The Influence of Chlorine on the Catalytic Decomposition of Methanol on Nickel Foil: Transition from Poison to Promoter upon Modification of Deposit

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The catalytic activity of a polycrystalline Ni surface with respect to the decomposition of CH_3OH is completely blocked by chlorine adsorbed as Cl_{ads}. CH_3OH adsorbs molecularly but desorbs without any trace of a chemical reaction. After Ar sputtering at 600 K and further heating at 700 K, Cl_{ads} is removed and the remaining chlorine is transformed into a nickel chloride. This comparatively small amount of nickel chloride is a promoter for the decomposition of CH_3OH. The reaction occurs according to the dissociative mechanism; CH_3O_{ads} dissociates to form CH_{3ads} and O_{ads}, while CO_{ads}, generated by dehydrogenation, dissociates to form C_{ads} and O_{ads}. Under equal conditions these reactions are not possible on a clean Ni surface. © 1985 Academic Press, Inc.

INTRODUCTION

Recent investigations of the elementary mechanisms of the catalytic decomposition of methanol on iron and nickel foils under steady-state flux conditions (*1–5*) have shown that kinetic control is influenced in a critical way by surface species present in a steady-state concentration which were generated during an initial induction period. This has been found for C_{ads} and/or O_{ads} on Fe (*1–4*) and for the enrichment of the Ni surface with H_{ads} (*5*). The conclusion is that the operative catalyst is formed by a self-consistently contaminated system but not by the clean preparation. Hence, the effect of poisons or promoters on elementary mechanisms should not be studied in static coadsorption experiments alone, as is often done, but the changes of valence, chemical bonding, and coordination at and in the surface, and even the incorporation of the chemical additives into the selvedge, need to be taken into account. An example of the different influence exercised by one additive according to its particular nature of incorporation or bonding is given in the present study, where we report on the effect of chlorine on the decomposition of CH_3OH on Ni foil.

It is well established that with clean Ni surfaces two different reaction patterns of CH_3OH decomposition can be observed depending on the flux intensity and/or the partial pressure of CH_3OH (*5*). With low CH_3OH flux the well-known sequence of consecutive H abstraction from the unruptured C–O skeleton is observed. The reaction starts with associative adsorption of CH_3OH, followed by formation of CH_3O_{ads} and further dehydrogenation of the undissociated C–O skeleton to form CO_{ads} and H_{ads}. CO and H_2 are the final products of this consecutive or associative mechanism. With very high CH_3OH flux the dissociative or multispecies mechanism is observed. This starts with the dissociation of CH_3OH_{ads} to form CH_{3ads} and OH_{ads}. Following reaction with H_{ads} bimolecular desorption of H_2O and CH_4 is observed; however, the majority of CH_{3ads} is further dehydrogenated and ends up as C_{ads}.

The reason for the transition from the associative to the dissociative mechanism is seen in the enrichment of the Ni surface with hydrogen due to the primary dehydro-

genation of CH_3OH in an induction period. Apart from the flux intensity of CH_3OH, enrichment of hydrogen in the Ni, as achieved by additional hydrogen dosing via an effusion beam directed toward the surface, leads to the dominance of the dissociative mechanism even at moderate CH_3OH flux. Also, very high surface roughness of the Ni favors the appearance of the dissociative reaction. On the other hand, the associative mechanism is dominant or even exclusively present when carbon and/or oxygen impurities are present in the Ni selvedge as may be induced after prolonged catalytic use in the dissociative reaction. In either case, the electron density close to the Fermi edge is observed in the photoelectron spectrum to be undisturbed or even increased for those Ni catalysts which catalyze the dissociative mechanism, and to be reduced for those Ni catalysts which catalyze the associative mechanism. The effect of chlorine is to be expected to interfere with these findings.

EXPERIMENTAL

The UHV apparatus has been described earlier (2, 6, 7). It is equipped with a supersonic molecular beam, an effusion beam, a surface manipulator able to cool the surface to liquid-nitrogen temperature and to heat it to 850 K, a quadrupole mass spectrometer, and a photoelectron (PE) spectrometer (UPS: 21.21 and 40.81 eV; XPS: 1486.6 eV). The experiments are done in the following sequence: the Ni surface is monitored by PES, cooled to liquid-nitrogen temperature, and subsequently covered with CH_3OH by a single exposure. Without further admission of CH_3OH stepwise raised temperatures are adjusted up to 800 K. Desorbing particles are analyzed by a quadrupole mass spectrometer, and surface species are analyzed at constant temperatures by PES. Experiments are performed with Ni surfaces contaminated by chlorine in two different modifications. No time-resolved or flux experiments (5, 6) have been performed so far on this problem.

