

Interaction of Propene with Pure and Hydrogen-Precovered Nickel Films. Studied by Means of Isothermal Reaction Mass Spectrometry and Thermal Desorption Spectroscopy

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A special experimental setup was used to study the equilibrium gas composition after interaction of propene with pure thin polycrystalline nickel films and nickel films precovered with hydrogen under ultrahigh vacuum conditions. Isothermal reaction mass spectrometry allows the analysis of the gas phase composition under equilibrium conditions. The analyzed gas phase consists of desorbed reaction products formed in the adsorbate phase after adsorption of propene on nickel films at 273 K. This technique was combined with thermal desorption spectroscopy and measurements of adsorption-induced changes in the electrical resistance of the polycrystalline films. After interaction with pure nickel films, in addition to propene, hydrogen, methane, propane, and butane could be detected as reaction products. The interaction of propene with nickel films precovered with hydrogen leads to a higher yield of butane and additionally to the formation of pentane. Thermal desorption experiments carried out after adsorption of propene at 77 K show only desorption of hydrogen, when the propene coverage was small. At higher coverages also propene desorbed.

Introduction

In recent years many investigations have been carried out in order to study the primary steps of the interaction of unsaturated hydrocarbons with the surfaces of unsupported transition metals under ultrahigh vacuum conditions. They include a variety of metals used as catalysts, like Fe, Ni, Pt, Rh, and Ru. Many different experimental methods have been applied, e.g., low energy electron diffraction (LEED),^{1,2} photoelectron diffraction,³ high resolution electron energy loss spectroscopy (HREELS),^{4–6} reflection absorption infrared spectroscopy (RAIRS),^{7,8} ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS),^{6,9,10} Auger electron spectroscopy (AES),¹¹ static secondary ion mass spectrometry (SSIMS)¹² and thermal desorption spectroscopy (TDS).^{11–14} Most of these tech-

niques provide experimental data that allow the identification of the structure and geometrical arrangement of the chemisorbed species. Usually the investigations were carried out with small hydrocarbons like ethene or ethyne and higher hydrocarbons like butenes or benzene, but only a few papers deal with the adsorption of propene on transition metal surfaces.^{5,6,11,12,15,16}

The aim of the present paper is different from that of the work mentioned above. It originates from questions that arose with current LEED, UPS, and TDS studies on the adsorption, reaction, and decomposition of propene on Ni(100) and Ni(110). The aim was to look for the coverage dependence of the formation of easily desorbable products, which have eluded observation by the methods referred to above. Isothermal reaction mass spectrometry (IRMS) has proven to be suitable in such cases, since it investigates the gas phase which is in isothermal equilibrium with the adsorbate.^{17–20} IRMS is therefore supplementary to the spectroscopic methods that give information on the adsorbate. However, IRMS cannot be applied to single crystals, so that metal films have to be used as adsorbents. Therefore TDS is additionally carried out as a link between single crystal and film results. The applied equilibrium measurements will be described in detail, since IRMS requires a special experimental technique, which cannot be performed in conventional all-metal ultrahigh vacuum systems.

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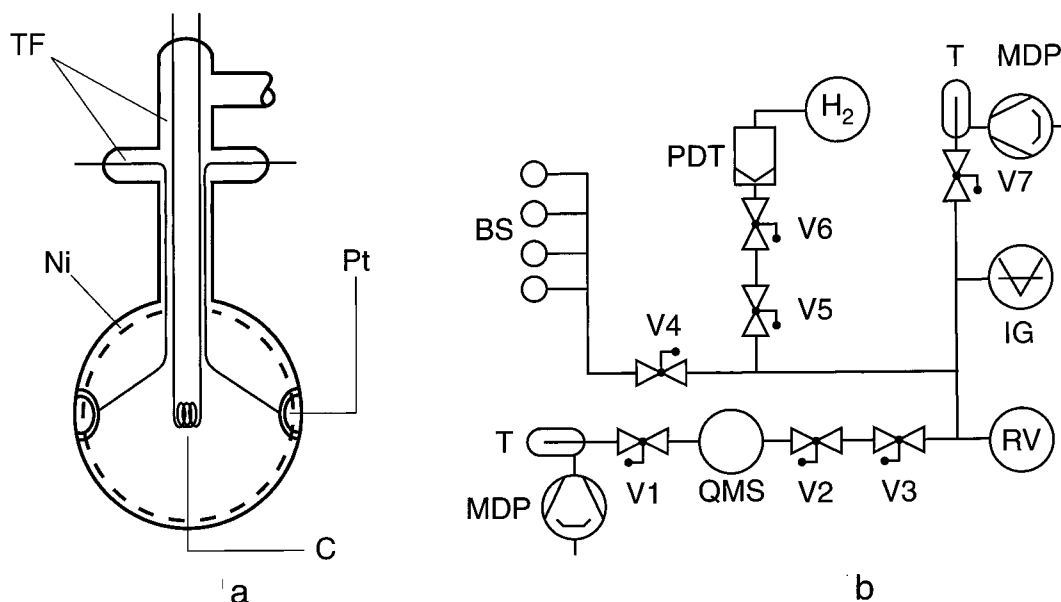


