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# Selective oxidation of isoprene to citraconic anhydride☆

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## Abstract

The isoprene oxidation to citraconic anhydride (CA, methylmaleic anhydride) over a V-Ti-O catalyst was studied with steady-state experiments, concentration cycling, fiber-optical in situ diffuse reflectance (DR) VIS spectroscopy and TGA. The results suggest both a reversible deactivation by deposits and a Mars–van Krevelen mechanism. Upon exposure to isoprene, the oxidized catalyst quickly changes its state, presumably by carbon deposition and reduction. This process is significantly faster than the regeneration under oxygen. In addition, the reaction seems to follow a ‘rake’ mechanism where CA is formed via a sequence of intermediates. The consecutive oxidation of CA leads to a selectivity maximum.

*Keywords:* Citraconic anhydride; In situ diffuse reflectance spectroscopy; Isoprene oxidation; Vanadia/titania catalyst; Concentration cycling

## 1. Introduction

The selective oxidation of hydrocarbons is a field of enormous economic importance, and intensive research has been carried out for decades [1,2]. Some reactions have been thoroughly studied by numerous research groups, e.g. the oxidation of methane, butane, propylene, etc. The present paper focuses on a less investigated reaction, the oxidation of isoprene to citraconic anhydride (CA).

CA, or methylmaleic anhydride, is a versatile compound. It may be used in the synthesis of antireversion agents used in the rubber industry [3,4] or in the copolymerisation, e.g. with styrene [5,6]. On a smaller scale, CA is studied as a building block for the synthesis of strigol-type germination stimulants [7] or of chemotherapy drugs [8]. Current synthesis methods are cumbersome respectively multistage processes (e.g. [9]), and a heterogeneously catalyzed oxidation of appropriate hydrocarbons is desirable.

Starting in the late 1960s, isoprene was investigated as a possible feedstock [10–12]. The reaction is strongly exothermic, and CA selectivity suffers from both consecutive and parallel reactions (Fig. 1).

In a pioneering study in 1967, Pichler et al. [10] investigated the production of CA starting with toluene, xylenes, cresols and isoprene, respectively. In contrast to the other reactants, isoprene led to acceptable selectivities of up to 21 mol%. Total oxidation was a major competing reaction. The oxidation was carried out over a tin vanadate catalyst. Varying the temperature a selectivity maximum to CA (16% at 28% isoprene conversion) was found. The maximum was attributed to a competition between CA formation and CA destruction by further oxidation.

These researchers [13–15], as well as others [16–19], filed a number of patents in the late 1970s, with most suggested catalysts consisting of vanadia, molybdena and antimony oxide as active components on various oxidic supports ($TiO_2$, $ZrO_2$, $SnO_2$). After this, it was only in 1999 that results on this reaction were again reported, by Trifirò and coworkers [20,21] and by ourselves [22–25]. A screening study [22] showed that the VTiO system yielded maximum CA selectivities of 20% and mainly carbon oxides as side products. It was superior to the MoTiO and the SbTiO system. The vanadium content was significantly higher than that of the low-V (monolayer) catalysts used in other oxidation reaction studies. This is also the case in butadiene oxidation and shows the similarity of the two reactants [26,27]. With the V-Ti-O catalyst, the CA maximum was closely related to an almost full isoprene conversion. Further studies [25] showed that selectivities of about 34% can be achieved with mixed oxide catalysts consisting of the oxides of vanadium, molybdenum and titanium.

Trifirò and coworkers studied the effect of the main operating parameters on the catalytic performance for a V-Ti-O catalyst [20,21]. Here, too, a selectivity maximum to CA was detected with temperature. It was assumed that the decrease of selectivity at higher temperatures is caused by combustion of CA. At lower temperatures the surface

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☆ This paper is dedicated to Prof. Bernhard Lücke on the occasion of his 65th birthday.

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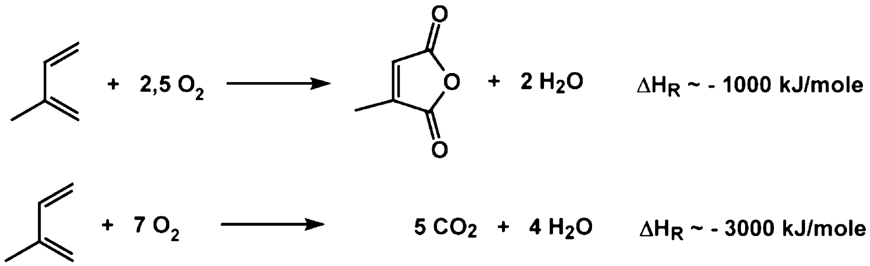

Fig. 1. Selective and total oxidation of isoprene.

of the catalyst is saturated with isoprene due to the strong interaction, and the availability of oxygen insertion sites decreases. Under these conditions the absorbed components can easily undergo total oxidation by adsorbed oxygen. This was supported by the observation that CA selectivity increased with the oxygen to isoprene ratio.

In the framework of an international multigroup microreactor project [28], the isoprene oxidation was carried out in a microchannel reactor [23,24]. The catalyst was applied as a thin layer onto the walls of the channels with a hydraulic diameter of 230–280 μm. The behavior in a fixed-bed and in the microchannel reactor upon a variation of the reaction conditions was qualitatively similar.

