

ELECTROSTATIC FIELD EFFECTS ON INTERMEDIATES OF CATALYTIC SURFACE REACTIONS

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Abstract

Pulsed Field Desorption Mass Spectrometry (PFDMS) has been applied to investigate reaction intermediates and products of "field sensitive" catalytic surface reactions.

During the reaction of methanol with single crystal planes of Ru and Rh ($T = 300 \dots 700 \text{ K}$, $p \approx 1,3 \cdot 10^{-5} \text{ Pa}$) field desorption mass spectra contain the parent ion, CH_3OH^+ and product ions, CO^+ , H^+ , H_2^+ as well as reaction intermediates COH_x^+ ($x = 1, 2, 3$). The initial dissociation of CH_3OH on Ru and Rh forms adsorbed CH_3O -species. The electrostatic field stabilizes COH_x -structures ($x = 1 \dots 3$), decelerating the catalytic surface decomposition to final products.

The interaction of NO with Pt(111)-planes normally leads to a non-dissociative chemisorption structure which can be reversibly desorbed. Electrostatic fields, $F_R > 4 \text{ V/nm}$, cause field induced surface dissociation. The products N_2O^+ , N_2^+ and O^+ are observed. Similarities with the behaviour of K-covered Pt(111)-planes are thus observed.

1. Introduction

The "electronic factor" in heterogeneous catalysis has been discussed, since G.-M. Schwab [1] observed an influence of the electron density in alloy catalysts on their catalytic activity. Early attempts to influence catalytic surface reactions by applied electrostatic fields failed, since available field intensities were insufficient [2]. In Pulsed Field Desorption Mass Spectrometry (PFDMS), external electrostatic fields can be altered continuously up to values beneath the desorption field strength, and influences on surface reactions can be studied.

For "field sensitive" reactions, intermediate surface structures of a catalytic reaction may either be stabilized or destabilized - retarding or promoting the reaction. The present communication gives examples for both cases.

2. Experimental

The experimental technique of PFDMS and its applications to kinetic studies of surface reactions have been described in detail elsewhere [3,4]. The principle of operation is to field desorb adsorbed species by means of high-voltage pulses and to chemically identify the respective ions by time-of-flight mass spectrometry. The field pulses (repetition frequencies up to 100 kHz, amplitudes up to $\approx 19 \text{ kV}$, half widths some 100 ns) are applied to a counter electrode (with a hole, 1mm diameter) in front of the Ru - or Rh - field emitter. A channel plate image intensifier with a probe hole is mounted at the entrance of the flight tube and allows field electron microscopy at reversed fields. The emitter can be tilted so that ions desorbing from different surface planes can enter the flight tube through the probe hole. The monitored area contains about 150 surface sites.

Experiments are performed with a continuous impact of CH_3OH -molecules (E-Merck, p.a. grade) and CHD_2OH (MSD Isotopes, 98.6 atom % D). The impinging molecules

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accumulate at the surface during the time interval, t_R , between the pulses. The next high-field pulse desorbs the adlayer and analyses its composition in a quantitative manner. Adsorption proceeds as t_R increases. The adsorbing particles can undergo a chemical reaction so that various intermediates and products form in the adsorbed layer. Kinetic information on these processes are obtained by varying t_R in a range of $t_R = 100 \mu\text{s} \dots 1 \text{ s}$.

An arbitrary field strength, F_R , between the pulses is applied in order to investigate the influence of the electrical field on the surface processes.

3. Methanol Decomposition on Rhodium and Ruthenium

The decomposition of methanol on Rh(100)-, Ru(001)-orientated emitters was studied. Both undeuterated, CH_3OH , and partially deuterated, CHD_2OH , were used in the experiments.

In the absence of a steady electric field between the pulses, the main species detected on rhodium were CH_3^+ , CO^+ , and H_n^+ ($n=1,2$). Smaller signals of H_yO^+ ($y = 0 - 3$), $\text{Rh}(\text{CO})_2^{2+}$ and $\text{Rh}(\text{CO})_3^{2+}$ may be detected.

