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Model Studies on Bimetallic Cu/Ru Catalysts

II. Adsorption of Hydrogen

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The chemisorption of hydrogen on pure and Cu-covered Ru(0001) surfaces was examined by means of low energy electron diffraction (LEED), work function ($\Delta\varphi$) measurements, and thermal desorption spectroscopy (TDS). H_2 adsorbs dissociatively on the Ru(0001) surface with an initial sticking probability $s_0 = 0.25\ (\pm 0.1)$. Two chemisorption states, β_1 and β_2 with adsorption energies of 10.5 (±2) and 16.5 (±1) kcal/mole, respectively, are observed. The saturation density is approximately 1.3×10^{15} atoms/cm^2 at $T = 150$ K, corresponding to a coverage $\theta_H = 0.85\ (\pm 0.15)$. The work function change depends in a complex manner on coverage and is strongly affected by surface impurities. Cu deposits on the Ru surface suppress the hydrogen adsorption capacity drastically. Whereas small amounts (~5% of a Cu monolayer) reduce the H saturation density of hydrogen by about 50% but have little influence on the heat of adsorption of hydrogen, E_{ad}, higher Cu concentrations (0.1–0.8 Cu ml) give rise to a decrease of E_{ad} by ~2–3 kcal/mole and cause a strong inhibition of the hydrogen chemisorption process. The results suggest that ensembles of up to 5–10 adjacent Ru atoms are involved in the hydrogen chemisorption bond whose concentration is steeply decreasing by addition of small amounts of copper. The conclusions are in agreement with those reached by Sinfelt *et al.* [*J. Catal.* **42**, 227 (1976)] with Cu/Ru "bimetallic cluster" catalysts.

1. INTRODUCTION

In a preceding paper (*1*) it was shown that thin Cu layers on a Ru(0001) single-crystal surface exhibit structural properties which are rather similar to those suggested by Prestridge *et al.* (*2*) for bimetallic Cu/Ru cluster catalysts. The present paper reports on hydrogen adsorption on clean Ru and well-defined Cu/Ru single crystal surfaces with varying Cu concentration. It will be shown that again fairly close analogies to the results obtained by Sinfelt *et al.* (*3*) are found. These authors demonstrated that the hydrogen uptake by supported bimetallic Cu/Ru cluster catalysts is drastically lowered by small (overall) concentrations of copper. Determination of the actual surface concentration of this element was, however, not possible under these conditions. The qualitative result is quite plausible since hydrogen chemisorbs readily on the platinum metals (*4*) but is only weakly bound on copper (*5*), so that the amount of adsorption on Cu is supposed to be negligibly small. It was the aim of the present paper to elucidate more quantitatively how copper affects the hydrogen chemisorption properties of a ruthenium single-crystal surface and whether the results by Sinfelt *et al.* can be confirmed and interpreted by a comparison with well-defined single-crystal data. Whereas the chemisorption of O_2, N_2, NO, or CO on Ru single-crystal surfaces has been examined in a number of papers (*6–9*), owing to the unique activity of this metal in catalyzing reactions important for the automobile exhaust problem, relatively poor data exist about the interaction between hydrogen and Ru. This might arise partly from the fact that H only forms a

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fairly weak chemisorption bond which requires cooling of the sample to temperatures below 300 K in uhv experiments. One of the first studies concerning hydrogen adsorption on Ru was performed by Kraemer and Menzel (*10*) who reported on field emission experiments with emphasis on work function change measurements. Room temperature adsorption on a Ru(1120) surface has been studied by Goodman *et al.* (*11*). Thermal desorption and molecular beam techniques were employed in order to elucidate binding energies and the adsorption/desorption kinetics. Danielsen *et al.* (*12*) reported on hydrogen adsorption energies and binding states on Ru(0001) evaluated from thermal desorption analyses. Quite recently, a fairly extensive photoemission, TDS, and work function study of the same system H/Ru(0001) was performed by Menzel *et al.* (*13, 14*) which revealed among others a rather complex variation of the work function with coverage.

In the present study we focused on the determination of adsorption energies and binding states as well as on the analysis of the sticking probability vs coverage dependence in order to obtain information on the influence of Cu addition to the Ru surface. Comparatively more detailed studies on the interaction of hydrogen with copper exist in the literature, in particular those by Pritchard *et al.* (*15, 16*). Mainly precise surface potential measurements gave clear evidence that the H chemisorption process takes place fairly slowly because the dissociation of the H_2 molecule as the rate-limiting step appears to be activated. Another informative study in this context has been reported by Balooch *et al.* (*5*) utilizing molecular beam techniques, where data about the activation barrier and the adsorption energy for hydrogen on Cu(110) and Cu(100) were given. Owing to the activation, the hydrogen uptake of Cu surfaces at low gas pressures and temperatures is certainly very small and almost negligible, in particular for Cu(111) (*15*). Thus, the system H/Cu/Ru may be regarded as consisting of one active (Ru) and one inactive (Cu) species. Whether the Cu atoms act only as a diluent just lowering the effective Ru surface area or if the adsorption is influenced in a more complex manner (as suggested by Sinfelt's data) was the main question of concern in the present work.

Characterization of the actual surface composition and structure was described in detail (*1*). Apart from the above mentioned "high"-pressure study by Sinfelt on Cu–Ru catalysts (*3*) no further measurements of hydrogen chemisorption on such systems are known. However, there are several publications on carbon monoxide or oxygen interaction with similar systems, e.g., with Cu-covered W surfaces (*17*). Concerning binary alloys, a fairly large number of gas adsorption studies is available in the literature, for example the CO/Cu–Ni system (*18–24*), the CO/Ag–Pd system (*25–28*), the CO/Au–Ni system (*29*), the H/Cu–Ni (*22*), and the H/Pt–Au system (*30, 31*). These investigations might be of some use also with respect to a discussion of the interaction of H with a Ru surface partly covered with Cu. The results of the alloy studies, however, are strongly influenced by the surface composition of the alloy system in question which often differs from that of the bulk for thermodynamic reasons (*32*) or because of a "corrosive" chemisorption (*33*). A system with immiscible constituents like the Ru–Cu overcomes this complication, since a definitive surface composition regardless of temperature can be adjusted by appropriate experimental conditions.

2. EXPERIMENTAL

Since details of the experimental procedure have been described (*1*), only a few additional remarks will be mentioned in this place: The first point concerns the importance of the surface cleanliness of the ruthenium substrate throughout the hydrogen adsorption measurements, since it is well-known that this adsorbate reacts extremely sensitively upon surface contaminants like carbon or sulfur. As already described (*1*), the most effective cleaning procedure of the Ru(0001) surface consisted of repeated Ar^+ ion sputtering followed by annealing periods and of an oxidation/reduction treatment in oxygen and hydrogen atmosphere, respectively. However a quite severe problem arose from the oxidation cleaning: The rear of the Ru crystal, which was not accessible for a Cu deposition and any kind of surface characterization, became also clean and contributed to the desorbed amount of hydrogen during the TDS experiments. A fairly elaborate experimental procedure involving the deposition of an inert gold layer onto the rear of the sample was necessary in order to suppress this spurious contribution which otherwise would simulate a noticeable hydrogen adsorption even on a Ru surface completely covered with copper.