The present paper carries on the investigation of the reaction by a systematic variation of parameters such as feed temperature, residence time or feed concentrations, respectively, in steady-state experiments. Further insight is obtained by unsteady-state experiments (switching between isoprene in nitrogen and air). In order to take the first steps towards a discussion on the molecular level, in situ DR VIS spectroscopy and TGA experiments are carried out. In particular, the spectroscopic data should be taken in situ with this kind of systems. Here, a fiber optical assembly is used that allows to take spectra at reaction temperature in a well-characterized catalytic reactor with a high temporal resolution (see [29–31]).

## 2. Experimental

### 2.1. Catalyst preparation

The catalyst was prepared by wet impregnation of $TiO_2$–anatase (Fluka; BET surface area about 9 $m^2/g$) with an aqueous solution of $V_2O_5$ (GfE, Nuremberg) in oxalic acid which was evaporated under stirring. The remaining precursor was dried at 120 °C over night followed by a calcination at 500 °C for 4 h. The obtained catalyst had a BET surface area of about 11 $m^2/g$. The V/Ti molar ratio was 3:1 which was verified by ICP–OES-analysis.

### 2.2. Catalytic Experiments

The catalytic measurements were carried out in a conventional flow apparatus at atmospheric pressure. The gases were dosed by mass flow controllers, as was the liquid isoprene (Fluka) with subsequent evaporation using nitrogen as carrier gas. Feeding CA (Aldrich) was effected by bubbling nitrogen through a heated (80 °C) saturator. An integral reactor ($\alpha$-$Al_2O_3$, inner diameter: 10 mm) with five heating zones was used. In the center of the reactor a ceramic capillary containing eight thermocouples was inserted to monitor the axial temperature profile.

The analysis of the organic products and permanent gases was carried out online with a GC which was equipped with three columns (HP-5, PoraPlotQ and molecular sieve 5 Å) and two detectors (FID, TCD).

The actual reaction was carried out in either one of two ways. In Sections 3.1 and 3.2, 0.5 g of pellets (0.8–1.12 mm diameter) diluted with inert spheres ($Al_2O_3/SiO_2$, 0.75–1 mm diameter) to a total of 8 ml were used. For temperature variations, it was found beneficial to decrease the temperature starting from a high value, rather than increasing temperature. At a certain temperature, CA selectivity would go through a maximum. This was usually the temperature of about 90% isoprene conversion. At these conditions, the overtemperature as measured with the axial thermocouples was 1–9 K above set temperature, depending on the isoprene feed concentration. Estimations showed that only under more severe conditions (overtemperature of to up to 25 K at even higher set temperatures and full conversion), pore diffusion limitation could set in.

In Section 3.3, experiments were carried out with the active catalyst being applied as a powder onto the inert $Al_2O_3/SiO_2$ spheres, yielding a mechanically resistant, catalytically active thin layer. The measured hot spot temperature was less than 3 K. The results compared well with those in Sections 3.1 and 3.2, confirming that the latter were not significantly influenced by heat or mass transport limitations.

### 2.3. In situ diffuse reflectance (DR) VIS spectroscopy

The in situ DR VIS spectroscopical experiments were conducted with an AVS-SD2000 (Avantes) spectrometer with a 2048 diode array in the range of 340–1015 nm. The slit was 200 micron, the integration time 195 ms, and the average of 10 single measurements was taken. Spectralon served as a reflectance standard. The spectra were taken with a fiber optical probe (Fiberguide Industries Inc.) that was axially

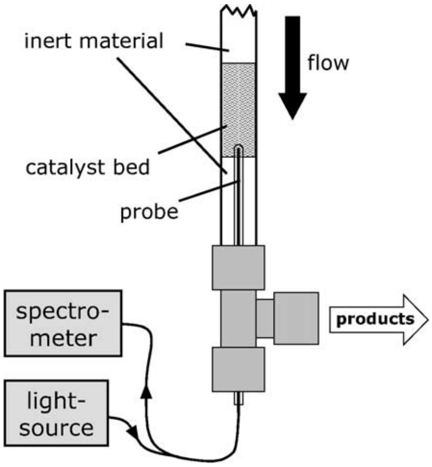

Fig. 2. Experimental setup for DR–VIS spectroscopy.

inserted in the reactor through a quartz-glass tube (Fig. 2). The tube was inserted from the gas exit side (rather than the gas entrance side) of the reactor, leaving most of the gas flow pattern and the catalyst bed undisturbed. The tip of the probe, and hence the location of the DR VIS measurement, was at the end of the catalyst bed, equivalent to the last tank of a tanks-in-series representation of a plug-flow reactor. Hence, the spectroscopic information can be attributed to the catalyst that is exposed to the gas composition as monitored by the analytics downstream.

### 2.4. TGA

TGA experiments with used catalyst were done in a NETZSCH TG 209 apparatus. The catalyst was weighed in an alumina crucible, the balance chamber was evacuated and afterwards flushed with nitrogen for three times to ensure that no oxygen was left. The sample was then heated under a flow of nitrogen with a rate of 10 K/min to a $T_{max}$ of 600 °C. After cooling the sample down under nitrogen, another subsequent TGA in a flow of air and with the same heating rate and $T_{max}$ was done with the very same sample, which was not removed from the TGA apparatus.

