons. Very recently, we investigated the influence of water on the catalytic oxidation of 1-butene using transient isotopic-exchange of ¹⁸O₂ and showed that ¹⁸O from H₂¹⁸O was incorporated into AcOH [27]. Nevertheless, the transfer of oxygen atoms from water to AcOH does not imply that water or OH groups participate in the formation of AcOH.¹⁸O can be introduced in AcOH structure due to the exchange between AcOH and H₂¹⁸O as well as between H₂¹⁸O and vanadium oxide centers. Sadovskaya et al. [28] studied in the model system, the isotopic O-exchange between water and oxygen from the monolayer of VOx-TiO2 in temperature range 50 - 500 °C using SSITKA technique. It was found that the oxygen exchange with the water proceeds over two types of vanadium species, i.e., hydrated (V-OH) and dehydrated (V-O-V and V=O), with different reactions rates and activation energies.

The aim of this communication is to clarify the role of water in the mechanism of AcOH formation in the oxidation of 1-butene over VO_x -TiO₂ catalysts. The present work is focused on the characterization of surface properties, i.e., acidity, oxidation state of the catalyst surface and water – catalyst surface interactions. Additionally the investigation of the reaction pathways of 1-butene oxidation on these catalysts is carried out. For this purpose, the dynamics of the reaction and the formation of oxidation products in presence and absence of oxygen and/or water vapor were studied. The detailed steady-state and isotopic transient kinetic studies were carried out to develop a consistent kinetic model for an unambiguous interpretation of the experimental results. In particular, the investigations were aimed to explain the considerable differences in the oxidation mechanism in presence and absence of water.

2. Experimental section

2.1. Catalyst

The VO_x -TiO₂ catalyst (6 wt-% V_2O_5) was prepared by spraydrying method of TiO₂ (Millenium GmbH) and vanadium oxide (Aldrich) in pilot plant of Consortium für Elektrochemische Industrie GmbH, München by mixing the aqueous slurry of TiO₂, V_2O_5 and vinyl acetate in the presence of air stream. Afterwards, the sample was first dried at 100 °C and then calcined at 400 °C for 5 hours in air atmosphere. After calcination, catalyst was pressed and sieved to 0.1 - 0.315. The catalyst was characterized by N₂ adsorption (ASAP 2000, micromeritics), NH₃-TPD, H₂-TPR, XPS and DRIFTS. The BET-surface area of the catalyst was 79 m²/g and the average pore diameter was 13 nm. A detailed description of the results of catalyst characterization was reported elsewhere [27].

DRIFTS: Infrared spectra in diffuse reflection were recorded with an infrared Fourier spectrometer Vector 22 (Bruker Optic GmbH; software OPUS 3.1) combined with a diffuse reflection unit "The Selector" (Specac Ltd., Kent, UK) and a stainless steel reaction chamber (Specac Ltd., Kent, UK). Prior to the analysis, the catalyst was saturated with water vapour in an air flow (50 ml/min) in temperature region 160–300 °C for 2 hours. After hydrothermal treatment, the samples were placed in stainless steel cup inside the reaction chamber and exposed to air for 1 hour at similar temperature to the hydrothermal pretreatment. After activation, the system was cooled down to 100 °C using dry nitrogen as purge gas. The spectra were recorded with a resolution of 2 cm⁻¹ in the range of 4000 – 1100 cm⁻¹.

XPS: The measurements of V 2p, Ti 2p and C 1s signals were performed using the Mg anode (K α = 1253.6 eV) as X-ray source (XR 50 from Specs GmbH). An accelerating voltage of 12.5 kV and a pass energy of 30 eV were used for the measurements. The hemisphere detector Phoibos 150 (Specs GmbH) was applied for the detection of photoelectrons. The spectra analyses including satellites and background subtraction (Shirley) were done with CasaXPS software. Because of the electrostatic charging of the samples, the binding energies were corrected. The binding energy value for C 1 s BE = 284.5 eV was used as a calibration standard for the corrections.

TPD of ammonia: The measurements were performed using a microreactor filled with catalyst (50 mg). The evolved gases were analyzed with a quadrupole mass spectrometer (Pfeiffer GSD 301). Prior to the analysis, the catalyst was pretreated in He flow (50 ml/min) at 160 °C K for 2 hours. After cooling down to 100 °C, the adsorption experiments were carried out by consecutive pulses of 1 ml ammonia until complete saturation of the surface was reached. After the removal of physisorbed ammonia by purging with helium, the sample was heated from 100 up to 600 °C (heating ramp of 10 K/min) in a He flow and the desorption of NH₃ was detected by MS (m/e 16). Additionally, NH₃-TPD measurements were carried out after hydrothermal treatment (10 vol.-% of water vapor) of catalyst at different temperatures.

Adsorption experiments: The measurements were carried out in the flow-through reactor with the catalyst packed in the basket coupled with electronic balance (Rubotherm; resolution 0.01 mg). Prior to the adsorption experiment the catalyst was pretreated in dry flow of N₂ at 300 °C or in the presence of 1-butene (1 vol.-%) at 220 °C. After pretreatment, the water stream was introduced into the flow (5 wt.-% water) and the change of catalyst weight was recorded.

2.2. Isotopic-transient-experiments

The reaction was performed in a quartz reactor (i.D: 0.5 cm; L: 10 cm) at atmospheric pressure in the temperature range of $160-280 \,^{\circ}\text{C}$ using 100 - 200 mg of catalyst (fraction 0.1 - 0.3 mm) diluted with 200 - 400 mg corundum of the same fraction (activation conditions: $280 \,^{\circ}\text{C}$ in the mixture of 5 vol.- $\%O_2$ in He) and a constant 1-butene to oxygen ratio of 1:4 (GHSV: $3600 \, h^{-1}$, const.). The oxidation of 1-butene over the VO_x-TiO₂ catalyst was carried out in presence and absence of both, H₂¹⁶O and H₂¹⁸O and the oxygen isotopes ${}^{16}O_2$ and ${}^{18}O_2$. A reaction mixture contained 1.2 vol.-% 1-butene, 5 vol.-% O₂ and balance He, whereas in case of the



Fig. 1. Main reactions pathways for oxidative C-C-scission of 1-butene to C₁-C₃ carboxylic acids and total oxidation.

reaction in presence of water the mixture contained additionally 17 vol.-% water vapor.