Figure 1. (a) Reaction vessel: C, Ni coil; Pt, platinum contact foils; Ni, evaporated film; TF, tungsten feedthroughs. (b) Schematic diagram of the UHV apparatus: V1–V7, ground-in ball and socket valves; BS, break seal ampoules; RV, reaction vessel; MDP, mercury diffusion pump; T, cooling traps; PDT, palladium thimble; QMS, quadrupole mass spectrometer; IG, ionization gauge.

Experimental Section

The study of the composition of the gas phase in equilibrium with the adsorbate requires experimental equipment that fulfills some prerequisites: (I) The investigations have to be performed under ultrahigh vacuum conditions. (II) The reaction system has to be separated from the pumps in order to allow equilibrium between the adsorbate and the gas phase to be established. (III) It has to be possible to remove a small amount of the gas phase for analysis without disturbing the equilibrium between the two phases. (IV) The whole UHV section of the apparatus has to be built of a material that is inert toward propene and its reaction products. Therefore the experiments were performed using a special UHV system made of Pyrex glass. Such a system has proved to be very suitable for investigations of this kind in earlier papers.^{17–20}

Figure 1a shows the reaction vessel (RV) for thin Ni film deposition and propene adsorption. It consists of a glass bulb of 500 cm³ with an inner wall area of 300 cm². This cell is equipped with two electrodes made of thin platinum foil Pt melted onto the glass and connected with tungsten feedthroughs (TF). The adsorbent is evaporated from a nickel coil (C) by electrical heating. (In reality the axis of the coil is oriented perpendicularly to the drawing plane.) This arrangement allows the measurement of the resistance of the nickel film Ni during its deposition as well as during propene and hydrogen adsorption.

The whole ultrahigh vacuum (UHV) section of the apparatus is schematically drawn in Figure 1b. Since the UHV system is built from Pyrex tubes and bulbs, it can easily be divided into small and larger sections by means of magnetically operated, greaseless ground-in ball and socket valves (V). Two three-stage mercury diffusion pumps (MDP) backed with liquid nitrogen cooling traps (T) produce a residual pressure of 2×10^{-8} Pa after several cycles of bake-out, measured with an ionization gauge (IG) of Bayard-Alpert type. When V1 and V7 are closed after the deposition and annealing of the nickel film, the measuring section is separated from the pumps and the cooling traps. Nevertheless ultrahigh vacuum is still maintained for at least 15 h. In order to precover the film with hydrogen, the spectroscopically pure gas is introduced by diffusion through a palladium thimble (PDT) and admitted in small doses via the twin valve V6/V5. Propene is admitted from break seal ampoules (BS) in exactly known quantities through valve V4, valves V5, V7, and V3 being closed.

In case of TDS experiments the propene is adsorbed at 77 or 273 K in small doses, until the required coverage is reached. Simultaneously the film resistance is recorded. Then the reaction vessel and the mass spectrometer are combined by opening V2/V3 and V1. A usual TD spectrum is taken with a constant heating

rate of 20 K/min, which has proven to give the best resolution with UHV apparatus of the type used.

IRMS experiments start with the adsorption at 273 K. Enough time is left to establish equilibrium between the adsorbate and the gas phase. This is checked by withdrawing a small amount of the gas phase via the twin valve V3/V2, which acts as a pipet, in fixed time intervals. Only then a further dose of propene is admitted and the procedure just described is repeated. In order to avoid back-diffusion of molecule fragments formed in the mass spectrometer, it is completely evacuated via V1 after each measurement.