## 3. Experimental results

### 3.1. Steady-state catalytic behavior

The product spectrum mainly consisted of the target product CA and the carbon oxides. Up to 14 additional organic byproducts were regularly detected. With GC–MS, several byproducts could be identified: 3-methylfuran, 3-furaldehyde, 3-methyl-dihydro-furan, 3-methylfuran-2(5H)-one and 2-methyl-2-butenal as $C_5$-hydrocarbons, and maleic anhydride, methyl-vinylketone and methacrolein as products with less than five carbon atoms. A few byproducts containing more than five carbon atoms were found in traces.

The isoprene conversion shows an exponential increase with temperature until full conversion is reached (Fig. 3). The selectivity to the main product CA shows a maximum of about 30%. This temperature of maximum selectivity to CA will be denoted by $T_{ms}$. It is located about 20 K below that of full conversion. Upon further increase of the set temperature, the CA selectivity decreases. At temperatures below $T_{ms}$, organic byproducts occur in higher amounts. Most organic byproducts disappear when the temperature of the CA-selectivity maximum is reached (see e.g. 3-methylfuran in Fig. 3). At temperatures well above $T_{ms}$, only a few components having a higher thermal stability are detected, e.g. maleic anhydride. The selectivities to the carbon oxides both pass through a minimum around $T_{ms}$. When comparing various runs at different conditions, it can be noted that the

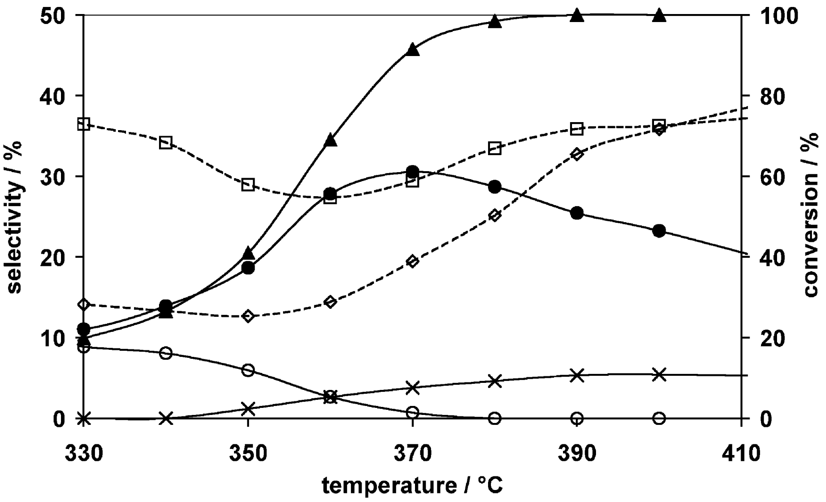

Fig. 3. Isoprene conversion and product selectivities vs. temperature (0.8 vol.% isoprene in air; $W/F_{tot} = 25$ g min/mol): isoprene conversion, ▲; selectivities to CA, ●; $CO_2$, □; CO, ◇; 3-methylfuran, ○; MA, ×.

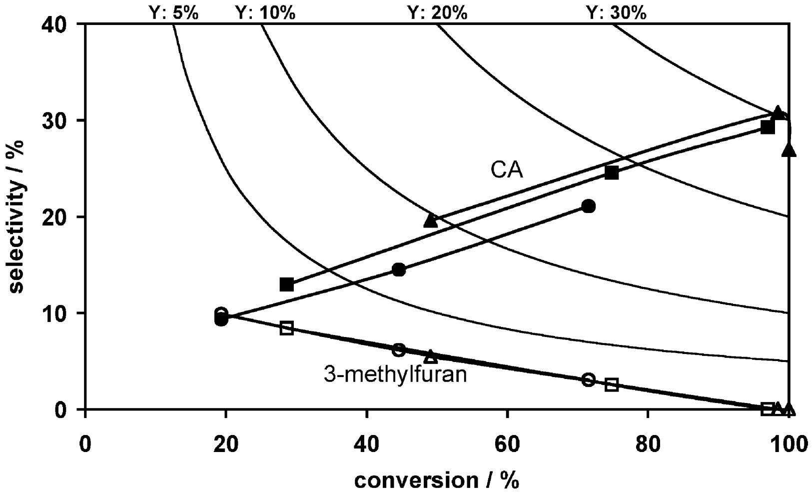

Fig. 4. Selectivities to CA (filled symbols) and 3-methylfuran (open symbols) vs. isoprene conversion for three temperatures (conversion is varied by altering W/$F_{tot}$ (12.5–50 g min/mol); 0.8 vol.% isoprene in air): 370 °C, ▲; 360 °C, ■; 350 °C, ●.

temperature range where CA was detected decreased in width with increasing non-isothermicity.

The selectivities to CA and 3-methylfuran are plotted versus isoprene conversion for three different temperatures (Fig. 4). The variation of conversion at a given temperature was attained by varying the residence time (W/$F_{tot}$), which was in turn modified by altering $F_{tot}$. The selectivity to CA increases with conversion in an approximately linear manner up to high degrees of conversion of about 95% and drops off upon a further rise of residence time and hence conversion. The curves for the three different temperatures are located close to each other and display similar slopes. This behavior is even more evident for 3-methylfuran. In this case all points lie on the same curve, irrespective of the temperature and residence time. The curve shows a linear decline with increasing conversion until a degree of conversion of about 95% is reached and no 3-methylfuran is detected any longer.