For isotopic transient experiments cylinders containing 10 vol.- % ¹⁶O₂ in He and 10 vol.-% ¹⁸O₂ in He, respectively, were used (purities: ¹⁸O₂: 95.5 vol.-%, balance ¹⁶O₂; H₂¹⁸O: 98.5 vol.-%, balance H₂¹⁶O). Before the isotopic experiments the catalyst was activated with a mixture of 5 vol.-% ¹⁶O₂ and He for 60 min and cooled to the desired temperature. After steady state conditions were achieved, ¹⁶O₂ was replaced by ¹⁸O₂. In case of experiments with water H₂¹⁸O the catalytic reaction was carried out first in absence of water and then in presence of H₂¹⁸O, which was dosed by a Liquid-Flow-Evaporator (Bronkhorst Hi-Tech) to the feed. The following isotopic transient experiments were performed: (i) in presence of H₂¹⁶O and H₂¹⁸O, respectively, by replacement of ¹⁶O₂ by ¹⁸O₂, (ii) in absence of water by replacement of ¹⁶O₂ by ¹⁸O₂, (iii) in absence and presence of water and ¹⁶O₂.

3. Calculation method

3.1. Model of transient regimes

The kinetics model of transient regimes in a plug-flow reactor can be written by the system of hyperbolic and ordinary differential equations (1):

$$\frac{dC_j}{dt} + \frac{1}{\tau} \frac{dC_i}{d\xi} = L_V \sum_{i=1}^K \alpha_{ij} r_i \quad j = 1, \dots, N_1$$

$$\frac{d\theta_j}{dt} = \sum_{i=1}^R \alpha_{ij} r_i \qquad j = N_1 + 1, \dots, N_2$$
(1)

with initial and boundary conditions:

 $t=0:\quad C_j{=}^0_j \quad, \theta_j=\theta_j^0$

$$\xi = 0$$
: $C_i = C_i^{inpu}$

where C_j is the concentration (molar fraction) of the gaseous component j; τ is the residence time (s); L_V is the total number of surface sites (mol) per mole of gas molecules present in the catalyst bed; θ_j is the concentration (mol/mol) of the surface species (including the vacant sites); r_i is the rate of the elementary step i; α_{ij} is the matrix of stoichiometric coefficients. The form of the right parts of the equations is determined by the kinetics scheme of reaction.

3.2. Model of isotope transfer

The model of isotope transfer carried out under steady-state conditions in plug-flow reactor can be written as the following system of differential equations (2):

$$C_{i}\frac{\partial C_{i}\alpha_{i}}{\partial t} + \frac{1}{\tau}\left(\alpha_{i}\frac{\partial C_{i}\alpha_{i}}{\partial\xi} + C_{i}\frac{\partial C_{i}\alpha_{i}}{\partial\xi}\right) = \beta\sum_{l=1}^{N_{i}}r_{l}\alpha_{l}$$

$$\theta_{j}\frac{\partial\alpha_{j}}{\partial t} = \sum_{l=1}^{N_{j}}r_{l}\alpha_{l}$$
(2)

with initial and boundary conditions:

$$t = 0 : \alpha_i = \alpha_i^0, \ \alpha_j = \alpha_j^0$$

$$\xi = 0 : \alpha_i = \alpha_i^{input}$$

where α_i, α_j – are the relative concentrations of isotopic fractions in the gaseous phase and adsorbed species, respectively. This model takes into account the change of isotope concentration in the reagents and surface intermediates both with time and along the catalyst bed. The form of the right parts of the equations is determined by the scheme of isotopic transfer from one substance to another.

3.3. The numerical analysis of experimental data

The numerical analysis of experimental data which corresponds to the solution of the inverse problem of the system of equations (1)or (2) was carried out through the minimization of next objective functional:

$$F(\bar{\vartheta}) = \sum_{i=1}^{N} \int_{0}^{tend} (x_i^{calc} - x_i^{\exp})^2 dt \to \min$$
(3)

where x_i^{exp} experimental concentration value in gaseous phase or isotopic fraction, x_i^{calc} calculated concentration value according to the model (1) or (2).

4. Results and discussion

4.1. 4.1.Catalytic activity and surface investigations of the catalyst

In present studies we investigated the effect of temperature on the selectivity of the formation of AcOH from 1-butene in the presence of water. It needs to be mentioned that the reaction proceeds via various intermediates such as 2-butanol, 2-butanone and 2,3butandione [3–6]. Ketone intermediate subsequently undergoes C-C oxidative cleavage to C_2 - C_3 aldehydes [29,30] which are then selectively oxidized to corresponding carboxylic acids including AcOH [31] (see Fig. 1). However, these intermediate steps proceed very fast, thus, are not limiting. The limiting step is formation of AcOH and desorption from the catalyst surface.

The selectivity to AcOH in the oxidation of 1-butene in the presence of water depends on the reactivity of each intermediate, i.e., activation parameter, and temperature of the reaction. At the same

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Conversion (X) and selectivities (S) to acetic acid, carbon dioxide and carbon monoxide during oxidation of 1-butene on VO_x-TiO₂ catalyst under dry gas flow condition (Dry) and in presence of 17 vol-% water (Water).

	Temperature (°C)					
Parameter	Conditions	160	200	220	250	280
Conversion (%)	Dry	4	14	39	64	100
	Water	5	24	46	69	100
S _{CH3COOH} (%)	Dry	22	36	56	66	46
	Water	31	51	61	68	45
S _{CO2} (%)	Dry	5	13	16	19	35
	Water	3	8	11	12	25
S _{CO} (%)	Dry	1.5	3	4.5	6	8
	Water	0.5	1	2.5	3	4.5

GHSV: 18000 h⁻¹; 1-butene 1.4 vol-%; O₂ 4.0 vol-%.



Fig. 2. Correlation of 1-butene conversion with selectivity to acetic acid at different temperatures in presence and absence of water. For reaction conditions, see Table 1.

time, the reaction temperature also has strong influence on the adsorption-desorption equilibrium of the catalyst surface, water and all the products of the reaction [24,34]. In the following section, an experimental data about the influence of water and temperature on the properties of the surface of the catalyst and their catalytic performance will be presented.

Summarized results of 1-butene oxidation in the presence and absence of water at different temperatures are shown in Table 1. Under wet conditions, higher conversions of 1-butene and higher selectivity to AcOH were observed in the temperature region of 160 – 250 °C.

Fig. 2 exhibits the comparison between conversion and selectivity to acetic acid at different temperatures. It clearly shows that addition of water results in the increase of the selectivity to AcOH, but only at lower temperatures up till ca. 220 °C. At higher temperatures the difference is negligible indicating that influence of water strongly depends on reaction temperature, i.e., prevalence of desorption of physisorbed water and dehydration of VOH and TiOH at temperatures above 250 °C.