In the course of the present study thermal desorption spectroscopy appeared to be the most powerful tool for obtaining information on hydrogen chemisorption on both the pure Ru and the Cu/Ru surfaces. That is why some comments on this technique are worthwhile. Hydrogen forms a rather weak chemisorption bond on Ru(0001), exhibiting low values for the heat of adsorption (less than 80 kJ/mole) (see Section 3.1) which is somewhat similar to the behavior of the Pt(111) surface (*34*). In order to get a hydrogen-saturated Ru(0001) surface it was therefore necessary to perform the adsorption prior to the thermal desorption at temperatures below room temperature (200–250 K). In a careful study using an inactive stainless-steel sample (which had the same dimensions as the Ru crystal and was mounted in the same manner) the desorption of H_2 under identical experimental conditions was found to be completely negligible. The contribution from the rear of the Ru crystal was suppressed by gold deposited as mentioned before, the contribution from the sides and edges of the sample was identified with that amount of hydrogen which desorbed after deposition of Au on the rear and several monolayers of Cu on the front face of the crystal. This amount (approximately 15% of the total saturation coverage) was always subtracted from the high exposure desorption traces. Of course, these side and edge effects cause a fairly high inaccuracy in the hydrogen coverage determination, in particular when dealing with highly Cu-covered surfaces, the H uptake of which is small.

A completely linear and reproducible heating rate (~10 K/sec) was used during the desorption run with the ion pump slightly throttled. The absolute coverage data given for the clean Ru sample has been obtained by a numerical integration of the desorption trace according to the relation:

$$n_{\mathrm{ad}} = \frac{S_{\mathrm{eff}}}{AkT_{\mathrm{g}}} \int_0^\infty P\, dt \qquad (1)$$

in which the effective pumping speed, S_{ef}, has been determined experimentally. A is the active sample area and T_{g} is the gas temperature.

Finally, a short comment has to be made on the calibration of the Cu surface coverage (a more detailed description can be found in (*1*)). The calibration is based on combined Auger–TDS measurements and utilizes the electron-mean-free-path energy dependence (*35, 36*) in a metallic solid. Assuming a uniformly deposited and homogeneous Cu layer on top of the Ru(0001) surface, just that amount of Cu is determined by TDS which is required for a suppression of the ejected Ru Auger electrons to a fraction of $1/e$. The corresponding area below that TDS peak is henceforth used as a standard which corresponds to roughly 6×10^{15} Cu atoms/cm^2. It provides reasonable measure for all Cu concentrations down to the submonolayer range just by a comparison of TDS peak areas. At this point, however, we would like to emphasize that some important conclusions of the present paper strongly depend on this determination of the Cu coverage. In a study which is still in progress we will pay even more attention to this particular point (*61*).

3. RESULTS

3.1. *The Interaction of Hydrogen with Clean Ru(0001)*

The chemisorption of hydrogen on a clean and well-annealed Ru(0001) surface was studied at different exposures ranging from 0.1 up to several 100 L (1 L = 1.333×10^{-4} Pasec) and at temperatures between 150 and 500 K. In no case did "extra" LEED spots appear in the diffraction pattern. At high surface coverages and with a stationary hydrogen pressure of 10^{-4} Pa a slight increase of the background intensity was observed indicating either a disordered overlayer or a hydrogen-induced change of the overall surface reflectivity for low-energy electrons. Therefore, from LEED investigations no further conclusions could be drawn.

A typical set of thermal desorption spectra taken from a Ru sample which had been exposed to H_2 at 220 K is shown in Fig. 1. Parameter is the hydrogen exposure (L), the dosing pressure being always 2.6×10^{-6} Pa. From this figure apparently two different H binding states are discernible which will be denoted as β_1 and β_2. Whereas the maximum rate of the β_1 state seems to be independent of coverage a second-order-like temperature shift of the β_2 state is observed. The saturation of the β_2 state is attained at approximately 1–2 L with the maximum desorption temperature at 380 K. However, since the two peaks cannot be completely resolved no clear distinction can be made between β_1 and β_2, therefore the numbers given are rather uncertain. The β_1 state is saturated at 60–75 L and desorbs at 325 K with maximum rate. Hydrogen–deuterium isotope exchange experiments reveal the atomic nature of both adsorption states, and from a comparison of the desorption areas $\int p dt$ it is suggested that both exhibit equal hydrogen population. The Ru(0001) face contains 1.59×10^{15} atoms per cm^2, and the saturation density obtained reveals approximately 1.3×10^{15} ($\pm 20\%$) H atoms cm^{-2}, which corresponds to a coverage $\theta = 0.86$. It therefore appears probable that the maximum hydrogen chemisorption capacity of the (0001) face corresponds to a ratio of 1 : 1 for the hydrogen and ruthenium surface atoms.

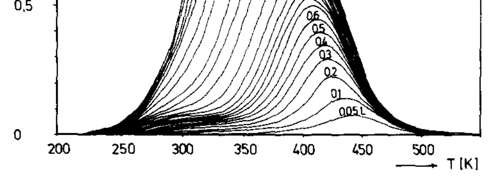

FIG. 1. A series of thermal desorption traces of hydrogen from a Ru(0001) surface. The adsorption was performed at T = 200 K, parameter is the exposure [L].

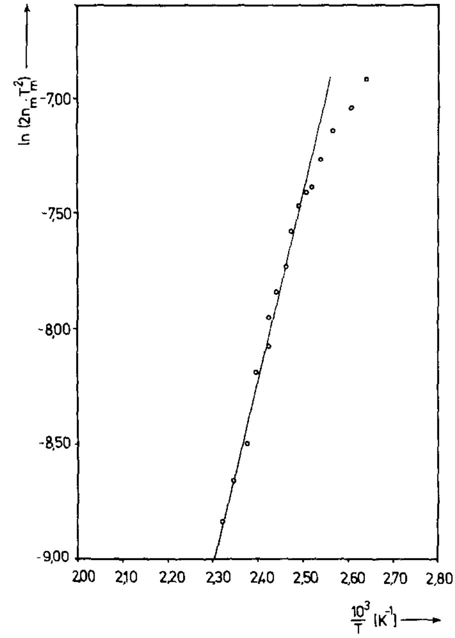

FIG. 2. Second order plot of $\ln(2n_{max}T_{max}^2)$ versus T_m^{-1} according to Redhead (37). ($2n_{max} = n_s$.)

The desorption curves reproduced in Fig. 1 also contain information on the activation energy for desorption, E^*. Conveniently, this can be obtained utilizing the simple method described by Redhead (*37*), assuming second-order kinetics and a coverage-independent E^* and frequency factor ν at low coverages. The result of this analysis for the β_2 state is shown in Fig. 2. A straight line obtained by a plot of $\ln(n_s T^2_{\max})$ versus T^{-1} indicates the applicability of the Redhead model at least at low coverages and yields an activation energy of approximately 16 kcal/mole = 67 kJ/ mole. The preexponential, ν, is determined from TDS curves obtained with different heating rates to be approximately 10^{-3} cm^2 H-atoms^{-1} sec^{-1}. However, deviations from the linearity at higher coverages as are evident from Fig. 2 suggest the use of a more realistic kinetic model to describe the desorption process. A more general desorption trace analysis has been proposed for example by King (*38*) and does explicitely consider the coverage dependence of E^* and ν. Application to the present data leads to a more complex E^* (θ) relation which is reproduced in Fig. 3. The adsorption energy of 16.5 kcal/mole (=β_2 state) is constant up to θ = 0.2 and then decreases steplike to 10 kcal/mole (=42 kJ/mole), when at higher coverage the β_1 state becomes populated. From a comparison of the adsorbed amount (cf. Fig. 1) with the gas exposure the sticking probability as a function of coverage was extracted which is shown in Fig. 4. The initial sticking coefficient is s_0 = 0.25 (±0.1). A pronounced decrease of s with increasing coverage θ is observed which actually exhibits some structure, namely a plateau at $\theta \approx 0.1$ and a steplike decrease at θ = 0.25. This structure appears to be correlated with the saturation of the β_2 desorption state and is evidence for the subsequent filling of the two TDS states.

