Surface Sensitivity of Hydrogen Evolution and Formaldehyde Reduction on Differently Oriented TiO₂ Anatase Nanocrystals

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Abstract
Selectivity of nanocrystalline anatase electrodes with different preferential surface orientation in formaldehyde reduction was assessed as a model of oxide-based catalyst for electrochemical CO₂ valuation. Cathodic behavior of TiO₂ (anatase)-based electrodes observed in formaldehyde reaction integrates, in fact, several processes including hydrogen evolution, formaldehyde reduction, and proton insertion into anatase structure. The electrochemical activity of the anatase-based cathodes is, regardless of the surface orientation, dominated by proton insertion. The proton insertion is more pronounced on {001}-oriented anatase than on {101}-oriented nanocrystals due to anisotropy of the proton transport in the anatase which is more facile in the (001) direction. Aside from the proton insertion, both anatase orientations also differ in selectivity in the formaldehyde reduction. While {101} surface orientation produces primarily hydrogen and methanol, the same process on {001}-oriented surfaces shows the ability to produce aside of methanol also hydrocarbons most likely methane. The overall activity towards the reduction of organics is, however, lower than that of metals.

Keywords Formaldehyde reduction · Titanium dioxide · Selectivity · DEMS

Introduction
The valuation of the carbon dioxide represents one of the imperative tasks in mitigation of the recent climate change. The CO₂ valuation is expected to be driven by a surplus of renewable sources of electric energy, which needs to be stored as chemical energy. This situation has sparked vigorous interest in possible direct conversion pathways for CO₂ into chemicals. Reductive conversion of carbon dioxide has been studied by different approaches such as thermochemical [1], biochemical [2], photochemical [3], and also electrochemical [4]. Given the fact that the carbon in CO₂ may receive up to 8 electrons, one has to naturally expect that the carbon dioxide reduction proceeds in a rather complex manner stressing the need to achieve a good selectivity control. Electrocatalysis, namely, the electrocatalytic reduction processes are deemed particularly important, and metals like silver and copper receive main attention in this context [4].

N-semiconducting oxides have been investigated in this context for direct photocatalytic CO₂ reduction [5]. Although the photocatalytic CO₂ reduction may seem to be rather departed from electrocatalytic CO₂ reduction, the activity and reactivity still should be governed by the same relationships as the reductions on metals. It should be kept in mind that the electronic structure of n-semiconductors in fact conforms to that of the metals if the external bias drives the Fermi level below the flat band potential E_{fb}. This type of behavior can be demonstrated on TiO₂ which is often used as a model material showing the behavior typical for n-semiconductors. Although the majority of the papers published on the (photo)electrocatalytic behavior of the TiO₂ polymorphs disregards the surface orientation or details of the electronic structure, TiO₂ remains the best understood n-semiconductor as far as the intrinsic properties are concerned. The titanium dioxide surface chemistry affects its electronic structure and follows the pH of the adjacent electrolyte solution in a Nernstian way [6]. Keeping in mind the rich polymorphism of the titanium oxides, it needs to be stressed that particularly the anatase polymorph is a convenient material for electrocatalytic reductions given the position of the flat band potential which is just positive of the 0 V (in the reversible hydrogen scale). This makes the anatase available for a wide variety of
reduction processes including the hydrogen evolution [7, 8]. Despite scarcity of anatase single crystals connected with the fact that the anatase structure is stabilized with surface energy; there are several studies addressing fundamental behavior of the anatase single crystal surfaces. These studies are, however, confined to high vacuums [9, 10]; the studies related to the electrochemical behavior of these surfaces are, alas, infrequent [11–13]. The activity of anatase in reduction processes was in detail studied for hydrogen evolution [7], oxygen reduction reaction [14, 15] or reduction of nitrobenzene [16].

In regard to the carbon dioxide valuation, it is believed that the oxides may represent a new class of viable catalytic materials. Their activity and selectivity in these processes are so far unknown. Given the richness of possible products of the CO2 materials, their activity and selectivity in these processes are far unknown. Given the richness of possible products of the CO2 reduction, it seems convenient to test the activity and selectivity of the model oxide catalyst on a system showing sufficient similarity to the CO2 reduction yet reducing the complexity of possible reaction pathways. Formaldehyde and its reduction can be recognized as one of such model systems given its presence among CO2 reduction intermediates; its concentration can be conveniently controlled in the electrochemical experiments [17].