At the same time the selectivity to CO_x was suppressed. The formation of CO₂ increased with the temperature from 5% to 35% under dry flow and from 3% to 25% in the presence of water. CO was also observed in the course of reaction, however, the selectivity was 3 -4 times lower than for CO₂. At low temperatures, 2-butanol is the main product of the reaction with the selectivity above 20% (not present in Table 1). However, due to its poor oxidative stability, its amount decreases in the product composition at higher temperatures to ca. 1.5%. The selectivity's towards this intermediate were slightly higher under wet conditions only at lower temperatures. Increase of the reaction temperature suppressed the formation of 2-butanol due to its further oxidative C-C scission (not present in Table 1). Additionally, the formation of furan and maleic anhydride as byproducts was observed resulting from isomerization of 2-butene followed by dehydrogenation to butadiene (not show in Table 1). However, this reaction pathway over VOx-TiO₂ catalyst is not favored as opposed to e.g., VPO. Thus, very low selectivities to furan and maleic anhydride (below 1%) were observed.

The influence of water on the formation of products in partial catalytic oxidation, oxidative dehydrogenation of C2-C3 hydrocarbons [13-25] and selective oxidation of acrolein [32] is also known from literature. Moreover, water influence on the selectivity towards carboxylic acids during the oxidation of C_2 - C_3 aldehydes over VOx-TiO₂ catalyst has been recently studied by our group [31]. The results showed that the selectivity increased in the presence of water and the total oxidation pathway was depressed. In general, the differences in activities (conversions) and selectivities in the absence and presence of water at various temperatures can be attributed to (i) different adsorption-desorption equilibriums of reactant and product molecules and (ii) direct involvement of water in the catalytic oxidation reaction. These results show that the water and reaction temperature play an important role in the formation of oxidation products. Obviously, this effect is associated with the modification of the surface of the catalyst and this phenomenon strongly depends on the temperature. Thus, surface sensitive techniques, i.e., DRIFT spectroscopy, XP spectroscopy and TPD of ammonia were applied to study these effects in more details. Additionally, the adsorption of water under anaerobic conditions was carried out as a model experiment to elucidate the effect of water on the properties of the catalyst.

Fig. 3a shows the DRIFT spectra of $\text{VO}_{x}\text{-}\text{TiO}_{2}$ catalyst after pretreatment with water at different temperatures. The broad



Fig. 3. DRIF Spectra of VOx-TiO₂ catalyst after pretreatment with water steam at different temperature. Hydrothermal treatment 15 vol% Water; balance Helium. Total Flow: 100 ml/min.



Fig. 4. The NH_3 -TPD profiles for VOx-TiO₂ catalyst after pretreatment with water vapour at different temperature.

absorption region between 3600 and 3000 cm⁻¹ corresponds to the physisorbed water. With the increase of the temperature from 160 to 350 °C the physisorbed water is removed from the surface of the catalyst and the broad band disappears. Physisorbed molecular water also appears at the vibrational frequency of 1650 cm^{-1} and similar decrease of the band can be observed with increasing temperature (see Fig. 3a). The sharp band at the frequency of 3650 cm^{-1} corresponds to the dissociatively adsorbed water or/and OH groups from hydrated titania species. These findings stay in the good agreement with the DFT calculations and experimental data presented by Czekaj et al. [33]. The bands associated with V-OH species could not be detected in the DRIFT spectra due to the low content of vanadium in VOx-TiO₂ catalyst, i.e., below 6 wt.-%.

The acidity of VOx-TiO₂ catalyst is also substantially affected by temperature. Fig. 4 shows the TPD of ammonia profiles of the catalyst pretreated at three different temperatures for different periods of time. In the case of catalyst pretreated at 160 °C the TPD-profile is very broad with Lewis and Brønsted type of acidic sites not clearly resolved. Nevertheless, there is a distinct shoulder in the profile at higher temperature region likely corresponding to the strong acidic centers of Brønsted type. Increase in the temperature of pretreatment to 300 °C resulted in the decrease of the acidity of the catalyst. In particular, the disappearance of Brønsted acidic centers can be observed. Brønsted centers are mainly associated with OH groups on the surface of the catalyst, either connected to vanadia species or titania surface. Higher temperatures promote dehydration of the surface resulting in the loss of Brønsted centers [24,34,35].

The catalytic experiments in the presence and absence of water under oxygen-free conditions were carried out to elucidate the role of water in the mechanism of the formation of different oxidation products (Fig. 5). After the input of 1-butene over freshly activated catalyst, the concentration of detected AcOH in the absence of water reaches the maximum after 25 min TOS following by a rapid decrease after 35 min TOS. In the presence of water, AcOH was detected immediately after 1-butane input with higher concentration and over longer period of time. This suggests that the oxygen from water is involved in the formation of AcOH. Additionally, faster detection of AcOH in the presence of water can be explained by more agile removal and/or desorption of this polar compound from the surface of catalyst.

Fig. 6 illustrates breakthrough curves for the adsorption of water over pretreated and calcined catalysts. The results show that more water is adsorbed on the catalyst pretreated with1-butene. In contrast, freshly calcined sample exhibited only very small uptake of water. This can be explained by the reaction of 1-butene with lattice oxygen. Depending on the origin of the oxygen, i.e., V=O termi-



Fig. 5. Formation of acetic acid in dry at wet flow during oxidation of 1- butene with lattice oxygen from VOx-TiO₂ catalyst in anaerobic condition.

nal oxygen in vanadia species, bridging oxygen in titania matrix (Ti-O-Ti) or bridging oxygen between vanadia species and titania matrix (Ti-O-V), different products of partial and total oxidation are formed such as CO_x and C_1 - C_3 carboxylic acids and aldehydes. Due to these reactions, vacancies in the matrix of the metal oxide are formed serving as free water sorption centers. On the other hand, the consumption of lattice oxygen inevitably leads to the reduction of vanadium oxide species and titanium oxide support. Thus, XPS investigation was carried out to identify the oxidation states of vanadium oxide surface species and titania matrix before and after pretreatment with 1-butene.

The signal of V 2p $_{3/2}$ of the freshly calcined catalyst is shown in Fig. 7a. Binding energy of the signal corresponds to vanadium species in the oxidation state +5. A small component at lower B.E. can be attributed to vanadium species in lower oxidation state, i.e., V^{4+.} After 6000 s TOS pretreatment of the catalyst with 1-butene (see Fig. 5), XPS signal of V 2p $_{3/2}$ shifted to lower binding energies indicating reduction of vanadium species, i.e., ca. 60% of vanadium was found to be in the oxidation state +4 and +3 (see Fig. 7b). More information could be derived from the Ti 2p $_{3/2}$ region of XP spectrum. Fig. 7d and e shows the comparison of Ti 2p $_{3/2}$ signals of freshly calcined sample and after pretreatment with 1butene. Before the reaction, Ti 2p $_{3/2}$ signal mostly corresponds to titania species on +4 oxidation state at 458.7 eV. Second component found at lower binding energy at 457.2 eV is very small and can be attributed to reduced titania surface species presumably on



Fig. 6. Breaktrhrough curves for the adsorption of water over freshly calcined catalyst and after pretreatment with 1-buten at 220 °C for 120 min.



