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WORKSHOP ON
"SURFACE SCIENCE AND CATALYSIS"
(4 - 8 May 1987)

BACKGROUND MATERIAL FOR LECTURES BY

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Theoretical Aspects of Surface Reactions.

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ABSTRACT

A short review is given of our present understanding of the trends in the chemisorption energies and activation energies for dissociation for simple gas molecules on the transition metals. The effect of adsorbed alkali atoms on the activation energy for dissociation is also discussed. This is then used to explain the trends in activity along the transition metal rows and the promoting effect of K for the ammonia synthesis reaction. The basis for the description is the development of a kinetic model for the ammonia synthesis which can describe quantitatively the macroscopic kinetics of a commercial catalyst under industrial conditions. The model relates the reaction rate directly to the properties of the chemisorbed reactants, intermediates and product as measured for model single crystal systems under ultra high vacuum conditions.

I. Introduction

One of the aspects about solid surfaces that has the largest fundamental and technical importance is the way in which chemical reactions are affected by the presence of a surface. Many reactions proceede with rates that are orders of magnitude larger at a surface than in the gas or liquid phase. For reactions with more than one possible product the presence of a surface can completely change the selectivity. One or both of these principles are used extensively in all industrial production of chemicals.

At the most general level the role of the surface can often be regarded as a means of stabilizing intermediates in the reaction. The synthesis of NH_3 directly from N_2 and H_2, for instance, is extremely slow in the gas phase because it requires a prohibitively large energy to break the N-N bond. At a metal surface the N atoms are stabilized by the chemisorption bond to the surface and this means that the reaction can proceede with a reasonable activation energy. Another effect of the surface is that it provides an effective energy dissipation medium. When it comes to understanding why some solids are better catalysts than others or why the addition of traces of other elements can increase or decrease the rate considerably, a much more detailed picture of the processes at the surface is needed. The same is true if we want to understand differences in selectivities between various surfaces.

Our understanding of the chemisorption process is still far from complete. So far the knowledge is almost exclusively about metal surfaces. Most is known about the static properties: chemisorption sites, bond lengths, binding energies etc.. The binding energy of simple atomic and molecular adsorbates can now be calculated as a function of distance outside the surface [1-5] and good agreement is found between experimental and theoretical results. There is also a qualitative understanding of the properties of the metal and the adsorbate determining bond lenths, vibrational frequencies, and trends in the binding energies from one metal to the next [4,5]. Even the adsorbate-induced relaxations and reconstructions of the surfaces is now beginning to be described [6]. One can say that the adiabatic potential energy surface is reasonably described for the simplest (atomic chemisorption) systems and that there is a qualitative understanding of some aspects of the potential energy hypersurfaces for more complicated systems [3,4,7].

Less is known about the dynamics of the adsorbate motion on the adiabatic potential energy surface. A large amount of information now emerges from molecular beam experiments. Molecular dynamics-like simulations of adsorbate dynamics have emphasized the complexity in the reaction dynamics introduced by the multi-dimensional nature of the adiabatic potential [8,9]. The coupling to substrate phonons is found to be an important energy transfer mechanism [9], but the coupling to the electron-hole pair excitations is also important, at least in some systems [10]. This is for instance evidenced by the occurence of chemiluminescence during adsorption of reactive molecules like O_2 or the halogens [10]. The question of the relative importance of the two energy dissipation mechanisms is still not resolved.

A kinetic description of chemical reactions is much simpler than a full dynamical description. Because of the thermal averaging, only certain features of the adiabatic potential energy surfaces, namely the minimum energy barriers separating the minima, enter into the rate [11]. The energy transfer processes and the complex motion on the multidimentional potential energy surface enter into the so-called pre-exponential factor. Usually one of the elementary steps in a chemical reaction is much slower than the others in which case the net rate of the reaction is equal to the rate of this step. The rest of the steps can be treated as equilibria and the equilibrium constants can be calculated from the properties of the intermediates. Several chemisorption systems are so well described experimentally under ultra high vacuum (UHV) conditions that it is possible to construct a surface reaction mechanism and use the UHV measurements to derive the kinetics for the reaction in question, which can be used without extra input to describe the reaction under high pressure and temperature conditions. This is the case for the the NH_3 synthesis over Fe [12,13] and for the reaction of CO with O_2 and NO over Rh [14]. More reactions are bound to follow shortly.