Aside from polarographic studies of formaldehyde reduction which bear only limited relevance [18, 19], the formaldehyde reduction was also studied on polycrystalline copper yielding methane and ethanol [20]. There are no reports describing the reduction of formaldehyde on oxides and anatase in particular. The interaction of the anatase with formaldehyde vapors has been studied though in connection with gas sensor development [21]. This study concluded that formaldehyde adsorbs at the anatase surface marking it a promising material for gas sensors. Theoretical studies of this adsorption interaction showed that formaldehyde is chemisorbed on the anatase surface forming a dimethylene structure [21].

This paper extends previous studies and reports in a systematic manner the electrocatalytic reduction of formaldehyde on nanoparticulate anatase surfaces. The reduction of formaldehyde in aqueous solutions was studied on anatase surfaces with preferential {101} and {001} orientation. The electrochemical and on-line mass spectroscopic data describing the behavior of anatase in formaldehyde reduction and its competition with hydrogen evolution are compared with the behavior observed on polycrystalline copper.

**Experimental**

**TiO2 Anatase Synthesis**

Anatase with preferential {101} surface orientation was prepared by hydrothermal synthesis from water-soluble Ti peroxocomplex [22, 23].

Ti powder (Goodfellow 99.9%) was dissolved in hydrogen peroxide (30% w/w), Aldrich p.a. and NH3 (25%, Aldrich p.a.); citric acid (Aldrich p.a.) was added in equimolar amount to Ti solution as a complexing agent. The solvent was evaporated at 80 °C to form a yellow gel-like substance. The gel-like substance was dissolved in 60% (m/m) solution of ethylenediamine. The transparent solution was hydrothermally treated in a PTFE-lined stainless steel autoclave at 200 °C for 24 h. Resulting precipitate was filtered, washed with water, dried in air, and calcined at 400 °C for 4 h.

TiO2 with prevailing {001} surface orientation was prepared by hydrolysis of 20 mL of titanium(IV) butoxide (purum, ≥ 97.0%, Sigma-Aldrich) with 2.4 mL of hydrofluoric acid (48%; Sigma-Aldrich) under vigorous stirring. The mixture was treated in autoclave at 200 °C for 24 h. The product was washed with Milli-Q water and dried at 100 °C for 5 h. The as-received material contained between 6.5 and 20 wt% of F as determined by energy-dispersive X-ray spectroscopy (EDS) analysis. Calcination of the material at 500 °C for 1 h decreased the F content practically to zero.

The purity of synthesized samples was assessed by powder X-ray diffraction performed using Rigaku Miniflex powder X-ray diffractometer using CuKα radiation. The particle shape and size was evaluated by scanning electron microscopy (SEM) using Hitachi S4800 microscope equipped with energy-dispersive X-ray spectroscopy (EDX).

The surface orientation of the prepared photocatalysts was determined by analysis of high-resolution transmission electron micrographs (HRTEM). Transmission electron microscopy (TEM) and scanning TEM (STEM) was carried out on a JEOL JEM 2200FS microscope operating at 200 kV (autoemission Schottky gun, point resolution 0.19 nm) with an in-column energy filter, a HAADF detector, and an EDX silicon drift detector Oxford Instruments X-Max attached. Images were recorded on a Gatan CCD camera with resolution 2048 × 2048 pixels using the Digital Micrograph software package [8].

**Electrode Preparation**

The TiO2 (anatase) electrodes were prepared on Ti mesh (Goodfellow, 20% open area) pre-etched in HClO4 (18% w/w) by drop casting method. TiO2 suspensions in absolute ethanol (10 g/L) were prepared by sonication for 1 h. TiO2 (anatase) samples were deposited on the substrate in a step-wise manner when 10 μL increments of suspension were dropped on the etched Ti substrate. The deposited layer was dried at 80 °C for 10 min after each increment. Procedure was repeated until the mass of the anatase layer reached 1–2 mg. The deposited anatase layers were stabilized by annealing at 400 °C in air for 4 h.

