SURFACE   SCIENCE   AND   CATALYSIS

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Abstract – Surface spectroscopic techniques may provide rather detailed information on the atomic processes occurring at solid surfaces. Some examples for applications of this 'surface science' approach to well-defined model systems and their implications on 'real' catalysis are presented. These comprise the characterization of catalyst surface (bimetallic Cu/Ru systems and ammonia synthesis catalysts) as well as studies on the elementary steps of catalytic reactions (synthesis of ammonia and oxidation of carbon monoxide).

INTRODUCTION

The elementary steps involved in a heterogeneously catalyzed reaction are in principle well known. These include adsorption and desorption steps (eventually associated by a variation of the molecular nature), surface migration as well as reactive and nonreactive interactions between the surface species. Thus a reaction path may be offered which is eventually more favourable and which proceeds under steady-state conditions with a higher rate than in the homogeneous phase. For a given catalyst this rate will then only be a function of the temperature and of the concentrations of the species in the fluid (i.e. gaseous or liquid) phase. Kinetic measurements will therefore always yield only rather indirect information on the reaction mechanism itself, and the situation is not very much improved if such studies are supplemented by measurements which are based on variations within the fluid phase (e.g. isotope exchange, selective adsorption etc.). In order to really understand the phenomenon of heterogeneous catalysis obviously more detailed information on the two following problems is needed: i) First of all the catalytically active surface regions have to be properly characterised on an atomic scale in order to be able to perform model studies with simpler systems which allow a systematic variation of the different parameters influencing the activity. ii) A much more elaborate task consists in identifying and characterising the surface species involved in the reaction in as much detail as possible. This information might then eventually be used in attempts for a proper theoretical description which represents the ultimate goal.

Until about a decade ago experimental techniques for direct spectroscopic investigation of surface processes were (with a few exceptions such as infrared spectroscopy) almost missing. In the meantime a great variety of methods became available which allow rather detailed insights into surface phenomena which comprise the field of 'surface science' (Ref. 1) and which have also been widely applied to problems of catalysis (Ref. 2). Studies of this type are, however, usually performed with model systems, namely well-defined clean single crystal faces (mostly of metals) and the conditions differ at a first sight appreciably from those of 'real' catalysis:
a) Only few catalysts are pure metals. The surface composition is usually ill-defined and may contain promotors. The activity may further be influenced by the support material. Therefore at first the actual surface composition and the chemical nature of the catalytically active surface under working conditions should be determined. Comparison with model systems can then be achieved by studying the influence of additives on the properties of clean surfaces.
b) Small catalyst particles expose various crystal planes and exhibit a variety of structural imperfections. This 'structural' factor can be studied by comparing the activities of different single crystal planes and by modelling the imperfections e.g. by introducing monoatomic steps or kinks in a well-defined manner. The importance of this latter aspect for example on reactions

involving C-C and C-H bonds was emphasized in great detail by Somorjai (Ref. 3). The situation is certainly much simpler if the reaction is 'structure-insensitive' (Ref. 4). c) Surface spectroscopic studies can only be performed at pressures below about 10^{-2} Pa. This 'pressure gap' can be partly overcome by using high-pressure cells from which the sample can be transferred into a spectrometer section for in situ surface analysis. This problem is, however, sometimes overstated: The transition to 'real' conditions is rather a question of surface concentrations than of gas pressure, and higher coverages can also easily be achieved by lowering the temperature which offers the advantage that surface intermediates have a longer lifetime (Ref. 2c). In cases where high pressures are needed for thermodynamic reasons (e.g. with ammonia synthesis) information on the microscopic surface reactions leading to the establishment of the equilibrium may equally well be obtained by studying the backward reaction which is accessible by low pressures. Nevertheless it has always to be checked carefully, to what extent the results obtained from model studies may be transferred to the conditions of practical catalysis. The following examples are intended to demonstrate the kind of information which can be obtained by this 'surface science' approach.