Fig. 7. Experimental XPS spectra and curve-fitting of the V 2p _{3/2} and Ti 2p _{3/2} for freshly calcined (a, d) VOx-TiO₂ catalyst and after treatment with 1-butene flow at 220 °C (b, e) and after pretreatment with 1-butene and water (c, f).

+3 oxidation state [36]. After the reaction, the whole signal of Ti 2p 3/2 became much broader and a tailing at lower binding energies appeared. Deconvolution of the signal showed much higher contribution of reduced titania species at lower binding energies suggesting strong influence of reactant and water on the surface of VOx-TiO₂ catalyst. This reductive effect can be explained by the mechanism of reaction in which the reacting olefin consumes the oxygen from vanadia species and lattice oxygen from titania support [37,38]. Resulting vacancies can later be hydrated with water molecules; however the surface cannot be fully reoxidized. Fig. 7c and f show the V 2p 3/2 and Ti 2p 3/2 XPS region for the pretreated catalyst with water and 1-butene. The spectra were taken after 6000 s TOS (see Fig. 5). The results show that the surface content of reduced V and Ti species is not as prominent as in the case of the catalyst pretreated with 1-butene only (see Fig. 7b and e). Nevertheless, the surface is more reduced than in the case of fresh calcined catalyst (see Fig. 7 a and d). The difference in the reduction degree of the surface for pretreated catalyst in the presence and absence of water can be explained by much higher formation of oxygenated products in the presence of water which can serve as a potential oxygen source, thus, facilitating reoxidation [23].

Fig. 8 shows a proposed mechanism of the formation of lattice vacancies and their hydration with water. The mechanism stays in the agreement with the results of water adsorption experiment and XPS studies over fresh and pretreated catalysts. In the real catalytic oxidation process, the reaction proceeds in the presence of oxygen via Mars van Krevelen mechanism. Thus, molecular oxygen is adsorbed on the active center on the surface of the catalyst subsequently reacting with hydrocarbon. Formed vacancy, i.e., reduced active center is then reoxidized by another oxygen molecule.

The second part of this work will be focused on the kinetic studies of the oxidation of 1-butene under aerobic conditions.

4.2. Transient kinetic studies

Prior to the transient studies, the catalyst was pretreated at 220 °C in oxygen atmosphere in the absence and presence of water for 1 hour. After that time, 1-butene was introduced to the flow.

Fig. 9a shows concentration-time profile of AcOH in wet flow. The AcOH was detected at the outlet of reactor immediately after the input of 1-butene and the steady-state conditions were reached after ca. 300 s. In contrast, in the absence of water, AcOH was found only after ca. 200 s. from the addition of 1-butene to the flow (Fig. 9b). In this case, the steady-state concentration of AcOH was 4 times lower than in the experiment in wet flow. After steady-state conditions have been reached the continuous flow of water was introduced into the gas feed. An impulse of increased concentration of AcOH was detected. Afterwards, steady-state conditions have been reached after ca. 1000s. Additionally, such impulses were detected also for other products of partial oxidation, i.e., 2-butanol and MEK. The delay in the detection of AcOH in the beginning of the experiment in dry flow can be explained by the saturation of the catalyst surface with AcOH followed by its total oxidation. In the beginning of the reaction, the total oxidation products are favored due to the high content of vanadium oxide species on +5 oxidation state. The reduction of these species in the curse of reaction leads to the decrease of total oxidation reaction rate. Thus, AcOH can be detected only after the rate of total oxidation reaction is sufficiently small. It should also be mentioned that the reaction order with respect to oxygen for total oxidation reaction is higher than for selective oxidation of 1-butene to AcOH. No delay of the AcOH detection in the wet flow experiment obviously indicates that water effectively suppressed the total oxidation reaction.

The concentration of AcOH at the maximum of the desorption peak is much higher than starting concentration of 1-butene. Thus, it can be assumed that this impulse is not connected with an increase of the oxidation reaction rate. Instead, it indicates that the addition of water increased the rate of desorption of the oxidation products from the catalyst surface.

Amount of AcOH adsorbed on the catalyst surface in the dry flow experiment can be estimated from the area of the desorption peak observed immediately after the addition of water. It corresponds to ca. 0.5×10^{19} molecules/m² which is close to the monolayer coverage. Concentration of other intermediates, i.e., 2butanol and MEK was very low and can be neglected. Therefore, the kinetic modeling was carried out taking into account simple model



Fig. 8. Mechanism of the oxidation with lattice oxygen from V- and Ti-Oxide during pretreament with 1-butene in anaerobic condition followed by adsoption of water.



Fig. 9. Time dependencies for the formation of acetic acid during oxidation of 1-butene on VOx-TiO2 catalyst at 220 °C in the presence of water (a) and in dry flow (b). Water concentration 15 vol%. Open circles: experimental dates, dotted and solid curves: calculated. The arrows indicate the addition of 1-butene and water to the feed.



Fig. 10. Simplified model of the transformation of 1-butene in partial and total oxidation.

with only one surface intermediate [X] - the adsorbed AcOH species (Fig. 10).

It was assumed that the formation of AcOH and CO₂ proceeds on one type of vanadium oxide active centers according to the following reactions:

1) $0_2 + 2[Z] \rightarrow 2[Z0]$ $C_4H_8 + 4[ZO] \rightarrow 2[X]$ 2) 3) $[X] \rightarrow AcOH + 2[Z]$ 4) $AcOH + 4[ZO] \rightarrow 2CO_2 + 2H_2O + 4[Z]$ 4a) $C_4H_8 + 12[ZO] \rightarrow 4CO_2 + 4H_2O + 12[Z]$

Results of kinetic modeling following these assumptions are presented in Fig. 9a and b. In the first model - curve 1a - it is postulated that formation of CO2 mostly proceeds via parallel reactions 4a ($r_4 = 0$). In the second model – curve 1b – CO₂ is formed only by the oxidation of acidic acid $(r_{4a} = 0)$. The results show that the second model describes the real experiment in dry flow more adequately. Numerical analyses were carried out by varying desorption constant and total oxidation constant. The best results were obtained in the case of high desorption constant and low total oxidation constant in the presence of water. However, the model was not consistent with the experimental results after desorption of AcOH was completed. The model showed that the steady-state conditions were reached immediately after desorption period, whereas in experiment, a gradual increase in the concentration of AcOH was observed over time. It is assumed that the increase is associated with slow transformation of active sites. Different vanadium oxide

active species have been identified depending on the reaction conditions, i.e., temperature, presence of water. This includes terminal V=O, bridging V-O-V, and hydrated V-OH species. Hydrated vanadium oxide species have been proposed as the most selective in the formation of AcOH [23]. Therefore, additional reaction equation, i.e., hydration of oxidized vanadium species, has been introduced to the kinetic model.