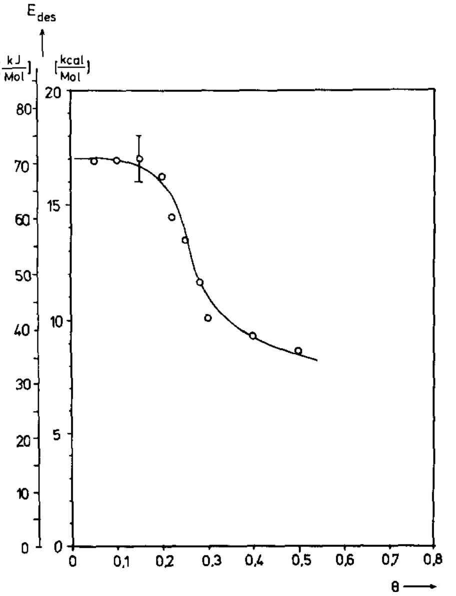

FIG. 3. Coverage dependence of the activation energy for desorption, E^*, as derived from a lineshape analysis of the curves of Fig. 1 according to King (*38*).

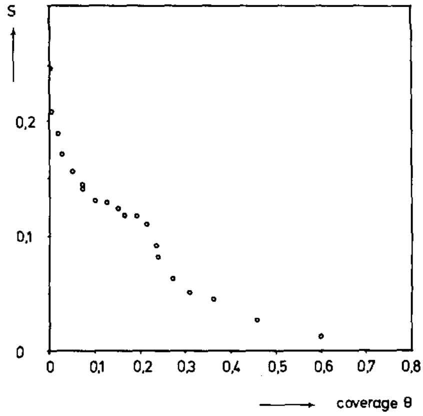

FIG. 4. Absolute sticking probability of hydrogen as a function of coverage θ, derived from the TD curves reproduced in Fig. 1.

The Ru(0001) surface shows a unique variation of the work function upon exposure to H_2. Extensive and systematic studies concerning this behavior have been performed by Feulner and Menzel (*13*), and the present results are in agreement with these findings. As is shown in Fig. 5 a carefully cleaned Ru(0001) sample kept at T = 200 K exhibits first an increase of the work function by approximately 15 meV followed by a continuous decrease of $\Delta\varphi$ down to −50 meV. These features slightly depend on the crystal temperature, presumably owing to a temperature influence on the population of both TD states each of them causing a dipole moment with reverse sign. Since no superstructure in LEED is

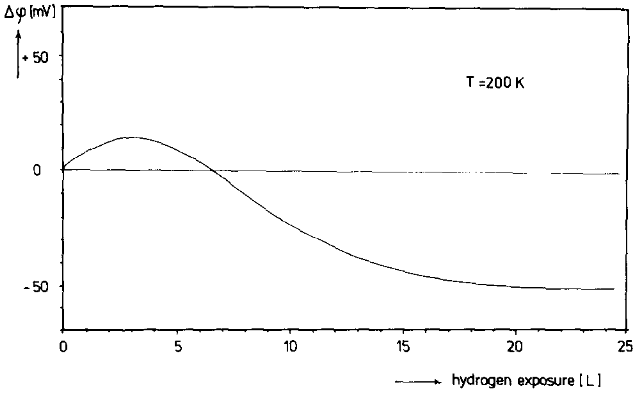

FIG. 5. Work function change Δφ for H_2/Ru(0001) versus the hydrogen exposure [L]. The sample temperature was 200 K.

found it is impossible to identify the two hydrogen species with adsorbate complexes of a different type of geometry. Other experimental techniques (for example vibrational spectroscopy) would have to be employed in order to elucidate the details of the $\Delta\varphi(\theta)$ function. The picture becomes even more complicated by the fact that traces of carbon impurities lead to a much stronger temperature dependence of the hydrogen-induced work function change: At temperatures around 150 K the behavior is almost identical with that of a clean Ru surface, whereas at room temperature increase of Δφ is no longer observed, but instead a pronounced decrease to values as low as −160 or −200 meV, depending on the C concentration. This observation, too, is in good agreement with results by Feulner and Menzel (*40*).

3.2. The Interaction of Hydrogen with Bimetallic Cu/Ru Surfaces

From the conclusions given (*1*) it can be inferred that a proper characterization of the bimetallic Cu/Ru system can be performed. Regarding various Cu surface concentrations, the following three regions may be distinguished: (a) the exclusive two-dimensional growth region (I), (b) the transition stage region (2 D → 3 D) (II), and (c) the 3 D Cu(111) epitaxial layer stage (III) (which, in principle, should exhibit a behavior similar to that of the bulk Cu(111)). With respect to Sinfelt's data range I with low Cu concentrations will be of particular interest. All coverage data for Cu given in the following section refer to a close-packed Cu(111) face ($\theta_{Cu} = 1.0$) which corresponds to a surface density of 1.77×10^{15} Cu atoms/cm^2.

As in the case of clean Ru(0001) and also Cu(111) surfaces H_2 does not form an ordered adsorbate phase on any Cu-covered Ru surface, at least not in the accessible pressure and temperature range. There is no evidence from LEED for a noticeable H-induced surface reconstruction as far as the geometry of the LEED pattern is concerned. However, no quantitative investigation of the LEED intensities was performed in the present case which might eventually indicate variations of the vertical spacings.

Figure 6 shows a series of thermal desorption curves obtained at 200 K from a Ru(0001) surface covered with Cu to approximately $\theta_{Cu} = 0.005$ (exclusive 2 D growth) after varying H_2 exposures. This set of curves has to be compared with that of the bare Ru reproduced in Fig. 1. It can be seen that neither the lineshape nor the position of the desorption maxima is significantly influenced while the total adsorbed amount (equal to the area below a TD curve) is suppressed considerably by the Cu deposit. This trend is even more evident from Fig. 7, where desorption

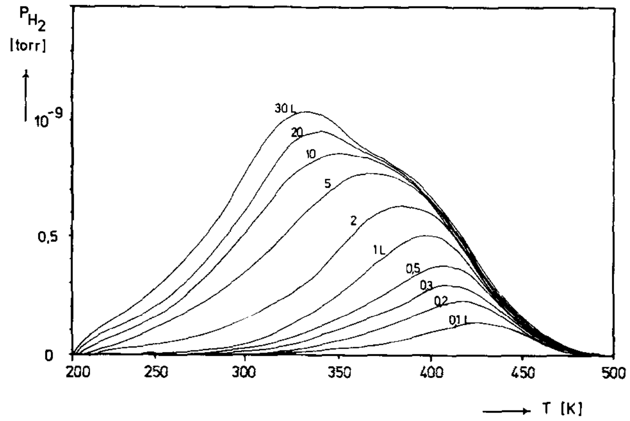

FIG. 6. Series of TD curves of hydrogen from a Ru(0001) surface covered with approximately 0.5% of monolayer (mL) copper. The adsorption was performed prior to desorption at T = 200 K, parameter is the exposure [L].