The cracking patterns of a mass spectrum contain the fragments of several compounds like pentane, butane, and methane. The evaluation method used in former papers^{18–20} has been improved: The cracking patterns of propene as well as those of the expected reaction products have been determined before starting the experiment. Important for these determinations are the same starting conditions of the gases in the break seal ampoules. All ampoules contain the same number of gas molecules. This guarantees that after expansion of the gases into the UHV system the same amount of gas is detected with the QMS. Therefore the measured QMS intensities of the several gases become comparable to one another. From these cracking patterns relative sensitivity factors for all peaks were determined and normalized to the base peak (the main peak of the spectrum) of the main reaction product propane. The relative concentrations of the products have been determined by a least-squares fit method after normalizing the recorded spectra and all possible product spectra to the base peaks and multiplying the results of the fit by the relative sensitivity factors.

The ordinates in the relevant figures (Figures 4 and 5) give very exactly the correlation between the partial pressures of the different gases. The partial pressures themselves are affected with a higher limit of error. The intensity of 10^{-7} in au corresponds to about 1 Pa.

Results and Discussion

Properties of the Adsorbent. The nickel films of an average thickness of about 10 nm are deposited onto the inner wall of the cell, which is cooled with a liquid nitrogen bath. The deposition rate is about 1 nm/min. The films are then annealed for 60 min at 333 K. Deposition and annealing are controlled by measuring the electric resistance of the film via the platinum contact foils. This process guarantees highly reproducible physical properties of the films, which have been examined using X-ray

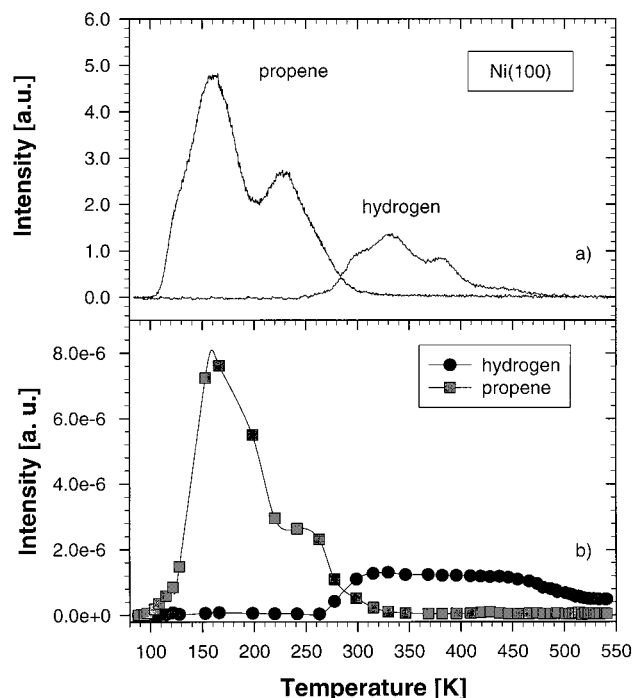


Figure 2. Thermal desorption spectra taken (a) after adsorption of 1.5 monolayers on Ni(100) at 105 K and (b) after adsorption of 2 monolayers on a Ni film at 77 K.

diffraction experiments²¹ and transmission electron microscopy.²² The films are compact, however, polycrystalline. The size of the crystallites is of the same magnitude as the film thickness. They exhibit a $\langle 111 \rangle$ -fiber texture. Due to the relatively high concentration of grain boundaries, the specific resistivity is higher than that of well-ordered bulk nickel by a temperature-independent amount, which is representative of the state of ordering according to Matthiessen's rule. The roughness factor, which is the ratio of microscopic to macroscopic surface area, was determined to be about 1.5.²³ AES and XPS measurements²⁴ show that these films are as clean as well-prepared single-crystal surfaces.

Thermal Desorption Spectroscopy. There are many examples which prove that the catalytic behavior of thin metal films of the kind described above is very similar to that of single-crystal surfaces, sometimes with the exception of the most densely packed faces.²⁵ Usually the catalytic activity of the metal films slightly exceeds that of single crystals due to the higher concentration of dislocations.

