J. Am. Chem. Soc. **1994,** *116,* 10041-10049

Interaction of Acetylene with Films of the Transition Metals Iron, Nickel, and Palladium

W. Alter, D. Borgmann,[*] M. Stadelmann, M. Wörn, and G. Wedler[*]

Contribution from the Institute of Physical and Theoretical Chemistry, University of Erlangen-Nuernberg, Egerlandstrasse 3, D-91058 Erlangen, Federal Republic of Germany

Received April 9, 1993. Revised Manuscript Received January 24, 1994[⊗]

Abstract: A special experimenal setup and application of isothermic reaction mass spectrometry (IRMS) allow the analysis of the gas phase which consists of desorbed reaction products formed in the adsorbate phase after adsorption of acetylene on Fe, Ni, and Pd films at 273 K under ultrahigh vacuum conditions. This technique, combined with temperature-programmed thermal desorption spectroscopy (TDS) and adsorbate-induced changes in electrical resistance of the adsorbent film, was used to compare the activities of Fe, Ni, and Pd concerning C–C bond breaking, self-hydrogenation, dimerization, and trimerization of acetylene. As products methane, hydrogen, ethane, butane/butene, and benzene appear in the gas phase when the coverage with acetylene is increased. There is strong evidence that the products are formed already at low coverages. Additionally adsorbed deuterium leads to isotope exchange.

Introduction

In recent years, many papers have been published dealing with the interaction of acetylene with transition metal surfaces, preferably with catalytically active metals such as Fe,[1-5] Ni,[6-11] Pd,[12-23] Rh,[24,25] and Ru.[26] Low-energy electron diffraction (LEED),[6,9,12,19,22,24-26] high-resolution electron energy loss spectroscopy (HREELS),[1,2,6-8,10,14,15,21,22,24,25] ultraviolet photoelectron spectroscopy (UPS),[5,12,16] X-ray photoelectron spectroscopy (XPS),[5,12,16,21] and Auger electron spectroscopy (AES)[4,5,10,11,17,19] were applied, because the authors were interested in the identification of the structures of the chemisorbed species and their geometric arrangement on the surface. In addition thermal desorption spectroscopy (TDS)[3,6,11-14,17-20,22-26] and measurements of changes in work function ($\Delta\Phi$)[3,5,6,12,17,19] were performed to characterize the adsorbates.

There is only a relatively small number of papers referring to the analysis of the gas phase consisting of desorbed reaction products formed in the adsorbed layer,[3,27-30] in spite of the fact that such measurements give supplementary information valuable for catalytic studies.

The interaction of acetylene with polycrystalline films of Fe, Ni, and Pd is studied with the aid of isothermic reaction mass spectroscopy (IRMS) and temperature-programmed thermal desorption spectroscopy (TDS). Both, the adsorption of acetylene alone and the coadsorption of acetylene and hydrogen are investigated. H_2 as well as D_2 and C_2H_2 as well as C_2D_2 are used as adsorbents. The applied methods are described in detail, since IRMS requires an experimental procedure, which cannot be performed in conventional all-metal ultrahigh vacuum systems.

Experimental Section

As it is the aim of the studies to analyze the gas phase consisting of reaction products formed, when acetylene interacts with the surface of the adsorbent, the experimental equipment has to fulfill some prerequisites: (i) The investigations have to be carried out under ultrahigh vacuum (uhv) conditions. (ii) The system adsorbent/adsorbate/gas phase has to be separated from the pumps in order to allow desorbable species to equilibrate between adsorption phase and gas phase. (iii) The apparatus has to be built of a material which does not interact with acetylene and possible reaction products. (iv) It has to be possible to withdraw a small amount from the gas phase for analysis without disturbing the phase equilibrium.

These criteria are not met with a conventional all-metal uhv apparatus. They are, however, met by an in-house-built all-glass apparatus, which is pumped by means of two-stage mercury diffusion pumps backed by liquid nitrogen cooling traps. After several cycles of bakeout a vacuum of 2×10^{-8} Pa is achieved. Mechanical valves are replaced by magnetically operated greaseless ground-in ball and socket valves. By means of such valves gas handling system with break-seal ampules, adsorption cell, pipets of known volume, quadrupole mass spectrometer, and pumping unit can be connected to or separated from each other. Details of this apparatus are published elsewhere.[3,27,29,30] The volume which is filled by the desorbed or displaced gases amounts to 2150 cm^3.

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[*] To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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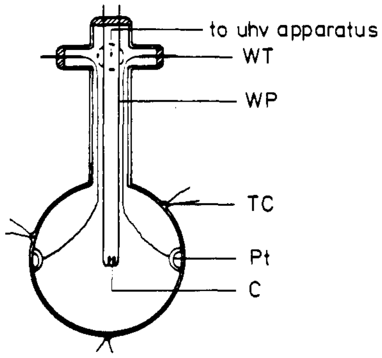

Figure 1. Reaction vessel: C, metal evaporation coil; Pt, contact foils; TC, thermocouples; WT, WP, tungsten feedthroughs.

The reaction vessel is shown in Figure 1. It is made of Pyrex glass. Under a vacuum of 2×10^{-8} Pa the adsorbent is evaporated from the metal (Fe, Ni, Pd) coil C by electric heating and deposited at 77 K on the inner wall of the glass bulb at a rate of 1 nm min^{-1} up to a thickness of about 10 nm. The films are then annealed for 1 h at 333 K. Deposition and annealing are controlled by measuring the electric resistance of the films via the Pt contact foils. Iron, nickel, and palladium films produced in this kind are as clean as well-prepared single-crystal surfaces as has been checked by AES and XPS.[3] Their surface areas are 300 cm^2, and their electric resistances are absolutely stable at temperatures of 77 or 273 K.

In the case of IRMS experiments the metal film is prepared as just described. The measuring part of the apparatus is separated from the pumping unit by closing the valves. By opening one break-seal ampule, a known number of acetylene molecules is admitted. The gas phase is then analyzed by withdrawing a known, small volume of gas via a pipet into the quadrupole mass spectrometer. This is done in fixed time intervals until no further change in composition is observed. Only then the content of a further ampule is admitted to the adsorbent.

In the IRMS experiments the adsorption of acetylene is followed by numerous reactions along a large variety of reaction paths leading to the formation of chemical species, part of which is also stable in the gas phase whereas another part only exists in the chemisorbed state on the surface of the adsorbent. The strength of the chemisorption bond of a distinct chemical species is often strongly dependent on the adsorption site. Usually, at least at room temperature, the adsorption systems are far away from chemical equilibrium, since the activation energies of equilibration are too high. Product molecules can only be *detected* in the gas phase when their adsorption bond is rather weak. Fortunately, this prerequisite is fulfilled in the case of small, saturated hydrocarbons and hydrogen on Fe, Ni, and Pd. In spite of the fact that desorption may also occur via different paths[40] each desorbable species present in the adsorption layer appears in the gas phase according to its equilibrium pressure which depends on temperature, coverage, and presence of coadsorbed species. This has been experimentally proven for many systems.[31,32,41] In the IRMS experiments establishment of such a phase equilibrium is postulated as soon as there is no change in the mass spectrum with time.