RESULTS

1. Adsorbed Chlorine: A Poison for the Reaction

CH_2Cl_2 is adsorbed at or below room temperature. Upon admission to the surface the molecule is decomposed to form $CH_{2_{ads}}$ and Cl_{ads} at temperatures as low as 150 K (8, 9). Heating to 400 K removes $CH_{2_{ads}}$ completely, with formation of CH_{ads} and C_{ads}, followed by migration of C_{ads} into the bulk, as is shown by XPS. Finally, a surface is generated which is contaminated by a strong coverage with Cl_{ads}, characterized by a 5.8-eV peak in the UP spectrum, and traces of C_{ads} at the surface. The UP spectrum of the d band is uniformly reduced.

This surface is cooled down to about 90 K and CH_3OH is condensed at the surface. Four UPS peaks of condensed CH_3OH are observed. The exact peak maximum is dependent on the thickness of the multilayer condensation in close resemblance to the condensation of CH_3OH on a clean Ni surface; with increasing layer thickness, higher values of binding energy E_B^F are observed (5, 9).

At temperatures of 140 K and above the four well-known UPS peaks (5.8, 7.2, 9.6, 11.8 eV) characteristic of the monolayer of molecularly adsorbed CH_3OH are observed (Figs. 1a–c). The change in work function of the surface is equal to the change observed for CH_3OH adsorption on clean Ni: $\Delta\Phi = -1.5$ eV (5). In contrast to the results on clean Ni (Fig. 1a) (5), no chemical reaction is observed upon further increase of temperature. Instead, the four peaks decrease continuously and uniformly; finally, at 240 K, CH_3OH_{ads} can no longer be traced at the Cl_{ads}-contaminated Ni surface which emerges unchanged from the adsorption and desorption of CH_3OH (Fig. 1b). This result is in contrast to the chemical reaction observed with clean Ni and with C_{ads}-contaminated Ni as well. In those cases, formation of CH_3O_{ads} is observed as indicated by the generation of two peaks at 5.6 and 9.5
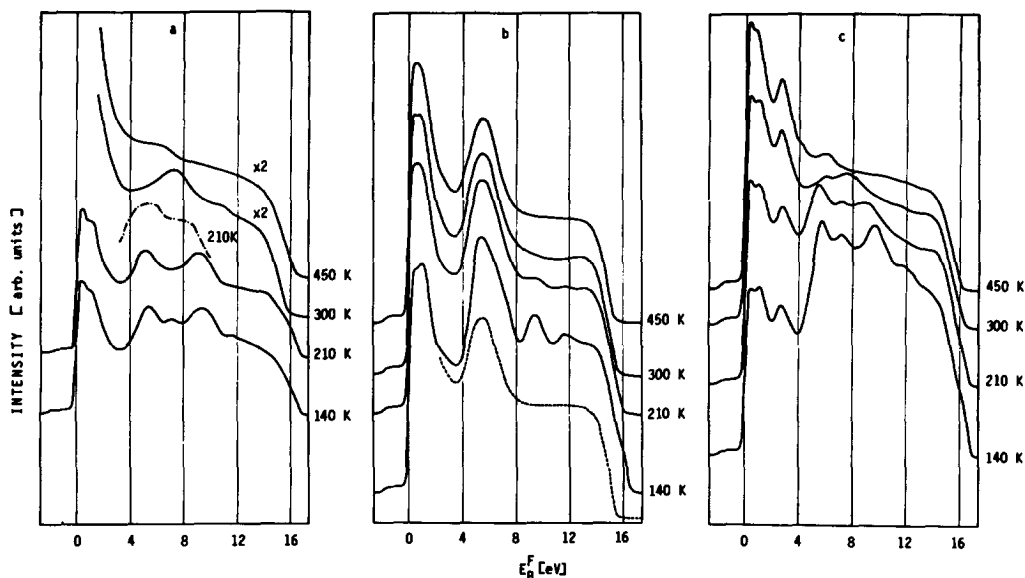
FIG. 1. Ultraviolet photoelectron spectrum (He(I), 21.21 eV) of adsorbed intermediates at different surface temperatures. (a) clean nickel, (b) Cl_{ads}-contaminated nickel, (c) nickel chloride-contaminated nickel. The dashed-dotted spectrum in (a) shows the intermediate on a clean but very rough Ni surface (5). The dotted spectrum in (b) shows the clean catalyst (Cl_{ads} on Ni) before admission and adsorption of CH_3OH.

eV together with the appropriate changes in work function at temperatures of about 160 K (5).