traces (always taken at an exposure of 1 L H_2) from Ru surfaces covered with increasing amounts of Cu are compared. These curves had been corrected with respect to the desorption contribution from the crystal edges and backside (cf. Section 2). The surprising reduction of the hydrogen uptake due to the presence of Cu is not only a result of a possibly reduced sticking probability, as is shown by Fig. 8, where the maximum hydrogen surface population which is held at $T = 150$ K on the surface *in vacuo* is plotted versus the amount of Cu present in the surface. Compared to the bare Ru surface already 4% of a copper monolayer ($= 7 \times 10^{13}$ Cu atoms/cm^2) causes a suppression of the hydrogen concentration on the surface by a factor of two, and $\theta_{Cu} = 0.20$ inhibits the hydrogen adsorption almost completely. It should be repeated in this context that the absolute Cu concentration data can be erroneous to within 30%. So the numbers given here show more of a trend rather than really quantitative data. Notwithstanding the more qualitative character of the TD results, a comparison with the Cu TD spectra (cf. Fig. 5b of (*1*)) shows that a reduction of the hydrogen uptake is already observed before the β_1 state occurs, as soon as this state grows exclusively no further adsorption of hydrogen takes place. Finally, another aspect is evident from the hydrogen thermal desorption spectra shown in Fig. 7:

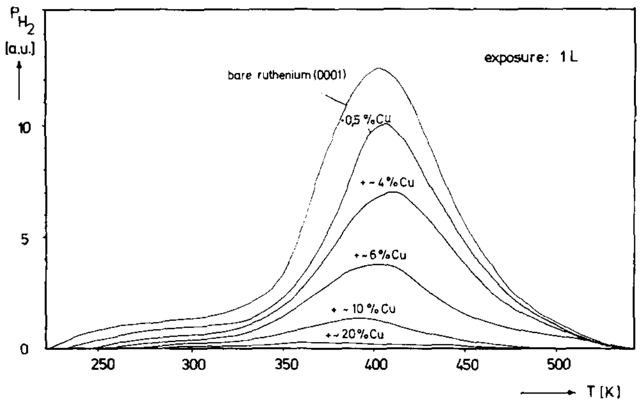

FIG. 7. Comparison of desorption traces obtained after 1 L hydrogen exposure from Ru(0001) faces with various amounts of Cu. Exposure was performed at 200 K.

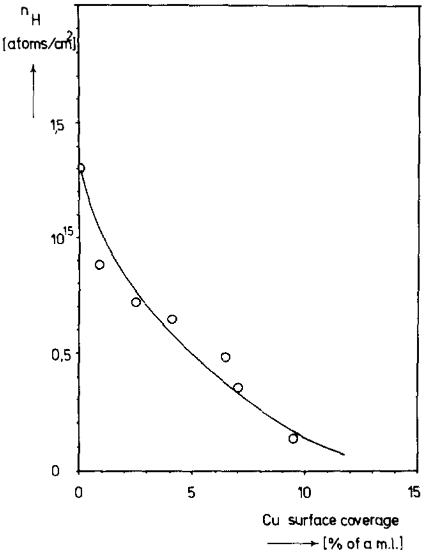

FIG. 8. Maximum amount of hydrogen adsorbed at T = 150 K on Ru(0001) faces covered with various amounts of copper as a function of the Cu surface coverage (in percentage of a ml).

The peak width at half maximum of all curves does not change significantly upon Cu addition but instead remains rather constant on a level of approximately 80–90 K. On the other hand, no additional desorption features can be observed which, e.g., could be ascribed to either a hydrogen species adsorbed exclusively on top of Cu atoms or at "mixed" Cu–Ru sites, even not at the saturation coverage which is attained in most cases after a H_2 exposure of approximately 30 L. Besides the striking depression of the adsorbed hydrogen amount some alteration of the position of the maximum of the desorption rate becomes evident from an inspection of Fig. 7, for copper surface concentrations above $\theta_{Cu} \approx 0.06$. From the temperature of the desorption maximum the (integral) activation energy for desorption was estimated by using the simple Redhead formalism (*37*) for a second order rate process. Figure 9 shows the thus developed activation energies (which are only an average and valid for small coverages) as a function of the copper concentration on the respective ruthenium surface. It can be seen that the activation energy, E^* (which, for nonactivated adsorption, equals the adsorption energy), is almost independent of the Cu concentration as long as this quantity does not exceed a level of approximately 10% of a Cu monolayer (corresponding to $\sim 2 \times 10^{14}$ Cu atoms/cm^2). However, at higher Cu surface densities, a distinct decay of E^* appears.

Figure 10 shows the variation of the sticking coefficient with hydrogen coverage for various Cu surface concentrations as extracted from TD experiments. The hydrogen coverage given in the graph is, for the bare Ru(0001) face, related to the H/Ru ratio of 1 : 1 (θ_H = 1.0 means a H surface concentration of 1.59×10^{15} atoms/cm^2). In the case of the bimetallic surfaces, the hydrogen coverage is referred to the actual Ru surface area (i.e., the real surface area multiplied by the mole fraction of Ru atoms). Apart from this correction, it appears rather difficult to define a reasonable measure for θ_H, since even for a low nominal H concentration locally a fairly large hydrogen density may exist which depends on the size of the bare Ru islands. Therefore Fig. 10 again shows a trend rather than a quantitative result.

A first glance at Fig. 10 may imply a continuous decrease of the initial sticking probability, s_0, as a function of the Cu surface concentration: Fig. 11 shows the

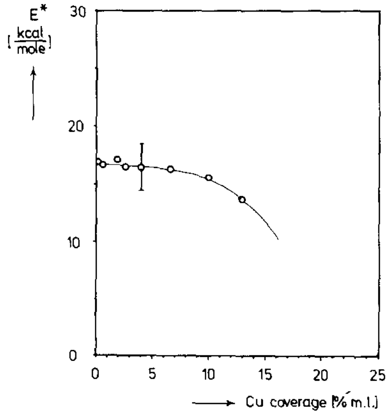

FIG. 9. Dependence of the activation energy for desorption, $E^*_{\beta_2}$, (as derived from a Redhead evaluation (*37*)) for various Cu surface concentrations from the Cu coverage (in percentage of a ml).

