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The Flux Induced Switch in the Mechanism of the Catalytic Decomposition of  $\text{CH}_3\text{OH}$  on Ni Foil as Studied by MBRS and Time-Resolved PES

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#### Summary

By means of molecular beam techniques and photoelectron spectroscopy, time-resolved in the appropriate cases, the elementary mechanisms of the catalytic decomposition of  $\text{CH}_3\text{OH}$  on Ni foil are disclosed. Emphasis is given to the investigation of continuous flux of the reaction rather than of static co-adsorption. With low  $\text{CH}_3\text{OH}$  flux the sequence of consecutive H abstraction from the unruptured C-O bond is observed, leading finally to the formation of CO and  $\text{H}_2$  - consecutive or associative mechanism. With very high  $\text{CH}_3\text{OH}$  flux - realized by the full application of the intensity of the supersonic nozzle beam - number and chemical nature of the intermediate species are markedly augmented and changed: a sharp transition occurs from the consecutive mechanism to the multispecies or dissociative mechanism. The latter is characterized by immediate rupture of the C-O bond, formation of  $\text{CH}_3\text{ads}$  and  $\text{OH}_{\text{ads}}$ , and reactions leading to  $\text{CH}_4$  and  $\text{H}_2\text{O}$ , NiC and NiO. The intermediates are identified and the pattern of the reaction network is analyzed.

#### Introduction

In the present work emphasis is given to the study of the continuous flux rather than to static experiments of co-adsorption and pre-adsorption. CO and  $\text{H}_2$  are the products of the catalytic decomposition of  $\text{CH}_3\text{OH}$  on various metals as is manifested by a number of mechanistic studies using MBRS (1) or PES and TDS (2-5) and also recently time-resolved PES (6,7). On the other hand, in the 1 Pa region at about 200 K formation of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  is dominant (8); also industrial conversion of  $\text{CH}_3\text{OH}$  to  $\text{CH}_4$  on Ni catalysts is applied (9). The obvious difference in reaction pathways must be due to the different pressure regimes. Hence, the partial pressures used hitherto in studies of elementary mechanism are insufficient. The use of molecular beam techniques, in particular the application of a supersonic nozzle beam with high particle intensity, might lead to the high particle flux and the necessary surface concentrations in order to be able to observe intermediates and reactions taken for granted in higher pressure regimes with the analytical methods necessary in an investigation of elementary steps.

#### Experimental

The UHV apparatus used in this study has been described earlier (6,7). The Ni surface

mounted on a manipulator can be cooled to liquid nitrogen temperature and heated up to 850 K. The surface is controlled by UPS ( 21.21 and 40.81 eV ) and XPS ( 1486.6 eV ). Particles desorbing from the surface are monitored by a quadrupole mass spectrometer. The essential feature of the experiment is the admittance of the reactants by a molecular beam: either an effusion beam of small divergence and a maximum particle intensity of  $10^{12}$  particles/ $\text{mm}^2\text{s}$  ( about  $10^{-4}$  Pa ) is used (1,10,11), or a supersonic nozzle beam with  $10^2$  times higher particle intensity (12). The latter beam can be chopped with frequencies up to 100 Hz in order to perform MBRS and time-resolved PES (6,7). Most of the experiments are done in the following pattern: the PE spectroscopically controlled Ni surface is cooled down to below 90 K. Subsequently the  $\text{CH}_3\text{OH}$  beam is turned on. Then, with the beam continuously on, stepwise raised temperatures are adjusted up to 800 K and PE spectra are taken for the different constant surface temperatures. Under flux conditions, the mean coverage of the surface due to a distinct species is a function of the ratio of the pertaining rate constants of formation and degradation of the species. Because of the temperature dependence of the rate constants there are always one or more species with the proper lifetime in order to prevail in the spectra taken at a given temperature. Particular experiments are started at higher temperatures, sometimes proceeding to lower temperatures. Also, for reasons of comparison to other studies or in identification experiments, the common adsorption and co-adsorption technique is applied. In order to ascertain the products desorbing from the surface temperature programmed reaction spectroscopy ( TPRS ) is applied in flux and single exposure experiments as well; the rate of heating is 0.6 K/s .

## Results and Discussion

### 1. Two mechanisms

In dependence on the  $\text{CH}_3\text{OH}$  flux two different mechanisms of methanol decomposition are observed. The discrimination of the two mechanisms is possible from temperatures as low as 140 K to temperatures as high as 440 K. At temperatures above, the surface coverage is decreased to an extent that the second of the two mechanisms can no longer be maintained.