With the ability of relating the properties of chemisorbed molecules and atoms directly to the kinetics of high pressure catalytic reactions we also get a chance to use our understanding of the adiabatic potential energy surface for chemisorption to explain some of the general questions in the field of catalysis. This is what we shall attempt in the present paper. We will use the kinetics developed for the ammonia synthesis to explain i) why the transition metals close to iron in the periodic table are the most active catalysts for this reaction and ii) why potassium promotes the reaction considerably. In the following we first briefly discuss the qualitative picture of the trends in atomic binding energies and activation energies for dissociation. The kinetics of the ammonia synthesis is then reviewed, and finally in Section IV the results are presented and discussed. The last section is a summary.

II.The adiabatic potential energy surface.

The adiabatic potential is a high dimensional hypersurface in the space spanned by the adsorbate and substrate coordinates. As discussed in the introduction, only certain aspects of the potential energy surface enter into the rate expression. It is therefore illustrative for such purposes to give a one-dimentional representatation showing only the minima and barriers along the lowest energy reaction path. An example of such a representation of a calculated potential energy surface for the adsorption of a molecule (H_2) on a metal surface (Mg(0001)) is shown in Fig.1(b) [7]. It has many resemblances with the usual Lennard-Jones picture [15] as indicated in Fig.1(c), except for an extra minimum between the physisorbed state and the dissosiated state. This is a molecularly chemisorbed state which is a precursor to the dissociation. Similar states have been observed experimentally or found theoretically for a number of molecules (N_2, CO, O_2 etc.) [3,12,16] and the H_2 state has recently been observed on stepped Ni(100) [17].

Fig.1(a) shows the one-electron densities of states corresponding to the total energy diagram in Fig.1(b). Far from the surface, the H_2 bonding states are filled and the adsorbate is essentially a closed shell entity. The first barrier it meets approaching the surface is also completely analogous to the barrier seen by rare gas atoms at a surface. Closer to the surface the anti-bonding H_2 state is shifted down due to the interaction with the metal electrons and starts getting filled. This provides an attraction which bends the energy curve over and eventually gives rise to the chemisorbed molecule minimum. In spite of the substantial degree of filling of the anti-bonding level there is still some H-H interaction left here, which must be overcome if the molecule is to dissociate. This is what gives rise to the second energy barrier. The dissociated state shows a single adsorbate-induced resonance well below the Fermi level. This picture is not restricted to H_2. All simple molecules have anti-bonding levels which must fill during the dissociation and the one-electron spectra of the dissociated state show valence level resonances well below the Fermi level. For transition metals the interaction with the d-electrons generally increases the stability and lowers the energy barriers.

Using the effective medium theory [18] it can be shown that the contribution to the total energy from the adsorbate - metal-d interaction can simply be added to the sp-electron contribution and that it can be described by the change in the sum of one-electron energies due to the interaction with the d-electrons [19]. The sp-contribution is basically what is seen in Fig.1. This will not vary substantially from one transition metal to the next. The trends in the binding energies along the transition metal series are given by the trends in the adsorbate - metal-d interaction. Fig.2 shows the result [19] of a simple calculation of the trends using the Newns-Anderson Hamiltonian [20]. Two cases are shown. One where the adsorbate level is well below the Fermi level corresponding to the atomic chemisorption case (c.f. Fig.1) and one where the adsorbate level is at the Fermi level corresponding to a molecule at the top of the barrier between the molecular and atomc chemisorption minima. Again we stress that the present arguments are independent of the specific system studied.

The atom chemisorption energies vary according to the model approximately as N_d-10, where N_d is the number of d-electrons in the transition metal. This behaviour is observed experimentally for all the simple gas atoms [21]. The quality of the simple picture can be judged for H chemisorption from Fig.3. The fact that the slope of the chemisorption energy vs. atom number in Fig.3 is almost constant indicates that the adsorbate - metal-d coupling matrix element does not vary much from one metal to the next.