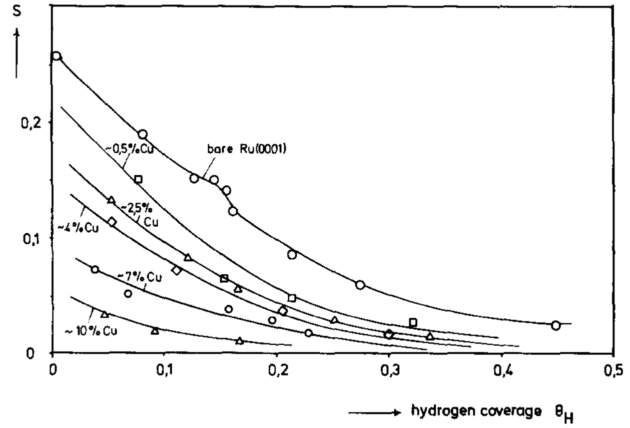

FIG. 10. Plots of the sticking probability/hydrogen coverage function for Ru(0001) planes with various amounts of Cu deposit. T_{ad} was in all cases ~200 K.

dependence of s_0 on the number of Cu atoms present on the surface. Actually a significant decrease of s_0 with increasing θ_{cu} arises. It has to be borne in mind, however, that the quantity s_0 has always been related to the number of Ru surface atoms derived from a simple geometric site balance. The desorption data instead show that the number of Ru sites being active in hydrogen adsorption is certainly much smaller (since the adsorbed amount decreases much more strongly than linear with the Cu concentration). In order to render a comparison of the hydrogen adsorption kinetics of Cu–Ru surfaces with various amounts of Cu possible some kind of "normalized" sticking coefficient, s', has to be introduced. s' is simply given by the ratio between s_0 (derived in the usual manner) and the corresponding hydrogen saturation density of the surface in question, which number is believed to be proportional to the true active Ru surface area. The resulting plot is reproduced in Fig. 12 and exhibits much less influence of the Cu concentration on the adsorption kinetics.

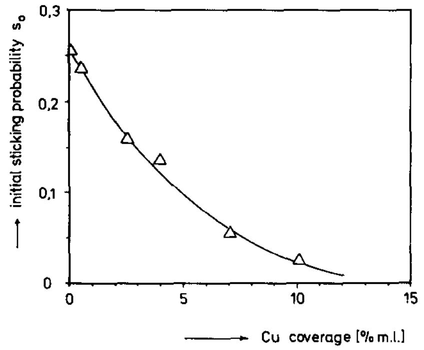

FIG. 11. Variation of the initial sticking probability for H adsorption, S_0, with the amount of copper preadsorbed. The data refer to T_{ad} = 200 K.

Some interesting results are obtained from the measurement of the work function change of a Cu–Ru surface exposed to hydrogen. Figure 13 shows for a variety of Cu surface concentrations how $\Delta\varphi$ depends on the hydrogen exposure (at T = 200 K), starting off with the bare Ru(0001) surface up to a face containing approximately 20% of a ml Cu. Below about θ_{cu} = 0.04 all curves behave fairly similarly to the clean Ru(0001) face, however with less pronounced features. An increase of $\Delta\varphi$ by 10 to 20 meV is followed by a broad maximum at about 2 L H exposure. Then the work function decreases again until after approximately 3–7 L the value of the uncovered surface is attained. Further hydrogen exposure causes a behavior which now strongly depends on the Cu concentration: Small Cu contents (i.e., θ_{cu} = 0.005 and 0.026) still effect a continuous decrease of the work function. Higher Cu deposits

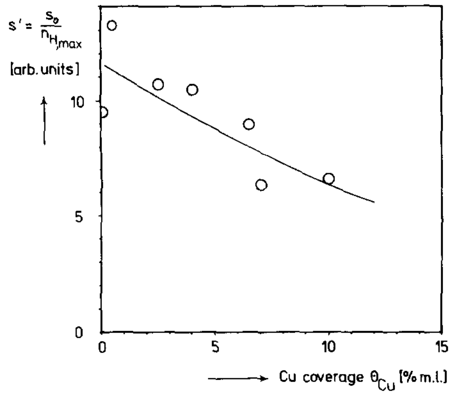

FIG. 12. Variation of the "normalized" sticking probability s' (see text) as a function of the amount of Cu deposit (in percentage of a ml).

($\theta_{Cu} \approx 0.04$) give rise to a very shallow minimum and a subsequent increase of $\Delta\varphi$ to at most 30–40 meV for $\theta_{Cu} = 0.075$. All these features are reversible with respect to the hydrogen coverage and end up with a constant value after approximately 30 L (saturation exposure at $T = 150$ K). However, in a very small Cu concentration range (corresponding to the termination of the 2 D and the onset of the 3 D growth) a unique behavior is found: After 5–10 L hydrogen exposure the work function increases continuously as long as H_2 gas is offered to the surface and keeps constant when the hydrogen gas is pumped off. The slope of the $\Delta\varphi$ (exposure) relation thereby strongly depends on the H_2 gas pressure: A high pressure causes a steep increase up to a final value of approximately 200–260 meV. This work function change is not reversible with respect to the exposure, that is to say, the desorption of the adsorbate (the concentration of which is quite small, cf. Fig. 7) does not restore the initial work function of the surface. The only plausible explanation that can be offered is that hydrogen chemisorption in this range causes a rearrangement of the Cu atoms (presumably 2 D ↔ 3 D) which is associated with an irreversible work function change. Cu amounts exceeding the 2 D stage and leading to the pronounced 3 D growth cause only very small work function variations upon hydrogen chemisorption which is in close agreement with the TDS results where the H uptake was shown to be practically zero for this range of Cu concentrations. No attempts were made to correlate the work function changes with the actual H surface coverage determined, e.g., from TDS experiments, since owing to the very small effects ($\Delta\varphi_{max} \leq 20$ meV, $\int p dt \leq 10^{-7}$ Pa sec) a considerable error is taken into a $\Delta\varphi - \theta$ relation, not to mention the ambiguity connected with the definition of the H coverage on a Ru surface diluted with copper.

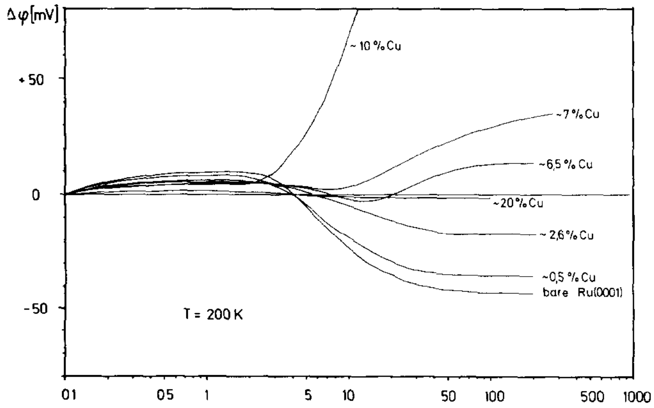

FIG. 13. H-induced work function change features as a function of the H_2 exposure (L) for different amounts of copper deposit. Note that the x axis is logarithmically compressed.