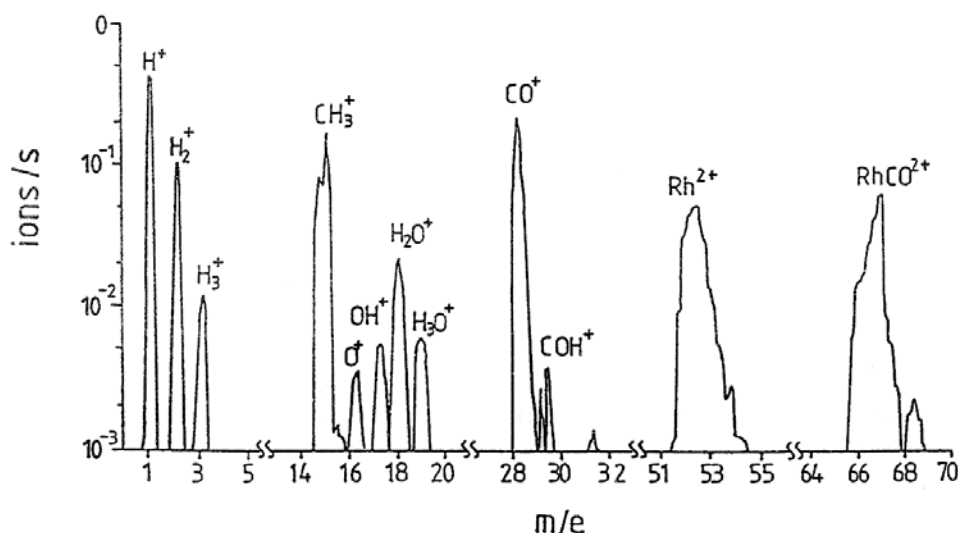


Fig 1 Mass spectrum of field desorbed ions from CH_3OH adsorbed on a rhodium tip in the absence of a steady electric field. $F_D = 26 \text{ V/nm}$, $t_R = 1 \text{ ms}$, $T = 298 \text{ K}$, $p = 1.3 \times 10^{-5} \text{ Pa}$ (Logarithmic intensity scale).

The mass spectra obtained were very different when a steady electric field was applied during the reaction. In the presence of fields above 2 V/nm , ionic intermediates of the methanol decomposition, COH_x^+ ($x=1 - 3$) and CH_3^+ as well as the parent molecular ion CH_3OH^+ , could be seen (Fig. 2a). Since the dipole moments of the different neutral species, COH_x have different magnitudes, an influence of the electric field on their surface concentrations is to be expected.

In order to avoid any ambiguities in the mass assignments of the different species, CHD_2OH was used in some of the measurements. Fig. 2b shows a mass spectrum taken at $F_R = 4 \text{ V/nm}$, where the prominent peaks were located at a.u. 17, 31 and 32; this corresponds to CHD_2^+ , COHD^+ and COD_2^+ (the latter two being deuterated isomers of COH_2^+). This experiment allows mass 15 to be correctly identified as CH_3^+ and not COH_2^{2+} ; and mass 30 has to be COH_2^+ and not C_2H_6^+ .

In order to check the dependence of methanol decomposition on the electric field, measurements were performed at various steady electric fields. During these measurements, a high desorption field strength, F_D , of 28 V/nm was maintained. Under these conditions, the adsorbed layer was quantitatively desorbed by the field pulses.

Fig. 3 shows the results from measurements using $1.3 \times 10^{-5} \text{ Pa}$ CH_3OH at 298 K with a