The activation energies for dissociation vary according to the simple model approximately as $(N_d-10)N_d$. This is at least in qualitative agreement with the observation that the tendency towards dissociation generally increases as one goes to the left from the noble metals Cu, Ag, and Au [22].

Returning to the picture of the dissociation process given by Fig.1 it is clear that the filling of the antibonding level will tend to make an adsorbing molecule slightly negative. This is in accordance with work function measurements. This also means that an adsorbing molecule will be very sensitive to variations in the electrostatic potential. This is the basis for the simplest model of the effect of surface impurities like alkali metals on the adsorption rate [23]. It can be seen from Fig.4 that an adsorbed alkali atom gives rise to a substantial increase in the electrostatic potential (as seen by a negative test-charge) at neighbouring sites due to the charge transfer from the alkali atom to the surface. An adsorbing molecule like N_2, CO, or O_2 will therefore be stabilized by the presence of adsorbed alkali atoms. The activation energy for dissociation is therefore decreased. Estimates based on Fig.4 indicate that the alkali-induced energy change is of the order 0.1 eV [23]. It can also be seen from Fig.4 that the effect is larger far from the surface where the molecular adsorption takes place than closer in where chemisorbed atoms have their equlibrium positions.

Electro-negative atoms like O, S, or Cl give rise to an electrostatic potential of the opposite sign than the electro-positive alkali atoms and therefore have the opposite effect on the activation energy for dissociation [23].

Other models of the poisoning and promotion of surface reactions have been proposed [24]. They focus on the change in the surface density of states induced by the presence of the poison or promoter atoms. It still remains to explore what effect such changes have on the molecule-metal interaction energies. It should be pointed out that adsorbed atoms could affect the adsorption process in more than one way. The electrostatic interaction will always be present, and can alone explain most experimental observations [23].

III. The kinetics of the ammonia synthesis.

The kinetic model we have developed to describe the ammonia synthesis is discussed in detail in a series of papers [13]. Here we only mention a few important points. The mechanism for the reaction derived from the literature [12,25] and the picture of the adsorption process given above is assumed to be the following:

$$N_2 + * \rightarrow N_2{-}* \tag{1}$$

$$N_2{-}* + * \rightarrow 2N{-}* \tag{2}$$

$$H_2 + 2* \rightarrow 2H{-}* \tag{3}$$

$$N{-}* + H{-}* \rightarrow NH{-}* + * \tag{4}$$

$$NH{-}* + H{-}* \rightarrow NH_2{-}* + * \tag{5}$$

$$NH_2{-}* + H{-}* \rightarrow NH_3{-}* + * \tag{6}$$

$$NH_3{-}* \rightarrow NH_3 + * \tag{7}$$

Here a * signifies a free site on the surface. The second step, which is the dissociation of the molecular precursor, is assumed to be rate limiting in accordance with a number of experimental observations [12,23]. The overall rate is then given by the difference between the forward and backward rate of step (2):

$$r=2k_2(\theta_{N_2*}\theta_* - \frac{1}{K_2}\theta_{N*}^2) \tag{8}$$

where θ_x is the coverage of x. K_2 is the equilibrium constant of step 2, and

$$k_2=k_0 exp(-E_{a2}/kT) \tag{9}$$

is the rate constant for step 2. k_2 is given from the N_2 sticking coefficient [13], which has been measured as a function of temperature on various Fe single crystal surfaces with and without adsorbed K [12]. Since we are trying to model a commercial catalyst which is promoted with K [26] we use the value for the optimally promoted surface. The sticking probability is approximately independent of the crystal face when K is present [12].

The coverages are given from the equilibrium constants for all the other steps. These can be calculated from the partition functions of the adsorbed and gas phase species, and the partition functions can be estimated from the binding energies and vibrational and rotational excitation energies. These have to a large extend been measured. The binding energies are deduced from thermal desorption measurements. This amounts to considering only the first two reaction steps. It is important to know the sticking coefficient before the binding energy is deduced because the desorption rate is related to it by the principle of microscopic reversibility [11].

