Bridging the "Pressure Gap" between Ultrahigh-Vacuum Surface Physics and High-Pressure Catalysis

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It is shown that it is possible to calculate the ammonia synthesis rate in a catalytic reactor at industrial conditions (150–300 atm, 375–500 °C) starting from measurements of the properties of the reactants on well-defined single-crystal surfaces under ultrahigh-vacuum conditions. A generalized form of Fowler and Guggenheim's statistical mechanical treatment of adsorption is used in conjunction with the reaction scheme proposed by Ertl *et al.* The calculation contains no adjustable parameters and reproduces experimental data over a broad range of conditions.
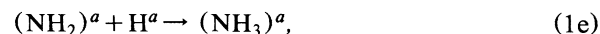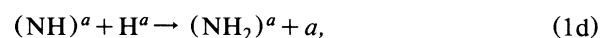
One of the main motivations behind the rapidly expanding effort in surface physics is the presumption that it will eventually lead to a new understanding of heterogeneous catalysis. This goal has come considerably nearer in the last few years. A number of important elementary reactions have been studied experimentally in great detail under ultrahigh-vacuum (UHV) conditions[1] and some progress has been made towards a theoretical description of these processes.[2] With the advent of UHV chambers which combine the usual electron spectroscopies with high-pressure microreactors, the measurement of high-pressure catalytic reaction rates for well-characterized single-crystal surfaces has been made possible.[3] It has been established in this way that single-crystal surfaces in a number of cases give rates per surface atom very close to those found on catalysts which consist of small (< 500 Å) particles dispersed on an oxide (e.g., Al_2O_3) support.[4] This shows that single-crystal surfaces are good models of real catalysts. It still remains to be shown that the processes (adsorption, desorption, etc.) studied in UHV cells (pressures 10^{-13}–10^{-7} atm) are the same as those proceeding at the pressures (1–10^2 atm) where most catalytic reactions run. The many orders of magnitude in pressure difference might change the reaction rate and mechanism through changes in surface coverages and composition.

The present Letter contributes to the bridging of this "pressure gap" by showing that, starting from a knowledge of the reaction scheme for the ammonia synthesis over an iron surface and UHV-chamber measurements of adsorption and desorption rates, the output from a catalytic reactor at 1–300 atm and 375–500 °C can be calculated in excellent agreement with measurements using an industrial Fe-based ammonia catalyst.

The basis for the present calculation is the work of Ertl and co-workers.[1] They have studied the adsorption of N_2, H_2, and NH_3 on clean and K-covered Fe single-crystal surfaces in great detail using a combination of Auger spectroscopy, photoelectron spectroscopy, work-function measurement, electron-energy-loss spectroscopy, and rate measurements. Metallic Fe with adsorbed K is expected to be a good model for a reduced industrial NH_3 catalyst, which consists of 200–400-Å Fe particles with small amounts of Al_2O_3 to prevent sintering.[5,6] The Fe surface is partly covered with K which is a promoter for the reaction[5,6]; i.e., it increases the reaction rate.

Ertl[1] has generalized the previously proposed[7] reaction schemes for the NH_3 synthesis:

$$N_2 + a \rightarrow N_2^a, \tag{1a}$$

$$N_2^a + a \rightarrow 2N^a, \tag{1b}$$

$$N^a + H^a \rightarrow (NH)^a + a, \tag{1c}$$

$$(NH)^a + H^a \rightarrow (NH_2)^a + a, \tag{1d}$$

$$(NH_2)^a + H^a \rightarrow (NH_3)^a, \tag{1e}$$

$$(NH_3)^a \rightarrow NH_3 + a, \tag{1f}$$

$$H_2 + a + a \rightarrow 2H^a, \tag{1g}$$

where (1b) is the rate limiting step. In (1) an a denotes a free surface site, and X^a is an adsorbed X atom.

Instead of starting from the usual NH_3-synthesis kinetics which, for instance, assume that there is a continuous distribution of binding energies for adsorbed nitrogen,[7] we use as a starting point a new kinetic model with a minimum of assumptions. Our basic approximation is that adsorbate-adsorbate interactions are neglected. Furthermore, we assume that

the surface is energetically homogeneous and that N_2, H_2, and NH_3 are ideal gases. Generalizing Fowler and Guggenheim's[8] treatment of adsorption to the case where many gases adsorb competitively, we obtain expressions for the equilibrium constants in terms of partition functions. For reaction (1a), for example, we have

$$K_1(P_{N_2}/p_0)\theta_a = \theta_{N_2^a}, \quad K_1 = Z_{N_2^a}/Z_{N_2}^0, \quad (2)$$

where θ denotes a coverage, p_0 is the thermodynamic reference pressure, $Z_{N_2^a}$ is the partition function for N_2^a, and $Z_{N_2}^0$ is the partition function for N_2(gas) at $P = p_0$.