5) $[ZO] \xrightarrow{+H_2O} [ZOH]$

As a consequence the following additional reactions involving hydrated vanadium species need to be considered as well:

- $1a) \quad 2[Z^H] + O_2 \rightarrow [ZOH]$
- $\begin{array}{l} 2a) \quad C_4H_8 + [ZOH]^{+(n-1)[ZOH]+m[ZO]} \\ 3a) \quad [X_1] \rightarrow AcOH + m[Z] + n[Z^H] \end{array}$

Expanding the model with these terms allows more accurate description of the experimental results (Fig. 9b, curve 2). Exact concentration of intermediate $\theta_{[X]}$ in dry flow calculated according to the model equals to ca. 80% of monolayer coverage. In the presence of water $\theta_{[X]}$ and $\theta_{[X_1]}$ is not higher than few %. Calculated value of the hydration reaction constant $k_5 = 0.0005 \text{ s}^{-1}$ is consistent with the value determined experimentally in the model reaction [28]. Thus, it can be concluded that transformation of V=O to V-OH species is responsible for a gradual increase in the concentration of AcOH (Fig. 9b).

These results show that the addition of water has two main effects: (i) an immediate effect, associated with the increase of desorption rate of AcOH from the catalyst surface and suppression of total oxidation rate, (ii) a prolonged effect, associated with the hydration of oxidized vanadium species which favor the selective oxidation. Nevertheless, it cannot be unambiguously concluded whether V-OH species are directly involved in the formation of reaction products. It can also be assumed that they

only participate in the activation of 1-butene and oxygen transfer proceeds over active lattice VO centers and/or adsorbed oxygen.

4.3. Isotopic kinetic studies

4.3.1. Analysis of the ¹⁶O, ¹⁸O isotope distribution in AcOH under

steady-state reaction conditions with H₂¹⁸O present in the feed Three isotopomers of AcOH was formed, i.e., CH₃¹⁶O¹⁶OH, CH₃¹⁶O¹⁸OH and CH₃¹⁸O¹⁸OH as a result of the reaction in presence of H₂¹⁸O. The total concentration of all three isotopomers was the same as the concentration of formed AcOH in the presence of H₂¹⁶O.

Under steady-state reaction conditions, at 220 °C the atomic isotope fraction of ¹⁸O in AcOH (α_{AcOH}^{18}) amounted to:

$$\alpha_{AcOH}^{18} = \frac{2 * CH_3 C^{18} O^{18} OH + CH_3 C^{16} O^{18} OH}{2 * (CH_3 C^{18} O^{18} OH + CH_3 C^{16} O^{18} OH + CH_3 C^{16} O^{16} OH)}$$

= 0.63

It can be seen from Figure 11 that distribution of isotopic AcOH molecules observed in experiment strongly differs from calculated equilibrium distribution α^{18}_{AcOH} :

$$f_{AcOH}^{18-18}(equilibrium) = (\alpha_{AcOH}^{18})^2 = 0.4$$

$$f_{AcOH}^{16-18}(equilibrium) = 2(\alpha_{AcOH}^{18})(1 - \alpha_{AcOH}^{18}) = 0.47$$

 $f_{ACOH}^{16-16}(equilibrium) = (1 - \alpha_{ACOH}^{18})^2 = 0.13$

Note that CH3¹⁶O¹⁸OH fractions are much smaller than the equilibrium values. As it will be shown below, this is a crucial point that allows discriminating some variants of isotope label transfer.

During the oxidation of 1-butene in presence of H₂¹⁸O, two competitive processes take place: isotope exchange with water, which enriches active sites with ¹⁸O, and reoxidation of catalyst by ¹⁶O₂ (Fig. 12).

Isotopic fraction of ¹⁸O in VOH (α_{VOH}^{18}) and VO (α_{VO}^{18}) depends on the ratio between the reaction rate of isotopic exchange W^{exch}_{VOH(VO)}







Fig. 12. Proposed scheme of ¹⁶O and ¹⁸O isotope transfer under steady state conditions in the presence of H₂¹⁸O.

and rate of reoxidation $R_{VOH(VO)}^{ox}$ (Eq. (4)).

$$\alpha_{VOH(VO)}^{18} = \frac{W_{VOH(VO)}^{exch} \alpha_{H_2O}^{18} + R_{VOH(VO)}^{ox} \alpha_{O_2}^{18}}{W_{VOH(VO)}^{exch} + R_{VOH(VO)}^{ox}}$$
(4)

where: $\alpha_{O_2}^{18} = 0$, $\alpha_{H_2O}^{18} = 0.98$. Kinetic data of the isotope exchange with water obtained with a similar sample of V₂O₅/TiO₂ catalyst under temperatureprogrammed (50-500 °C) and isothermal (200 °C) regimes have recently been presented [28]. The exchange of oxygen atoms between water and vanadium oxide was shown to be rather intensive in this temperature range. The exchange involved both VOH and VO sites. In comparison with water, the rate of dioxygen isotope exchange with vanadium oxide is negligible. Rate constants of VOH and VO oxygen exchange with adsorbed water (at 200 °C) and activation energies were obtained: $k_{VOH}^{exch} \approx 0.5 \, s^{-1}$, $E_{VOH}^{exch} \approx 0$, $k_{VO}^{exch} \approx 2 * 10^{-3} \, s^{-1}$, $E_{VO}^{exch} = 70 \, \text{kJ/mol}$, as well as equilibrium constants of water adsorption $K_R \approx 10 \text{ s}^{-1}$, and adsorption heat Q = 45 kJ/mol. After recalculation to our reaction conditions, the rates of isotope exchange equalled to: $W_{VO}^{exch} \approx 10^{-3} \text{ s}^{-1}$ (per one site), and $W_{VOH}^{exch} \approx 0.2 \, \mathrm{s}^{-1}.$

Rate of reoxidation of V-OH and V-O centers can be calculated based on the rates of reactions proceeding on both centers. It is assumed that the total oxidation takes place only over V-O center and selective oxidation to AcOH over both V-O and V-OH centers. Formation of AcOH from 1-butene requires two oxygen atoms transferred from active centers. Thus, three possible combinations of active species participating in oxygen transfer can be proposed, i.e., VOH+VOH, VOH+VO and VO+VO with corresponding pathway contributions δ_1 , δ_2 and δ_3 , where $(\delta_1 + \delta_2 + \delta_3 = 1)$. Reoxidation rates for VO and VOH can be expressed as follow:

$$R_{VOH}^{ox} = R_{AcOH}(2\delta_1 + \delta_2)$$

$$R_{VO}^{ox} = R_{AcOH}(\delta_2 + 2\delta_3) + 3R_{CO}$$

where $R_{ACOH} = \frac{C_{ACOH}}{\tau L_{\nu}} = 0.003 \text{ s}^{-1}$, $R_{CO_2} = \frac{C_{CO_2}}{\tau L_{\nu}} = 0.0025 \text{ s}^{-1}$ - rate of AcOH and CO₂ formation calculated for one center (TOF).