In TDS experiments, acetylene is admitted to the adsorbent in some doses up to a requested coverage, while the cell is kept at 77 K. For analysis, the reaction vessel is combined via the mass spectrometer with the pumping unit. The vessel is heated with a constant rate of 16 K min^{-1}. The complete mass spectrum or only the intensities of those masses which are important for the analysis are recorded depending on temperature.

Since the adsorption of gases as well as reactions in the adsorbed layer influence the electric resistance of the adsorbent (film) in a characteristic manner, the electric film resistance is also recorded depending on time during the gas adsorption.

The controlling of the mass spectrometer as well as the data storage are managed by a personal computer.

The experiments will demonstrate that, as a consequence of the adsorption of acetylene, hydrogen, methane, ethane, butane/butene, and benzene are formed and appear in the gas phase. In blank experiments carried out in absence of a deposited film, but with the metal coil in the measuring cell, the mass spectrum only shows the admitted gases. However, when the mass spectrometer or the ionization gauge is switched on for times considerably exceeding that necessary to take the mass spectrum, acetylene reacts on the hot filaments under formation of new compounds. Therefore all filaments were switched off before acetylene was admitted in the adsorption experiments. The gases formed during the analysis in the quadrupole mass spectrometer were pumped off.

In order to obtain the basic spectra necessary for quantitative analysis the intensities of suitable masses in the mass spectra of the pure gases, which could be expected as products after the admission of acetylene to the adsorbent, were measured as a function of the ion current of a Bayard–Alpert gauge. By means of this calibration it is at least possible to measure the partial pressures of the different components in the gas phase in nitrogen equivalents.

In contrast to the surface of single crystals the surface of evaporated metal films consists of various crystallographic planes and is not smooth. The roughness factor (the ratio of microscopic to macroscopic surface area) is about 1.5, when the films are prepared as described above.[42,43] The experimental procedure yields an exact value of the number of admitted acetylene molecules per centimeter squared of macroscopic surface area (${}^1N_{ad}$), which is identical to the number of adsorbed acetylene molecules per centimeter squared as long as acetylene cannot be detected in the gas phase. A considerable part of these molecules will suffer structural and/or chemical changes in the adsorbed state. In the following, ${}^1N_{ad}$ will be used as a measure of coverage. It is much more reliable than the coverage expressed in molecules of acetylene per surface metal atom all the more since reactions occur in the surface layer. A monolayer coverage corresponds to about ${}^1N_{ad} = 1 \times 10^{15}$ acetylene molecules cm^{-2} macroscopic surface area. Contrary to single-crystal experiments the coverage cannot be related to the number of surface atoms of the adsorbent. Here the monolayer is defined as the number of adsorbed particles which cover a square centimeter of surface area when they are closely packed.

Results and Discussion

Isothermic Reaction Mass Spectrometry. Figure 2 shows, by way of example, the typical change of the mass spectrum of the gas phase, when increasing amounts of acetylene (from a to e) are adsorbed on an Fe film at 273 K. The numbers in the spectra indicate the relative sensitivities applied; the insets, the fragmentation schemes of the products. There is no difficulty in analyzing the quantity of hydrocarbons formed; however, since fragmentation of hydrocarbons in a quadrupole mass spectrometer always produces hydrogen, the uncertainty in the quantitative determination of desorbed hydrogen is high.

Although the products appearing in the gas phase above Fe, Ni, and Pd are essentially the same, there are typical differences concerning partial pressures and the respective coverage of the film with acetylene at which they can be detected for the first time. Figure 3, parts a, b, and c, refer to experiments performed with Fe, Ni, and Pd films, respectively.

In any case hydrogen, methane, ethane, butane and/or butene, and benzene are found. Acetylene, the original material, appears in the gas phase only at high coverages exceeding a monolayer by far. In none of the cases can C_3 or C_5 products be detected. This leads to the assumption that the formation of desorbable products only occurs via hydrogen abstraction, C–C bond breaking, dimerization, and trimerization of C_2 entities.

Methane is always the first product appearing in the gas phase. This is due to the fact that it is only weakly bonded to the catalyst.[28,33,34] On Fe and Ni films there are two plateaus in the curve partial pressure of methane versus acetylene coverage with a step at that coverage, at which also ethane desorbs. On Pd films the methane signal reaches its maximum value far below that of the monolayer. The total amount of methane formed at ${}^1N_{ad} = 0.5 \times 10^{15}$ acetylene molecules cm^{-2} is lowest on Fe and

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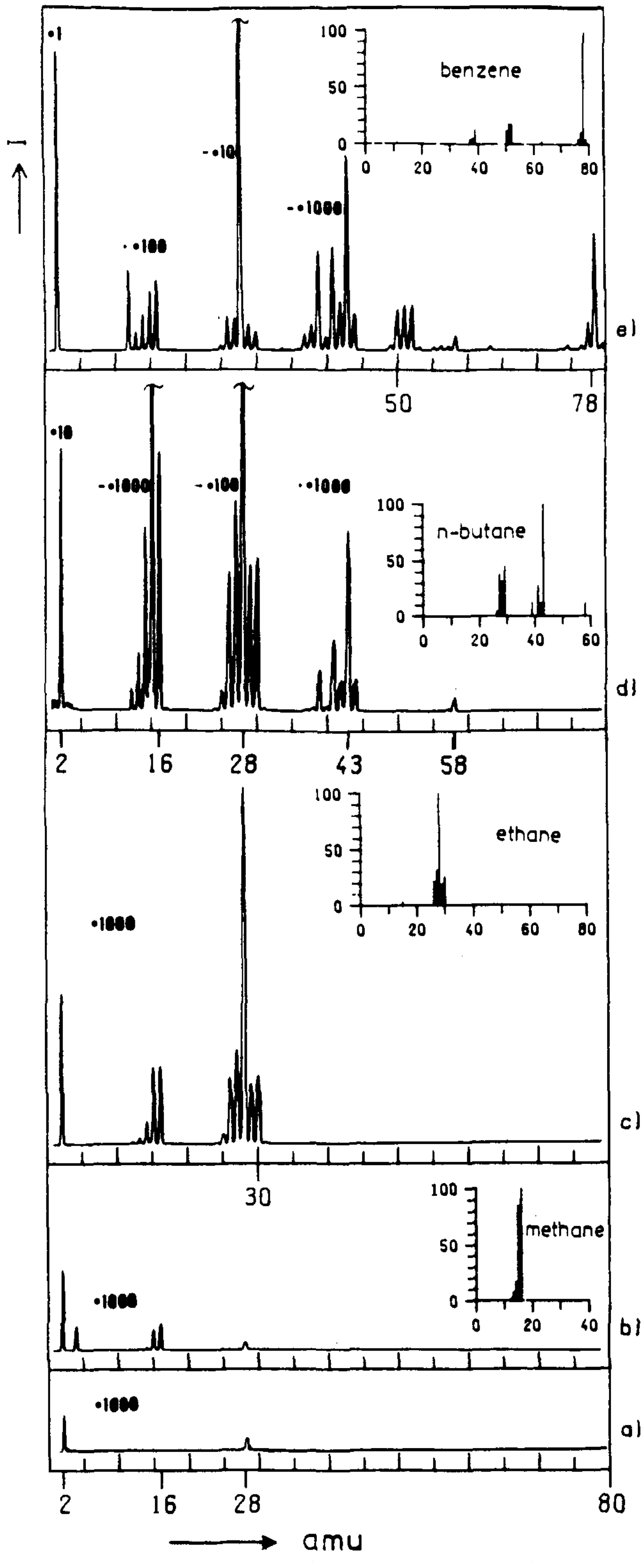

Figure 2. Mass spectra obtained after adsorption of increasing amounts of acetylene (from a to e) on an Fe film at 273 K. The numbers in the spectra indicate by which factor the peaks have been multiplied. The insets show the fragmentation schemes of the products.

highest on Pd, corresponding to 0.04, 0.14, and 7.2% of admitted C_2H_2 in case of Fe, Ni, and Pd, respectively.