The resulting calculated ammonia production is compared to measured values in a test reactor with a commersial catalyst under a broad range of conditions in Fig.5. In order to model the plug flow test reactor it is nessecary to devide the reactor up into small segments. The gas compostion in each segment is given from the conversion in all the previous segments. The only knowledge about the catalyst used in the calculations is the area of metallic Fe, which is measured independently by CO chemisorption.

The agreement between theory and experiment seen in Fig.5 gives confidence that the model describes the essential features of the reaction. We can go on to look at the coverages of adsorbed species down through the reactor. The coverages will change as the gas phase composition changes due to the ammonia production. Fig.6 shows the coverages for a typical set of conditions. It is seen that the coverage of free sites is very small and that basically all of the sites on the surface are covered by atomic N, which has by far the largest binding energy. This is why the N chemisorption energy is the most important parameter in the problem together with the N_2 sticking coefficient. The other binding energies and all of the excitation energies can be changed substantially without changing the result [13].

IV. Understanding the trends in activity.

We can now combine the understanding of the trends in binding energies and activation energies as a function of the metal and the presence of additives with the kinetics of the ammonia synthesis. This should allow us to describe the trends in the catalytic activities.

First we shall consider the variations in the catalytic activity along the transition metal rows [13]. We use the variation of the chemisorption energies and the activation energies for the dissociation process with the number of d-electrons N_d discussed in Section II:

$$E_{chem}=E_{chem}^{0}+c_1(N_d-10) \tag{10}$$

$$E_a=E_a^{0}+c_2N_d(N_d-10) \tag{11}$$

We neglect the dependence of these energies on the d-band width and the coupling matrix element. As discussed in connection with Fig.2 there is some justification for this, but it is clearly a crude approximation which can only be expected to give the general trends. This, for instance, means that we cannot describe the differences in the activities for transition metals in the same group. If one is interested in the activity of a given metal the chemisorption properties of the reactants on this surface should be measured in detail.

The values of the parameters in Eq.(10) and (11) for nitrogen adsorption are chosen to be $E_{chem}^{0}=-0.10$ eV, $E_a^{0}=1.95$ eV, $c_1=0.057$ eV, and $c_2=0.094$eV. These values correctly reproduce the detailed measurements for Fe(111) [12] that form the basis for the description of the reactior over iron described above. They also give a sticking probability for N_2 on W(100) of the order one as found on the most reactive faces [27]. Finally, they give thermal desorption peak temperatures for atomically chemisorbed N on W(100) [27] and Ni(100) [28] within 20 K of experiment. It must be stressed that the parameter set is not unique. Other sets could be used to reproduce the experimental results used. This procedure is not meant to give quantitative results, but merely to give reasonable parameters from which the *trends* can be described. The variation of the H chemisorption energies with N_d is determined from Fig.3. The chemisorption energies for the other surface intermediates are varied in proportion to the variations in the N chemisorption energy. As discussed in Section III the values of these parameters are not very important for the ammonia production. The same is the case for the vibrational and rotational excitation energies, which are assumed the same as for Fe everywhere.

The variation of the catalytic activity measured as the ammonia production for a fixed area of the catalyst with the number of d-electrons is shown in Fig.7. The figure clearly has the 'volcano' shape observed for a large number of reactions [29,30]. It also shows N_d around 7 (Fe, Ru) to be the most active catalyst in agreement with experimental experience [30]. Having established that the model reproduces the known facts about the trends in the activities we can use it to unders and the origin of the trends. From the above discussion it is rather simple [19]. The optimum catalyst is a compromise between a high N_2 sticking coefficient and a low N chemisorption energy. A high rate constant for the rate limiting step is of cause always desirable. Since the activation energy for dissociation is minimum towards the middle of the transition metal series the dissociation rate is maximum here. A low N chemisorption energy is desirable because this gives a low θ_{N*} and a high coverage θ_* of free sites where the reaction can take place. The chemisorption energies are lowest to the right in the transition metal series. $N_d=7$ is the compromise. To the right of $N_d=7$ there is plenty of free surface but the dissociation is slow, whereas to the left the dissociation is fast but the surface is covered completely with N.