The polycrystalline copper mesh (Goodfellow, 37% open area) was used as a working electrode for comparative
measurements. The copper mesh was pre-treated in 5% (w/w) H₃PO₄ at a potential of +1.8 V vs RHE for 1 min prior to formaldehyde reduction experiments.

**Electrochemical Experiments**

The formaldehyde reduction was studied in the stationary and flow-through arrangements using 0.02 M formaldehyde (36.5–38%, Sigma Aldrich) in 0.1 M KHCO₃ (Sigma-Aldrich) solution in Millipore Milli-Q quality water. The solution was purged with Ar prior to the experiments.

All electrochemical experiments were performed in combination with on-line mass spectroscopic detection of volatile reaction products (differential electrochemical mass spectrometry – DEMS approach). One compartment Kel-F cell with anatase (or copper) working electrode and Pt and Ag wire as an auxiliary and reference electrode, respectively, was employed in static arrangement. The potential was controlled by PAR 263A potentiostat. The measured potentials were recalculated and are quoted in reversible hydrogen electrode (RHE) scale. The electrochemical reduction of formaldehyde was studied in potentiostatic mode at potentials ranging from −0.21 to −1.11 V vs. RHE. In all experiments, the OCP potential was firstly applied for 2 min to establish a steady state. The formaldehyde reduction was subsequently performed at a constant pre-set potential. The reduction step lasted for 2 min in stationary cell and was reduced to 30 s in the flow-through cell experiments.

Schematic representations of stationary and flow-through cells are shown in Fig. 1. The DEMS apparatus consisted of a Prisma QMG220 quadrupole mass spectrometer (Balzers) connected to a HiPace 80 turbomolecular drag pumping station (Balzers). Electrochemical cell was connected to DEMS apparatus via PTFE membrane with 0.2 μm pore size (Sartorius Stedim Biotech).

To complement the DEMS approach in product detection, a long-term electrolysis combined with subsequent IR (Nicolet, iS50 FTIR, Thermo Scientific) analysis was employed. The electrolysis was performed at a constant potential (−0.71 V vs RHE) in a single compartment cell with 1.6 mL of 20 mM formaldehyde in 0.1 M KHCO₃. The typical charge recorded during the electrolysis was 3.6 C. After electrolysis, the solution was analyzed in the following way. Fifty μL of solution after electrolysis was mixed with 2 mL of acetonitrile, and the mixture was injected into a thin layer cuvette placed in IR spectrometer.

**Processing of DEMS Signals**

To avoid ambiguity resulting from an overlap of the fragments present in mass spectra of formaldehyde and expected reaction products, we have adjusted the measured DEMS signal with m/z of 29 to compensate for its presence in the mass spectrum of methanol. The contribution of methanol to measured signal with m/z of 29 was calculated from the DEMS signal with m/z 31 (which does not interfere with other compounds expected in the system) using known fragmentation of methanol obtained by calibration on our experimental setup. This contribution was subtracted from the raw values recorded on DEMS channel of m/z of 29 to obtain the characteristic signal following formaldehyde consumption.