Depending on the relation between rates of different reaction pathways δ_1 , δ_2 and δ_3 , reoxidation rates R $^{\rm ox}$ $_{\rm VOH}$ can change in the region between 0 (when $\delta_1 = \delta_2 = 0$) and 0.006 s⁻¹ (when $\delta_1 = 1$). In any case, this value is essentially lower than the rate of oxygen exchange with water W_{VOH}^{exch} . Therefore, ¹⁸O isotope fraction in VOH will be close to the isotope fraction in water vapor:

$$0.98\Big|_{\delta_1=\delta_2=0} \ge \alpha_{VOH}^{18} \ge 0.97\Big|_{\delta_1=1}$$

On the contrary, rate of VO sites reoxidation strongly exceeds the rate of their isotope exchange with water, and at any δ_1 , δ_2 , δ_3 the ¹⁸O fraction in VO will be close to isotope fraction in dioxygen:

$$0.075 \Big|_{\delta_1 = \delta_2 = 0} \le \alpha_{VO}^{18} \le 0.12 \Big|_{\delta_1 = 1}$$

With the known isotopic composition of the catalyst surface, we can calculate the isotopic composition of AcOH that corresponds to different ratios of the pathways proceeding on different sites.

A) Suppose that only VO sites take part in the formation of AcOH $(\delta_1 = \delta_2 = 0)$. In this case, the isotope fraction of ¹⁸O in AcOH at the time of their formation will be equalled to α_{VO}^{18} , and distribution of isotopic AcOH molecules will be determined solely by probability factor and will correspond to equilibrium distribution. If the AcOH \leftrightarrow [H₂¹⁸O_{ADS}] exchange is ignored, the isotopic composition of AcOH will be as follows: $\alpha_{AcOH}^{18} = 0.12$, $f_{AcOH}^{16-18} = 0.21$ (Fig. 13, variant A1). If one of oxygen atoms in AcOH (most probably C-OH) exchanges with [H₂¹⁸O_{ADS}], this will provide an evident prevalence



Fig. 13. The values of f_{ACOH}^{16-18} and α_{ACOH}^{18} calculated by different models and compared to experimental values.

of CH₃C¹⁸O¹⁸OH fraction. The maximum value of α_{ACOH}^{18} may attain 0.56, with $f_{ACOH}^{16-18} = 0.88$ (Fig. 13, variant A2). Alternatively, supposing both oxygen atoms of AcOH exchange equiprobably with [H₂¹⁸O_{ADS}], the distribution of isotopic molecules will also correspond to the equilibrium one. α_{ACOH}^{18} may attain the value observed in experiment, 0.63, with $f_{ACOH}^{16-18} = 0.47$ (Fig. 13, variant A3). Thus, in any case when the label appears in AcOH via isotope exchange, the f_{ACOH}^{16-18} fraction will be greater or equal to the equilibrium one.

B) Let us suppose that both VO and VOH sites take part in the formation of AcOH. Then the isotope fractions in AcOH will be determined as follows (ignoring the secondary exchange of AcOH with water):

$$\begin{aligned} \alpha_{AcOH}^{18} &= (\delta_1 + 0.5\delta_2)\alpha_{VOH}^{18} + (0.5\delta_2 + \delta_3)\alpha_{VO}^{18} \\ f_{AcOH}^{16-18} &= \delta_1 2\alpha_{VOH}^{18} (1 - \alpha_{VOH}^{18}) + \delta_2 (\alpha_{VOH}^{18} (1 - \alpha_{VO}^{18}) + \alpha_{VO}^{18} (1 - \alpha_{VOH}^{18})) \\ &+ 2\delta_3 \alpha_{VO}^{18} (1 - \alpha_{VO}^{18}). \end{aligned}$$

At a certain rate ratio of AcOH formation routes, namely at $\delta_1 = 0.48$, $\delta_2 = 0.24$, $\delta_3 = 0.28$, we obtain the calculated isotopic composition of AcOH that corresponds to that observed in experiment (Fig. 13, variant B).

Analysis of isotopic distribution shows that V-OH center directly participates in the formation of AcOH, although the calculated values can be slightly overestimated due to exclusion of oxygen exchange between AcOH and adsorbed water, i.e., $AcOH \leftrightarrow [H_2^{-18}O_{ADS}]$. In the next part of the work the estimates were refined by numerical modeling of the isotopic distribution of AcOH molecules under transient conditions.



Fig. 14. Formation of different isotopomers of AcOH during the oxidation of 1butene on a VO_x -TiO₂ catalyst at 220 °C, in absence and presence of H_2 ¹⁸O. The arrows indicate the addition of 1-butene and isotopic water to the feed.

state conditions, H₂¹⁸O was added to the feed resulting in a sharp increase in the concentration of AcOH and then attaining a steady state concentration level, which was 2–3 times higher than that of AcOH formed in absence of water.