The large amount of methane formed on the Pd film corresponds to the observation that it takes a very long time until no further changes in time occur in both mass spectrum and film resistance.

The main product is ethane, independent of the metal used as catalyst. Its partial pressure in nitrogen equivalents exceeds that of the other hydrocarbons by at least half an order of magnitude. This is more than the ratios of the ion gauge sensitivity factors. The total amount corresponds to about 16% of a monolayer, i.e. about 5×10^{16} molecules. At its appearance hydrogen also desorbs in the case of Fe and Ni films. Most likely hydrogen is replaced by acetylene when the total coverage approaches a monolayer. Under these conditions hydrogen seems to be most active concerning hydrogenation of additionally admitted acetylene. The amount of hydrogen in the gas phase is higher in the case of Fe films. When Pd films are used as catalysts hydrogen can only be detected at much higher coverages. It has to be kept in mind that all the hydrogen atoms necessary to transform CH into CH_4 or C_2H_2 into C_2H_6 have to be gained by hydrogen abstraction from C_2H_2. Pd seems to promote this abstraction reaction better than Fe and Ni do as can be deduced from the fact that on Pd the largest amount of CH_4 is formed and ethane is observed at rather low coverages. On the other hand and contrary to Fe and Ni, Pd is able to absorb large amounts of hydrogen, and, indeed, hydrogen appears in the gas phase only when the film surface is saturated with acetylene.

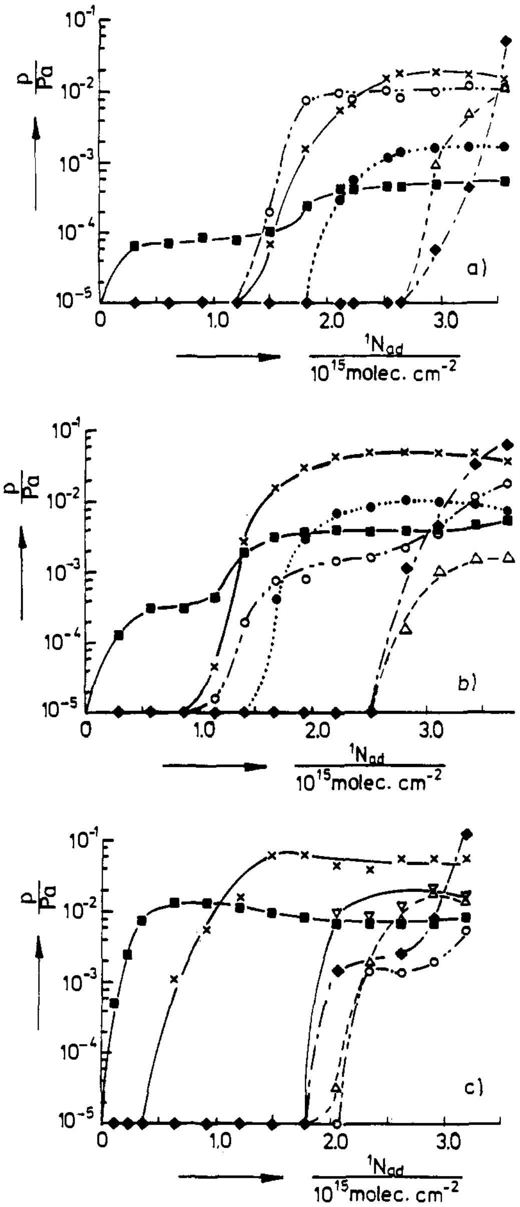

Figure 3. Partial pressures in nitrogen equivalents depending on the number of acetylene molecules admitted to an (a) Fe, (b) Ni, and (c) Pd film at 273 K (IRMS): (■) methane, (×) ethane, (○) hydrogen, (●) butane, (◆) acetylene, (▽) butene, and (△) benzene.

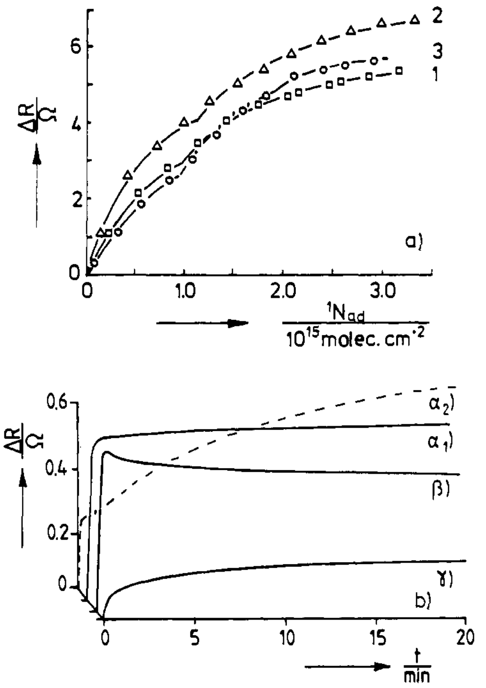

Figure 4. (a) Change in resistance of an Fe (1), Ni (2), and Pd (3) film depending on the number of acetylene molecules admitted per square centimeter of geometric surface area at 273 K; and, (b) change in resistance during a single admission of acetylene depending on time: admission at α_1, sub-monolayer (Fe or Ni); α_2, sub-monolayer (Pd); β, monolayer (Fe or Ni); and γ, multilayer coverages (Fe or Ni).

As a C_4 product only butane can be detected when the catalyst consists of Fe. Figure 3b demonstrates that on Ni films a considerable amount of butane is also formed. A detailed analysis of the mass spectra taken after the admission of 2.8×10^{15}, 3.1×10^{15}, and 3.7×10^{15} C_2H_2 molecules cm^{-2} shows that the intensity of peak 41 amu increases from 45 to 61 and finally to 78% of the peak height of 43 amu. This is strong evidence for formation of butene besides butane. When Pd films are used as catalysts only butene is detected as C_4 product (Figure 3c). At first it seems to be contradictory that on Pd, the highly active hydrogenation catalyst, only unsaturated C_4 hydrocarbons are formed under the experimental conditions. Hydrogenation of C_1 and C_2 species as well as sorption of hydrogen atoms by Pd seem to be favored before hydrogenation of C_4.

When, finally, the admitted acetylene can no longer be completely adsorbed, benzene is replaced from the surface. In this respect there is no big difference in the behavior of Fe, Ni, and Pd.