#### 1.1. Consecutive mechanism

When the surface is covered with  $\text{CH}_3\text{OH}$  by single exposure and likewise in experiments applying the weak flux of the effusion beam, with increasing temperature the well known sequence of consecutive hydrogen abstraction is observed, starting after non-dissociative adsorption of  $\text{CH}_3\text{OH}$  with the formation of  $\text{CH}_3\text{O}_{\text{ads}}$  and, after consecutive deprivation of the intact C-O bond of hydrogen, finally leading to CO and  $\text{H}_2$  (1-5,13, 14). A synopsis of the species formed and the regimes of dominance at the surface in a static experiment is presented in Fig. 1. The figure includes formation and desorption of reaction products observed by mass spectrometry performed either simultaneously to the PES or in separate TPRS experiments. In close resemblance to the spectroscopic results observed with Fe catalyst (7) the spectra of the various species are clearly printed and distinguished. The substantial difference to the mechanism on Fe is given

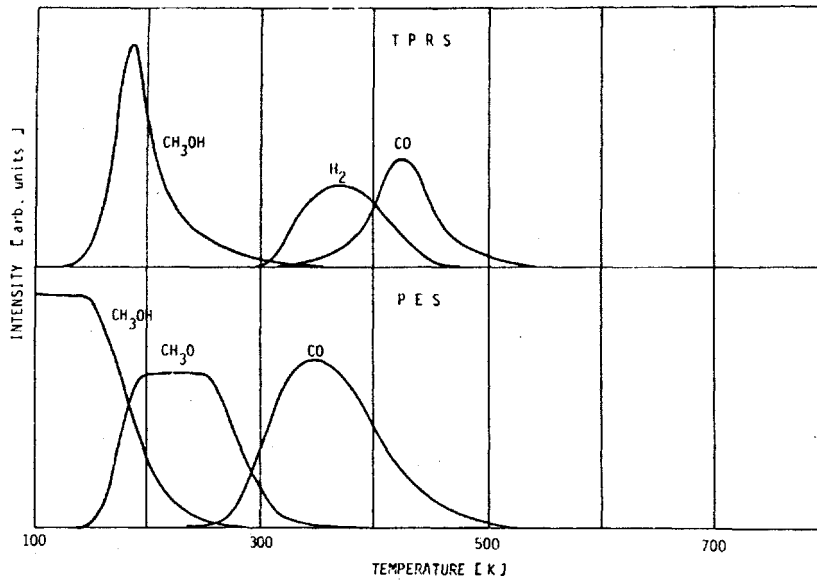


Fig. 1 Surface species and gaseous products of single exposure and low intensity beam experiments. The curves represent summarized results of different experiments.

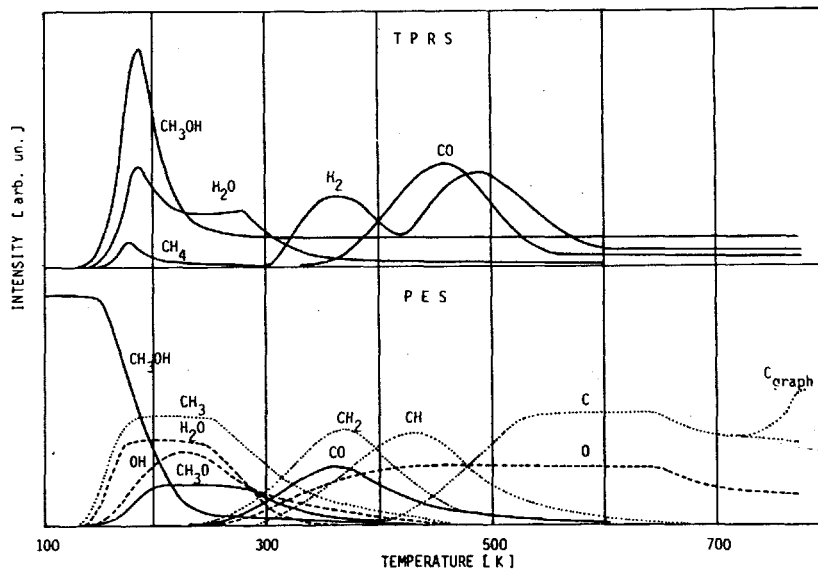


Fig. 2 Surface species and gaseous products of high intensity (supersonic nozzle) beam experiments. The curves represent summarized results of different experiments.

by the stability of the C-O bond throughout the reaction on Ni.