**Results and Discussion**

**Material Characterization**

The reduction of formaldehyde was studied on two types of nanocrystalline TiO₂ anatase featuring different surface orientation. Both types of nanocrystalline anatase were crystallographically phase-pure. The powder diffraction patterns and
SEM images of both samples are shown in Fig. 2. While both diffraction patterns show all reflections characteristic for anatase polymorph of TiO$_2$, there is a slight difference in the relative intensities of the individual reflections which indicates a change in the preferential growth of the nanocrystals. The diffraction pattern of the platelet-featuring anatase material shows suppressed intensity of the (004) reflection compared to needle-like anatase nanocrystals. The suppression of the (004) reflection indicates the crystals are truncated in the direction of the $z$ axis which identifies the exposed platelet terminating faces as perpendicular to the $z$ axis. The majority of the exposed surface therefore should conform to $\{001\}$ surface orientation. The same surface orientation was also confirmed by the HRTEM analysis (see Fig. 3). The diffraction pattern observed for spindle-like particles does not show any deviation from the randomly grown anatase and does not provide any base for the surface orientation. The dominating surface orientation can still be determined from HRTEM data as it is shown in Fig. 3 and as was in detail explained in reference [8]. The HRTEM analysis found the surface of spindle-like anatase to be formed mainly by $\{101\}$-oriented facets. The individual nanocrystal orientation based on combination of XRD and HRTEM can be used also as a fundament of the preferred orientation of the electrodes based on the synthesized nanocrystals. Since the SEM of the prepared electrodes does not suggest any preferential arrangement of the crystals in the electrodes, it is reasonable to assume that the surface representation on the individual nanocrystals does not deviate significantly from that of the entire electrode surface. It is difficult to verify if this preferred surface orientation is preserved at the conditions of the electrocatalytic experiments, yet the reproducibility of the electrochemical behavior independent of the electrodes history suggests that their surface orientation remains unchanged.

**Formaldehyde Reduction**

**Static Cell**

As can be expected for the n-semiconducting materials, the anatase electrodes show electrochemical activity at reduction potentials when the applied potential lowers below the flat band potential ($E_{fb}$). The flat band potential of anatase single crystals has been reported to be $-0.084$ V vs RHE for $\{001\}$-oriented or $-0.1$ V vs RHE [8] and $-0.024$ V vs RHE for $\{101\}$-oriented anatase orientations [12]. Although $E_{fb}$ is pH dependent, it remains constant in reversible hydrogen electrode scale (RHE). Stepping the electrode potential to potentials negative to $E_{fb}$ triggers immediate cathodic current response. The current response at constant potential (see Fig. 4a) decreases with time and reaches a steady state value after 10–15 s. The cathodic current is accompanied with a DEMS signals attributable to formaldehyde removal from the system (see curve of the fragment with m/z of 29 in Fig. 4a). (See the details of the DEMS data processing given in the Experimental Section). The apparent formaldehyde consumption is matched by DEMS signals of fragments characterized by m/z = 2, m/z = 31, and m/z = 15 attributable to electrode process products (see Fig. 4). To accentuate the specificity of the anatase cathodes, the data obtained on anatase TiO$_2$ electrodes were compared in Fig. 4a with data characteristic for polycrystalline Cu electrode. It also needs to be noted that the observed behavior may be in principle affected also by
a contribution from the Ti substrate. This behavior is, however, not significantly pronounced as shown in Fig. 4b.

While in the case of polycrystalline Cu electrode the DEMS-based signals of the formaldehyde consumption as well as those of the product formation follow immediately the cathodic current onset in the case of anatase-based cathodes, one observes a significant time-lag between the passage of the cathodic current and its reflection in the consequent chemical change in the DEMS signals, namely, in formaldehyde consumption. The time-lag between the onset of the cathodic current and detection of the chemical changes is the same for all fragments regardless of their possible assignment to individual reaction products. This time-lag at which the DEMS starts to reflect the reduction process is characteristic for the given surface orientation of the anatase material products as well as for the applied electrode potential. The time-lag of the reaction products formation is generally longer for the {001}-oriented surface and decreases with increasing overpotential regardless of the prevailing surface orientation (see Fig. 5). The observed time-lag can be also converted to the charge which needs to pass before reaction products can be detected shows a significantly different course for both anatase surface orientations. While in the case of the {101}-oriented surface the charge needed to drive the formation of the volatile reaction products is independent on the electrode potential in the case of the {001}-oriented anatase, the charge preceding the detection of the volatile products decreases with increasing overpotential and reaches a steady-state value only at potentials negative to $-1.0 \text{ V vs RHE}$.