There is a clear correlation between the processes deduced from Figure 3 and changes in the electric resistance of the metal films in dependence on both, number $^1N_{ad}$ of admitted (and adsorbed) acetylene molecules (Figure 4a) and time (Figure 4b). Figure 4a shows that adsorption of acetylene leads to an increase in resistance. The symbols mark the resistance measured as final value after the discontinuous admission of the doses of acetylene. Figure 4b demonstrates how the resistance of an Fe film changes with time after admission of acetylene. There are three typical shapes of the curves. A rapid increase in R with time followed by a slight further increase is observed, when only adsorption and reaction of acetylene in the surface layer combined with desorption of loosely bound methane takes place (curve α_1, submonolayer range). A rapid increase followed by a slight decrease in R occurs when, due to completion of monolayer coverage, replacement of hydrogen and butane are dominant (curve β). The very slow increase in R and replacement of benzene have to be correlated (curve γ). When the curves of Figure 4a obtained in more than hundred experiments of this kind are compared it becomes evident that at the coverages at which the curves of type α (β) change to type β (γ) a more or less pronounced point of inflection can be observed in the curves ΔR vs $^1N_{ad}$. The curves drawn in Figure 4a demonstrate this behavior.

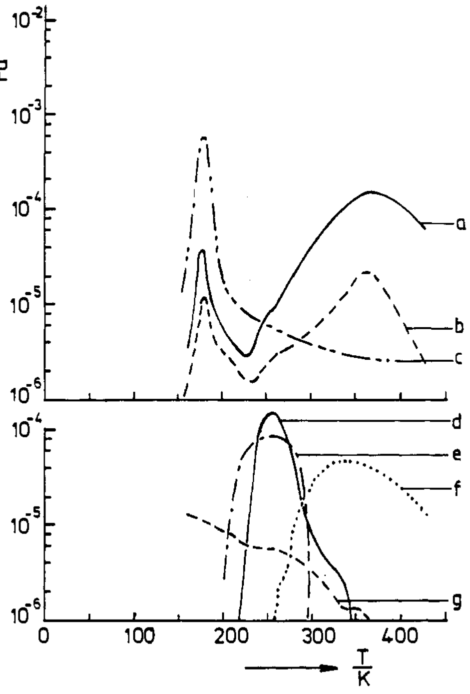

Figure 5. TPD spectra taken after adsorption of about half a monolayer of acetylene at 77 K: (a) hydrogen, (b) methane, (c) acetylene, (d) benzene, (e) butene, (f) butane, and (g) ethane.

In spite of the fact that the chemisorption-induced changes in film resistance have not yet satisfactorily been interpreted from the theoretical point of view,[35-37] they often give valuable hints to events occurring in the adsorption layer. In order to prove this statement two curves α are drawn in Figure 4b. Shape α_1 is observed in the case of Fe or Ni, where only a small amount of methane is produced and the mass spectrum does not change significantly with time after the adsorption of acetylene. Shape α_2 is typical of Pd in the low coverage range, where a large amount of CH_4 is formed and a distinct time dependence of the mass spectrum is observed.

It is essential to note that the number of molecules that appear in the gas phase is small in comparison to the number of admitted molecules. The pressures in nitrogen equivalents observed above the metal surfaces saturated with acetylene at 273 K range from 10^{-3} to 10^{-1} Pa. It should be kept in mind that the surface of the films is 300 cm^2 and the gas volume is only 2150 cm^3 and the loss of gas by pumping is negligible. That means that the number of hydrocarbon molecules of a distinct species in the gas phase amounts to a few percent of the admitted acetylene molecules or even less. IRMS experiments indicate which substances can be formed when acetylene interacts with the metal surface. It does not tell us anything about the chemical nature of the majority of the species which remain adsorbed. For such a purpose other spectroscopic methods have to be applied as mentioned in the Introduction.

Temperature-Programmed Thermal Desorption Spectroscopy. The chemical nature of the adsorbent has only little influence on the desorption spectrum, when acetylene is adsorbed at 77 K on films of Fe, Ni, or Pd up to comparable coverages and the temperature is increased with the same rate. Therefore only TD

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Table 1. Thermal Desorption Spectra of the Systems Fe/C_2H_2, Ni/C_2H_2, and Pd/C_2H_2[a]

metal	C_2H_2	H_2	CH_4	C_2H_6	C_4H_{10}	C_4H_8	C_6H_6
Fe	180–230 (d)	190–230 (d) >110 (r)	210–230 (d) 190–350 (r)	150–230 (d) 150–310 (r)	230–250 (d) 280–390 (r)		240–350 (d)
Ni	130–200 (d)	150–200 (d) >140 (r)	150–190 (d) 150–400 (r)	140–190 (d) 140–390 (r)	200–240 (d) >250 (r)	150–280 (d)	230–350 (d)
Pd	180–220 (d)	190–210 (d) >100 (r)	150–220 (d) >110 (r)	110–190 (d) >110 (r)		150–350 (d) >350 (r)	220–290 (d)

[a] Desorption temperature in kelvins; narrow peaks indicating desorption of species already present in the adsorbate are designated d; broad peaks indicating desorption of species formed only by the increase in temperature, r.

spectra obtained for the system Ni/C_2H_2 are discussed in detail.

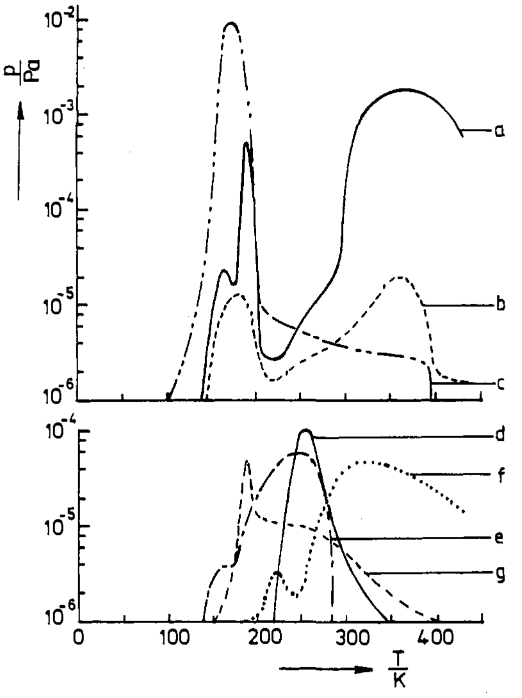

Figure 6. TPD spectra taken after adsorption of a monolayer of acetylene at 77 K: (a) hydrogen, (b) methane, (c) acetylene, (d) benzene, (e) butene, (f) butane, and (g) ethane.

When about half a monolayer of acetylene is adsorbed at 77 K the desorption spectra of Figure 5 are recorded during heating to 450 K. Acetylene (c) is only desorbed at about 175 K, together with some hydrogen (a) and methane (b). There are two types of desorption signals of the products, narrow and very broad ones. The former are usually typical of desorption of a species which was already present at the surface at lower temperatures, while the latter are typical of the formation of a desorbable species over a wide range of temperature. So the desorption curves of butene (d) and benzene (e) indicate that these substances were already present on the surface considerably below room temperature. Hydrogen (a) abstraction and formation of butane (f) by hydrogenation of an unsaturated C_4 species as well as further formation of methane (b) occur over a wide range of temperature. The desorption curve of ethane (g) follows that one of acetylene (c).