The model of transient regime upon addition of H_2 ¹⁸O is represented by a set of nonstationary kinetic equations (Eq. (1)) written in accordance with the reaction steps 1–5 and 1a-3a. They were supplemented with isotope kinetic equations (Eq. (5)) describing changes in the concentration of isotopic AcOH molecules and the ¹⁸O fraction in VO (to simplify the calculation, ¹⁸O fraction in water vapor and VOH was rounded off to 1):

$$\frac{dC_{AcOH}^{1818}}{dt} + \frac{1}{\tau} \frac{dC_{AcOH}^{1818}}{d\xi} = L_V (r_{2a1} + r_{2a2}\alpha_{VO}^{18} + r_2(\alpha_{VO}^{18})^2 - k_3 C_{AcOH}^{1818} \theta_{ZO}^2) + L_V \left\{ 0.5k_1 C_{AcOH}^{1816} \right\} \\
\frac{dC_{AcOH}^{1618}}{dt} + \frac{1}{\tau} \frac{dC_{AcOH}^{1618}}{d\xi} = L_V (r_{2a2}(1 - \alpha_{VO}^{18}) + 2r_2\alpha_{VO}^{18}(1 - \alpha_{VO}^{18}) - k_3 C_{AcOH}^{1618} \theta_{ZO}^2) + L_V \left\{ k_2 C_{AcOH}^{1616} - 0.5k_1 C_{AcOH}^{1816} \right\} \\
C_{AcOH}^{1616} = C_{AcOH} - C_{AcOH}^{1818} - C_{AcOH}^{1618} \\
\frac{d\alpha_{VO}^{18}}{dt} \theta_{VO} = W_{VO}^{exch} \theta_{VO}(1 - \alpha_{VO}^{18}) - (r_{2a1} + 2r_2 + 4r_3)\alpha_{VO}^{18}$$
(5)

4.3.2. Analysis of the isotope distribution in AcOH under transient conditions after input of $H_2^{18}O$

Fig. 14 shows the formation of AcOH at 220 °C in presence of H_2 ¹⁸O. The reaction was first studied in the absence of water, similar to the experiment described in chapter 4.2. After reaching steady

where, $r_{2a1} = k_{2a2}C_{BUT}\theta_{VOH}$ and $r_{2a2} = k_{2a2}C_{BUT}\theta_{VOH}$ - rates of reactions proceeding with the participation of VOH+VOH, VOH+VO centers; $r_{2a1} + r_{2a2} = r_{2a}$. Terms in parentheses correspond to isotopic exchange between AcOH and [H₂¹⁸O_{ADS}]. If both oxygen AcOH atoms are exchanged with [H₂¹⁸O_{ADS}] with the same probability, then $k_1 = k_2$.



Fig. 15. Modeling of transient regimes upon addition of H₂¹⁸O to the feed (points – experiment, lines – calculation).

If the rate constant of the formation of VOH centers remains unchanged ($k_5 = 0.0005 \text{ s}^{-1}$), then the calculated concentration of isotopic AcOH molecules increases slower than in the experiment (Fig. 15a). It can be proposed that during the desorption of products, the probability of the transformation of unoccupied active centers will be increased. Formally, it can be expressed as dependency of rate constant of step 5 on the desorption rate, i.e., $k_5 = k_5^0 (1 + a(r_2 + r_3))$, where $k_5^0 = 0.0005 \, \text{s}^{-1}$ – rate constant of the transformation VO→VOH in the absence of reaction. Thus, after addition of water to the reaction mixture, calculated rate for the formation of VOH centers and consequently the amount of formed isotopic AcOH molecules will increase (Fig. 15b and c). Calculated variants showed in Fig. 15b and 15c differ in k_i values. In the first case (Fig. 15b) $k_i = 0$, while in the other (Fig. 15c) $k_i > 0$. The last case (Fig. 15c) describes the dynamics of the AcOH formation the most adequately.

Results of the modeling showed that exchange with $[H_2^{18}O_{ADS}]$ strongly affects the isotopic distribution of AcOH molecules under transient conditions. However, under steady-state conditions this effect is negligible, and isotopic composition of AcOH is developed mainly at the formation step. Contributions of the routes involving different active sites to the total steady-state rate of AcOH formation were calculated in the view of subsequent isotope exchange of AcOH with water:

at VOH + VOH sites : $\delta_1 = 0.42$



at VO + VO sites : $\delta_2 = 0.30$

In this case, the calculated concentration of centers θ_{VOH} and θ_{VO} equaled to \approx 30% and \approx 70%, of the total amount of vanadia surface species, respectively. Thus, the turnover frequency (*TOF* = R/θ) over VOH centers is about three times higher than over VO centers.

4.3.3. Analysis of 18 O transfer from O₂ to AcOH under steady-state conditions (SSITKA)

Fig. 16a shows the change of ¹⁸O isotopic fraction in AcOH (α_{ACOH}^{18}) after switching from ¹⁶O₂ to ¹⁸O₂ under steady-state conditions in dry flow at 220 °C. Labelled ¹⁸O appears in AcOH immediately after ¹⁶O₂ \rightarrow ¹⁸O₂ switching and reaches the steady-state conditions after ca. 3000 s.

Logarithmic dependency of the isotopic fraction on time, i.e., $\ln(1 - \alpha_{ACOH}^{18}(t))$ clearly exhibits convexity, typical for a reaction with buffer step [39,40]. The number of exchanged oxygen atoms was calculated according to Eq. (6).

$$N_0 = \int_0^t (1 - \alpha_{AcOH}^{18}) dt \times U \times 2C_{AcOH} / g / S \approx 8 \times 10^{19} \, \text{at} / m^2, \qquad (6)$$



Fig. 16. Comparison of SSITKA experiments with ¹⁸O₂ in dry (a) and wet flow (b).



Fig. 17. Proposed scheme for oxygen transfer from gas phase to oxidation product in the absence of water.

This number is one order of magnitude higher than the monolayer coverage. This indicates that oxygen from the bulk of vanadium oxide serves as a buffer. Thus, the ¹⁸O transfer from O_2 to AcOH in dry flow can be illustrated with the scheme showed in Fig. 17.

The scheme describes the isotope response α_{AcOH}^{18} quite accurately (Fig. 16a, solid line). Estimated effective diffusion coefficient of labeled oxygen atoms in the bulk of vanadium oxide equals to $D/L^2 = 8 \times 10^{-3} \text{ s}^{-1}$.

In presence of water vapor $(H_2^{16}O)$, the dynamics of isotope response upon ${}^{18}O_2$ substitution of ${}^{16}O_2$ in the feed differs from that in a dry flow. Firstly, the characteristic time of transient regime, which is determined by a ratio of intermediates concentration to conversion rate, strongly decreases due to a faster rate of the reaction. Secondly, the isotope fraction of ${}^{18}O$ in AcOH attains a level that is much lower than the ${}^{18}O$ fraction in O_2 , which is caused by a concurrent process of isotope exchange of the catalyst oxygen with $H_2^{16}O$. Noteworthy is a profound change in the form



Fig. 18. Proposed scheme for oxygen transfer from gas phase to oxidation product in the presence of water.

of isotope response. The curve has a pronounced sigmoid shape and the ¹⁸O label in AcOH appears with a considerable delay, i.e., a few tens of seconds. The difference of the response curves in a dry flow is most clearly seen in logarithmic coordinates. In this case, the $\ln(1 - \alpha_{AcOH}^{18}(t))$ dependence is concave, which is typical for the consecutive mechanism of surface transformations. Interestingly, the numerical modeling shows that concentration of oxygen-containing intermediates appearing in the consecutive mechanism strongly exceeds the monolayer coverage and is close to oxygen concentration in the bulk of vanadium oxide. The scheme of ¹⁸O transfer from O₂ to AcOH describing most adequately the results of experiment in presence of water vapor is shown in Fig. 18.