CHARACTERIZATION OF CATALYST SURFACES

Bimetallic Cu/Ru surfaces
Although Cu and Ru form no solid solutions, small catalyst particles ('bimetallic clusters') consisting of these metals were found to exhibit quite attractive catalytic properties for hydrocarbon reactions (Ref. 5). Based on the raft-like structure of these particles it was suggested that they probably consist of a thin Ru layer covered by less than a monoatomic layer of Cu atoms. In order to answer the question whether Cu atoms tend indeed to spread over a Ru surface instead of forming separate particles (as suggested by the bulk phase diagram) the following model experiment was performed (Ref. 6): Well-defined amounts of Cu atoms were deposited on a clean Ru(0001) single crystal surface and the resulting system was characterized by means of low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and thermal desorption spectroscopy (TDS). It turned out that the Cu atoms indeed form first a monoatomic layer on the Ru surface before threedimensional crystal growth is starting. The reason is an energetic one and can be seen from a series of thermal desorption spectra reproduced in Fig. 1 which were recorded after increasing amounts of Cu had been deposited: Up to a monolayer copper desorbs at a somewhat higher temperature than from bulk copper itself. The chemisorption energy of Cu on Ru is about 3 kcal/mole higher than the sublimation energy of (threedimensional) copper. The free energy of Cu-Ru interaction is on the other hand smaller than that for the Ru-Ru interaction so that no alloy formation takes place.

Hydrogen adsorption experiments with these single crystal systems (Ref. 7) revealed a strong decrease of the strongly chemisorbed amount with Cu concentrations forming only a fraction of a monolayer. This result is quite similar to the findings by Sinfelt et al. (Ref. 5) with 'bimetallic cluster' catalysts and is regarded to be responsible for the pronounced change in catalytic selectivity. This example shows how by proper 'tayloring' of a model system characterization of catalyst surfaces may be achieved.

Ammonia synthesis catalysts
Industrial ammonia synthesis is performed with promoted iron catalysts. XPS studies (Ref. 8) with commercial unreduced catalysts revealed that the surface region contains only relativley little Fe, but is strongly enriched by K , Al , Si etc. The bulk concentration of K , for example, was only 0.5%, but the surface was found to consist to 20% or even more of this element. Treatment of the catalyst in a N_2/H_2 mixture at 400°C causes an increase of the Fe surface concentration and simultaneously a reduction of this element into its metallic state. The latter effect is illustrated by fig. 2 showing spectra from the Fe2p(3/2) core-levels at various stages of reduction which exhibit a 'chemical shift' due to the variation of the oxidation state. Spectrum f corresponds to the situation under steady-state catalytic conditions and is identical to that obtained from an atomically clean iron surface. The valence state of the other cations is not affected by this treatment.