Fig. 5a shows the rates of isoprene consumption and CA formation versus the feed concentration of isoprene at 330 °C. The rate of isoprene consumption shows no dependence on the feed concentration. The formation of CA is about constant for the higher feed concentrations (0.4–0.8 vol.%) as well. At the low feed concentration of 0.2 vol.% the corresponding degree of conversion is fairly high (about 65%) compared to the values for the other isoprene concentrations (20–33%).

The oxygen feed concentration has a stronger influence on the reaction (Fig. 5b). It was varied between 10 and 30 vol.% at 0.8 vol.% isoprene (oxygen-to-isoprene ratio ≈ 12–40, i.e. always oxygen excess). Both isoprene consumption and CA formation show an increase with the oxygen feed.

### 3.2. Unsteady-state catalytic behavior

In order to study the dynamic behavior, concentration cycling was carried out. The catalyst was preoxidized under

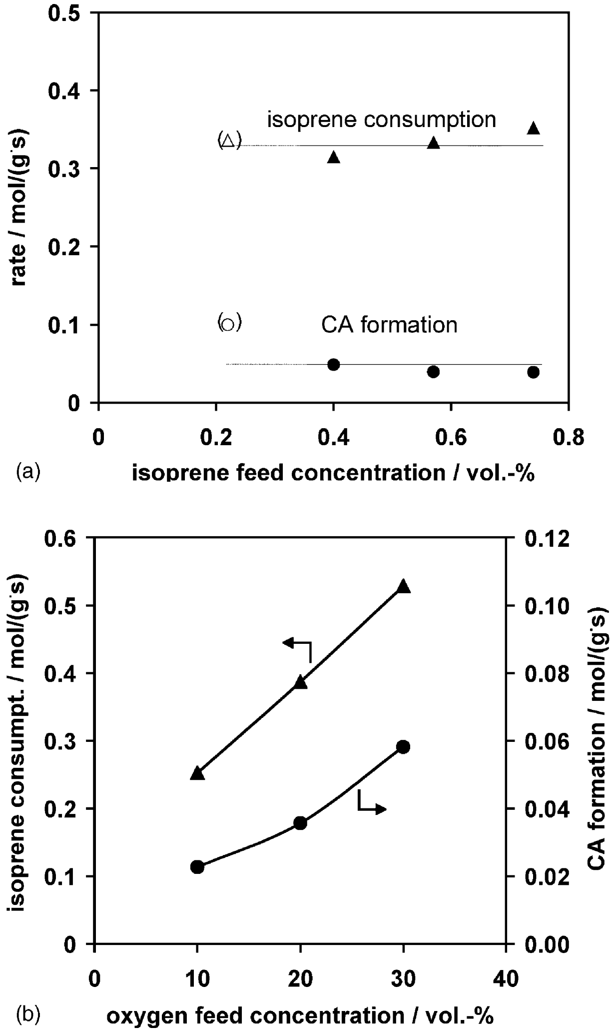

Fig. 5. Rates of isoprene consumption and CA formation vs. (a) isoprene feed concentration (20 vol.% oxygen) and (b) oxygen feed concentration (0.8 vol.% isoprene); $W/F_{tot} = 25$ g min/mol; $T = 330$ °C.

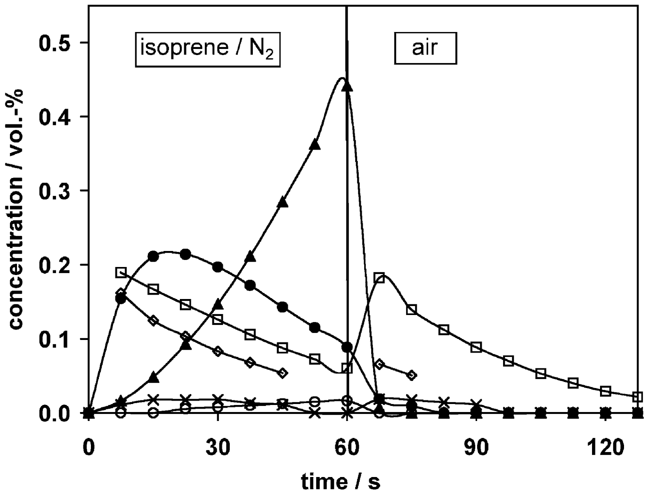

Fig. 6. Unsteady-state operation: $t = 0$ s, switching from air to isoprene/$N_2$ (0.8 vol.% isoprene; $W/F_{tot} = 25$ g min/mol; $T = 360\,°C$); $t = 60$ s, switching back to air; outlet concentrations of isoprene, ▲; CA, ●; 3-methylfuran, ○; MA, ×; $CO_2$/5, □; CO/5, ◇ (the concentrations of the carbon oxides are divided by their stoichiometric coefficients).

flowing air. At $t = 0$, the feed was switched to 0.8 vol.% isoprene in nitrogen for 60 s, then the feed was switched back to air. The composition of the outlet was monitored as a function of time (Fig. 6). After switching to isoprene, both carbon monoxide and carbon dioxide outlet concentrations increased from zero to finite values and then decreased with an almost negligible positive curvature. CA displayed a maximum in time after about 15 s. The decline had a slope comparable to that of the carbon oxides. The isoprene concentration in the outlet increased in a sigmoidal manner with a slight positive curvature in the beginning. If isoprene was fed longer than 60 s, the outlet concentration approached a constant value with negative curvature (not shown here). Maleic anhydride displayed a maximum similar to that of CA, but at a much lower intensity. 3-methylfuran could also be detected; interestingly, its concentration increased over the entire period of isoprene dosage.