Taking into account that in a dry flow the reaction proceeds mainly on VO sites while in the presence of water on VOH sites the following conclusions can be drawn. VO centers are mainly formed during direct interaction with gaseous oxygen. In turn, VOH centers can be formed either from bulk oxygen or during interaction with added or reaction water.



Fig. 19. Proposed mechanisms of selective oxidation (a) and total oxidation (b) of 1-butene.

Table 2

Elementary reactions and kinetic parameters used in the modelling of 1-butene oxidation with the formation of AcOH and CO₂ following the mechanism proposed on Fig. 18.

Stages/Reaction	Rate expression	Constants (s ⁻¹)		
		in absence of water		in presence of water
Catalytic reaction over VO centers 1) $O_2 + 2[Z] \rightarrow 2[ZO]$ 2) $C_4H_8 + 4[ZO] \rightarrow 2[X]$ 3) $[X] \rightarrow AcOH + 2[Z]$ 4) $AcOH + 4[ZO] \rightarrow 2CO_2 + 2H_2O + 4[Z]$	$r_{1} = k_{1}C_{O_{2}}\theta_{[Z]}$ $r_{2} = k_{2}C_{4}H_{8}\theta_{[ZO]}$ $r_{3} = k_{3}\theta_{[X]}$ $r_{4} = k_{5}e_{(X)}e^{-2}$	0.001	>0.5 0.2	0.024
Catalytic reaction over VOH centers 1a) $[Z^H] + [O]_{BULK} \rightarrow [ZOH]$ 1b) $O_2 \rightarrow [O]_{BULK}$	$r_{1a}^{BRUTTO} = k_{1a}C_{O_2}\theta_{[Z^H]}$	2	>0.5	0.0
2a) $C_4H_8 + 4[ZOH] \rightarrow 2[X_1]$ 3a) $[X_1] \rightarrow AcOH + 2[Z^H]$ Transformation of centers	$r_2 = k_2 C_{C_4 H_8} \theta_{[ZOH]}$ $r_3 = k_3 \theta_{[X_1]}$		0.7 >0.3	
$5) [ZO] \rightleftharpoons [ZOH]$	$ \begin{aligned} r_5 &= k_5(\theta_{[ZO]} - K_R \theta_{[ZOH]}) \\ k_5 &= k_5^0 (1 + 5(r_3 + r_4)) \end{aligned} $			$k_5^0=0.0005$ $K_R=2.5$

5. Summary

According to numerical modeling results of the oxidation of 1butene can be summarized by the scheme shown in Fig. 19.

The scheme illustrates that the selective oxidation of 1-butene to AcOH proceeds in two different catalytic cycles, i.e., one involving VO and other VOH centers (Fig. 19a). Additionally, VO centers participate in the total oxidation to CO_2 and H_2O (Fig. 19b). Rate constants for the proposed mechanisms obtained from kinetic and transient isotopic investigations are summarized in Table 2.

The obtained data shows that rate constants of steps 3, 4 and 5 (see Fig. 19) are influenced by the presence of water. The increase of desorption rate constant of AcOH in the presence of water is expected phenomenon and can be interpreted on the basis of adsorption-desorption mechanism proposed by Tamaru [41]. In their work, it was shown that desorption of reaction products during catalytic conversions is accelerated by the presence of ambient gas. In our case, water can be regarded as ambient medium influencing desorption of reaction products.

Decrease in the AcOH total oxidation (step 4, Fig. 19b) in presence of water was explained in literature either by blocking the active VO centers by adsorbed water [2–8] or transformation of vanadia centers upon interaction with water [18,22,23]. Jehng et al. used Raman spectroscopy to investigate the transformation of vanadium oxide species at different temperatures [24]. It was found that the ratio between VO and VOH centers strongly depended on the pretreatment temperature. In our work, we showed that during desorption of products in the course of reaction, the probability of transformation of active centers increases. It is associated with hydration of vacancies formed during the reaction of 1-butene with lattice oxygen and desorption of oxygen containing products. It should be emphasized that transformation of vanadium oxide centers strongly influences the total kinetic of reaction, i.e., conversion and selectivities to different oxidation products. For example, the estimated reaction constants of the formation of AcOH over VOH centers is ca. 3.5 times higher than over VO centers (see k_2 and k_{2a} , Table 2). At the same time, the reaction rate constant of total oxidation in the presence of water is ca. 3.2 lower than in dry flow (see k_4 , Table 2).

Proposed mechanism explains the disappearance of the water effect on the activity and selectivity with increasing temperature. Obviously, high temperature leads to the decrease of the water concentration on the catalyst surface [42,43] and the influence of water on the desorption rate of AcOH (step 3) and on the rate of total oxidation (step 4) decreases. At the same time, the decrease of the concentration of adsorbed water shifts the equilibrium VO \leftrightarrow VOH to the formation of [VO] centers, which are less active towards selective oxidation than [VOH].

6. Conclusions

Elaborative studies using different spectroscopic and transient techniques allowed the detailed description of the role of water in the catalytic oxidation of 1-butene over VO_x -TiO₂ catalysts. NH₃-TPD and DRIFTS studies confirmed strong temperature influence on the acidity of the catalysts and the amount of adsorbed water. XPS investigations suggested that both, oxygen from vanadia and titania matrix lattice oxygen participated in the oxygen transfer during the formation of oxygenated products.

Addition of water during oxidation of 1-butene under steadystate conditions led to the significant increase of the reaction rate in the temperature region between 160 - 250 °C. At the same time, the increase in the selectivity to desired product was observed. Above 270 °C the effect of water was negligible. The influence of water is associated with two factors. Firstly, an increase in the desorption rate of $C_x H_y O_z$ adsorbed products, notably carboxylic acids due to addition of water. This effect appears immediately after the injection of water to the reaction feed. Secondly, gradual hydration of the catalyst surface resulting in the formation of VOH species.

Kinetic modeling of transient isotopic exchange experiments predicted the presence of two different types of active vanadium oxide centers, i.e., VO and VOH. Hydrated centers exhibit high activity in partial oxidation of 1-butene in contrast to dehydrated VO centers which favor total oxidation. Estimated turnover frequency of 1-butene to AcOH over VOH centers is ca. 3 times higher than over VO centers.

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