When the TD experiment is started with a monolayer coverage of acetylene (Figure 6) a much larger amount of only acetylene and hydrogen are desorbed between 150 and 200 K. The desorption curves of the other products are not strongly influenced by the increase in the educt coverage. This indicates that the products of the catalytic reaction are formed or preformed already at low coverage. This statement will strongly be supported by special studies discussed later on.

It is interesting to note that between 250 and 300 K the desorption of butene (e) strongly decreases, however, that of butane (f) increases. Evidently, just in this temperature range butene is hydrogenated by the hydrogen gained by abstraction as follows from the increase in hydrogen pressure (a) at the low-temperature side of the broad H_2 desorption peak. This also explains why in the IRMS experiment at 273 K (Figure 3b) only butane and no butene is observed.

In general the TD spectra obtained for the systems Fe/C_2H_2 and Pd/C_2H_2 agree with those of Ni/C_2H_2. The results compiled in Table 1 refer to adsorption of about a monolayer of acetylene. Again there are narrow peaks indicating desorption (d) of substances already formed at lower temperatures and broad ones which point to formation of the molecules due to reactions (*r*) over a wide range of temperature.

The original material acetylene shows desorption maxima at 220, 180, and 200 K on Fe, Ni, and Pd, respectively. Contrary to the desorption peaks of most of the other substances the peak height is strongly influenced by the amount of acetylene admitted if the coverage exceeds half a monolayer. The desorption temperature is much lower as should be expected from the strength of bonding of chemisorbed acetylene on the metal surfaces. Therefore the acetylene which desorbs at 200 K could not have been in direct contact with the metal surfaces.

The hydrogen pressure continually increases with increasing temperature and passes through a flat maximum between 350 and 400 K in the case of Fe and Ni and above 480 K in the case of Pd. There is no doubt that this hydrogen is only formed by reactions in the adsorbed layer, which become possible with increasing temperature. A narrow desorption peak at about 200 K is superimposed in any case. It is due to thermal desorption of hydrogen formed at low coverages at the adsorption temperature (77 K).

Methane, obviously formed at low coverages at 77 K, desorbs between 150 and 220 K (see also refs 28, 33, and 34), whereas a lot of methane originates in reactions up to about 400 K. A desorption of methane from Ni or Fe films between 150 and 220 K is not in contradiction to the observation of Beckerle et al.[44] who observed desorption of physisorbed methane below 60 K, however from Ni(111) surfaces.

Ethane behaves very similar to methane.

The most interesting observation concerning the influence of the chemical nature of the adsorbent is the fact that, in case of Fe only butane, but no butene desorbs, whereas in case of Pd butene, but no butane appears in the gas phase. This is in agreement with the results of the IRMS experiments. When acetylene is adsorbed on Ni, the TD spectrum points to the formation of both butane and butene as has been discussed before.

Benzene desorbs over a range of about 100 K. It is difficult to decide from TD spectra whether it is already formed at the adsorption temperature or during the thermal desorption experiment. Observations to be discussed later on point to a formation at the adsorption temperature.

As already mentioned, only the desorbed amount of acetylene and, to a less extent, that of hydrogen is dependent on the amount of adsorbed acetylene. This is not true for methane, ethane, butane/butene, and benzene. This points to a formation of these substances in the low coverage regime.

TDS studies indicate which substances can be formed when acetylene interacts with the metal surface. They do not give any direct information on the chemical nature of the adsorbate and

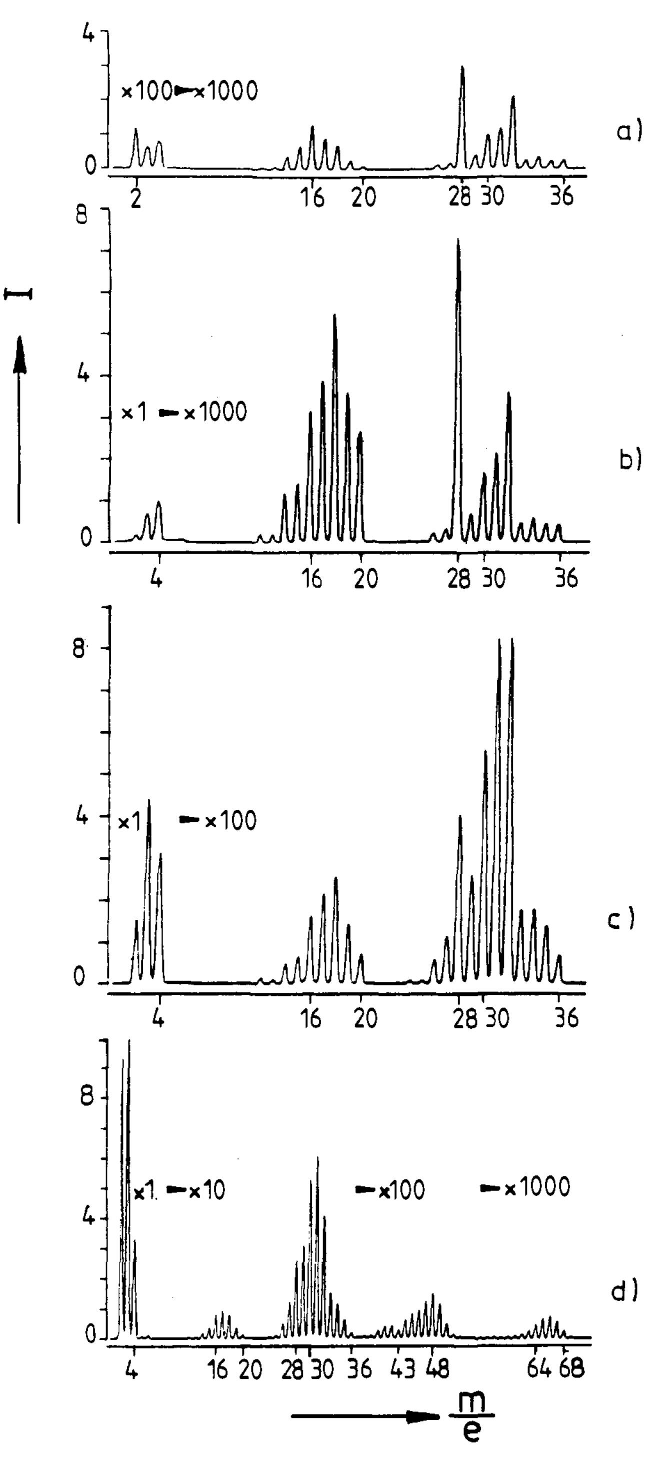

Figure 7. Mass spectra taken from an Fe film at 273 K precovered with 1.5×10^{15} D_2 molecules cm^{-2} and after admission of 0.1×10^{15} (a), 0.5×10^{15} (b), 1.0×10^{15} (c), and 2.2×10^{15} (d) C_2H_2 molecules cm^{-2}. The numbers in the spectra indicate by which factor the peaks have been multiplied.

the kind of the adsorption bond. Electron spectroscopic studies deliver more information in this respect. Therefore XPS, UPS (He I and He II), as well as AES and measurements of changes in work function, were also applied in case of the system Fe film/C_2H_2.[5] The results of these experiments strongly support the conclusions concerning the state of the adsorbate indirectly drawn from ΔR measurements, IRMS, and TDS: Acetylene can be adsorbed in multilayers, chemical reactions occur at low coverages. Furthermore, they indicate what happens to the residual carbon: It is deposited on the catalyst surface in both carbidic and graphitic forms.