In the subsequent oxidation half-cycle, considerable amounts of both carbon dioxide and carbon monoxide appeared in the outlet, decreasing in an almost exponential manner with time. Maleic anhydride appeared for about 30 s.

Performing this experiment at three different temperatures (330, 360 and 390 °C, not shown) revealed that the carbon oxide formation in the air half-cycle is significantly faster at high temperatures. In the isoprene half-cycle, the curves (especially the CA curves) are hardly different for the three temperatures. It should be noted that with the present set-up (GC-analysis), a time-resolved mass balance was not possible with satisfying accuracy.

### *3.3. In situ diffuse reflectance (DR) VIS spectroscopy*

Preliminary experiments were carried out to identify the relevant spectral regions. An in situ DR VIS spectrum was taken of the catalyst that had just been preoxidized in air. A second spectrum was taken after the catalyst had been used in isoprene containing atmosphere at low reaction temperatures. Differences in these two spectra occur in the VIS-region at wavelengths above 550 nm merging in a broad absorption band. For monitoring the catalyst state as a function of operating parameters, the reflectance at 660 nm was chosen as an indicator. At this wavelength, a maximum difference in the reflectance spectra was observed.

The time resolved temperature variation in the co-feed mode is shown in Fig. 7. The temperature was decreased by steps of 10 °C every 80 min. The product gas composition and the reflectance at 660 nm are shown with time on stream. The product gas composition shows the typical temperature behavior, with full isoprene conversion and increasing CA selectivity upon temperature decrease. Coming from 450 °C, the reflectance remains almost constant, independent from temperature. After changing the set temperature to 390 °C,

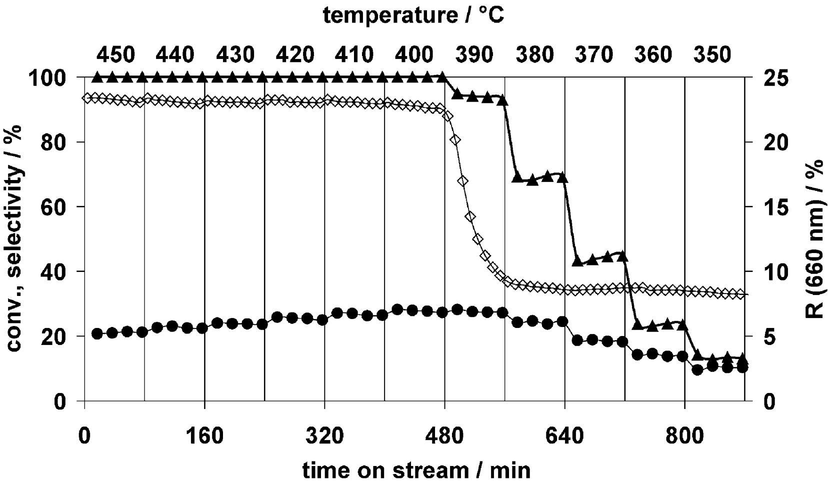

Fig. 7. Time on stream behavior of: isoprene conversion, ▲; CA selectivity, ●; reflectance, ◇ by lowering the temperature stepwise by 10 °C every 80 min (0.8 vol.% isoprene in air; $W/F_{tot} = 9$ g min/mol).

isoprene breaks through. At that temperature, a sudden decrease of the reflectance is detected. The transient of the reflectance is slower than that of the concentrations in the outlet.

While isoprene and CA attain their steady-state values in less than 20 min, the reflectance changes for more than 80 min. Upon further decrease of the temperature, the reflectance becomes independent from the temperature again even though conversion and selectivities change. It seems that the catalyst is mainly in one of only two states, depending on whether isoprene is present or not.

Additional unsteady-state experiments were performed with the fiber-optical probe in the catalyst bed. The inlet gas was switched from purely oxidizing atmosphere to a pure isoprene/nitrogen mixture (like in Section 3.2). Again a sudden decrease of the reflectance is observed when isoprene breaks through (Fig. 8a). In contrast to the co-feed mode, this happens within seconds. The complete cycle (air to isoprene to air) is depicted in Fig. 8b. It is evident that the change of the catalyst induced by oxygen is much slower than the counteracting change induced by isoprene.

### 3.4. TGA

During a steady-state experiment, the reaction was stopped at 355 °C (i.e. below maximum CA selectivity, $T < T_{\mathrm{ms}}$) by flushing the reactor with nitrogen and cooling it down under nitrogen atmosphere. The two subsequent thermogravimetric analyses of the catalyst are depicted in Fig. 9. In the first TGA under an inert nitrogen atmosphere the catalyst showed a weight loss of about 1.5 wt.% in the temperature range of 300–450 °C. The second subsequent TGA in air yielded an increase in weight by about 3.5 wt.% in the temperature range of 380–480 °C. Note that the overall procedure had therefore led to a net mass gain (about 2 wt.%) of the sample. Additional information was taken