The observed experimental trend outlines the complexity of the reduction processes on n-semiconducting oxides as, e.g., TiO$_2$. It needs to be born in mind that the titanium dioxide itself can be subject of reduction [16] leading to proton insertion into anatase structure to compensate for the lowered charge (Ti(IV) to Ti(III) reduction) in the cationic sublattice [24, 25]. It needs to be stressed that this process contributes to the overall cathodic current and does not yield any detectable (i.e., volatile) reaction product. This process has comparable driving force with conventional two-electron proton reduction to hydrogen and similarly as the hydrogen evolution is likely to cause an increase of the pH in the electrode’s vicinity. In fact, the observed delay of the hydrogen detection after the cathodic current clearly shows a competition between Ti(IV) to Ti(III) reduction and hydrogen evolution on anatase.
The proton insertion apparently prevails over the hydrogen evolution particularly at low overpotentials when the overall reaction rate is relatively low. The competition between both processes can be related to the availability of the adsorbed hydrogen at the surface which makes the indispensable intermediate in the hydrogen reduction reaction (HER).

The hydrogen adsorption at titania surfaces has been theoretically treated using DFT models [8] outlining striking difference of the hydrogen adsorption on \{101\}-oriented anatase with respect to adsorption on different surface orientations. While \{100\}- or \{001\}-oriented anatase adsorbs the hydrogen rather strongly suggesting the hydrogen evolution being controlled by energetically demanding hydrogen desorption, the \{101\}-oriented anatase, on the other hand, adsorbs hydrogen weakly leaving the control of the hydrogen production to relatively low surface concentration of the adsorbed hydrogen. It needs to be noted that the hydrogen adsorbed at the surface is also available for needed charge compensation of the Ti (IV) to Ti (III) reduction. The higher apparent extent of the Ti (IV) to Ti (III) reduction on \{001\}-oriented anatase is also

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![Fig. 4](image-url) # Springer

**Fig. 4** a The cathodic current and based DEMS signals for reactant and products of formaldehyde reduction triggered by a polarization of polycrystalline Cu, \{001\}-oriented anatase and \{101\}-dominated anatase to $-0.8$ V vs RHE. Experimental conditions: degassed 20-mM HCHO in 0.1 M KHCO$_3$, applied potential $-0.8$ V vs RHE, static cell. b Cyclic voltammograms of 20 mM formaldehyde in 0.1-M KHCO$_3$ on pre-etched Ti mesh (black curve) and on anatase TiO$_2$ \{001\} electrode (red curve). Experimental conditions: static cell, a scan rate of 10 mV/s...
augmented by the anisotropy of diffusion properties of anatase as shown, e.g., in Li diffusion experiments [26]. The ratio of the charges needed to observe MS detection of reaction products on {001}- and {101}-oriented anatase electrodes. The symbol assignment is given in the figure legend. Data were extracted from chrono-amperometric experiments. Experimental conditions: 0.1 M KHCO₃, static cell.

The potential-dependent mass spectroscopic signals with m/z of 2, 15, and 31 reflect that the electrode process includes, in addition to Ti (IV) to Ti (III) reduction, also at least two more cathodic reactions producing volatile and detectable reaction products. These reactions can be identified as hydrogen evolution (m/z 2) and alcohol formation (m/z 31). While both mentioned fragments can be assigned unequivocally to a definite reaction product, the remaining fragment with the m/z of 15 can in general originate from various organic compounds. Assuming that the formaldehyde consumption can be linked with formation of the methanol (m/z of 31), one needs to check if the fragment of m/z of 15 originates from fragmentation of methanol. This can be verified by comparing relative intensity of the signal of the m/z of 15 with respect to that of the methanol-related signal with m/z of 31 (see Fig. 6). As follows from Fig. 6, the {101}-dominated anatase yields the ratio of DEMS signals with m/z of 15 and 31, respectively, close to a theoretical value of 0.37. This ratio seems to be independent on the applied potential pointing indicating that the methanol is the only product of the formaldehyde reduction on {101}-oriented anatase. In the case of the {001}-oriented anatase, the m/z = 15 to m/z = 31 ratio seems to decrease with increasing overpotential. The characteristic ratio of the fragments with m/z of 15 and m/z of 31 starts to deviate from the value characteristic for methanol at −0.7 V and increases, namely, at −0.5 V. This trend apparently suggests possible formation of additional organic compounds at potentials positive to −0.6 V vs RHE. It needs to be noted that this coincides with the region where the charge needed to generate measurable amounts of volatile products on {001}-oriented anatase increases.