Thermal desorption spectroscopy is a good means to compare the adsorption of propene on Ni(100)¹⁰ as well as on nickel films. This is done in Figure 2. The TD spectrum in Figure 2a was taken in a usual all-metal UHV system with a heating rate of 5 K/s after adsorption of about 1.5 monolayers of propene at 105 K. It consists of two desorption maxima of propene at 160 and 230 K, respectively. The only other gas that can be detected is hydrogen with a big peak at 330 K, one peak at 380 K and two shoulders at 300 K and between 400 and 500 K. Schoofs and Benziger,¹¹ who also applied TPD to the adsorption

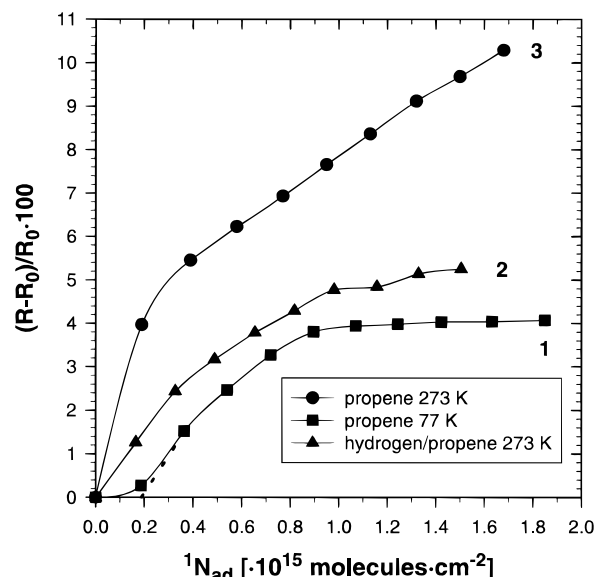


Figure 3. Change in resistance of Ni films in dependence on propene admission: curve 1 at 77 K, curve 2 at 273 K after preadsorption of 0.5 monolayer of hydrogen, curve 3 at 273 K.

system Ni(100)/propene were not able to observe the first desorption peak of propene, since they started their experiment at temperatures that were too high. They also observed hydrogen as the only reaction product. The resolution of their TD spectrum does not exhibit further details.

Figure 2b shows the desorption spectrum that was obtained after admission of 1.85×10^{15} molecules of propene per cm^2 , i.e., after adsorption of about 2 monolayers of propene on a nickel film at 77 K. The heating rate amounted to 20 K/min. The spectrum is dominated by an intense peak of desorbing propene with a maximum at 160 K and a shoulder at 240 K. As in the case of propene adsorption on the single crystal, hydrogen desorption starts at 260 K and extends to more than 500 K. The agreement between the results obtained on the single crystal and on the film is very good.

The propene adsorption on Ni(100) was also investigated by means of UPS and XPS.¹⁰ From these studies it can be deduced that the first desorption peak (160 K) is due to desorption of physisorbed propene from the multilayer and desorption of a weakly π -bonded species, whereas the peak at about 240 K results from desorbing chemisorbed propene.

The desorption of hydrogen clearly indicates that at elevated temperatures decomposition of propene takes place. The onset of the desorption of hydrogen coincides very well with the desorption of hydrogen chemisorbed on clean nickel.^{26,27} Therefore it can be supposed that the decomposition of propene takes place not only at 260 K but also at lower temperatures, while the formed hydrogen remains chemisorbed. This question cannot be decided by TDS. Here IRMS is a suitable method.

The multilayer adsorption, in the case of the experiment with the nickel film, follows not only from the amount of admitted propene but also from the change in electric resistance that is plotted in Figure 3. Curve 1 refers to propene adsorption at 77 K. After admission of 0.9×10^{15} molecules of propene per cm^2 , when the relative change in electric resistance amounts to 4% of the resistance of

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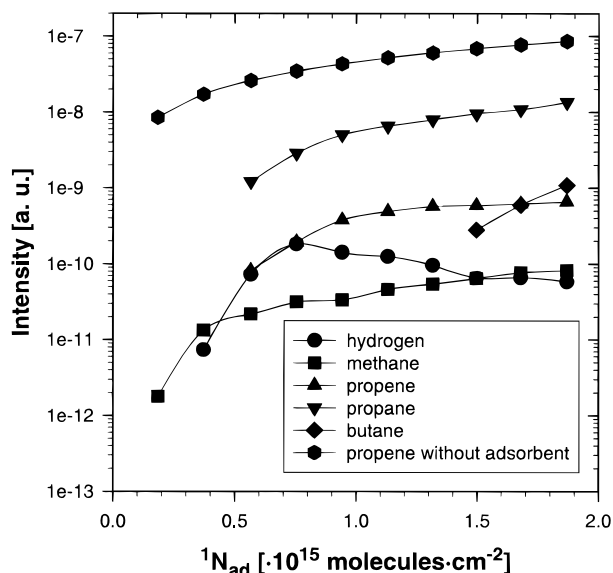