### 1.2. Multispecies mechanism

When the high flux of the full supersonic nozzle beam is applied to the Ni surface, even at temperatures as low as 140 K broad PES peaks, characteristic of the simultaneous generation of a variety of different surface species at the given temperature, are observed in UPS and XPS as well. The prevailing reaction is the dissociation of the C-O bond to form  $\text{CH}_3\text{ads}$  and  $\text{OH}_{\text{ads}}$ , also  $\text{H}_2\text{O}_{\text{ads}}$  is observed, accompanied by minor amounts of  $\text{CH}_3\text{O}_{\text{ads}}$ . A synopsis of the species formed and the regimes of dominance at the surface in a flux experiment with high beam intensity is given in Fig. 2. Likewise the figure includes the results of TPRS. The manifold of species as indicated by the intensive broad PES peak is maintained throughout the temperature range as high as 350 K. At temperatures above, desorption of CO is strong, hence the coverage with surface species is decreased. Furthermore, the H abstraction from  $\text{CH}_3\text{ads}$  is marked, leading to  $\text{CH}_{\text{ads}}$  and  $\text{C}_{\text{ads}}$ ; a similar abstraction from  $\text{OH}_{\text{ads}}$  leading to  $\text{O}_{\text{ads}}$  is observable. Finally, going to even higher temperatures as high as 700 K, there remain the atomic species only in close similarity to Fe (7) with a strong recombination reaction to form gaseous CO, accompanied by formation of NiC-like  $\text{C}_{\text{ads}}$  and NiO-like  $\text{O}_{\text{ads}}$ . No formation of  $\text{CO}_2$  was traced, hence a disproportioning of CO according to the Boudouard reaction (15,16) can be excluded. The essential feature of the multispecies mechanism is the early rupture of the C-O bond of  $\text{CH}_3\text{OH}$  forming  $\text{CH}_3\text{ads}$  and  $\text{OH}_{\text{ads}}$ . This is clearly to be distinguished from a dissociative reaction of  $\text{CO}_{\text{ads}}$  after loss of hydrogen.

### 1.3. Factors influencing the transition between mechanisms

Apart from flux intensity or partial pressure the transition from the consecutive to the multispecies reaction is influenced by several other parameters of the Ni catalyst. Enrichment of hydrogen in the Ni as achieved by additional hydrogen dosing via the effusion beam leads to the dominance of the multispecies mechanism even at moderate  $\text{CH}_3\text{OH}$  flux. Also very high surface roughness of the Ni favours the appearance of the multispecies reaction. On the other hand, the consecutive mechanism is dominant or even exclusively present when oxygen and/or carbon impurities are present in the Ni as may be the case after prolonged catalytic use in the multispecies reaction.

### 2. Identification and spectroscopic characterization of surface species

An unambiguous attribution of the observed PE spectra to the chemical formula of the surface species is obtained either by expansion of the catalytic decomposition over a wide temperature interval; this is possible, in particular, for the consecutive mechanism. Then, the dominance of one species on the surface is clear, its chemical nature is supported by the species previous or subsequent in the reaction sequence. This identification is not possible in the multispecies mechanism. Hence, a number of surface species are generated at the surface in separate experiments by admission via molecular beam or single exposure of those compounds which dissociate in two surface groups one of which is the species under study.

## 2.1. Consecutive mechanism

In the consecutive mechanism ( Fig. 1 ) the following species are identified: physisorbed and condensed methanol  $\text{CH}_3\text{OH}_{\text{cond}}$ , the chemisorbed species  $\text{CH}_3\text{OH}_{\text{ads}}$ ,  $\text{CH}_3\text{O}_{\text{ads}}$  in the flat lying position, and  $\text{CO}_{\text{ads}}$ . The electron binding energies referenced to the Fermi level are given in Table 1 together with the temperature regimes of dominance on the surface. The identification of the  $\text{CH}_3\text{OH}$  species is as usual by compari-