The UPS results are confirmed by XPS (Fig. 2), with E_B^F remaining at the values of CH_3OH_{ads}: O $1s = 533$ eV; C $1s = 287.3$ eV (5). The decrease of peak intensities with increasing temperature is uniform and no O- or C-containing species other than CH_3OH_{ads} can be traced. Apart from the Cl_{ads} contamination (Cl $2p$ 268.8 eV) at temperatures above 230 K, the surface is clean (Fig. 2b).

2. Chlorine Incorporated as Nickel Chloride: A Promoter for the Dissociative Mechanism

As a result of Ar-sputtering of the Cl_{ads}-covered surface at 600 K for half an hour, the 5.8 eV UPS peak of Cl_{ads} is completely extinguished, and the Cl $2p$ XPS peak (268.8 eV) is significantly reduced but still present: Cl_{ads} is removed from the surface, but minor parts remain in the selvedge. By both UPS and XPS it is shown that C_{ads} is

completely removed. Subsequent heating of the Ni above 700 K for about 1 h creates a new peak at 2.8 eV and decreases the work function ($\Delta\Phi = -0.3$ eV).

A similar observation with Ag has been attributed to the interaction of the p orbitals of chlorine with the d band of Ag (10). With Ni above 700 K it is generally agreed that nickel chloride forms (11, 12). Most remarkable is the influence of the formation of nickel chloride on the d electrons of the Ni surface. Whereas by Cl_{ads} and likewise O_{ads} or C_{ads} the electron density at the Fermi edge is distinctly reduced, the electron density in the immediate vicinity of the Fermi edge is not influenced by the formation of nickel chloride; instead, the flank of the d band at about 1.3 eV below the Fermi edge is suppressed. The formation of nickel chloride in the selvedge is different from the formation of nickel oxide with respect to the effect on d electrons, since nickel oxide reduces the electron density at the Fermi edge.

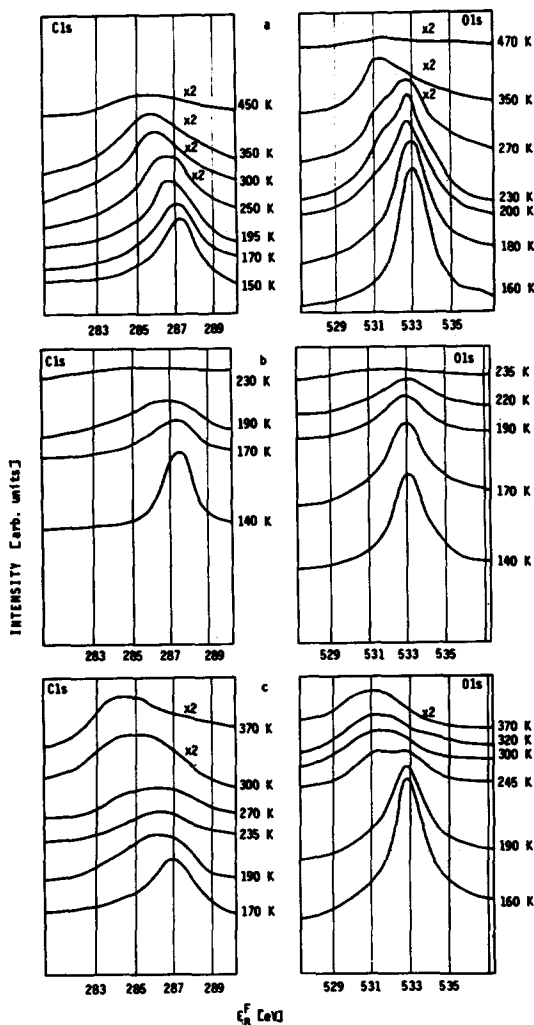Condensation of CH_3OH at 90 K and sub-

FIG. 2. X-Ray photoelectron spectrum (Al$K\alpha$, 1486.6 eV) of adsorbed intermediates at different surface temperatures. (a) Clean nickel, (b) Cl_{ads}-contaminated nickel, (c) nickel chloride-contaminated nickel.