Table 2. Comparison of Theoretically Expected and Experimentally Observed Isotope Exchange in Methane at 273 K

product	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
		Adsorbent Fe[a]			
statistically	0.9	11.0	50.0	100.0	75.0
experimentally	6.6	3.5	22.3	100.0	72.7
		Adsorbent Ni[b]			
statistically	0.9	11.0	50.0	100.0	75.0
experimentally	0.5	2.0	52.3	100.0	85.0
		Adsorbent Ni[c]			
statistically	75.0	100.0	50.0	11.0	0.9
experimentally	69.6	100.0	60.7	16.1	0.6
		Adsorbent Pd[d]			
statistically	0.9	11.0	50.0	100.0	75.0
experimentally	0.4	1.8	7.5	24.7	100.0

[a] Preadsorption of D_2, 25% hydrogen (in C_2H_2), 75% deuterium.
[b] Preadsorption of D_2, 25% hydrogen (in C_2H_2), 75% deuterium.
[c] Preadsorption of H_2, 75% hydrogen, 25% deuterium (in C_2D_2).
[d] Preadsorption of D_2, 25% hydrogen (in C_2H_2), 75% deuterium.

Adsorption of Acetylene on Ni Surfaces Partially Precovered with Hydrogen. Coadsorption of acetylene and hydrogen was studied at 273 K using various experimental procedures. When the influence of additional hydrogen on the product spectrum in IRMS experiments was investigated the metal film was precovered with H_2 to different extents prior to the admission of the doses of C_2H_2. When isotope exchange was of interest first D_2 and then C_2H_2 or at first H_2 and then C_2D_2 was admitted.

For example, Figure 7 shows mass spectra taken at 273 K when several doses of C_2H_2 were admitted to an Fe film precovered with 1.5×10^{15} D_2 molecules cm^{-2}. The number of admitted C_2H_2 molecules were 0.1×10^{15} (a), 0.5×10^{15} (b), 1.0×10^{15} (c), and 2.2×10^{15} (d) C_2H_2 molecules cm^{-2}. After the first dose of C_2H_2 all possible kinds of CH_xD_{4-x} $(0 \le x \le 4)$ and $C_2H_yD_{6-y}$ $(0 \le y \le 6)$ are observed. The same holds for butane and benzene when they appear in the gas phase at higher coverages. The relatively high peak at 28 amu is due to a slight contamination with CO.

When Ni or Pd are used as adsorbents very similar results are obtained. Preadsorption of H_2 followed by admission of C_2D_2 also leads to all possible isotope compositions.

However, differences become evident when the theoretically expected and the experimentally observed compositions are compared. In Table 2 the available results are compiled. Taking into account that the experimental setup was not planned for quantitative precision measurements of this kind the experimental data (at least of the main products) agree with the statistically expected ones, when the reaction took place on Fe or Ni. In the case of Pd, however, they differ considerably. On Fe and Ni the preadsorbed hydrogen (or deuterium) and the deuterium (or hydrogen) contained in the acetylene have the same chance to hydrogenate CH or CD to methane. On Pd the isotope already contained in the acetylene molecules is much less active in the hydrogenation reaction than the preadsorbed isotope. This result is consistent with the observation that the self-hydrogenation reaction on Pd only leads to butene and not to butane.

Figure 8 shows the result of an IRMS experiment carried out on Pd at 273 K after preadsorption of 1.8×10^{15} molecules H_2 cm^{-2}. It should be compared with Figure 3c. The preadsorbed hydrogen at once hydrogenates the admitted acetylene molecules, so that, contrary to Figure 3c, a large amount of ethane is formed after the first admission of acetylene. The final pressure of methane is reduced by 1 order of magnitude. Again only butene and no butane are observed in the gas phase. The formation of benzene is not influenced by the presence of preadsorbed hydrogen. The fact that the higher hydrocarbons are detected at higher C_2H_2 doses than in absence of preadsorbed hydrogen is due to the direct hydrogenation of acetylene to ethane.

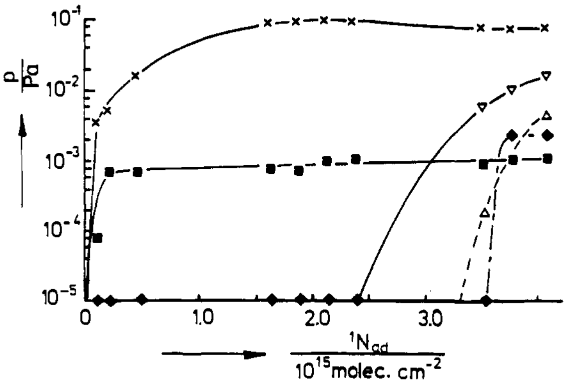

Figure 8. Partial pressures depending on the number of acetylene molecules admitted to a Pd film at 273 K after preadsorption of 1.8 × 10^{15} H_2 molecules cm^{-2}: (■) methane, (×) ethane, (♦) acetylene, (▽) butene, and (△) benzene.

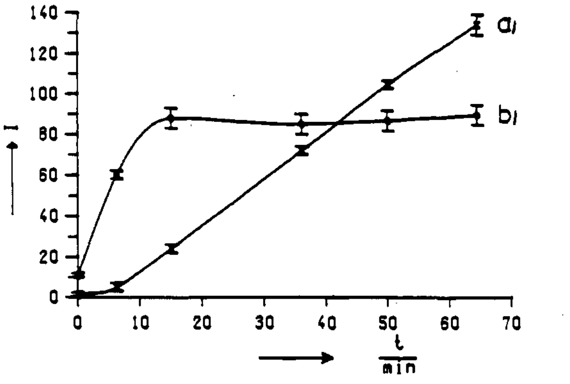

Figure 9. Intensities of the molecule ion peaks of (a) methane and (b) ethane as a function of time for the first admission of acetylene in Figure 8.

That the hydrogenation of acetylene is the favored reaction follows also from Figure 9 in which the intensities of the molecule ion peaks of methane and ethane are plotted as a function of time for the first admission of acetylene in Figure 8. Only when the ethane peak (b) approaches its final value the methane peak (a) begins to increase. Even after 1 h it has not yet arrived at the maximum value.

Coadsorption of C_2H_2 and C_2D_2. This study concentrates upon the behavior of methane and benzene. In spite of the fact that generally the whole mass spectra were taken (see e.g. Figure 2) here only the ranges from 12 to 20 amu (as long as only the methanes are present in the gas phase) and from 70 to ≤ 84 amu (the range of the fragmentation scheme of benzene that is not superimposed by signals originating from other hydrocarbons) are discussed.

C_2H_2 used in the following experiments was absolutely pure, whereas C_2D_2 contained a small amount of C_2H_2, which was taken into account in the quantitative calculations.

Measurements carried out with C_2D_2 as adsorptive revealed exactly the same results as those performed with C_2H_2. This means that there is no isotope effect and the conclusions drawn from the experiments discussed before are also valid when C_2D_2 adsorbs on Fe, Ni, and Pd.