Although the methanol seems to represent the prevailing reaction product regardless of the used electrode material, its formation cannot be simply ascribed to direct reduction of formaldehyde. One needs to reflect the possibility of Cannizzaro-type disproportionation of formaldehyde resulting from local increase of pH in the electrode’s vicinity [27]. Assuming this type of formaldehyde disproportionation, one should expect a formation of formate along the methanol. Since the formate/formic acid cannot be detected using DEMS due to its low volatility, its formation needs to be proved by other experimental technique. Infrared spectroscopy could in general be used to prove the formation of formates. However, even the solutions subjected to long-term electrolysis were found to be formate-free (see Fig. 7). Formate anion is characterized by two pronounced absorption bands located at 1157 and 1182 cm⁻¹ [28] which are clearly missing in the spectra of the solution which was subject of the long-term electrolysis.

To firm establishing the reaction mechanism (and ruling or confirming the presence of Cannizzaro reaction), one may also run the formaldehyde reduction experiments in a flow-through cell where reproducible concentration and pH distribution in the cell can be expected and buffering effects of the bicarbonate/carbonate equilibrium may be neglected.

![Fig. 7](image-url)
Flow-Through Cell

The formaldehyde reduction on anatase cathodes in a flow-through arrangement shows qualitatively similar trends as those observed in stationary cell. The DEMS signals reflecting the formation of the cathodic products on anatase again show a time-lag with respect to the onset of the cathodic current. This time-lag decreases with increasing overpotential; its magnitude is, however, significantly shorter than in the case of static cell and never exceeds 10 s. In contrast to the behavior observed in the static cell, one encounters a different time course of the DEMS-based signals reflecting different reaction products. The time-lag of the onset of the produced hydrogen (m/z of 2) behind the cathodic charge is shorter than those of the fragments reflecting the formation of the organic products (m/z of 31 and 15) of the electrode process (see Fig. 8a). It also needs to be noted that the lag of the hydrogen formation-related signal is more pronounced in absence formaldehyde.

The trends observed in experiments carried out in stationary and flow-through DEMS cells reflect the relationship of the individual cathodic reactions composing the overall electrode process. One may assume that the electrode process consists of electrocatalytic hydrogen evolution and formaldehyde reduction. The significant difference between time-lag observed for the hydrogen production in static and flow-through cells suggests that the competition between HER and proton insertion into anatase structure are further affected by the mechanism of the hydrogen evolution. One can consider two possible reaction sequences describing the hydrogen evolution:

\[
\begin{align*}
* + H^+ + e^- & \leftrightarrow *H \\
*H + H^+ + e^- & \rightarrow * + H_2
\end{align*}
\]

and

\[
\begin{align*}
* + H_2O + e^- & \rightarrow *-H + OH^- \\
*H + H_2O + e^- & \leftrightarrow * + H_2 + OH^- 
\end{align*}
\]

The first reaction sequence relies on presence of protons; the concentration of which is rather low and decreases with time, namely, in stationary cell. It may be, therefore, envisaged that the (limited) supply of protons (electrolyte solution pH > 9) in stationary cell gets exhausted relatively fast so the HER proceeds mainly by reaction sequence (3)-(4), which is, apparently, kinetically less favored. The situation gets altered in flow-through arrangement when the electrolyte composition change is much less pronounced, and the system can sustain the more facile reaction sequence (1)-(2).

The data available from flow-through cell arrangement also suggest a competition between hydrogen evolution and formaldehyde reduction evidenced by a different time-lag of the DEMS signals attributable to formaldehyde reduction and that of HER (see Fig. 8b). This competition can be identified by blocking of the HER adsorption in the presence of formaldehyde.