sequent increase of temperature in a procedure completely analogous to the one described above for the Cl_{ads}-covered surface leads to different results at temperatures above 140 K. In the UP spectrum the four peaks characteristic of CH_3OH_{ads} do not decrease uniformly. Instead, the development of two peaks at 5.6 and 9.5 eV indicates the formation of CH_3O_{ads} at temperatures of about 200 K. The peak energies are slightly shifted with respect to the values observed with clean Ni, 5.2 and 9.2 eV (Fig. 1a and

Ref. (5)), which might be due to the presence of nickel chloride in the surface. At about 260 K the rise of a peak at 7.6 eV in between the two decreasing methoxy peaks indicates the formation of CO_{ads} by dehydrogenation of CH_3O_{ads}; this peak is dominant at 300 K (Fig. 1c). The change in work function $\Delta\Phi = +0.2$ eV is in the same direction as with the formation of CO_{ads} on a clean Ni surface (5), but less pronounced than there ($\Delta\Phi = +0.6$ eV). The second UPS peak of CO_{ads} at 11 eV, as observed on single crystal planes and, in particular, with He(II) (40.81 eV) radiation, is commonly very weak in a He(I) spectrum of a polycrystalline surface. The correct identification of CO_{ads} by the two peaks has been secured in separate experiments using He(I) and He(II) as well (9).

The UPS observations are corroborated by XPS (Fig. 2c). Even at 190 K, a drastic shift of the C 1s peak is observed; $E_B^F = 286.4$ eV and is significantly lower than the C 1s value observed with the Cl_{ads}-contaminated surface (C 1s 287.3; O 1s 533.0 eV). The shift of the C 1s peak, compared to the rather constant O 1s peak (532.4 eV), is due to the coupling of the C atom to the surface, i.e., the formation of a CH_3O_{ads} species lying down on the surface. Whether the lying CH_3O_{ads} has already lost one H atom, being then in fact a CH_2O_{ads}, at that time is not yet clear. The shift to lower binding energies might also be due to the closer approximation of the carbon upon transition from CH_3OH_{ads} to an inclined or lying CH_3O_{ads} species (increase of extra-atomic relaxation). With increasing temperature in the range 220 to 370 K a C 1s peak at 285.3 eV is observed. At about 220 K a shoulder at 531.2 eV starts to evolve from the O 1s peak. These values are characteristic for CO_{ads}. These features increase in intensity at temperatures above room temperature, but at about 370 K they decrease; a simultaneous broadening on the low-energy flank of O 1s and also C 1s indicates the onset of CO dissociation.

The nickel chloride-contaminated Ni sur-

face is catalytically active; dehydrogenation of CH_3OH_{ads} via CH_3O_{ads} occurs to form CO_{ads}. However, upon closer inspection of the UP spectra, e.g., the spectra taken at 145 and 210 K in Figs. 1a and c, a significant difference between the nickel chloride-containing Ni surface and the clean Ni surface is seen. There are no differences in peak position or relative intensity between the two spectra of the monolayer of CH_3OH_{ads} at 145 K. At 210 K the spectrum of the CH_3O_{ads} on the nickel chloride-contaminated surface exhibits a distinct peculiarity which can be traced already at temperatures above 160 K: the methoxy peak at 9.5 eV is considerably less intense than the methoxy peak at 5.6 eV. Bearing in mind the attribution of the 5.6-eV peak to an O $2p$ orbital and the 9.5-eV peak to a superposition of the π_y and σ_{xz} orbitals, the decrease of the intensity of the latter peak shows that part of the CH_3O_{ads} is dissociated to form CH_{3ads} and O_{ads}. The UP peak of both CH_{3ads} and O_{ads} are situated between 5 and 6.5 eV (9), and hence the different intensity at 5.6 and 9.5 eV. Crucial data for the various CH_n species are obtained by a group of experiments with CH_3Cl and CH_2Cl_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_{ads} and CH_{3ads} or CH_{2ads}, respectively, is scrupulously followed and the spectra of the generated $CH_{n_{ads}}$ species are taken prior to further degradation. Subsequently, the sequence of degradation to form C_{ads} is resolved (9).