It is well known that aluminium and silicon oxides act as 'structural' promotors, i.e. they ascertain only a high degree of dispersion. Potassium on the other hand is an 'electronic' promotor, i.e. it affects the activity per unit area of iron (Ref. 9). It is thus concluded that
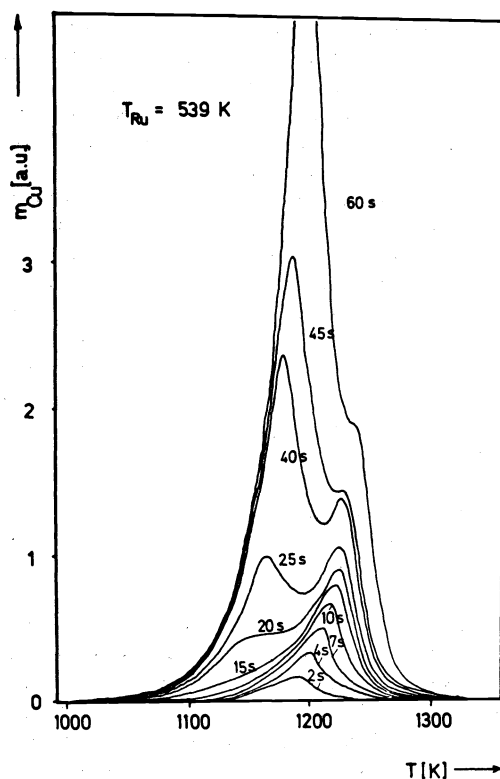
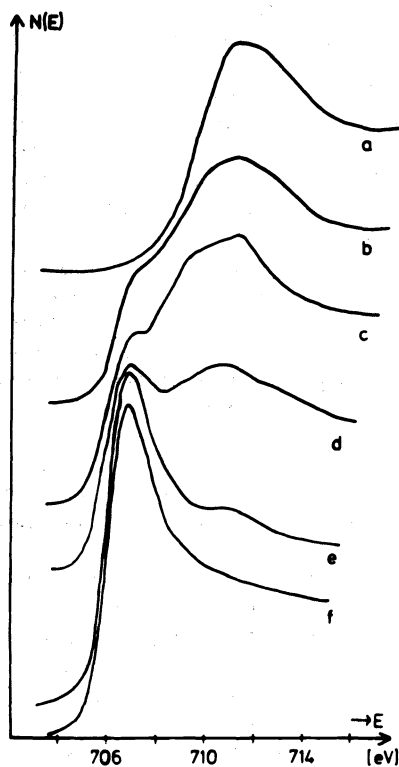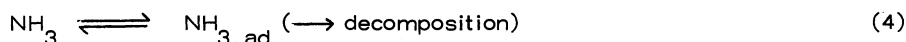Fig. 1. Thermal desorption spectra of Cu from a Ru(0001) single crystal surface.

Fig. 2. XP-spectra of the Fe2p(3/2)-level of an industrial ammonia catalyst at various stages of reduction. a: Unreduced, f: completely reduced.

clean Fe single crystal surfaces are a good starting point for model studies on this reaction, whereby the promotor action of potassium can be investigated separately by well-defined addition of this element.

REACTION   MECHANISM

Synthesis of ammonia

The question of the surface composition under working conditions is closely related with that
of the mechanism of the catalytic reaction. For the ammonia synthesis reaction this problem
was tackled in an extended series of experiments with various iron surfaces (Ref. 10). It was
found that the molecules involved in the reaction may undergo the following adsorption-desorp-
tion steps:

$$H_2 \;\rightleftharpoons\; 2\,H_{ad} \tag{1}$$

$$N_2 \;\rightleftharpoons\; N_{2,ad} \tag{2}$$

$$N_{2,ad} \;\rightleftharpoons\; 2\,N_{ad} \tag{3}$$

$$NH_3 \;\rightleftharpoons\; NH_{3,ad} \;(\longrightarrow \text{decomposition}) \tag{4}$$

It turned out that all these adsorbed species desorb in vacuo below $200^{\circ}C$, with the exception
of the atomic nitrogen species, N_{ad} , which recombines and desorbs only above 450° with
an appreciable rate. If under conditions far from equilibrium, (i.e. decomposition of NH_3
negligible) and at temperatures below $450^{\circ}C$ the reaction is run near atmospheric pressure and
the surface composition is analyzed afterwards in situ after evacuation but with the catalyst
still at elevated temperature, by this procedure obviously the N_{ad}-concentration will not be
affected due to its high thermal stability so that the surface analysis yields the surface
concentration of atomic nitrogen under working conditions.

This information can be used to solve the question whether ammonia synthesis proceeds via
a molecular or an atomic nitrogen species and furthermore to establish the nature of the
rate-limiting step: If the reaction proceeds via $N_{2,ad}$ according to the above scheme in a
parallel reaction $N_{2,ad}$ will also dissociate into N_{ad} and the surface will become saturated
with this species (if $T < 450^{\circ}C$) under steady-state reaction conditions, irrespective of the
H_2 pressure.