Figure 4. Measured product distribution (normalized to propane) in dependence on the number of admitted propene molecules per cm^2 at 273 K, 10^{-7} au corresponds to about 1 Pa.

the clean film, no further change in resistance can be observed. This is clear evidence that the additionally admitted molecules adsorb without direct contact to the nickel surface, i.e., a multilayer is built up. At low coverages the curve relative change in resistance versus coverage exhibits a sigmoidal shape. This is an artifact that is based on adsorption of nearly the whole amount of the first dose of admitted propene on the cooled, baked-out walls of the upper part of the reaction vessel before reaching the metal film. The number of adsorbed propene molecules is by 0.2×10^{15} molecules per cm^2 smaller than the number of admitted molecules (see the dotted line). Such an effect is not observed when the experiment is carried out at 273 K.

Isothermal Reaction Mass Spectrometry. Interaction of Propene with the Pure Nickel Surface. In the IRMS experiments doses of about 0.2×10^{15} molecules of propene per cm^2 were discontinuously admitted at 273 K. After each dose of propene, equilibrium between the adsorbate and the gas phase was allowed to establish. Five reaction products could be detected in the gas phase. Their normalized intensities are plotted in Figure 4 in dependence on the number of propene molecules admitted per cm^2 . The uppermost curve (black hexagons) indicates the intensity that would be expected when no gas whatever would be adsorbed; i.e., the values of the abscissa are directly proportional to the values of the ordinate. As explained in the Experimental Section, these intensities give a very exact ratio between the partial pressures of the different gases. The partial pressures themselves are subject to a higher error. An intensity of 10^{-7} au corresponds to about 1 Pa. That means that the partial pressures of the desorbed reaction products in Figures 4 and 5 lie in the range between 10^{-5} and 10^{-1} Pa.

After the admission of the first dose of propene only a very small amount of methane can be detected in the gas phase. Its amount increases after the second dose by about 1 order of magnitude. Simultaneously hydrogen appears in the gas phase. From the third dose onward, in addition propene and propane can be detected. Only from the eighth dose forward is butane observed. The normalized intensities, i.e., the partial pressures of all reaction

products, increase with the increase of the number of admitted propene molecules, with the exception of hydrogen.

The third dose leads to the appearance of the educt propene in the gas phase. This indicates that the monolayer coverage has been exceeded. This follows also from the relative change in resistance (curve 3 in Figure 3, black circles). However, in contrast to the behavior of the relative change in resistance with adsorption at 77 K, it does not become constant at monolayer coverage but exhibits a further increase, as is the case when reactions occur in the adsorbed layer, which produce additional species acting as additional scattering centres for the conduction electrons.

The formation of propane, which, with its appearance, is the main product, indicates that self-hydrogenation takes place. Since no hydrogen has been admitted, the hydrogen needed for the hydrogenation of the admitted propene has been formed from the decomposition of the chemisorbed propene.

Methane is also formed by self-hydrogenation. It appears as the first reaction product in the gas phase since its desorption energy is extremely small. The same is valid for the saturated hydrocarbons propane and butane (the desorption energy increases with the length of the molecules). The decrease in the intensity of hydrogen indicates a decrease in its coverage due to the hydrogenation reactions and—maybe—displacement by fragments with higher adsorption energy.

At the end of the experiment the gas phase consists of 8% butane, 5% propene, 1% methane, and 0.5% hydrogen referred to the main product propane.

This IRMS experiment supports the assumption that the hydrogen observed with TDS is, at least to some extent, formed by decomposition of propene at temperatures lower than 260 K. The fact that the other reaction products cannot be observed with TDS can be explained by their extremely small concentrations under the condition of TDS.

Isothermal Reaction Mass Spectrometry. Interaction of Propene with the Nickel Surface Precovered with Hydrogen. The influence of partial precoverage of the nickel surface with hydrogen on the product spectrum after adsorption of propene at 273 K is shown in Figure 5. The precoverage amounted to exactly half a monolayer. This can easily be checked by measuring the change in resistance during hydrogen adsorption. It is well-known^{26–28} that the change in resistance of the nickel film passes through a maximum just at half a monolayer of hydrogen.