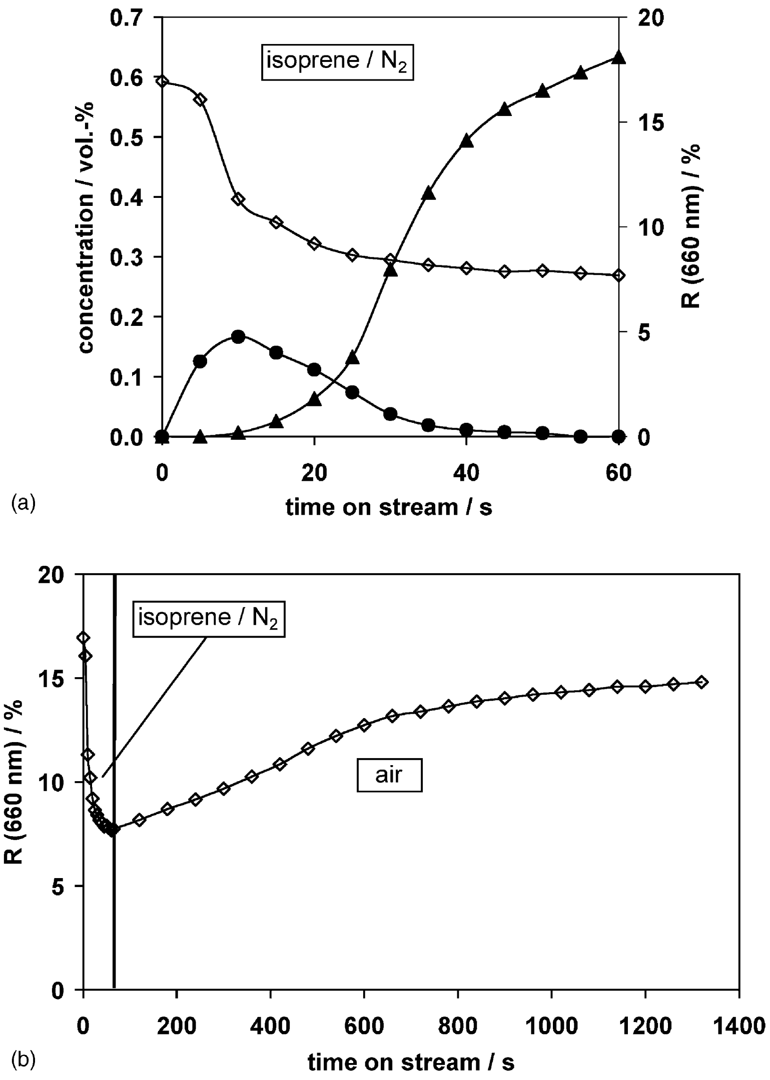

Fig. 8. VIS-measurement at unsteady-state operation: (a) isoprene half-cycle; (b) one whole cycle (isoprene and air; 0.8 vol.% isoprene in $N_2$ and air, respectively; $W/F_{\mathrm{tot}} = 9$ g min/mol; $T = 420$ °C); isoprene, ▲; CA, ●; reflectance, ◇.

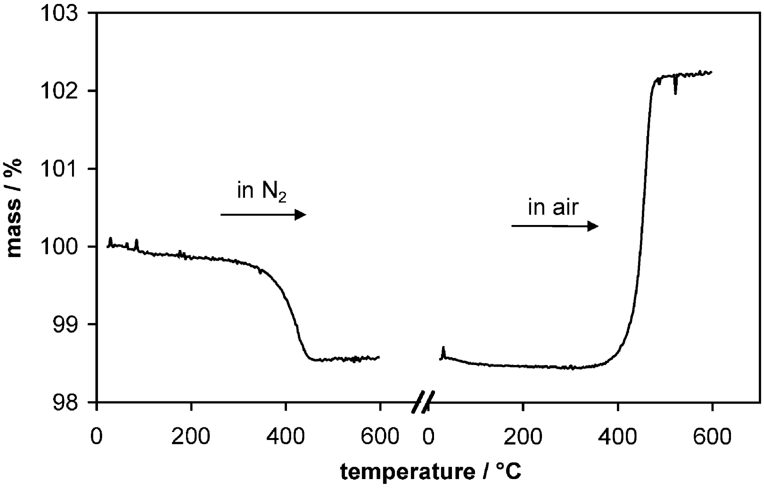

Fig. 9. Two subsequent TGA (in $N_2$ and air, heating rate = 10 K/min) of one used catalyst sample.

from visual inspection of the sample: it was dark both after the reaction and after the non-oxidative TGA. After the second, oxidative TGA run, however, it had regained the orange color of the fresh, oxidized catalyst sample.

## 4. Discussion

### 4.1. Increase of CA selectivity with increasing conversion

Numerous selective oxidation reactions are known where the selectivity to the desired product decreases with increasing conversion. However, for some reaction systems, e.g. the oxidation of butene to maleic anhydride [32] or of toluene to benzoic acid [33] over vanadia catalysts, the selectivity to the target product shows a maximum with temperature and corresponding conversion. In the present study the experiments show as well that the CA selectivity clearly exhibits a maximum with temperature (Fig. 3) and also with residence time (Fig. 4). The maximum with temperature is consistently found for this reaction in various different seups [10,12,21,23], but differing from some of these works, in these experiments the selectivity maximum to CA is always achieved near full reactant conversion.