Table 1

PE spectroscopic data of species present in the consecutive mechanism  
( static experiment or very low flux intensity )

species	T regime [ K ]	$E_B^F$ [ eV ]				C1s		O1s	
		( 21.21 and 40.81 eV )				( 1486.6 eV )			
$\text{CH}_3\text{OH}_{\text{cond}}$	90 - 140	6.1	8.2	10.5	12.6	287.6	534.0		
$\text{CH}_3\text{OH}_{\text{ads}}$	90 - 160	5.5	7.1	9.5	11.6	287.3	533.0		
$\text{CH}_3\text{O}_{\text{ads}}$	160 - 290	5.2		9.2		286.7	532.6		
$\text{CO}_{\text{ads}}$	270 - 400		7.5		11.2	285.5	531.3		

son with the gas phase spectra (7,17); the difference between condensation in multilayers and adsorption in the monolayer is realized by different exposure time or thermodesorption of the condensed multilayers. Furthermore,  $\text{CH}_3\text{OH}_{\text{cond}}$  and  $\text{CH}_3\text{OH}_{\text{ads}}$  are distinguished by the different relaxation time of  $E_B^F=534$  eV and  $E_B^F=533$  eV in time-resolved PES. The spectra of  $\text{CH}_3\text{O}_{\text{ads}}$  and  $\text{CO}_{\text{ads}}$  are in accordance to the literature (3,18,19). The changes in work function of the covered surface support the geometric formulation of the species. Multilayer condensation of  $\text{CH}_3\text{OH}$  decreases the work function:  $\Delta\phi=-1.6\text{eV}$ . Due to desorption of  $\text{CH}_3\text{OH}$  and formation of the methoxy species the work function increases:  $\Delta\phi=+0.6\text{eV}$ . Prolonged observation of the methoxy covered surface gives rise to the observation of a gradual further increase of the work function (  $\Delta\phi=+0.3\text{eV}$  ) without any change in the peak area of the UP spectra. Hence, a geometric rearrangement of species must take place without alteration of the surface coverage and the chemical formula ( slight shift of  $E_B^F$  values ). This is attributed to the transition from standing to lying  $\text{CH}_3\text{O}_{\text{ads}}$ . Finally, the formation of  $\text{CO}_{\text{ads}}$  by dehydrogenation leads to an inversion of the surface dipole, the work function increases by  $\Delta\phi=+1.2\text{eV}$  and is now higher than the work function of the clean Ni.

## 2.2. Multispecies mechanism

In the multispecies mechanism ( Fig. 2 ) a large variety of species is identified:  $\text{CH}_3\text{OH}_{\text{cond}}$  and  $\text{CH}_3\text{OH}_{\text{ads}}$  as in the consecutive mechanism; in addition  $\text{CH}_3\text{ads}$ ,  $\text{CH}_2\text{ads}$ ,  $\text{CH}_{\text{ads}}$  and  $\text{C}_{\text{ads}}$  ( NiC ), furthermore  $\text{C}_{\text{graph}}$ ,  $\text{CH}_3\text{O}_{\text{ads}}$  and  $\text{CO}_{\text{ads}}$  are present as in the consecutive mechanism. New species are  $\text{OH}_{\text{ads}}$ ,  $\text{H}_2\text{O}_{\text{ads}}$  and  $\text{O}_{\text{ads}}$  ( NiO ). The electron binding energies referenced to the Fermi edge of Ni of these species are given in

Table 2. The very essential data of the various  $\text{CH}_n$  species are obtained by a group of experiments with  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  adsorption on the surface either by single exposure or by dosing with the weak effusion beam. By slowly increasing the temperature of the surface the event of dissociation into Cl and  $\text{CH}_3$  or  $\text{CH}_2$  respectively is scrupulously followed and the spectra of the generated  $\text{CH}_n$  species are taken prior to further degradation. Subsequently, the sequence of degradation to form  $\text{C}_{\text{ads}}$  is resolved (20).