To increase the activity of, say, Fe significantly, the activation energy for dissociation must be decreased without an increased stability of the chemisorbed atom. This cannot be acomplished by changing the metal. The best thing to do is to add adsorbed K. As discussed in Section II this decreases the activation energy without affecting the chemisorbed atoms nearly as much. This is the basis for the use of K as promotor in all commercial ammonia catalysts. Adsorbed K increases the sticking probability by decreasing the activation barrier or equivalently increasing the stability of the chemisorbed molecule by 0.1 eV [12]. This can account semi-quantitatively for the promoting effect seen in the high pressure catalytic reaction as illustrated in Fig.8. Here the ammonia concentration is shown as a function of distance down a reactor is shown in two cases: one using the usual sticking coefficient of the K promoted surface as in Fig.5 and one using the smaller N_2–* binding energy corresponding to the sticking probability on the clean Fe(111) surface [12].

In Fig 8 we also show the measured ammonia concentration out of a reactor with the usual catalyst and a catalyst prepared without any K. The effect of K is very significant. It must be pointed out that the difference in ammonia concentration seen corresponds to about a factor of six in the rate. The calculated rate is somewhat higher than the experimental one for the unpromoted catalyst. This is presumably to a large extend because we have used the sticking probability for the most active (111) surface for all of the Fe surface. This must result in an overestimate.

The poisoning effect of chemisorbed oxygen can be described in a similar way. The oxygen is introduced in the system as traces of water in the synthesis gas. This is discussed in detail in Ref.13.

V.Summary.

In summary we have shown that in spite of its incompleteness the theoretical description of the interaction potentials for chemisorption of simple gases is so developed that it can provide an understanding of qualitative features in catalysis. We can understand the origin of the 'volcano' shaped relation between catalytic activity and the position of the metal catalyst in the transition metal series found for many reactions. Our discussion has been based mainly on the ammonia synthesis, but qualitatively the same picture will be valid for other reactions as well. The promotiong effect of alkalies and the poisoning effect of oxygen on the rate of ammonia synthesis can also described.

There is still a long way before we understand the full dynamics of adsorption and reactions. Rate constants cannot be calculated from first principles, but must be measured. The measurements can be performed on well characterised single crystal models and we have shown that such measurements can be used in the description of the complex phenomena at a catalyst surface operationg under high pressure and temperature conditions.

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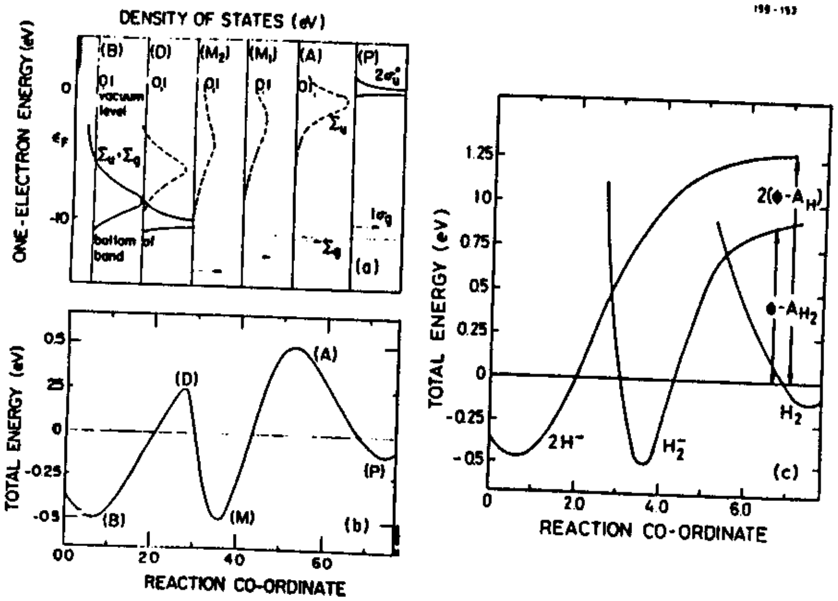