4. DISCUSSION

4.1. Hydrogen on Ru(0001)

The interaction between hydrogen and a clean and well-annealed Ru(0001) surface fits quite well into the picture which exists already for hydrogen adsorption on other densely packed transition metal surfaces, e.g., H/Ni(111) (*41*), H/Pd(111) (*42*), and H/Pt(111) (*34*). The adsorption occurs always in two binding states, β_1 and β_2, which both contain hydrogen *atoms* and are separated by an energy of approximately 2–6 kcal/mole = 0.09–0.26 eV. Danielson *et at.* (*12*) reported recently on an activation energy for H_2 desorption from Ru(0001) of 22 (±4) kcal/mole as derived from TDS data, using Redhead's method. The data underlying this evaluation, however, scatter considerably, and it is believed that the 22 kcal/mole reflects only a (small) portion of H atoms chemisorbed in the initial coverage range. Compared to this result our E^* value of 16.5 (±1) kcal/mole appears to be fairly low, but it has been determined independently from the TD traces using Redhead's method (*37*) and the lineshape analysis proposed by King (*38*) and by Falconer and Madix (*43*). Unfortunately, no isosteric heat data are available for the present system. A plausible explanation for the deviation of 5–7 kcal/mole cannot be offered at the moment, however, Danielson *et al.* (*12*) might have used a surface with a considerably high defect concentration (which could account for the high E^* and the high initial sticking probability of 0.4 as well). It should be mentioned that recent results from Menzel's group (*13*) also show evidence for a fairly low activation energy. Combining $E^* = 16.5$ kcal/mole with the dissociation energy of H_2 (103.2 kcal/mole) yields $E_{\text{Ru-H}} = 59.8$ kcal/mole (= 2.60 eV) for the strength of the metal–hydrogen bond which is similar to the numbers obtained for other H-transition metal systems: $E_{\text{Ni-H}} = 2.74$ eV, $E_{\text{Pd-H}} = 2.69$ eV, and $E_{\text{Pt-H}} = 2.47$ eV (*4*). The occurrence of a second adsorption state (labeled β_1) exhibiting an activation energy approximately 4–6 kcal/mole lower than the β_2 state is observed for coverages beyond $\theta = 0.2$–0.3 and is tentatively explained by the operation of indirect interaction forces between the adsorbed hydrogen atoms in a manner as described theoretically for the H/W(100) system by Grimley and Torrini (*44*) and Einstein and Schrieffer (*45*), and recently for a jellium surface by Lau and Kohn (*46*). Direct orbital overlap or geometric site arguments cannot account for the energy difference between both states, since even at saturation coverage (which, in accordance with the study by Danielson *et al.* (*12*), can be assumed to be $\theta = 1.0$) no restriction with respect to a most favorable adsorption sites should exist, nor is the nearest-neighbor distance sufficiently narrow. The β_1 state is also reported by Danielson *et al.* (*12*), but much less pronounced than in our case. The results by Feulner and Menzel (*13*) also show the β_1 state which, as with our TD curves, could not be resolved from the β_2 state. The order of the desorption reaction turns out to be *two* as is most likely for a dissociatively chemisorbed species. Accordance also exists with respect to the initial sticking probability which clearly differs from the fairly small numbers ($s_0 \leq 0.1$) reported for the H/Ni(111) (*41*), the H/Ni(100) (*47*), or the H/Pt(111) system (*34*). Danielson *et al.* (*12*) estimate $s_0 = 0.4$ and Feulner and Menzel (*13*) arrive at $s_0 = 0.3$ which values are within the limits of the present determination, $s_0 = 0.25$ (±0.1). The fact that the initial sticking coefficient is markedly higher for the H/Ru(0001) system than that observed for other densely packed hexagonal VIIIb metal surfaces (it almost reaches the level of the s_0 values characteristic for the H/W(100) system) cannot be understood at the moment, but might be related to the fairly low work function ($\varphi = 4.5$ eV (*10*)) of the clean Ru(0001) surface (*4*, *48*). No ordered hydrogen adlayer is found with Ru(0001), even not at 100 K, a result which was also confirmed by Feulner and Menzel

(*13*) by LEED observations. The lack of a long-range order might be due to a smooth energy surface of the Ru(0001) which does not restrict the surface diffusion of the adsorbed hydrogen to an appreciable extent. Eventual adsorbate–adsorbate interactions then have to be rather weak compared to the thermal energy kT at 150 K, which fact, however, would be somewhat inconsistent with the fairly large energy difference (~4–6 kcal/mole) suggested from the temperature separation of the β_1 and β_2 state in the TD spectra. This behavior is different from the H/Ni(111) system, where below 270 K an ordered H overlayer was found (*41, 49*), but very similar to the Pd(111)/H system which also did not exhibit the formation of any ordered hydrogen phase (*34*).

Mainly three characteristic features concerning the H-induced work function change have to be emphasized: (i) the very small overall effects ($\Delta\varphi$ ranges from +20 meV to −40 meV at most), (ii) the reversal of sign of the dipole moment, and (iii) the temperature dependence of $\Delta\varphi$ (which, to some extent, might be caused by a coverage effect as discussed below), not to mention the enormous sensitivity of $\Delta\varphi$ against carbon surface impurities. The initial increase of $\Delta\varphi$ in the course of the chemisorption process cannot be explained by assuming a preferred initial adsorption into ledge and kink sites caused by crystallographic defects as was a proper interpretation for the Pt(111)/H system, where similar $\Delta\varphi$ features were observed (*34, 39*). The amount of hydrogen leading to the initial work function increase is too large compared to the possible number of defect sites and, furthermore, does not depend on the annealing treatment of the Ru sample (which governs the defect concentration). A quite similar $\Delta\varphi$ behavior was recently observed with the H/Fe(110) system (*52*). No unequivocal correlation between the work function behavior and the population of the two desorption states can be made, although it seems likely to attribute the initial increase of $\Delta\varphi$ to adsorption into the β_2 and the final decrease to adsorption into the β_1 state (the extent of which increases, when the adsorption temperature is lowered). The intermediate $\Delta\varphi$ range could be caused by a more or less simultaneous adsorption into both states (the distribution of which also depends on the temperature), with the absolute height of the $\Delta\varphi$ maximum governed by the fraction of H atoms adsorbed in the β_2 state. The temperature dependence of the H-induced $\Delta\varphi$ as well as the very small overall changes render a use of $\Delta\varphi$ as a coverage monitor difficult. Therefore no attempt was made to determine the relation between $\Delta\varphi$ and the number of the adsorbed hydrogen atoms which would (among others) reflect the electronic interaction between H and Ru in the course of the chemisorption process. Little help in understanding this interaction is obtained from uv photoemission work which has been reported by Steinkilberg and Menzel (*14*). Like H/Ni(111), H/Pd(111), or H/Pt(111) (*50, 51*), only rather faint alterations of the energy distribution curve of the emitted photoelectrons are observed after the adsorption of hydrogen, namely, a fairly broad additional emission in the energy range between 6.5 and 7 eV which is tentatively explained as being caused by a H 1s resonance with sp- and d-electron states of the ruthenium. Coupling phenomena of this kind are discussed for H/transition metal systems in more detail by Demuth (*51*).

As a concluding remark, it should be stressed that the nature of the H–Ru bond does in no case deviate significantly from that of other VIIIb metal/H systems, as far as the densely packed crystal faces are concerned: The chemisorption occurs in an atomic form, and the bond energy of 2.6 eV fits well into the scheme. The presumably fairly small dipole moment of the adsorption complex suggests a nearly completely covalent character of the H–Ru bond which is generally predicted for H transition metal bonds by several chemisorption theories and experimentally confirmed several times (*4, 60*).