Table 2

PE spectroscopic data of the additional species present in the multispecies mechanism ( experiment with supersonic nozzle beam )

$\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{O}$  and CO see Table 1

species	T regime [ K ]	$E_B^F$ [ eV ] ( 21.21 and 40.81 eV )	C1s	O1s ( 1486.6 eV )
$\text{CH}_3_{\text{ads}}$	160 - 400	6.5	285.8	
$\text{CH}_2_{\text{ads}}$	250 - 450	5.5 - 5.8	285.1	
$\text{CH}_{\text{ads}}$	290 - 500	5.2	283.8	
$\text{C}_{\text{ads}}$ ( NiC )	400 - 700	4.3	283.5	
$\text{C}_{\text{graph}}$	above 770	-	284.8	
$\text{OH}_{\text{ads}}$	160 - 400	5.5		530.8
$\text{H}_2\text{O}_{\text{ads}}$	160 - 300	6.5		532.6
$\text{O}_{\text{ads}}$ ( NiO )	270 - 800	5.5		530.0

### 3. Discussion of the mechanisms and of the causes of the transition

#### 3.1. Foundation of the multispecies mechanism

As is seen in Fig. 2 in the temperature range of 140 to 400 K a large variety of species is simultaneously present on the surface; the peaks characteristic of the single species merge into a very broad peak of up to 6 eV fwhm. Since almost any species composed of C, O and H could be incorporated in those peaks, the experimental supports for the identification of intermediate species must be given in some detail.

i) With rising temperature the intensity of the O1s peak decreases very sharply in comparison to the slower decrease of the C1s peak intensity. This behaviour is in clear distinction to the behaviour in a static experiment ( single exposure ), where both peak intensities decrease in parallel. Hence, the divergence between O1s and C1s intensity on the surface can be understood only by a dissociation of the C-O bond and an excess of desorption of O containing products over desorption of C containing products. Formation and desorption of  $\text{CO}_2$  is carefully checked and must be discarded.

ii) Already at low temperatures ( 170 K ) desorption of  $H_2O$  is observed (8,21); desorption of  $CH_4$  is present but with significantly lower intensity. From this a dissociation into  $CH_3_{ads}$  and  $OH_{ads}$  is rather straightforward; recombination of  $OH_{ads}$  with  $H_{ads}$  to form  $H_2O$  is faster than formation of  $CH_4$ .

iii) A very careful study of formation of further gaseous products, e.g.,  $CH_2O$ ,  $(CH_3)_2O$  or other hydrocarbons, does not show formation of such products, even in minor traces.

iv) Hence, a distinct enrichment of the surface with carbon must be postulated, which in fact is established by PES. The higher intensity in XPS rather than in UPS shows that a large amount of the carbon penetrates into the selvedge of the Ni.

v) As is seen in Fig. 2, apart from the desorption peak of  $H_2$ , well known from adsorption-desorption experiments of  $H_2$  on Ni (18,22), a second distinct  $H_2$  desorption is observed in the multispecies reaction with the maximum about 100 K above the common desorption peak. The second formation and desorption of  $H_2$  expands over a rather broad temperature region. It is attributed to the gradual dehydrogenation of adsorbed  $CH_3$ ,  $CH_2$  and  $CH$  species. This has been shown at temperatures above 400 K for  $CH_n$  species at Fe too (7,23).

vi) The broad multispecies peaks can be computed by superimposition of the peaks of the components, the agreement with the experimental UPS and XPS peaks is quite well. Of even higher significance is the close agreement of the shifts of the multispecies peaks to smaller binding energies with rising temperature: the peak measured at 170 K is equal to the superimposition of the signals of  $CH_3OH_{ads}$ ,  $CH_3O_{ads}$ ,  $H_2O_{ads}$ ,  $OH_{ads}$  and  $CH_3_{ads}$ . Due to the desorption capability of  $H_2O_{ads}$  the respective binding energy exhibits a relaxation response to the opening and closing of the nozzle beam, whereas the other parts of the UPS spectrum stay constant. The peak measured at 280 K equals the superimposition of the signals of  $CH_3O_{ads}$ ,  $CO_{ads}$ ,  $OH_{ads}$ ,  $CH_3_{ads}$  and  $CH_2_{ads}$ . The peak measured at 450 K equals the superimposition of the signals of  $CH_2_{ads}$ ,  $CH_{ads}$ ,  $CO_{ads}$ ,  $O_{ads}$  and NiC. Finally, the peak measured at 800 K equals the superimposition of the signals of NiO, NiC and  $C_{graph}$ .