FIG.1. (a) One-electron density of states and (b) total binding energy for an H_2 molecule approaching a Mg(0001) surface with the moleculaer axis parallel to the surface and oriented along the <100> direction above a Mg atom, as a function of position along the reaction coordinate connecting the local minima and saddle points of the adiabatic potential energy surface. The extrema on the potential are denoted: (P) Physisorbed state. (A) Activation barrier for molecular adsorption. (M) Molecularly adsorbed state. Here the density of states is shown both in the outer (M_1) and inner (M_2) part of the well. (D) Activation barrier for dissociation. (B) Two isolated H atoms chemisorbed in the two-fold bridge site. In (c) we show a schematic picture derived from (a) showing how (b) can be interpreted as originating from a series of diabatic states, which can be described approximately as H_2, H_2^-, and $2H^-$, respectively. ϕ denotes the metal work function and A_x the affinity of x. It is easily seen how (local) changes in ϕ will change the stability of H_2^- and the height of the activation barriers.

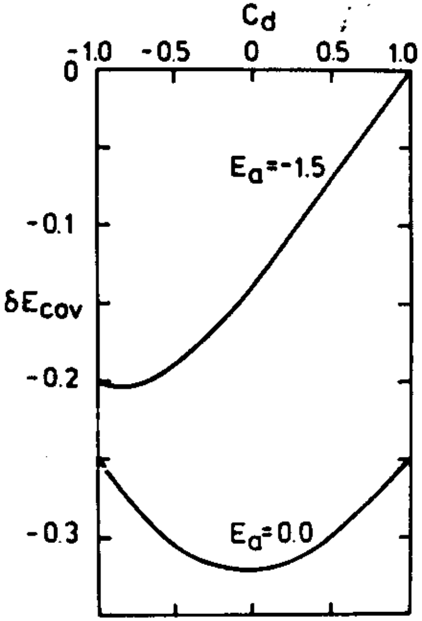

FIG.2. The change in the sum of the one-electron energies when a one-electron state with energy E_a interacts with a band of one-electron states. The calculation is performed within the resonant level model (after Newns, Ref. 20) using a semi-elliptical band. The one-electron energy difference, which is responsible for the trends in the interaction energy of an adsorbate and a transition metal surface, is shown as a function of the position of the center of the band, or equivalently, the degree of filling of the band, for two cases: one where the adsorbate level is at the Fermi level and one where it is well below. Energies are measured relative to the Fermi level and in units of half the band-width. The hopping matrix element is assumed constant and equal to 0.5. Moderate changes in this does not change the trends. From Ref. 19.

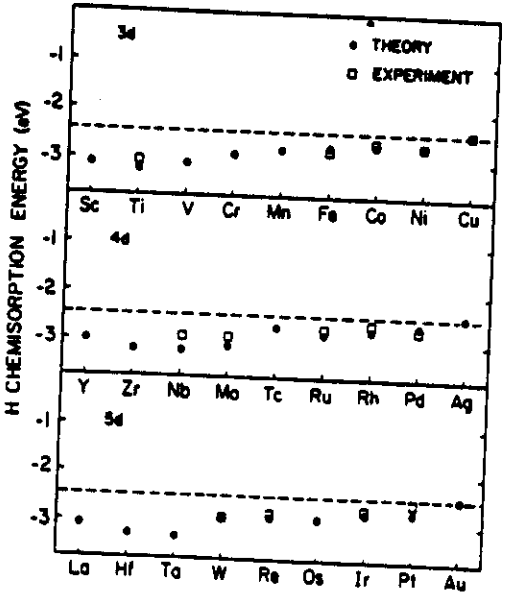

FIG.3. Comparison between calculated and experimental hydrogen chemisorption energies for all the transition metals. From Ref.5.