4.2. Hydrogen on Bimetallic Cu–Ru Surfaces

Differences between the adsorption properties of alloy or bimetallic cluster surfaces on the one hand and of the pure constituents on the other may arise mainly for two reasons: Either the local binding site geometry is altered upon alloying (owing to the substitution of site atoms), a phenomenon which is known as "ensemble effect" or a variation of the electronic environment of the adsorption sites will lead to altered interaction forces with different binding energies or even a different binding mechanism (ligand effect) (*53*). Furthermore, also the physisorbed state of a molecule (commonly referred to as a "precursor state") may become changed with alterations of the overall adsorption/desorption kinetics. Concerning, e.g., the dissociative chemisorption of hydrogen gas, the dissociation step may become accelerated or retarded only by slight alterations of the respective potential energy curves thereby influencing the rate processes on the surface in question by orders of magnitude. Sachtler and co-workers have investigated in great detail a number of surfaces of binary alloys, for example Cu–Ni– (*21*) or Ag–Pd– alloys (*28*), and they have discussed their results in terms of the ensemble and ligand effect.

In the case of the present bimetallic Ru/Cu system an important structural consequence arises from the immiscibility (which was also ascertained for Cu–Ru cluster catalysts utilizing ESCA by Helms and Sinfelt (*54*) Δ): The Cu atoms are not incorporated into the outermost Ru crystal surface but are instead located on top of Ru atoms in a level which reveals a mean perpendicular distance of approximately 2.25 Å to the adjacent Ru surface layer (a threefold hollow adsorption site assumed). This situation will lead to a Cu–Ru surface with a pronounced roughness which depends on the number and distribution of the adsorbed Cu atoms. Simultaneously, a fairly high variety of possible new adsorption sites for hydrogen is formed: Mixed adsorption sites (containing Cu and Ru atoms in various ratios) are now available as well as sites which exhibit a completely new coordination—due to the presence of Cu, e.g., kink and terrace sites are formed. As noted before, Cu is quasi-inert with respect to hydrogen *molecules* under uhv conditions, and the question arises, whether a single Cu atom or a small Cu ensemble in the vicinity of bare Ru patches is capable of adsorbing H atoms which have been formed by dissociation on the Ru part of the surface. The amount of the H atoms attached to Cu surface atoms then would be governed by the heat of adsorption for H on Cu which is supposed to be less than 10 kcal/mole (*15, 16*). An inspection of adsorption isotherms reported by Alexander and Pritchard (*15*) for hydrogen on polycrystalline Cu films with preferred (111) orientation clearly shows that (a normal preexponential factor of $\sim 10^{-2}$ cm^2/(H atoms sec) assumed) the temperature of the H desorption maximum would be certainly below 150 K. As a consequence, this weakly held hydrogen atoms would be hardly detectable in our experiments, owing to the apparative restrictions with respect to the lowest attainable temperature ($\sim$150 K) and the highest accessible dosing pressure ($\sim 10^{-3}$ Pa). At any rate our results (i.e., the strong inhibition effect of Cu atoms with respect to the more strongly held H atoms) suggest the necessity of a fairly large ensemble of Ru atoms for a H atom to become adsorbed as will be discussed further below.

Regarding the nature of the adsorption sites on a bimetallic surface in the first place, it can be immediately concluded from our hydrogen TD spectra taken at 150 K (cf. Fig. 7) that no additional desorption states appear when Cu is deposited on a Ru surface, nor is there any significant peak broadening observed. This is an indication that hydrogen does not adsorb on "mixed" sites containing both Ru and Cu with a binding energy only slightly different from a pure Ru site. Whether or not a weakly held hydrogen species (either atoms or molecules) exists on the surface cannot be decided from our TD experiments as noted before. Therefore a "spill-over" effect from the Ru to the Cu (which is, e.g., reported by Anderson *et al.* (*31*) for H adsorption on Au–Pt catalysts under high-pressure conditions) cannot be precluded. On the contrary, it seems most likely that with the Cu/Ru(0001) system, too, a weakly bound hydrogen species would be observable, if the pressure range could be extended up to the 10^{-1} Torr range. Such a weakly held hydrogen form was reported by Sinfelt *et al.* (*3*) on bimetallic Cu–Ru-supported catalysts, which, however, was at T ~ 300 K only stable in the presence of a few Torrs of hydrogen gas.

From an inspection of the activation energy of desorption, E^* (cf. Fig. 9), it is seen that within the limits of accuracy no variation of E^* with θ_{Cu} is found up to Cu contents of about 10% aml. This behavior strongly suggests that the addition of Cu does not produce a noticeable heterogeneity among the Ru adsorption sites. A quite similar result has been obtained by Yu *et al.* (*22*) for hydrogen adsorption on Cu–Ni alloys with varying composition where in a wide range no measurable influence of the alloy composition on the activation energy for hydrogen desorption could be detected. The observed shift of the desorption maximum at higher Cu contents, however, indicates a loss in hydrogen binding energy by about 2 kcal/mole when Cu is present in concentrations exceeding 10–20% of a monolayer. Since it was shown (*1*) that chemisorption of Cu on Ru is associated with a slight electron transfer it becomes plausible that at higher Cu concentrations the overall (i.e., delocalized) electronic properties of the Ru surface become slightly altered, which "ligand" effect could be made responsible for the slight observed decrease of the hydrogen chemisorption energy.

The most striking result of the present work is the dramatic suppression of the amount of chemisorbed hydrogen as soon as Cu is added to the surface. Since the ligand effect presumably will not play an important role and can therefore not account for this effect, one has to assume that an "ensemble" consisting of several adjacent Ru atoms is required for a hydrogen molecule to become dissociated and chemisorbed, that is to say one hydrogen molecule needs a fairly high number *n* of neighboring Ru atoms.

Following Yu *et al.* (*22*), the population of adsorption sites consisting of *n* active atoms randomly distributed in a bimetallic surface with the mole fraction X_a, can be taken to the proportional to $X_a{}^n$. The uptake of adsorbed gas should be proportional to $X_a{}^n$, too, if one assumes that the area under the desorption curve (obtained under saturation conditions) directly reflects the number of the above-stated adsorption sites. With this in mind, a log–log plot of the hydrogen amount adsorbed versus the mole fraction X_{Ru} of the active Ru atoms should yield a straight line with slope *n*. To a first approximation, the Ru surface concentration ($\propto X_{\mathrm{Ru}}$) can be determined by subtracting the known number of deposited (2 D-) Cu atoms from the total number of Ru atoms present in the Ru(0001) surface. In doing this and by taking the data of Fig. 8, the diagram reproduced in Fig. 14 is obtained which reveals a slope of $n \approx 10$, indicating a fairly large size of the Ru multiplet required for hydrogen adsorption in a surface diluted with copper. Even if it is assumed that the Cu surface concentrations as derived from AES–TDS data in a manner as outlined (*1*) are too small by 50% (which certainly limits the maximum degree of error) a value $n \approx 5$ results. The same procedure to determine *n* has, for example, been employed by Yu *et al.* (*22*) in the case of hydrogen adsorption on Cu–Ni alloys, which revealed $n = 4$, i.e., the H uptake

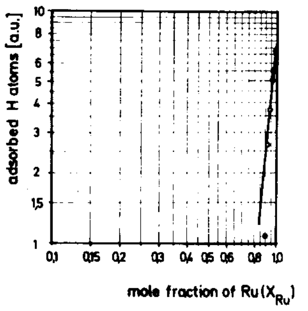

FIG. 14. Log–log plot of the maximum number of hydrogen atoms adsorbed on partly with Cu covered Ru(0001) surfaces versus the Ru surface concentration (mole fraction X_{Ru}).