If on the other hand the reaction proceeds along

$$N_{ad} + 3\,H_{ad} \longrightarrow NH_3 \;,$$
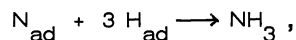
which forms a consecutive reaction to steps (2) and (3), then it can be easily seen that the
stationary N_{ad}-concentration will (at constant temperature and constant N_2 pressure) decrease
with increasing H_2 partial pressure.

Fig. 3 shows results for a Fe(111) surface (which has the highest catalytic activity), namely
the variation of the steady-state N_{ad}-concentration (as determined by Auger electron spectro-
scopy) with the H_2-pressure, while the N_2-pressure (150 torr) and the temperature ($310^{\circ}C$)
were kept constant. The data show clearly the behavior predicted by the atomic mechanism and
demonstrate moreover that in a stoichiometric $H_2 : N_2$ mixture (and under conditions far from
equilibrium) the stationary N_{ad}-concentration will be very small which means on the other
hand that dissociative nitrogen chemisorption is the rate-limiting step.

This latter process was studied with various Fe single crystal planes and revealed to be rather
complex: The effective sticking probability is only of the order of 10^{-5} to 10^{-7} (compared
with 10^{-1} for hydrogen). Nitrogen dissociation is associated with a small activation energy be-
tween 1 and 7 kcal/mole (depending on the surface orientation) and increases with increasing
coverage (which is one of the basic assumptions underlying the Temkin rate law). At $400^{\circ}C$
the rates differ by about two orders of magnitude between Fe(110) and Fe(111), the (111) plane
being the most active one. Except with Fe(100) the presence of atomic nitrogen causes
complex reconstructions of the topmost layers of the solid, therefore 'surface nitride' is a more
appropriate description of these phases.

The promoting action of potassium consists in a pronounced increase of this rate of dissociative
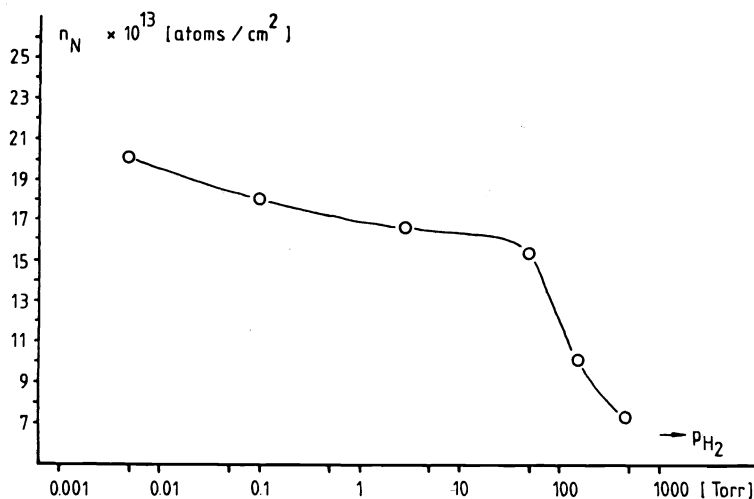nitrogen chemisorption (Ref. 11). This effect is achieved by an increase of the adsorption energy

Fig. 3. Steady-state surface concentration of atomic nitrogen on a Fe(111)-surface as a function of H_2-pressure at a constant N_2-pressure of 150 Torr and $T = 310°C$.

of molecular nitrogen which is accompanied by a lowering of the activation energy barrier for dissociation. The strengthening of the $M-N_2$ bond (by about 3 kcal/mole) is caused by the enhanced electron density in the vicinity of a K^+ ion on the Fe surface, as was suggested previously by Ozaki et al. (Ref. 12).