For the oxidation of butadiene to maleic anhydride [27] or the *o*-xylene oxidation to phthalic anhydride [34], a similar behavior is found. Maximum selectivity is attained near full reactant conversion. The selectivities to intermediates decrease with temperature and vanish at full conversion. This has been described by a ‘rake’ mechanism where the reactant is progressively transformed through a series of adsorbed intermediates. The intermediates may form observable intermediate products in the gas phase. In the isoprene oxidation, quite a number of observed byproducts (e.g. 3-methylfuran) will be precursors to CA. Once formed, they can either desorb (at low conversion), or react further to eventually yield CA (at higher conversion), respectively. Note that the concentrations of numerous byproducts (e.g. 3-methylfuran) vanish in the same temperature range of full conversion. This observation had already been reported by Castiglioni et al. [21].

Trifirò and coworkers explained the increase of CA and other oxygenated hydrocarbons by the availability of selective oxygen insertion sites [21]. They assume that at low temperatures (hence low conversion) the surface of the catalyst is saturated with adsorbed compounds hindering the adsorption and insertion of oxygen. They explain the formation of carbon oxides at these conditions by the fact that the adsorbed compounds are easily attacked by non-selective oxygen species. It is reported that alkenes in contrast to alkanes adsorb on the same site as oxygen, thus undergoing a competitive adsorption [35]. Hereby the effect of the rake mechanism is enhanced. Decreasing the conversion by lowering the temperature inhibits the formation of the high oxygenated products like CA in our case not only because of the temperature itself, but additionally by the decrease of availability of selective oxygen at the surface. Both the saturation of the surface with hydrocarbons and the limited availability of oxygen is confirmed by the experiments in Fig. 5: a change in the isoprene feed concentration does not affect the rate of isoprene consumption or CA formation when the surface is already saturated with isoprene. However, an increase of the oxygen content in the feed accelerates both rates.

Fig. 4 reveals yet another remarkable phenomenon, best demonstrated by the selectivity to 3-methylfuran: the selectivity depends on the degree of isoprene conversion irrespective of the combination of temperature and residence time that leads to that degree of conversion.

### 4.2. Decrease of CA selectivity due to consecutive reactions

At first sight, CA feed experiments in the absence of isoprene are no suitable tool to study the isoprene oxidation:

being an unsaturated reactant, isoprene is likely to adsorb, inhibit oxygen adsorption and hence suppress the further oxidation of the product CA (compare e.g. with the butadiene oxidation [32,35]), which is different for the isoprene-free CA feed experiment. However, at full isoprene conversion, no more isoprene is present from a certain axial position in the catalyst bed on. Downstream of this position, the conditions are similar to pure CA feed experiments.

Experiments with feeding 0.1–0.5 vol.% of CA in air over a V-Ti catalyst revealed that CA is oxidized to the carbon oxides at moderate temperatures [23]. No organic products like maleic anhydride or acetic acid were detected in these experiments. The decrease of the CA selectivity beyond full isoprene conversion (Figs. 3 and 4) may therefore be due to its further oxidation. Since the selectivity to maleic anhydride remains constant and the selectivities to the carbon oxides increase (Fig. 3), this suggests that CA is further oxidized to $CO_x$ and is no precursor for significant amounts of other organic products such as maleic anhydride. In addition, the constant selectivity to maleic anhydride with increasing temperature (Fig. 3) indicates that maleic anhydride has a higher thermal stability than CA. The structural difference is the allylic methyl group which suggests that an attack of CA via that group may not be ruled out. The detection of 3-furaldehyde during the steady-state experiments at low temperatures illustrates that the allylic methyl group may indeed be attacked.

### 4.3. Unsteady-state experiments

The appearance of carbon oxides upon switching from isoprene/nitrogen to air (Fig. 6) indicates that carbon-containing species are deposited on the surface. This further confirms the assumption of a catalyst surface saturated with adsorbed compounds as described above (reminiscent of the *o*-xylene oxidation [36]). After switching to air, CA or maleic anhydride were sometimes observed. This suggests that the carbon was neither solely adsorbed as carbon oxides nor solely as polymeric species.

After switching from air to isoprene/nitrogen, the CA concentration in the outlet passes through a maximum while the carbon oxides immediately start at high selectivities which then decrease in a monotonous manner (Fig. 6). It is not likely that adsorption of CA slows down its appearance at the reactor exit, since its concentration quickly drops to zero after switching off the isoprene feed. Rather, a dependence of selectivity on the degree of catalyst oxidation can be assumed. This kind of selectivity maximum with oxidation state has been discussed by Cavani et al. [37]. At an oxidation state that is too high, the formed CA would be further oxidized. At an oxidation state below the optimum value, isoprene would not be transformed fast enough to CA, but rather be prone to competing reactions or to desorption of precursors. And indeed, as time on isoprene stream increases, so does the amount of the supposed CA precursor 3-methylfuran (Fig. 6). Of course, this tentative explanation requires further experimental validation.

### 4.4. In situ DR VIS spectroscopy

Because of the strong UV absorption of the titania support, the spectroscopic measurements focused on the VIS region [38]. The oxidized catalyst differs from the catalyst that was exposed to the reaction mixture by an absorption around 660 nm. Without further spectroscopic evidence, any attribution remains tentative. One possible explanation would be based on *d–d* electronic transitions of V(IV) and/or V(III) cations (see, e.g. [39]), indicating a reduction of the vanadium oxide. However, these transitions are usually of low intensity. Also, the unsteady-state experiments reveal that carbon-containing species are deposited on the catalyst surface. Alternative explanations would therefore be a deposition of carbon-containing species that absorb in the visible region, or oxygen vacancies that are induced by chemisorbed alkenes. At this point, it should suffice to state that we will follow the absorption at 660 nm as an indicator of the state of the catalyst even if we cannot attribute it exactly to a well-described state on the molecular level. More research on the proper attribution has been initiated using various techniques such as DRIFTS, Raman spectroscopy, TGA, etc. However, the results described in the present paper will be sufficient to further elucidate certain issues.