increases in proportion to the fourth power of the surface Ni concentration. However, a correct interpretation of results obtained from such a crude consideration appears to be questionable for several reasons. First, the assumption of a multiplet of n adjacent active atoms is justified only if the atoms are randomly distributed over the substrate and do not show any correlation among each other. Regarding the present Cu/Ru system, it seems most likely that only a few individual Cu atoms exist on the surface, but rather ensembles consisting of several atoms. In this case, the destruction of Ru multiplets with a minimum size required for H adsorption is less severe than if the same number of single Cu atoms are randomly mixed into the Ru surface. In order to obtain a quantitative result, one has to treat the statistical problem as follows: To calculate the number of pairs, triplets, quadruplets, etc. of Ru atoms within a surface of a known overall geometry, when a certain distribution of single Cu atoms, pairs, triplets, quadruplets, etc. is given. Such a calculation turns out to be simple, if Cu ensembles of uniform size and shape are randomly distributed over the surface. In reality, however, no clusters of uniform size and shape are present but instead a distribution of Cu clusters containing n' atoms with n' running from 1 to (perhaps) 7, depending on the deposition parameters. For clusters with $n' > 2$ the distribution of the shape (linear or nonlinear) has to be considered. In the present case unfortunately both distribution functions are unknown, and a quantitative statistical treatment on the basis of the available data appears therefore to be hopeless. In the case of binary alloys, a first approach to this problem was suggested by Dowden (*55*). He considered the influence of ensembles of active atoms within a surface of inert atoms with respect to chemisorption and catalysis and derived statistical equations to determine, e.g., the probability that (in a bimetallic surface of known composition AB) a given atom will be of a desired type and that it will have a certain number m of nearest neighbors of the same type in an ensemble of a given number n of atoms. The derived expressions are rather simple and easy to calculate for a statistical mixture of both kinds of atoms. Complications arise, however, if short-range ordering occurs, but may be handled using additional formalisms according to Cowley (*56*) and Shante and Kirkpatrick (*57*). The overall result of Dowden's considerations is a rapid decay of the sum of binomial probabilities as soon as ensembles with an appreciable size consisting only of one type of atoms are regarded which is in qualitative agreement with our present findings. It should be mentioned in this context that statistical computations have been made in the group of Harsdorff (*58*) concerning the growth and nucleation problem of gold atoms on an alkali halide surface, however with a very good experimental data material available as provided by a direct counting of size and shape of particles utilizing electron microscopy. In concluding this section, the rapid decrease of the amount of chemisorbed hydrogen has clearly to be due to a pronounced "ensemble" effect: Obviously a fairly high number of neighboring Ru atoms (between about 5 and 10) is necessary for the chemisorption of hydrogen, although a more quantitative analysis is not yet possible.

Next some possible reasons for this surprising effect will be discussed: (i) Either the dissociation of a H_2 molecule proceeds only at sites consisting of more than two neighboring Ru atoms, or (ii) the chemisorption energy of a H atom will be drastically lowered as soon as a fairly large ensemble of surface atoms surrounding the actual adsorption site does not consist exclusively of Ru atoms.

The first aspect would mainly affect the adsorption kinetics, and in fact the initial sticking coefficient decreases strongly with increasing Cu content as shown in Fig. 11. As mentioned before this figure is somewhat misleading since the sticking coefficient was not derived with respect to the "active" Ru atoms in the surface layer, which obviously represent only a small fraction of the total number of the Ru surface atoms. Figure 12, where a sticking probability $s' = s_0/\theta_{H,\max}$ is plotted versus θ_{cu}, shows indeed only a little decrease of s' with the Cu surface concentration. If the role of Cu consists only in an influence on the adsorption kinetics, e.g., by building up an activation barrier for dissociative adsorption at neighboring Ru atoms, these Ru atoms should equally become populated by surface diffusion. That means that dissociation would take place on bare Ru ensembles and the formed H atoms would then be "spilled-over" to those Ru atoms which are located in the vicinity of Cu atoms (provided that these sites are not completely surrounded by Cu atoms forming a high activation barrier for surface diffusion). As a consequence the maximum adsorbed amount should be influenced much less by the presence of Cu atoms which would primarily affect the adsorption kinetics. Obviously this is not the case.

It appears therefore that the second explanation holds, i.e., the strength of the metal–hydrogen bond is determined by coupling to a fairly large number of metal atoms. A recent structural analysis of the H/Ni(111) system revealed that in this case the hydrogen atoms are located in threefold coordinated sites (i.e., attached to three neighboring Ni atoms) and that interactions between adsorbed H atoms are reaching next-neighbor distances (*59*). That means that if the three next-nearest neighbors are included an "ensemble" of at least six Ni atoms results which affect the chemisorption bond. If this picture is transferred to the Ru(0001) surface (which exhibits the same symmetry) the right order of magnitude for the critical ensemble size results. Since metallic sp-electronic states contribute significantly to the H chemisorption bond (*60*) the relatively strongly delocalized character of this bond becomes also plausible from this point of view.

In addition these results show that attempts to determine the mole fraction of platinum metal atoms present in the surface of an alloy by "titration" by means of hydrogen chemisorption might be questionable. Instead the resulting data will rather represent the portion of the surface which is active in reactions involving chemisorbed hydrogen. At least qualitative agreement exists between these conclusions and the results obtained with other systems. Stephan *et al.* (*30*) reported that the uptake of hydrogen irreversibly adsorbed at 78 K on a Pt surface decreases by a factor of two if it is alloyed by ~20% Au. The results by Yu *et al.* (*22*) with CuNi-alloys exhibit also a strong decrease of the hydrogen coverage with increasing Cu content, as outlined already above.

The discussion will be concluded by a comparison of the present findings with those of a study with Cu/Ru "bimetallic cluster" catalysts: Sinfelt *et al.* (*3*) measured hydrogen adsorption at room temperature and distinguished between "weakly" and "strongly" adsorbed species. The latter was defined as not being pumped-off at room temperature and can obviously be identified with the state of chemisorption investigated in the present work (whose rate of desorption becomes appreciable only above 300 K, cf. Fig. 1). In a typical experimental run it was found that the incorporation of 5% Cu decreased the amount of strongly adsorbed hydrogen to about one-tenth of its value found with pure Ru, i.e., a behavior quite similar to that observed in the present work. Unfortunately no quantitative comparison is possible since in Sinfelt's work no determination of the Cu surface concentration was possible but only of the overall composition.

Another observation was that with increasing temperature of the catalyst pretreatment the amount of adsorbed hydrogen was decreasing. This was ascribed to a more uniform spreading of the Cu atoms on top of the Ru substrate, an assumption which fits well into the picture of the growth mechanism previously described in detail (*1*).

Finally, a striking correlation between the ethane hydrogenolysis activity of Cu-Ru catalysts and their capacity for strongly chemisorbed hydrogen was reported by Sinfelt *et al.* (*3*), from which the necessity of an adjacent pair of bare Ru surface sites for the hydrogen chemisorption process was derived.

The pronounced similarity between Sinfelt's results and our own findings clearly justifies (at least for the Cu–Ru system) to model a real bimetallic cluster catalyst by a single crystal system (as was already assumed (*1*)). Therefore not only elementary steps of gas adsorption may be studied on these systems but also primary processes involved in hydrocarbon/hydrogen reactions.

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