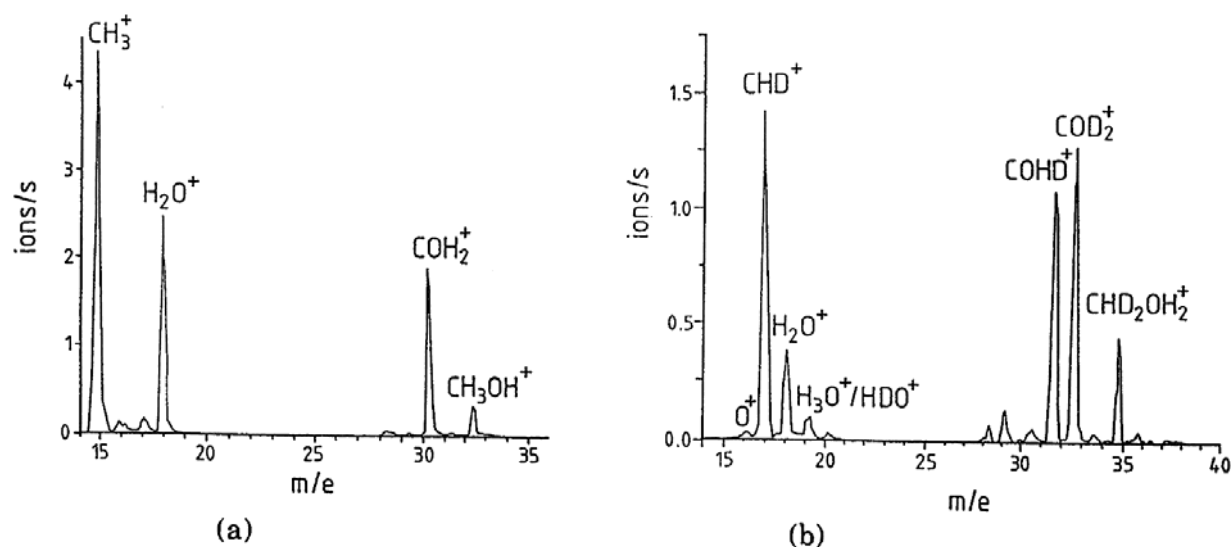


Fig. 2. Mass Spectrum of field desorbed ions in the presence of a steady electric field, $t_R = 4 \text{ V/nm}$, from: (a) CH_3OH , $t_R = 1 \text{ ms}$ (b) CHD_2OH , $t_R = 250 \text{ } \mu\text{s}$. $T = 298 \text{ K}$, $p = 1.3 \times 10^{-5} \text{ Pa}$, $F_p = 24 \text{ V/nm}$ (linear intensity scale)

high pulse repetition frequency of 4000 Hz. The various ionic species differed in their dependence on the steady reaction field, F_R . The field-free ($F_R = 0$) decomposition reaction during $t_R = 250 \text{ } \mu\text{s}$ led to the formation of large amounts of adsorbed carbon monoxide and hydrogen which were desorbed as CO^+ and as H^+ and H_2^+ respectively. The intensity of the CO^+ was approximately one quarter the $\sum n\text{H}_n^+$ ($n = 1, 2$) ion count, in accordance with the overall stoichiometry of methanol decomposition. Moderate intensities of CH_3^+ and H_2O^+ were also observed at low F_R ; COH^+ and $\text{Rh}(\text{CO})_2^+$ were detected only in small amounts under these conditions while COH_2^+ ions were absent from the mass spectra.

At higher reaction fields, $F_R \cong 2 \text{ V/nm}$, the intensities of CO^+ and H_n^+ started to drop while those corresponding to the reaction intermediates increased. In particular, COH_2^+ was formed and its intensity increased steeply. At high F_R values ($F_R \cong 4 \text{ V/nm}$), the mass spectra were dominated by CH_3^+ , H_2O^+ and COH_2^+ ions as seen in Fig. 2a. The intensities of all other species were considerably lower and tended to level off. Under these conditions, the chemisorbed carbon monoxide was preferentially desorbed as RhCO_2^+ . The combined $\text{Rh}(\text{CO})_2^+$ and CO^+ intensities at high F_R were smaller than the CO^+ count rate at low F_R . On the other hand, the overall intensity of the detected ions increased with increasing F_R . This results from an enhancement of the impingement rate of the gaseous methanol, which being a polar molecule, is attracted into the inhomogeneous electric field at the tip.

From these results, it can be seen that a steady electric field reduces the rate of methanol decomposition and stabilizes the intermediate stages. Fig. 4 shows that different field strengths, F_R , are required, to stabilize the COH_2^+ species as the temperature is increased. At 298 K, COH_2^+ appeared at $F_R = 2.6 \text{ V/nm}$ respectively. The higher F_R required when the temperature was raised, is due to a higher rate of methanol decomposition. Obviously, the interaction energy of the polar adsorbates with the electric field constitutes an enhanced activation barrier for the decomposition reaction.

In a separate experiment, the field dependence of the back reaction $\text{CO}_{(\text{ad})} + x\text{H}_{(\text{ad})} \rightarrow \text{COH}_x(\text{ad})$ was tested. A mixture of carbon monoxide and hydrogen ($P_{\text{CO}} = 1.3 \times 10^{-6} \text{ Pa}$, $P_{\text{H}_2} = 1.3 \times 10^{-5} \text{ Pa}$) was admitted and a steady field between 0 and 10 V/nm was applied. No COH_2^+ nor CH_3O^+ species were observed even at high F_R . A small signal of COH^+ (<4% of CO^+) was seen at $F_R = 0 \text{ V/nm}$. Its intensity remained constant within the range of F_R values studied (compare with Fig. 3). Hence it can be concluded that a field-induced formation of COH_x species ($x = 1 - 3$) from adsorbed carbon monoxide and adsorbed hydrogen does not occur and that all COH_x^+ ions detected are truly intermediates of methanol decomposition.