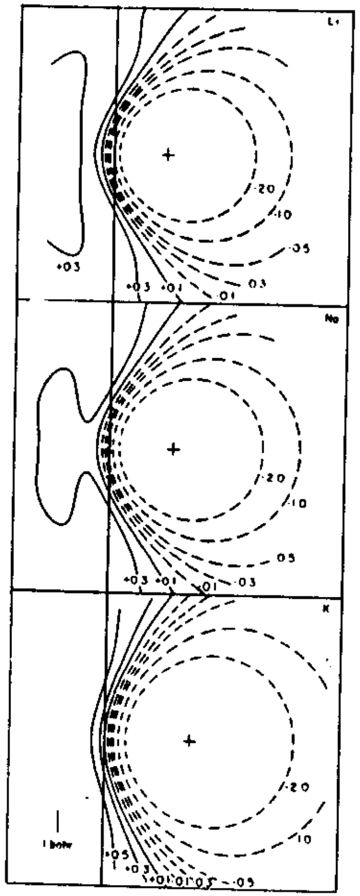

FIG.4. The induced electrostatic potential due to adsorbed alkali metals on a jellium (r_s=2) surface. The adsorbed atoms are at their calculated equilibrium positions. Contour values of +-2, +-1, +-0.5, +-0.3, and +-0.1 are shown within a sphere of radius 7 bohr. The vertical line denotes the jellium edge. From Ref. 23.

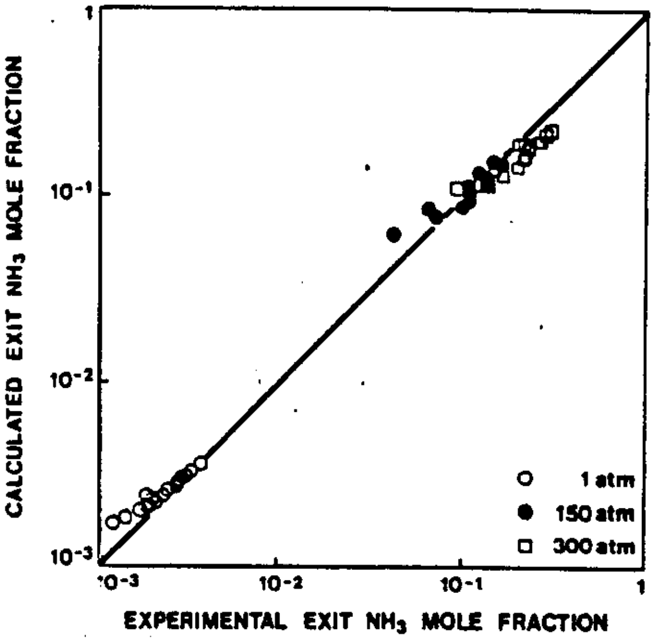

FIG.5. Comparison of the calculated and experimental ammonia production over a Topsøe KMI catalyst. The data set spans a broad range of pressures (1-300 atm), temperature (375-500 C) and gas velocities. The synthesis gas is a 1:3 mixture of N_2 and H_2. From Ref. 13.

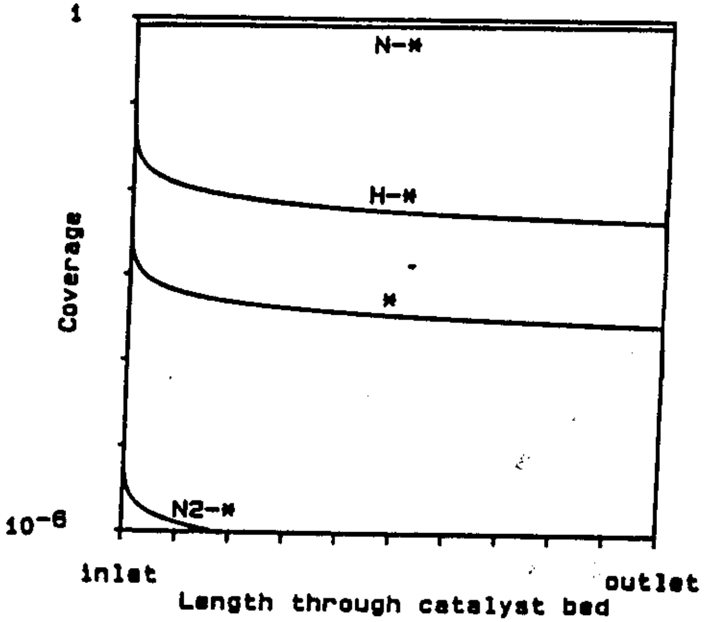

FIG.6. Variation of the coverage of various species down an ammonia reactor with a K promoted Fe catalyst at 100 atm, 400 C, stoiciometric inlet gas. From Ref. 13.