Without going into further details on the elucidation of the other reaction steps, it will only be shown how the existence of adsorbed NH as a surface intermediate was demonstrated by surface spectroscopic methods:
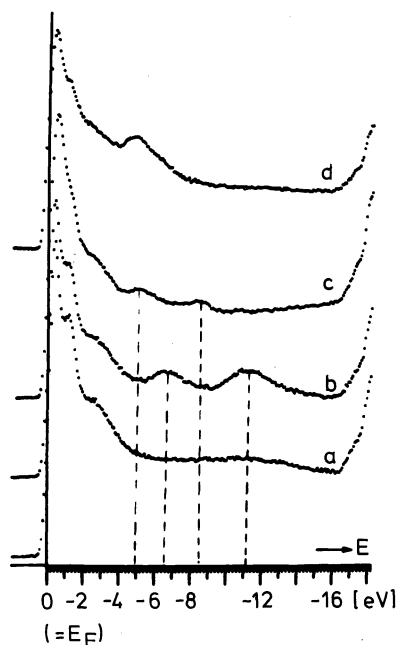

Fig. 4. UP-spectra from a Fe(110) surface
a) clean surface, b) after ammonia adsorption at 175 K ($NH_{3,ad}$),
c) NH_{ad} formed at 350 K, d) N_{ad} formed by heating to 500 K.

Fig. 4 shows a series of ultraviolet photoelectron spectra (UPS) from a Fe(110) surface at various stages of interaction with ammonia. Exposing a clean surface (curve a) to NH_3 below room temperature leads to the formation of a $NH_{3,ad}$-layer (curve b) which is characterized by two maxima at 6.7 and 11.2 eV below the Fermi level E_F (arising from ionization of the

N lone-electron pair and of the N-H bonds, respectively). Interaction with ammonia at 80°C on the other hand causes the build-up of an NH_{ad}-layer with maxima at -5.2 and -8.4 eV (curve c) and simultaneous formation of hydrogen. This species dissociates further upon heating above 120°C leading to the appearance of N_{ad} (as characterized by a single maximum at -4.9 eV) and to desorption of H_2. The intermediate formation of NH (with maximum concentration at 80°C) on the surface becomes further evident from experiments with secondary ion mass spectrometry (SIMS) as can be seen from fig. 5.
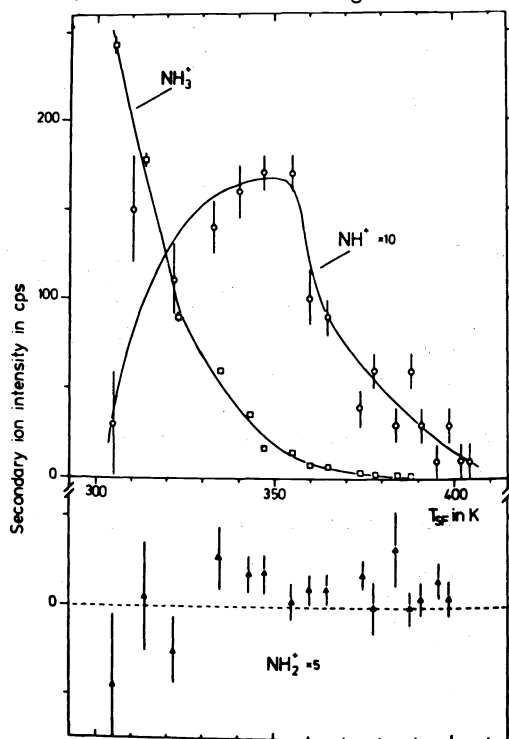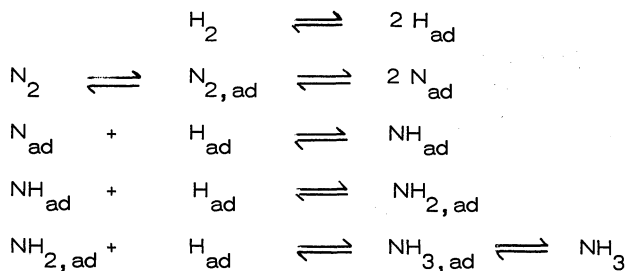

Fig. 5. SIMS-data for an ammonia covered Fe(110) surface as a function of temperature.