The complete poisoning effect of Cl_{ads} is removed and converted to a definite promoting effect by conversion of traces of Cl_{ads} left after Ar sputtering into a nickel chloride. Catalytic reaction now occurs again; part of the reaction follows the associative mechanism via CH_3O_{ads} to form CO_{ads}, and part the dissociative mechanism to form CH_{3ads} and O_{ads}. Considering the necessity of applying either high CH_3OH intensities or additional large doses of hy-

drogen in order to be able to observe the dissociative mechanism (5), the possibility to observe the dissociative reaction in an experiment after single exposure of the surface with CH_3OH must clearly be called a consequence of promotion of the catalytic selectivity.

At temperatures above 370 K the distinct difference of the catalytic activity of the nickel chloride-promoted Ni surface in comparison to the clean Ni surface continues. Whereas monomolecular desorption of CO_{ads} is exclusively present in experiments with the clean Ni, leaving behind at temperatures above 500 K the Ni surface as clean as after Ar sputtering, the dissociative mechanism is most strongly present after promotion of the surface with nickel chloride. The work function increases further ($\Delta\Phi = +0.4$ eV), which points to dissociation of CO_{ads} to form C_{ads} and O_{ads} (13). Simultaneously with the decrease of the 7.6-eV peak of CO_{ads} the formation of weak but clearly traceable C $2p$ and O $2p$ peaks at 4.4 and 5.5 eV is observed. These peaks of C_{ads} and O_{ads} disappear only after prolonged heating at and above 600 K because of the removal from the surface by either bimolecular desorption or diffusion into deeper layers of the catalyst. Either process leads to a decrease of the work function ($\Delta\Phi = -0.5$ eV). Hence, the initial value of the work function of the reactant-free, nickel chloride-contaminated surface is restored.

To summarize the experimental results, nickel chloride is a promoter of the Ni surface with respect to the decomposition of CH_3OH. Not only has the poisoning power of Cl_{ads} vanished but the reaction follows the dissociative mechanism insofar as a large part of the CH_3O_{ads} and all the CO_{ads} are dissociated to form CH_{3ads} and C_{ads}, respectively, and O_{ads}. With clean Ni surfaces the dissociative mechanism can be achieved in the presence of high concentrations of H_{ads} only. The antagonism of Cl_{ads} and nickel chloride can be observed with surfaces containing both impurities at the same time. There, the poisoning effect of

Cl$_{ads}$ is dominating over the promoting effect of nickel chloride.

DISCUSSION

In discussing the reasons for dissociation of C–O and C–C bonds on metals consideration is generally given to both electronic and geometric factors (*10–13*). High electron density in the close vicinity of the Fermi edge of the metal is assumed to be an essential property, but not the exclusive one. In case of Ni the high electron density close to the Fermi edge is favorable for the dissociation of CO; however, the geometric factor seems to counteract. Only with highly indexed planes and with highly disordered surfaces is the geometric obstacle circumvented and dissociative adsorption produced. This is supported by the observation that the dissociative mechanism of CH$_3$OH decomposition is observed on very rough Ni surfaces, generated by Ar sputtering without thermal annealing (*5*) [see also Fig. 1a]. Hence, it is possible that the nickel chloride contamination creates a fitting surface disorder on an atomic scale which is stable even at temperatures as high as 700 K. Most remarkable in this context is the fact that the electron density at the very edge of the *d* band is not affected by the nickel chloride deposit, in contrast to NiO, O$_{ads}$, C$_{ads}$ or Cl$_{ads}$. The high-temperature stability of the nickel chloride deposit makes it superior in promoting activity to surface disorder and roughness of clean Ni which are annealed after some time at temperatures above 500 K. For the same reason it is also superior to hydrogen solved in the Ni lattice; the hydrogen content is reduced at elevated temperatures (*5*).

Although these mechanistic details are not clarified up to now, the essential point must be emphasized. This is the inversion of the effect of added chlorine after severe use of the catalyst, as modeled in this study by heat treatment and Ar sputtering. In fact, the working catalyst is represented more closely by the nickel chloride-contaminated selvedge than by the Cl$_{ads}$-contaminated surface. This being so, coadsorption studies with presumed poisons or promoters cannot disclose the mechanism which is effective with the self-consistent system of the working catalyst.

ACKNOWLEDGMENTS

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