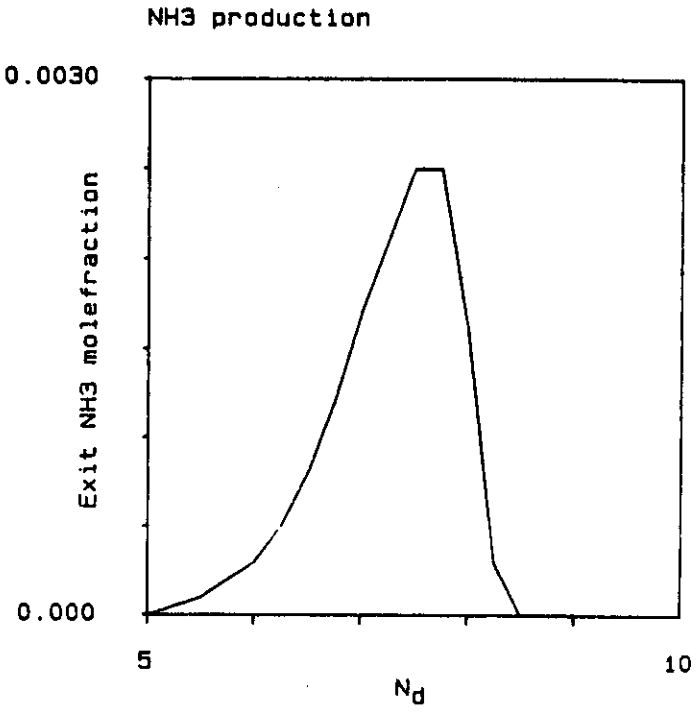

FIG.7. Trends in the ammonia production from 1 m^2 of catalyst as a function of the number of d-electrons in the substrate. The reaction conditions are kept constant(1 atm, 400 C, stoiciometric gas). The binding energies and activations energies are estimated as discussed in the text. From Ref.13.

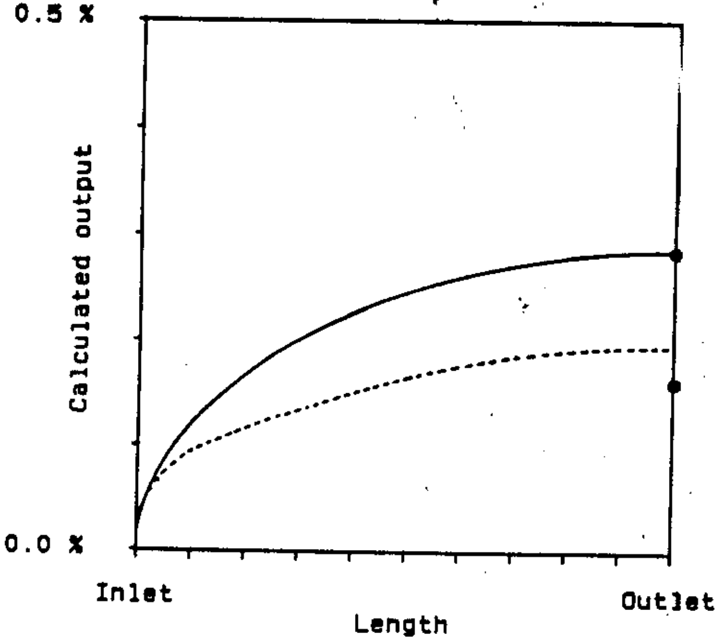

FIG.8. The variation in the ammonia concentration down a reactor at 1 atm, 400 C, using the sticking propability for an unpromoted and a K promoted Fe surface. The measured concentration at the outlet for the commersial catalyst (with K) and a model catalyst without K is indicated. From Ref.13.