The total reaction mechanism has to be formulated as follows:

$$H_2 \rightleftharpoons 2 H_{ad}$$

$$N_2 \rightleftharpoons N_{2,ad} \rightleftharpoons 2 N_{ad}$$

$$N_{ad} + H_{ad} \rightleftharpoons NH_{ad}$$

$$NH_{ad} + H_{ad} \rightleftharpoons NH_{2,ad}$$

$$NH_{2,ad} + H_{ad} \rightleftharpoons NH_{3,ad} \rightleftharpoons NH_3$$

and agrees with earlier suggestions in the literature (Ref. 6).
A schematic potential energy diagram for the whole sequence of reaction steps involved in the synthesis of ammonia on iron is reproduced in fig. 6.

Oxidation of carbon monoxide
The formation of CO_2 by oxidation of CO over platinum metal catalysts is certainly the reaction which has been studied most extensively in the past years and whose elementary steps appear to be best understood (Ref. 13). Results with model systems may be safely transferred to real conditions: Experiments with different Pd single crystal planes for example revealed that the reaction is structure-insensitive as can be seen from fig. 7 where the steady-state rate of CO_2 formation is plotted as a function of temperature (Ref. 14). This result has recently been confirmed with small Pd catalyst particles of varying size (15).
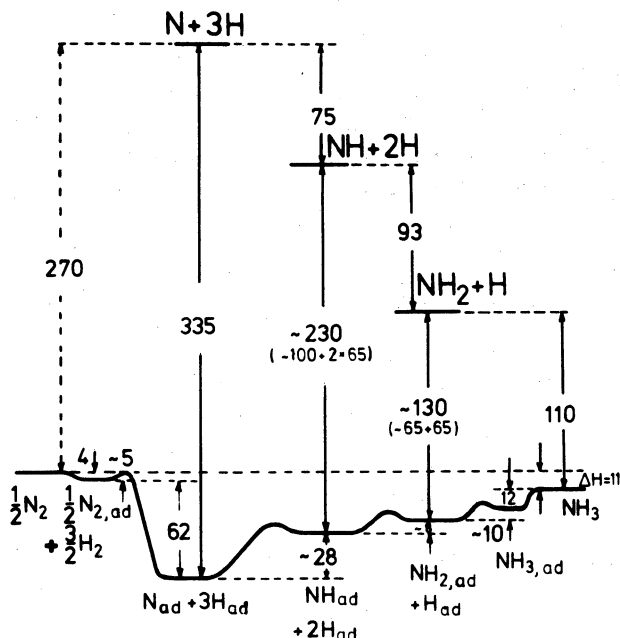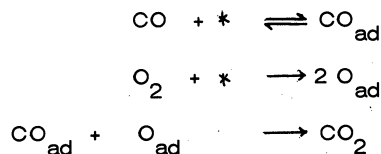
Fig. 6. Potential energy diagram for ammonia synthesis on iron surfaces (energies in kcal/mole).

It is now well established that the overall reaction proceeds along the following steps:

$$CO + * \rightleftharpoons CO_{ad}$$

$$O_2 + * \longrightarrow 2\,O_{ad}$$

$$CO_{ad} + O_{ad} \longrightarrow CO_2$$

* denotes schematically a free adsorption site, which represents, however, different arrangements of surface atoms for CO and oxygen as will be outlined below. Product formation occurs via a Langmuir-Hinshelwood mechanism; Eley-Rideal mechanisms of the type $CO + O_{ad} \rightarrow CO_2$ (or even $CO_{ad} + \frac{1}{2}O_2 \longrightarrow CO_2$) could clearly be ruled out by means of modulated molecular beam experiments (Ref. 16).