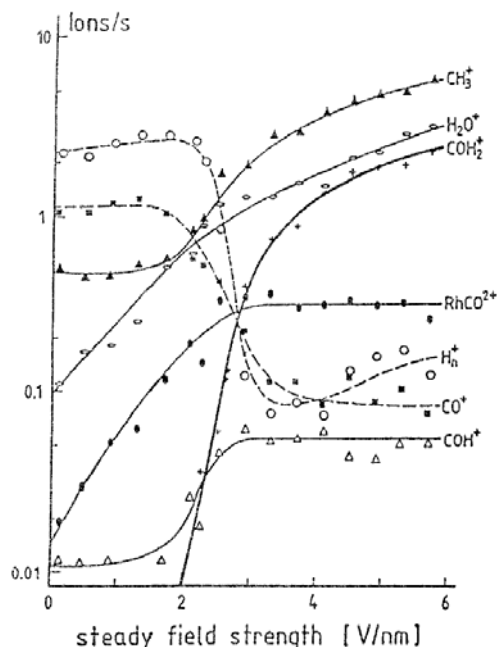


Fig. 3 Variation of the steady electric field, F_R , during the reaction interval, $t_R = 250 \mu\text{s}$.
 $F_D = 28 \text{ V/nm}$, $T = 298 \text{ K}$, $p = 1.3 \times 10^{-5} \text{ Pa}$.

An interesting observation was made in the course of experiments using CHD_2OH on rhodium where relatively intense peaks at the masses 1, 2 and 5 are assigned to H^+ , H_2^+/D^+ and HD_2^+ . The remarkably high intensity of HD_2^+ strongly suggests a field-induced cleavage of bonds in the CHD_2O species.

We now compare our results with earlier investigations on ruthenium [5]. Besides stabilizing the intermediate stages of methanol decomposition, the electric field can also induce bond cleavage. In the temperature range from 300 K to 460 K, equal ion intensities of CH_3^+ and oxygen in the ruthenium oxides - RuO^+ , RuO_2^+ , RuO_2^+ - were observed, indicating that these species are formed from the adsorbed methoxy. It is known from EELS work [6] that methoxy binds to the surface of ruthenium via the oxygen atom with a decrease in the work function. This suggests a net electron transfer from the CH_3 group to the metal. Thus, under the influence of a positive electric field, the resulting surface dipole is stabilized. The desorption pulses may cleave the $\text{CH}_3\text{O-Ru}$ surface bond to form CH_3O^+ as well as the $\text{CH}_3\text{-O}$ bond, resulting in CH_3^+ . Indeed, both species are detected. CH_3^+ is approximately 100-times more abundant than CH_3O^+ , but this ratio is independent of temperature, which proves that they are formed from the same surface species. The high intensity of the CH_3^+ shows that the steady decomposition of the methanol is impeded by the presence of adsorbed carbon monoxide which could not be removed even by the highest desorption field pulses.

However at temperatures above 460 K, the CH_3^+ intensity decreased. This is interpreted in terms of a "blocking model" where at temperatures above 460 K, carbon monoxide thermally desorbs and no longer blocks sites for methanol decomposition. Hence, the steady decomposition of methanol can proceed and the methoxy concentration decreases.

4. NO Decomposition on Pt(111)

Measurements of adsorption and thermal desorption of NO on various planes of a platinum field emitter gave the result that dissociative adsorption or decomposition of NO on Pt(111), even in the stepped region near the (111), could not be observed at room temperature.

However, applying a steady electric field $F_R > 4 \text{ V/nm}$ caused rapid decomposition of the NO molecules.

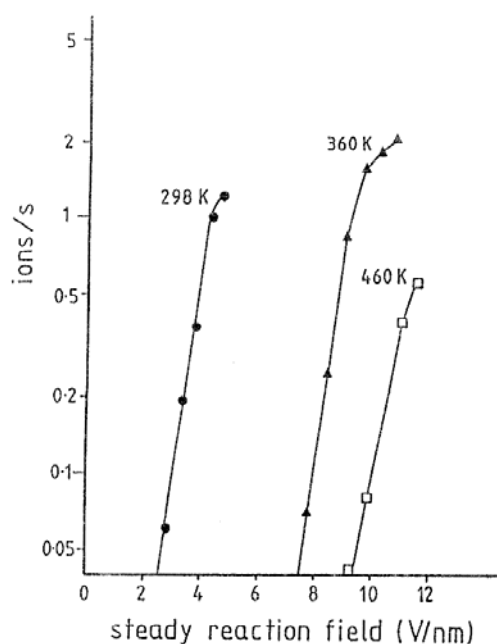


Fig. 4 Steady field strength dependence of COH_2^+ desorption at different temperatures, $t_R = 250\mu\text{s}$, $p = 1.3 \times 10^{-5}\text{Pa}$ for measurements at 298 and 360 K; $p = 5.2 \times 10^{-5}\text{Pa}$ for measurements at 460 K.