### 3.2. Temperature limits of the multispecies mechanism

The flux experiments described hitherto were started at 80 K, followed by successive increase of reaction temperature. This procedure has the disadvantage that those species formed at low surface temperature which do not recombine to desorbing products because of insufficient surface coverage or energetic reasons are preserved and trapped at the surface into higher temperature regimes. In order to circumvent this limitations a number of additional experiments, either time-resolved at constant temperature, either starting at elevated and proceeding to lower temperatures, is performed by which the multispecies mechanism is further characterized. Also, the arguments thus gained give further support to the correlation of species and observed

superimposed PE signal.

i) As is seen in Fig. 1, no surface species are detected at temperatures above 550 K though decomposition to CO and H<sub>2</sub> still proceeds. The reduced reaction probability is due to the significant decrease of the sticking probability of CH<sub>3</sub>OH at elevated temperatures (1). Also with the high intensity beam between 750 and 550 K only the formation of CO and H<sub>2</sub> is observed; the Ni surface stays perfectly clean. By means of beam modulation, the sensitivity of detection of surface species is increased by about two orders of magnitude, however, even a modulation experiment does not exhibit any surface species. On the other hand, recombination and desorption of CO is observed in the temperature range between 650 and 800 K, when C<sub>ads</sub> and O<sub>ads</sub> are generated and stored at lower temperatures ( Fig. 2 ). But again, also with the C<sub>ads</sub> and O<sub>ads</sub> contaminated Ni surface further dissociative reaction of CH<sub>3</sub>OH is not observed; the trial to observe any time response of the C<sub>ads</sub> as is possible with Fe foil (7) is negative. In summary, at temperatures above 550 K on clean and on contaminated Ni surfaces the consecutive reaction only can be detected in the given pressure regime.

ii) At temperatures about 500 K only part of the broad multispecies peak offers a response to the opening and closing of the supersonic beam. This is observed with the high energy flank of the Cls peak; the peak contains CH<sub>2ads</sub>, CH<sub>ads</sub>, NiC and CO<sub>ads</sub>. The fast response of the flank is due to the throughway reaction pathway of CO<sub>ads</sub>, which is formed by dehydrogenation and consumed by desorption. The other parts of the peak do not respond since there is no further desorption outlet for the CH<sub>n</sub> species, once CH<sub>3ads</sub> is further decomposed. An equal observation holds for the high energy flank of the Ols peak; the peak contains the signals of O<sub>ads</sub> and CO<sub>ads</sub>. Hence, any fast bimolecular recombination of C<sub>ads</sub> and O<sub>ads</sub> to form CO can be ruled out in that temperature region. The results found with the flanks of the Cls and Ols peaks are likewise observed with E<sub>B</sub><sup>F</sup> = 7.5 eV in the broad multispecies peak in the UP spectra; the binding energy is characteristic for nondissociated CO<sub>ads</sub>. In conclusion, dissociation of CH<sub>3</sub>OH to form CH<sub>3ads</sub> and OH<sub>ads</sub> no longer takes place, the same is true for further reactions of the CH<sub>nads</sub> species. However, the reaction channel of associative dehydrogenation, though narrow, is still open.

iii) At 400 K the supersonic nozzle beam with highest possible intensity is opened towards the clean Ni surface. Within minutes the formation and the increase of coverage of CO<sub>ads</sub> is registered by UPS, whereas those energies characteristic of CH<sub>nads</sub>, OH<sub>ads</sub> and O<sub>ads</sub> are of minor intensity. Also the work function changes in the way typical for coverage of the surface with CO<sub>ads</sub>. After further observation of the surface with the beam continuously on, a decrease of the work function accompanied by a further increase of the CO<sub>ads</sub> coverage is observed. The decrease in work function is due to the parallel formation of CH<sub>nads</sub>, OH<sub>ads</sub> and O<sub>ads</sub> as shown by the UP spectrum. After closing the beam a rapid decay of the CO<sub>ads</sub> intensity is observed whereas the dissociatively formed species remain on the surface. At 300 K an equal experiment shows faster response; up to now the dissociative species cannot be distinguished by larger



time constants from the associative species. Temperature increase with the beam on leads to enrichment with C1s intensity and depletion of O1s intensity, i.e., desorption of  $H_2O$  and enhanced formation of  $CH_n$  ads. These experiments, in particular the slower evolution of dissociated species in comparison to undissociated  $CO_{ads}$ , suggest - apart from the establishment of the upper temperature limit for the multispecies mechanism - that the generation of hydrogen on the surface by abstraction from the undissociated species is a necessary presupposition for the inducement of the C-O bond dissociation. Since  $H_{ads}$  rapidly desorbs from the Ni surface at temperatures above 400 K (1), also in thermodesorption experiments 400 K is observed as the temperature of desorption of the strongest bound  $H_{ads}$ , e.g. (18,22), it is reasonable that the consecutive reaction still continues at higher temperatures as long as the sticking probability of  $CH_3OH$  is not zero, however, dissociation of the C-O bond of  $CH_3OH$  is no longer possible. This will be continued below.