Steady-state rate of CO_2 formation at Pd surfaces

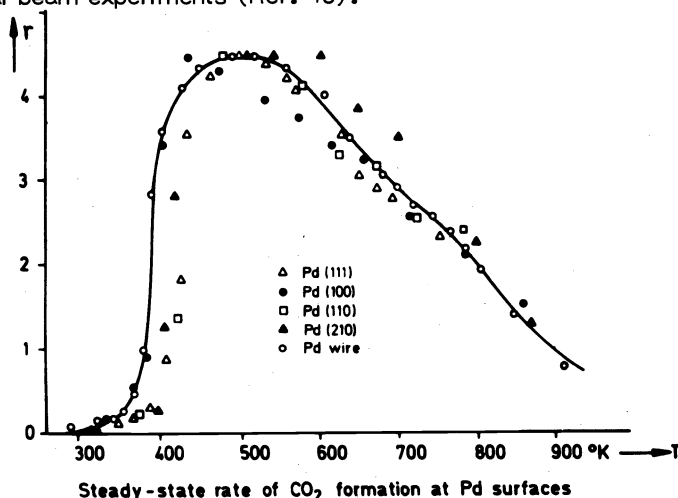Fig. 7. Steady-state rate of CO_2 formation as a function of temperature on different Pd surfaces.

CO adsorbs non-dissociatively with a high sticking coefficient and with adsorption energies between 30 and 40 kcal/mole (Ref. 13). As an example for the surface configuration of this

species fig. 8 shows the structure for CO on Pd(100) at $\theta = 0.5$ as determined by a LEED intensity analysis (17). The bridge-bond at this coverage is also characterized by frequencies of 1900 cm^{-1} for the C-O and of 340 cm^{-1} for the metal-CO vibrations, respectively. In general, adsorbed CO tends to form densely packed layers at high coverages, the maximum density being always about 1×10^{15} cm^{-2} as determined by steric effects.

By contrast oxygen adsorbs dissociatively (via a molecular 'precursor' state) and with a lower sticking probability. The adsorption energy is around 60 kcal/mole, that means about 90 kcal/ /mole for the strength of the M-O bond. The saturation density is not determined by the 'size' of the adsorbate, but instead relatively open overlayer structures are formed such as the 2x2-structure on the hexagonal (most densely packed) planes as shown in fig. 9.

This structural difference between O_{ad} and CO_{ad} has important consequences: If the CO coverage exceeds a certain limit oxygen chemisorption will become completely inhibited. A surface saturated with preadsorbed oxygen will on the other hand still be able to adsorb appreciable amounts of CO. Thus CO acts as an inhibitor for the reaction and its desorption is rate-limiting under steady-state conditions in the low temperature range. The detailed properties of coadsorbed O + CO phases are rather complex and include the formation of separate domains consisting of O_{ad} or CO_{ad} as well as the possible existence of mixed phases, depending on the relative concentrations, sequence of admission etc.(Ref. 18). Interactions between the adsorbed particles affect their effective adsorption energy and thereby also the activation energy for reaction.
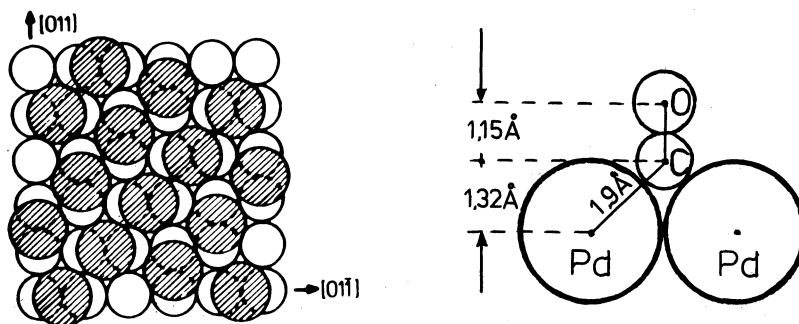

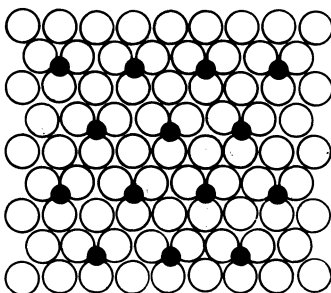Fig. 8. Structure model for CO adsorbed on a Pd(100) surface at $\theta = 0.5$

Fig. 9. Structure model for the 2x2-structure formed by chemisorbed atoms on Pd(111).