The results are displayed in fig. 5. The stepped Pt(111) surface region was probed. Without a reaction field, F_R , only NO^+ desorption occurred (besides some field evaporation of the substrate material).

In the lower steady field range only NO^+ ions are detected. At moderate fields, however, various other species, N_2O^+ , N_2^+ and O^+ , appear additionally. The intensities of these species increase steeply with rising F_R values. The onsets for N_2O^+ and O^+ desorption are coincident at $F_R \approx 4 \text{ V/nm}$, the N_2^+ ions come up somewhat later. The intensities of N_2O^+ are observed to reach about the same level as those of NO^+ for small F_R . Further augmentation of the field strength is associated with decreasing NO^+ rates. Both N_2^+ and O^+ intensities increase continuously within the measured range of F_R values, however, the O^+ ions are much less abundant.

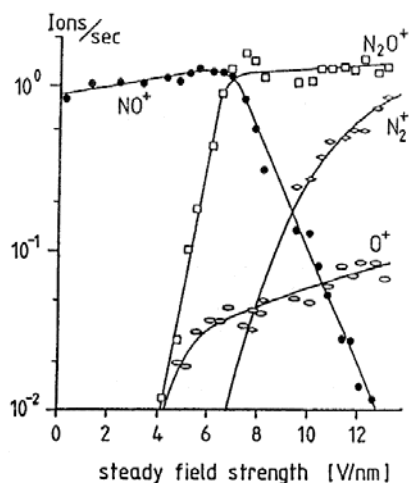


Fig. 5 Field induced decomposition of NO on Pt, measured on a stepped surface with (111) orientation of the terraces.

$F_D = 24 \text{ V/nm}$, $t_R = 10\text{ms}$, $p = 6.7 \cdot 10^{-5} \text{ Pa}$, $T = 298\text{K}$

The general result of fig. 5 is the field induced decomposition of NO. The chemical nature of the products and their high ionic intensities prove this process to occur in the adsorbed layer rather than in the gas phase near the surface where the field strengths are high, too. We note that the ionic traces remain essentially the same for increasing surface temperatures as long as there is no loss of NO_{ad} due to thermal desorption.

The surface oxide level in the monitored area is low as evidenced by the small O^+ ionic rates. This is unexpected in view of the stoichiometry of the field induced decomposition. Further investigations are currently performed in order to clarify this point.

The observed structure sensitivity of platinum in the decomposition reaction of NO is in accord with the known catalytic behaviour of the metal. While the stepped Pt(111) surface adsorbs NO only in its molecular form, the stepped Pt(100) surface also decomposes NO. Although step sites are generally regarded as active in N-O bond breaking we must conclude that this does not apply always. Banholzer et al. [7] developed a model in order to explain the plane to plane variations of the catalytic decomposition activity.

5. Conclusion

The results show the influence of the field in stabilizing the intermediate stages of methanol decomposition so that high amounts of CH_3^+ and COH_2^+ ions can be observed. To some extent, the field is able to counteract a faster reaction rate brought about by an increase in temperature. Furthermore, the field induces bond cleavage within the molecule, e.g., C-O bond breaking in the methoxy gives rise to CH_3^+ and adsorbed oxygen on the surface. The observation of H_3^+ (HD_2^+) suggests a concerted C-H (D) bond breaking from adsorbed methoxy. The oxygen left from the field cleavage reacts to form oxides in the case of ruthenium while on rhodium, it reacts with hydrogen from the methanol decomposition to form water which thermally desorbs below room temperature.

The field induced decomposition of NO over Pt presents another example for drastically changing chemical reactivities in high external electrostatic fields. Recently, Kiskinova et al. [8] reported the potassium promoted NO decomposition over macroscopic Pt(111) single crystal surfaces to produce nitrogen and oxygen as well as N_2O due to secondary reactions. The potassium, adsorbed as K^+ , is considered as an electronic promoter which transfers electrons into the antibonding 2π molecular orbitals of the adsorbed NO molecule. This leads to weakening of the N-O bond and, finally, to its scission. The field assisted NO decomposition cannot be explained by electronic effects only. The adsorption of NO is associated with an increase of the work function, thus there is a net electron transfer to the adsorbate. The electrostatic interaction of the resulting dipole with the (positive) external field may be associated with a bending of the molecule and its ultimate dissociation. Adjacent NO_{ad} species may associate during this process so that the detection of high amounts of N_2O^+ and N_2^+ becomes conceivable.

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