iv) At 150 K time-resolved PES is performed at  $E_B^F = 533 eV$  (O1s of  $CH_3OH_{ads}$ ) (Fig.3). The fast decrease of the amplitude is the most remarkable result. It shows that the initially formed surface species  $CH_3O_{ads}$ ,  $CH_3_{ads}$ ,  $OH_{ads}$  and  $H_2O_{ads}$ , apart from the

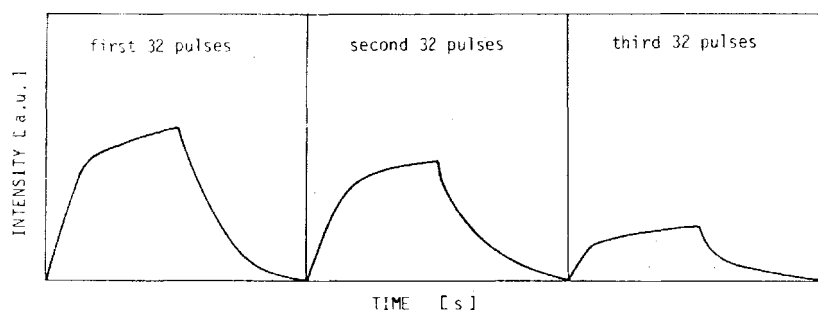


Fig. 3 Time-resolved PES at 533 eV. Four successive experiments. Each curve is the result of cyclic addition of 32 pulses of 50 s period. The fourth 32 pulses add up to a horizontal line.

desorbing  $H_2O$  do not react further at that temperature but block the surface. Due to simultaneous physisorption of  $CH_3OH$  the time-resolved signal ( first 32 pulses ) shows two distinct relaxation times: fast response of  $CH_3OH_{cond}$  ( flank of 534 eV peak ) and slow response of  $CH_3OH_{ads}$  ( maximum of 533 eV peak ). A time-resolved experiment at 534 eV shows the fast relaxation only, which is matched in TPRS. The blocked surface reduces the sticking probability of  $CH_3OH$  close to zero.

### 3.3. Effect of hydrogen

It is established that the experimental parameter that causes the transition between the two mechanisms is the intensity of the  $CH_3OH$  flux. However, it is not clear what is the chemical reason of the transition from the consecutive dehydrogenation of the associated C-O bond to the primary dissociation of  $CH_3OH$  into  $CH_3_{ads}$  and  $OH_{ads}$ ,

though a number of observations just outlined points to the decisive role of  $H_{ads}$ . This is further clarified in a number of experiments. In addition, the outcome of these experiments gives further insight into the inhibiting or promoting operation of residual species at the surface with respect to the catalytic flux (7).