From these few remarks two points should become plausible:
i) The kinetics of the LH-reactions will in general not obey a simple rate law of the form $r = k \theta_o \cdot \theta_{co}$ which will only hold for a system of randomly distributed non-interacting partic-

les. ii) Even for an a priori uniform single crystal surface the 'true' activation energy, E^*_{LH}, is not constant, but due to the various intermolecular interaction forces depends on the fractional coverages of the reactants. Values for E^*_{LH} of 14 and 25 kcal/mole for Pd(111) (Ref. 16) and between 10 and 22 kcal/mole for Pt(111) (Ref. 19) have been determined. So it will also not be possible to formulate a generally valid rate-equation in terms of the partial pressures and of temperature, despite the rather simple sequence of elementary steps.
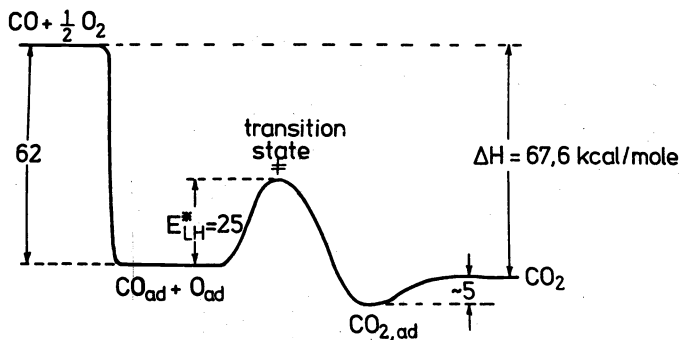

Fig. 10. Potential energy diagram for CO oxidation on Pd(111).

A schematic potential energy diagram for this reaction on Pd(111) at low coverages is reproduced in fig. 10.

A final interesting question concerns the mean energy of the CO_2 molecules coming off the surface: Deviations from a cosine-angular distribution of the produced CO_2 molecules were observed with Pt(111) (Ref. 19, 20) which result suggests that the reaction product leaves the surface with excess translational energy.

Velocity measurements revealed indeed that CO_2 formed on Pt at 880 K exhibits a mean translational energy in the motion perpendicular to the surface of more than 3000 K which corresponds to an excess energy of about 7 kcal/mole (Ref. 21). Inspection of fig. 10 indicates that in this case the product molecules obviously leave the surface on their way down from the transition state without becoming thermally accommodated with the surface ($\hat{=}$ $CO_{2,ad}$). Investigations on the energy distributions (including vibrational and rotational excitations) of species formed in exothermic surface reactions will certainly open a very interesting and fruitful field for future research on the reaction dynamics in heterogeneous catalysis.

CONCLUSIONS

The purpose of this contribution was to outline with a few selected examples what kind of information on heterogeneous catalysis can be obtained by using the methods of 'surface science'. A very great variety of suitable experimental techniques is now available which could not completely be mentioned. The presented examples represent relatively simple systems, for which on the other hand rather detailed insights could be obtained.

Many other catalytic reactions appear to be much more complex. This holds for example for all processes involving C-C and C-H bonds, where the characterisation of the catalytically active surface on an atomic scale seems to present a particular difficulty (Ref. 2b). The effects of promotors, poisons, structural irregularities and of the support material present wide and still almost unexplored fields for future research. Work on these aspects as well as on the mechanism of a series of other important catalytic reactions is in progress in many laboratories. Some results will be presented during this conference and it can safely be concluded that considerably more knowledge on the elementary processes in heterogeneous catalysis emerging from research along the presented lines will be available at the next congress of this type.

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