In a series of experiments at first a dose of C_2H_2 (about 0.35 × 10^{15} C_2H_2 molecules cm^{-2}) was adsorbed at 273 K on Ni. The second dose consisted of a comparable amount of C_2D_2. Then mixed doses of equal amounts of C_2H_2 and C_2D_2 were admitted. The first two admissions of acetylene led to the appearance of methane in the gas phase; ethane could be observed at $^1N_{ad}$ = 1.3 × 10^{15} and butane, butene, and benzene at $^1N_{ad}$ = 2.0 × 10^{15} acetylene molecules cm^{-2}. An increase of $^1N_{ad}$ above 4.8 × 10^{15} acetylene molecules cm^{-2} did not lead to any further changes in the product spectrum.

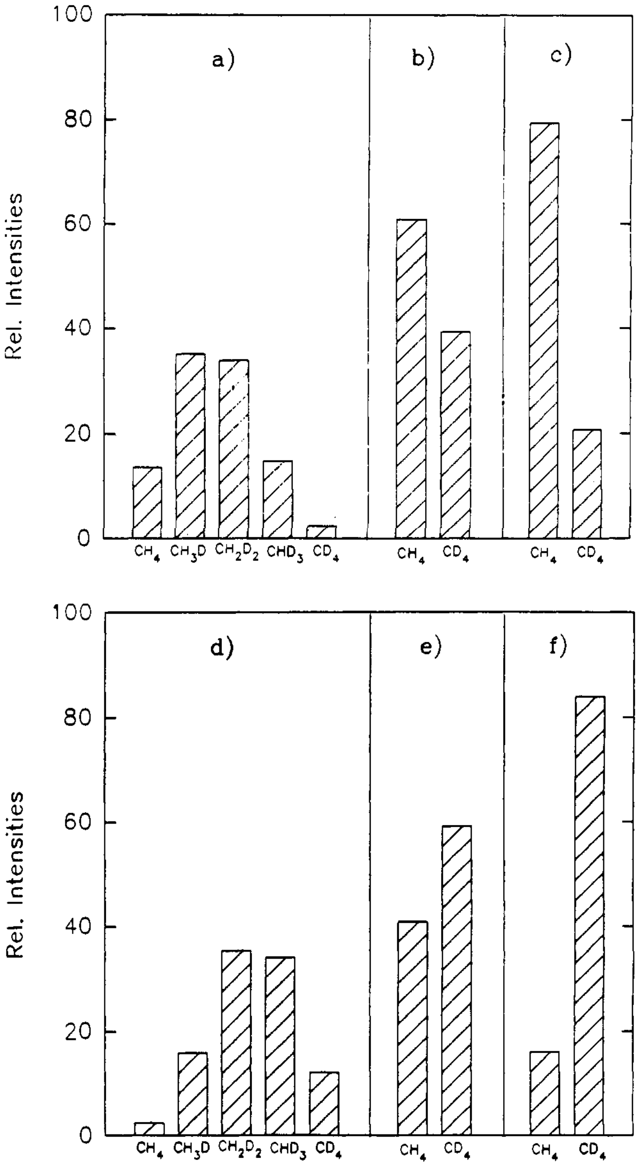

Figure 10. Methane formation after admission of C_2H_2 and C_2D_2 (first dose C_2H_2, a, b, and c; first dose C_2D_2, d, e, and f): (a and d) assuming complete isotope mixing; (b and e) assuming only formation of CH_4 and CD_4; and (c and f) experimental data.

A second experiment (B) differed from the first one (A) only in the sequence of admission of C_2H_2 and C_2D_2, the first dose consisted of C_2D_2, the second one of C_2H_2.

The mass spectrum of the gas phase after the first dose of C_2H_2 in experiment A showed signals from 12 to 16 amu and that after the first dose of C_2D_2 in B signals from 12 to 20 amu including odd values of amu due to the content of C_2H_2. Both spectra were taken as characteristic of the fragmentation schemes of C_2H_2 and C_2D_2 in these experiments.

After admission of the second dose of acetylene (C_2D_2 in A, C_2H_2 in B), the mass spectra of the gas phase revealed signals of all values of amu between 12 and 20 in both cases. Methane was the only product in the gas phase so that the mass spectrum was not superimposed by fragments of other products. Assuming complete isotope mixing, CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 should be observed with the distribution represented in Figure 10, parts a and d, respectively. However, the mass spectra proved to be the superposition of the fragmentation schemes of CH_4 and CD_4 only. The ratio of the partial pressures of CH_4 and CD_4 did not agree with the ratio of admitted C_2H_2 and C_2D_2 (Figure 10, parts b and e, respectively). It was dominated by the isotope admitted with the first dose and amounted to 3.8:1 and 1:5.2

(Figure 10, parts c and f, respectively) instead of 1.5:1 in experiment A and of 1:1.4 in experiment B.

With reference to both, the fact that only 0.1% of the hydrogen contained in the admitted acetylene appears in form of methane in the gas phase the adsorption layer and the coverage dependence of the methane pressure (Figure 3b) the following conclusions can be drawn from the results shown in Figure 10: (i) Due to the small heat of adsorption of methane on Ni nearly all the methane that can be formed in the adsorption layer under the given experimental conditions desorbs immediately.[33] (ii) In spite of the large number of collisions of the methane (deuteriomethane) molecules present in the gas phase with the surface they are not able to react with deuterium (hydrogen) produced by decomposition of deuterioacetylene (acetylene) during a subsequent admission of the original material. Under these conditions isotopic equilibrium cannot be established. (The situation is quite different when a large amount of hydrogen (deuterium) is additionally adsorbed.) (iii) The dominance of that methane which is formed from the first dose of acetylene is a consequence of the fact that, in the monolayer range, the production of methane decreases from dose to dose (see e.g. Figure 3b).

When the coverage exceeds a monolayer other products desorb and the mass spectrum between 12 and 20 amu is no more characteristic of methane. Further admissions of nearly equal amounts of C_2H_2 and C_2D_2 finally (at $N_{ad} \geq 3.2 \times 10^{15}$ cm^{-2}) lead to desorption of benzene into the gas phase. The mass spectrum at amu ≥ 78 consists preferably of the masses 78, 80, 82, 84 indicating that benzene must have been formed from intact acetylene molecules. The intensities of signals at odd values of amu, which give a hint to isotope exchange, are very small. The bars in Figure 11, parts a and c, show the relative intensities of the molecule ions which were to be expected when all admitted acetylene molecules in experiment A and B, respectively, had the same chance to take part in the formation of benzene. The bars in Figure 11, parts b and d, represent the experimental data. There is clear evidence that the species admitted with the first dose (C_2H_2 in experiment A, Figure 11b, C_2D_2 in experiment B, Figure 11d) are dominating. This result clearly demonstrates that the benzene molecules are formed or preformed at low coverages. Since they are rather strongly bonded to the Ni surface, they are displaced from the surface only at high total coverages.