![Figure 7](image_url) FTIR spectra of (a) initial solution of formaldehyde in 0.1-M KHCO₃ (b) standard 5-μM solution of formic acid in 0.1-M KHCO₃/ acetonitrile, (c) solution after electrolysis

![Figure 8](image_url) a The time course of DEMS signals with m/z of 2 and m/z of 31 recorded during potentiostatic formaldehyde reduction at −0.8 V vs RHE in flow-through cell. The experimental conditions: 20 mM HCHO in 0.1 M KHCO₃, applied potential −0.81 V vs RHE, the flow rate was 0.09 mL/min. b The potential dependence of time-lag of the mass spectroscopic signals of produced hydrogen for reductively polarized {001}–oriented anatase electrodes in presence and absence of 0.02 M formaldehyde. The symbol assignment is given in the figure legend. Data were extracted from chrono-amperometric experiments in 0.1 M KHCO₃ in flow-through cell at flow rate of 0.09 mL/min
As in the case of the stationary cell, also in the flow-through cell, methanol formation represents the dominant product of the formaldehyde reduction process on {101}-oriented anatase. Similarly, statistically significant over-stoichiometric ratio of the fragments with m/z of 15 and 31 with respect to that of methanol is observed on {001}-oriented surface, namely, at low overpotentials (see Fig. 9). Qualitative trend in the ratio of the fragments with m/z of 15 and 31 is qualitatively similar to that observed in stationary cell and suggests that formaldehyde reduction under these conditions transfers higher number of electrons than at higher overpotentials. Such a trend is not completely surprising since photocatalytic reductions transferring multiple electrons to the same target molecule were reported on anatase nanoparticles previously [5]. For instance, even quite stable CO₂ is reduced on anatase in 6 electron processes producing methane [5]. The photocatalytic experiments cannot be directly compared with conventional electrochemical experiments since the energy of the electron-transfer is controlled by the conduction edge position in the photocatalytic experiments. On the other hand, the band structure of anatase fixes the conduction band edge rather close to the E₁₈, so the energy at which the CO₂ reduction occurs in photocatalysis rather corresponds to more positive potential than explored in this work. The strong preference of the {101}-oriented anatase for methanol formation while {001}-oriented anatase maintains activity also for higher utilization of CO₂ can be tentatively linked with stronger hydrogen adsorption on {001}-oriented anatase which allows to form and maintain significant hydrogen surface coverage, namely, at low overpotentials.

The data gathered in flow-through cell also rule out the contribution of Cannizzaro-type disproportionation as the processes forming the methanol during electrochemical formaldehyde reduction. The prevalence of Cannizzaro disproportionation requires the amount of formed methanol to grow with growing hydrogen production which represents the main driver for an in situ pH increase in the system. The correlation of the methanol formation and hydrogen production can be expressed as a ratio of the DEMS signals with m/z of 2 (characterizing the evolved hydrogen) and of m/z 31 (describing methanol) (see Fig. 10). As follows from Fig. 10, the
formation of methanol decreases with increasing hydrogen production (i.e., with increasing pH) suggesting clearly that formaldehyde to methanol conversion is of heterogeneous nature.

Conclusions
The electrochemical reduction of formaldehyde was studied on anatase TiO$_2$ with differently oriented surfaces conforming to {001} and {101} orientation in static and flow-through DEMS cells. Regardless of the arrangement, the formaldehyde is reduced to methanol on TiO$_2$ anatase. While at the {101}-oriented anatase one observes mainly a formation of hydrogen to accompany the methanol production, the {001}-oriented anatase retains ability for a transfer of more than one electron in reduction of formaldehyde, namely, at low overpotentials. Overall activity of the {001}-oriented anatase in formaldehyde reduction exceeds that of the {101} orientation. The reduction of formaldehyde on anatase surfaces is apparently hindered by several other processes. The first competitive process preventing formaldehyde reduction is the reduction of electrode material itself, when Ti(IV) is reduced to Ti(III). This process demonstrates itself as a time delay of spectroscopy-based signal of product formation before Ti(III). The other competitive process was identified as cathodic H$_2$ evolution. The hydrogen evolution can proceed either by proton discharge or by water reduction. It can be shown that the water reduction represents the main mechanism of the hydrogen evolution unless the reduction proceeds under controlled convection conditions. The difference in hydrogen adsorption strength on {101}- and {001}-oriented anatase surfaces is most likely responsible for different activity and selectivity of both anatase surface orientation in the formaldehyde reduction. The formaldehyde conversion into methanol may be triggered also by Cannizzaro disproportionation initiated by the local pH increase. The presence of the Cannizzaro reaction was not, however, confirmed.

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