As in the case of the experiment described in the preceding section, propene was discontinuously admitted in doses of about 0.2×10^{15} molecules propene per cm^2 onto the surface precovered with half a monolayer of hydrogen. Again the uppermost curve (black hexagons) indicates the normalized intensity, which would be expected, when no propene is adsorbed. From the first dose onward, propane is the main product. That means that the preadsorbed hydrogen immediately hydrogenates the propene. As in the absence of preadsorbed hydrogen, methane is formed, which indicates decomposition of propene on the free part of the surface. Over the whole experiment no propene can be observed. Butane appears already with the fifth dose. Even pentane is formed from the seventh admission of propene onward. At the end of the experiment, the gas phase consists of 50% pentane,

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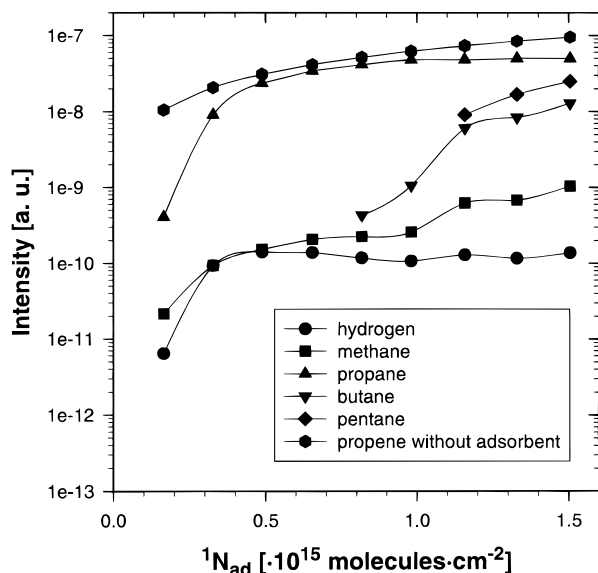


Figure 5. Measured product distribution (normalized to propane) of a nickel film, which was precovered with half a monolayer of hydrogen, in dependence on the number of admitted propene molecules per cm 2 at 273 K, 10^{-7} au corresponds to about 1 Pa.

26% butane, 2% methane, and about 0.5% hydrogen referred to propane.

This experiment shows that the propene adsorption on the nickel film results in both breaking of carbon-carbon bonds of the propene and formation of larger molecules from the fragments. Due to the higher amount of hydrogen, hydrogenation reactions are preferred, so that not only butane but also pentane can desorb. Since a larger amount of hydrocarbon desorbs than in the case discussed in Figure 4, the increase in resistance (curve 2) is smaller than that shown in curve 3.

In the case of the TDS experiments, hydrogen abstraction takes place over a wide range of temperatures leading finally to graphitic and carbide carbon. This could be confirmed by XP spectra taken after the TDS experiment on the single crystal surface.

Summary

The investigations include the adsorption and reaction of propene at 273 K on polycrystalline nickel films and nickel films precovered with half a monolayer of hydrogen as well as the thermal desorption of propene and its reaction products after adsorption of propene at 77 K. Thermal desorption after adsorption of a multilayer of propene at 77 K results in propene desorption with an intense peak at 160 K and a shoulder at 240 K. The only reaction product under these conditions is hydrogen, which desorbs with a broad peak between 260 and 500 K. In order to investigate the gas phase that is in isothermal equilibrium with the adsorbate, IRMS experiments were carried out. Small doses of propene were admitted, and after equilibration of the gas phase with the adsorbate, the composition of the gas phase was determined. At small propene doses, methane is the only reaction product that can be detected. At increasing doses, at first hydrogen and then propene and propane—the main reaction product—appear in the gas phase. At very high doses also butane can be detected. Therefore the main reaction under these conditions is the self-hydrogenation of propene with a small amount of carbon-carbon bond breaking and the desorption of the higher hydrocarbon butane, which might have been formed at lower propene coverages.¹⁹

On the contrary reaction of propene with a nickel film precovered with half a monolayer of hydrogen leads to propane, methane, and hydrogen already after the first propene admission. At higher doses, at first butane and then additionally pentane appear in the gas phase. During the whole experiment, no propene can be detected. Due to the higher amount of hydrogen, hydrogenation reactions are preferred, so that not only butane but also pentane can desorb into the gas phase.

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