Isotope Exchange at High Coverages. When C_2D_2 doses are admitted at 273 K to a Ni film until C_6D_6 is observed in the gas phase ($N_{ad} = 3.6 \times 10^{15}$ cm^{-2}) and subsequently H_2 is admitted, hydrogen/deuterium exchange is observed. It starts with ethane and butane/butene. As the methane signals are strongly superimposed by the fragments of the higher hydrocarbons no conclusions can be drawn concerning the isotope exchange with methane. The mass spectrum of benzene is only influenced when the amount of adsorbed hydrogen is markedly increased. The exchange reaction occurs rather slowly as can be seen from the time dependence of the mass spectra taken after adding a new dose of H_2. The species containing H atoms are formed at the cost of deuteriohydrocarbons already present in the gas phase. All these observations point to an exchange mechanism including readsorption of molecules from the gas phase. Therefore the observed isotope exchange supports again the statement that the gas phase and the adsorption phase are in phase equilibrium.

In another experiment a Ni film was dosed with C_2H_2 up to the appearance of C_6H_6 in the gas phase at 273 K. The following doses consisted of C_2D_2. It was not possible to detect any isotope exchange with the molecules in the gas phase. Evidently there is no deuterium abstraction at these high coverages.

Conclusions

The application of isothermal reaction mass spectrometry, temperature-programmed thermal desorption spectroscopy, and measurement of changes in resistance has yielded some new aspects concerning the interaction of acetylene with thin polycrystalline films of Fe, Ni, and Pd at low pressures ($p < 10^{-1}$ Pa) and low temperatures ($T < 300$ K).

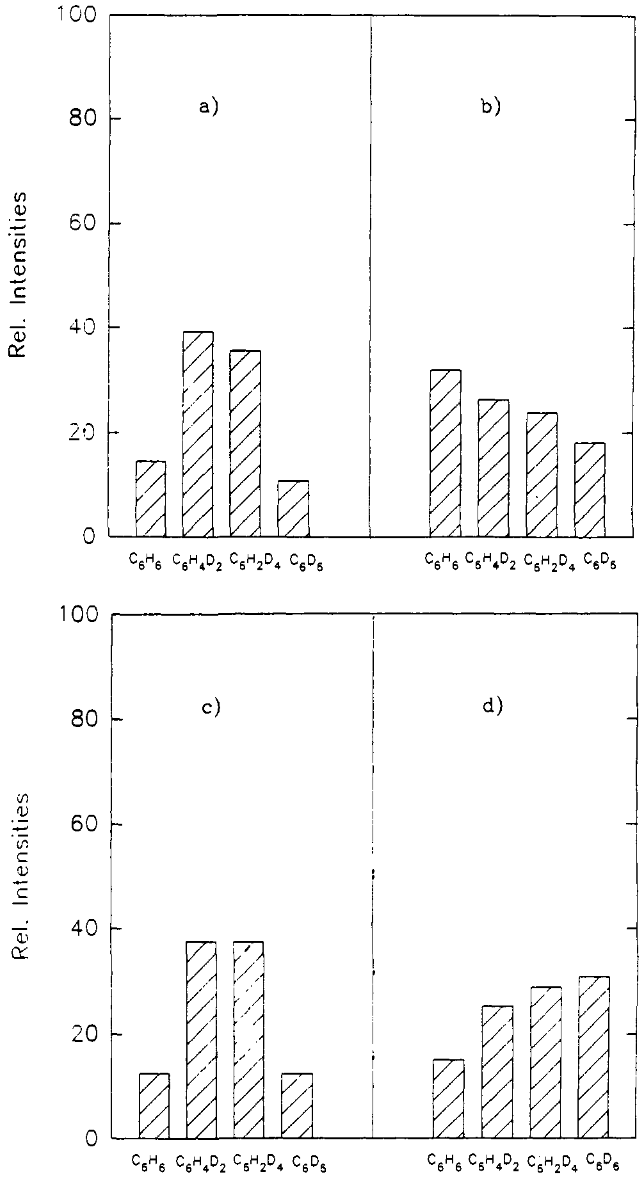

Figure 11. Benzene formation after admission of C_2H_2 and C_2D_2 (first dose C_2H_2, a and b; first dose C_2D_2, c and d): a and c, theoretical data and b and d, experimental data.

Studies using single-crystal surfaces as adsorbents have shown that acetylene adsorption is face specific.[8,9,38] Evaporated films prepared as described in the Experimental Section exhibit a fiber texture usually with the closest packed plane parallel to the substrate.[39] Their surface, however, consists of a large variety of differently indexed planes. Therefore, differences in the behavior of Fe, Ni, and Pd films toward acetylene have to be traced back to their chemical nature and not to specific structural properties.

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In many respects these three transition metals behave toward acetylene in a similar way: They promote the formation of CH_4, H_2, C_2H_6, C_4 hydrocarbons, and benzene which all can be detected in the gas phase, even at rather low temperatures. That means that the metals promote C–C bond breaking, self-hydrogenation, dimerization, and trimerization of acetylene. Differences become evident with regard to the quantity of the products: At 273 K the amount of methane observed in the gas phase at monolayer coverage corresponds to 0.04, 0.14, and 7.2% of admitted C_2H_2 in case of Fe, Ni, and Pd, respectively. The hydrogen pressure is highest in the case of Fe and lowest in the case of Pd. In absence of additional H_2 hydrogenation of butene occurs most easily on Fe and seems not to take place on Pd. Only butane is observed with Fe, but with Pd only butene is formed; both C_4 hydrocarbons are detected with Ni films.

Both TDS and application of deuterated acetylene indicate that the hydrocarbons are formed or preformed as long as the total coverage on the surface is small. Their appearance in the gas phase depends on the strength of their chemisorption bond. They can also be replaced by other coadsorbed species when the latter are more strongly bound.

Additionally pre- or postadsorbed hydrogen (deuterium) leads to isotope exchange reactions.

The relationships observed in this paper cannot be compared with literature data since similar IRMS measurements are not available. There are, however, papers which support a lot of the observations made here.

The best overlap seems to exist with the findings of the Lambert group.[12,20,23] These authors thoroughly studied the interaction of acetylene with Pd, especially Pd(111) single-crystal surfaces under ultrahigh vacuum conditions over a wide range of temperatures. They applied surface-sensitive methods such as ARUPS, XPS, LEED, changes in work function, TDS, and molecular beam measurements. Products were observed via TDS: hydrogen, ethylene, and C_4 and C_6 hydrocarbons. There were no C_3 and C_5 products according to the results of this paper. Obviously the authors did not detect methane and ethane. This is not in contradiction with the findings of this paper since under the conditions of Lambert's experiments methane and ethane must have desorbed before TDS started. The observations concerning residual carbon are in agreement with our findings on iron films. Experiments using C_2H_2 and C_2D_2[20] yield results concerning benzene formation which can be compared with the above mentioned observations on iron films. Contrary to the experimental procedure applied in this paper, Lambert's experiments allow an investigation of the molecular pathways in the cyclotrimerization of acetylene so that they are able to describe a C_4 intermediate.[19]

Indeed, there is a large gap between the conditions (pressure and temperature) under which model studies as in this paper and technical catalytic processes occur. Nevertheless, the primary steps in the adsorbed layer and the reaction mechanism should be comparable as has recently been proven in the case of cyclotrimerization of acetylene over supported palladium catalysts.[23] Similarities and differences in the behavior of Fe, Ni, and Pd toward acetylene as discussed in this paper should also influence reactions under technical conditions.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Forschergruppe Reakob) and the Verband der Chemischen Industrie.