The time resolved monitoring of the catalyst, accompanied by the analysis of the reaction products, yields insight in the velocities of the processes determining the catalyst activity. The steady-state experiments show a decrease in reflectance when the catalyst is exposed to isoprene. The catalyst seems to have two stable states depending on the presence or absence of isoprene (Fig. 7), which may be either the deposition of carbon-containing compounds or the reduction of the vanadia. A similar but accelerated change between these two states is also observed in the unsteady-state experiments. The exposition to isoprene initiates a fast and deactivating process (Fig. 8a). In contrast, oxygen exposure gives rise to a slow and activating process (Fig. 8b), either the burn-off of carbon-containing compounds or the reoxidation of the reduced vanadia. Hence, the observed behavior may be due to a reversible deactivation by carbon-containing compounds, to a reversible oxygen storage (Mars–van Krevelen mechanism), or to a combination of both. The limiting process, no matter whether it is the reoxidation of a reduced catalyst or the burning of the residues, will be accelerated by increasing oxygen concentrations. This is in agreement with the positive influence of oxygen (Fig. 5b). This influence explains the slower change of the reflectance (about 80 min) in the co-feed experiment in contrast to the fast transition (less than 20 s) in absence of oxygen in the unsteady-state experiment.

The experiment with catalytically activated microstructured plates supports the hypothesis of two different states: if the reaction was quenched at maximum CA selectivity, the catalytic channels were dark near the inlet and orange near the outlet. The change of color was an abrupt rather than a gradual one. At less than full isoprene conversion, the catalyst was dark over the entire channel length. It is noteworthy that this discoloring may serve as a memory/indicator of the flow equidistribution over the channels.

### 4.5. TGA

The simple TGA experiment may provide insight into the relative amount of deposition of carbon-containing species and of vanadia reduction during the reaction. The weight loss in nitrogen atmosphere is attributed to the removal of the carbon-containing compounds, either via desorption or via oxidation by oxygen stored in the catalyst. This first run left the catalyst in a dark state, suggesting that either not all residues had been removed, or that part of the V(V) had been reduced, giving rise to an absorption in the visible range. In order to clarify this, the sample was not removed from the TGA setup but rather exposed to oxidizing conditions. An increase in weight was now observed under oxidizing conditions which must stem from an insertion of oxygen into the catalyst.

It seems safe to assume that the second TGA run led primarily to V(V). If one assumes for a moment that the catalyst had been in its V(V) state during the reaction and before the first TGA, the weight loss during TGA 1 should have been greater than the weight gain during TGA 2. However, the weight gain exceeded the weight loss, suggesting that the catalyst must have been in a reduced state during reaction.

In order to obtain a rough estimate, a uniform oxidation state is assumed for the vanadium. The determined mass losses and gains indicate an oxidation state of the vanadium between +5 and +4, which would have to be discussed in the framework of non-stoichiometric phases $V_2O_{5-x}$ as suggested by Haber et al. [40]. The deposition of carbon-containing compounds may even be coupled to the reduction because it is reported that olefins adsorb more strongly at reduced vanadia sites [41]. More sophisticated TGA experiments, possibly while monitoring the gas phase, will be necessary to clarify the situation.

## 5. Conclusions and Outlook

In the isoprene oxidation an unusual maximum of the CA selectivity with temperature and residence time corresponding to an increasing selectivity with increasing conversion is found. The decrease of the CA selectivity sets in at almost full conversion. The second important experimental result is that the oxygen concentration has a strong positive influence on the reaction rates whereas the rates are independent on the isoprene concentration in the feed. These results are explained by a competitive strong adsorption of isoprene with oxygen known for alkenes. At low temperatures the catalyst surface is saturated with organic compounds. At higher temperatures or oxygen concentrations this saturation is reduced, corresponding to an increased availability for oxygen and hence increased conversion. The increasing selectivity with increasing conversion is also explained by the rake mechanism where the reactant is progressively transformed through a series of adsorbed species with increasing oxygen content.

Both the unsteady-state experiments and the TGA support the assumption of adsorbed organic compounds on the catalyst surface as well as the oxygen storage capabilities of the catalyst (Mars–van Krevelen mechanism). The oxygen availability for isoprene oxidation appears to be a function of the oxidation state of the catalyst, but is also influenced by the hindered oxygen adsorption. The time resolved monitoring of the catalyst VIS spectra during the reaction revealed that the catalyst is either in one of two states depending of the presence (low activity) or absence (high activity) of isoprene. The velocity of the deactivating process appears much higher than that of the activating process.

Further spectroscopic investigations will be performed to elucidate the exact nature of these catalyst states. Changes in the oxidation state and the modification of the catalyst surface by reactant and product adsorption are discussed. A detailed kinetic analysis of the experiments is also undergoing and should give further hints towards the understanding of the isoprene oxidation to CA, especially of the influence of oxygen.

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