The essential chemical reason for the dissociation of the C-O bond in  $CH_3OH$  is a high concentration of chemisorbed and dissolved hydrogen on the Ni surface. The solubility of hydrogen in Ni is smaller than in Pd though still higher than in other metals, in particular in polycrystalline Ni along the grain boundaries (24). The presence and decisive role of  $H_{ads}$  is shown by the following experimental results. Since in the multispecies mechanism even at the highest possible beam intensity there is always at temperatures between 160 to 290 K the formation of  $CH_3O_{ads}$  observed, though in inferior amounts, it is reasonable to assume, that the accumulation of this hydrogen in the Ni selvedge gives rise to the bond rupture in  $CH_3OH_{ads}$ . Hence, when the experiment is started at higher temperatures ( up to 800 K ) and continued to lower temperatures, the amount of hydrogen produced and stored in the temperature region between 160 to 400 K is not present and the share of the dissociative mechanism is decreased. Still, because of the high intensity and the low divergence of the  $CH_3OH$  beam, the generation of hydrogen on the Ni surface by abstraction from a minor part of the  $CH_3OH$  flux is the most effective method of H enrichment of the Ni selvedge. This is due - apart from the experimental limitations that do not allow for a hydrogen nozzle beam - mainly to the limited effectiveness of hydrogen enrichment when molecular hydrogen is offered to the surface because of the insufficient sticking of  $H_2$  in comparison to  $CH_3OH$ . However, the qualitative pattern of the multispecies reaction can be reproduced on a hydrogen enriched Ni surface: by the effusion beam  $H_2$  dosing is performed at the very pressure limit of operation of the PE spectrometer ( about  $10^{-5}$  Pa ). The Ni surface is heated to 600 K and cooled down slowly to 100 K in the  $H_2$  flux during 2 hours.  $CH_3OH$  then is adsorbed on the H enriched Ni in a single exposure, and the temperature raised stepwise as usual. No difference in the pattern of surface species in comparison to the consecutive mechanism ( Fig. 1 ) is detected up to room temperature. However, above room temperature a significant difference is observed: formation and desorption of  $CO_{ads}$  are less pronounced,  $CH_n$  species are traced on the surface. Furthermore, the final surface contamination with  $C_{ads}$  and  $O_{ads}$  above 450 K is detectable, whereas in the static or low intensity beam experiment started with a clean Ni surface ( without hydrogen ) the final surface above 550 K - after desorption of the associatively formed CO and  $H_2$  - is as clean as after Ar sputtering. The significance of the experiments just outlined is supported by an experiment with a low intensity  $CH_3OH$  beam and simultaneous  $H_2$  dosing: again, the share of the multispecies mechanism is increased with respect to equal beam intensity without  $H_2$  dosing. However, due to the pumping limitations no complete spectroscopic investigation over the total temperature range is possible under these conditions. The results just outlined are even more pronounced in equal experiments performed with the rough Ni surface as obtained after Ar sputtering without annealing.

The decision whether the hydrogen enrichment operates via an electronic bulk or ensemble effect or via chemical attack of the C-O bond in analogy to hydrocracking is not yet clear, however, arguments for an electronic interpretation seem to prevail. The d band population of the Ni surface close to the Fermi edge is markedly increased as is seen by comparison of PE spectra of clean, hydrogen enriched by dosing, and hydrogen enriched by multispecies reaction, surfaces. The residence time of the primary products  $\text{CH}_3_{\text{ads}}$  and  $\text{OH}_{\text{ads}}$  of bond cleavage is a further argument against hydrolysis of the C-O bond. These products are formed without hydrogen uptake, and their further reaction to form  $\text{CH}_4$  and  $\text{H}_2\text{O}$  is clearly separated from their generation at the surface. The appearance of  $\text{CH}_3_{\text{ads}}$  in principal opens up the reaction pathways known from Fischer-Tropsch synthesis, even more in the presence of  $\text{CO}_{\text{ads}}$ . However, apart from formation of  $\text{CH}_4$  no other characteristic products are found. Instead, a large part of  $\text{CH}_3_{\text{ads}}$  is further dehydrogenated and the final generation of NiC and  $\text{C}_{\text{graph}}$  is observed ( Fig. 2 ). The C deposit in either way leads to a significant alteration of the catalytic properties of the Ni surface. In fact, even under conditions favourable to the multispecies reaction, then the narrow pathway of consecutive dehydrogenation is observed. This is attributed to the inhibition of hydrogen adsorption and hydrogen uptake of the selvedge. The counterbalance of C contamination and H enrichment is seen in the narrow peak of the d band close to the Fermi edge, it is severely suppressed by C contamination.

#### Conclusion

It is established that the consecutive mechanism of the decomposition of  $\text{CH}_3\text{OH}$  on Ni ( stepwise dehydrogenation of the unruptured C-O bond ) switches to the dissociative mechanism ( primary dissociation into  $\text{CH}_3$  and OH ) upon drastic increase of the applied  $\text{CH}_3\text{OH}$  flux. The transition between the two mechanisms shows that any experimental results on elementary reactions, which are obtained with low covered surfaces, are to be extrapolated with great care if at all to higher pressure regimes. On the other hand, the example given opens up an experimental pathway in order to characterize surface intermediates and elementary reaction steps in a steady state operation situation of the catalyst under reactant flux several orders of magnitude higher than in co-adsorption experiments. In particular, time-resolved PES has the power to resolve the complex spectroscopic information. The results on the dissociative or multispecies mechanism contain further examples of the kinetic control of mechanism under steady state operation by surface species generated during an induction period ( hydrogen on Ni ). Hence, not the clean preparation but a self consistently contaminated system forms the operative catalyst.

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