The rate of NH_3 synthesis is equal to the net rate of the slowest step

$$r = 2k_2(\theta_{N_2^a}\theta_a - \theta_{N^a}^2/K_2), \quad (3)$$

where K_2 is the equilibrium constant for step (1b) and

$$k_2 = A \exp(-E/kT) \quad (4)$$

is the rate constant for step (1b). The factor 2 in (3) enters the calculation because two molecules of NH_3 will be produced through the reaction scheme (1) for each turnover of step (1b).

When step (1b) is rate determining, implying that all the other steps in (1) have much shorter relaxation times, we can express the coverages in Eq. (2) directly in terms of the partial gas-phase pressures of the reactants and product and the equilibrium constants $K_1, \ldots, K_7$. We can therefore derive an expression for the rate in closed form:

$$r = k_2 K_1 \left[\frac{P_{N_2}}{p_0} - \frac{P_{NH_3}^2 p_0}{K_G P_{H_2}^3} \right] D^{-2}, \quad (5)$$

where

$$D = 1 + K_1 \frac{P_{N_2}}{p_0} + \frac{P_{NH_3} p_0^{0.5}}{K_3 K_4 K_5 K_6 K_7^{1.5} P_{H_2}^{1.5}} + \frac{P_{NH_3}}{K_4 K_5 K_6 K_7 P_{H_2}} + \frac{P_{NH_3}}{K_5 K_6 K_7^{0.5} P_{H_2}^{0.5} p_0^{0.5}} + \frac{P_{NH_3}}{K_6 p_0} + \frac{K_7^{0.5} P_{H_2}^{0.5}}{p_0^{0.5}},$$

and K_G is the gas-phase equilibrium constant for the overall reaction. Examination of this expression shows that our model observes the principle of microscopic reversibility and that the reaction is always predicted to go towards the thermodynamic equilibrium for the gas phase.

To calculate the rate from Eq. (5) we need the rate constant k_2 and the equilibrium constants $K_1, \ldots, K_7$. Since the N_2 chemisorption energy is very small (44 kJ/mole),[1] K_1 is very small except at extremely low temperatures and the term involving K_1 in D can be neglected. This corresponds to neglecting the buildup of N_2^a on the surface. K_1 then only enters in Eq. (5) multiplied with k_2. This product is given by the N_2 sticking probability (at zero N_2^a coverage)

$$\sigma = k_2 K_1 d(2\pi mkT)^{1/2}/p_0, \quad (6)$$

where d is the density of sites on the surface and m is the N_2 mass. The other equilibrium constants are calculated from the partition functions as in Eq. (2).

The partition function for each of the intermediates can be written as a product of contributions from all of the degrees of freedom:

$$Z = (\Pi_i Z_{vib,i})(\Pi_j Z_{rot,j}) \exp(-E/kT). \quad (7)$$

The last term is the electronic contribution, which only contains the ground-state energy E. Electronic excitations have been neglected. The internal atomic or molecular excitations are too high in energy to contrib-

ute. For adsorbates in close contact with a metal and an appreciable adsorbate-induced one-electron density of states at the Fermi level, ϵ_F, the possibility of low-energy excitations around ϵ_F does exist. The density of excited electron-hole pair states is, however, proportional to the excitation energy ω for small ω,[9] and the low-energy electron-hole-pair excitations are therefore expected only to contribute little to the partition function.

We approximate all the vibrational and rotational degrees of freedom of both the free and adsorbed species by harmonic oscillators and free rotors, respectively. The corresponding partition functions Z_{vib} and Z_{rot} can then be expressed directly in terms of the fundamental excitation quanta, most of which have been measured.[10,11]

The N_2 sticking coefficient σ and its activation energy have been measured for both clean and K-covered Fe surfaces.[1] For the clean surfaces the values depend on the crystal face studied, but when K is present the values are insensitive to the surface structure.[1] K was found to increase the N_2 adsorption rate considerably, mainly by decreasing $E_{N_2^a}$.[1] This has been explained by an attractive interaction between adsorbed K and the dissociating N_2 molecule which is mainly electrostatic in character.[12] It is believed that the increase in N_2 dissociation rate by adsorbed K is the explanation for the promoter effect of K in commercial Fe-based ammonia catalysts.[1] In trying to mimic a commercial catalyst we have therefore used the data of Ertl et al. for

the K-covered-Fe surfaces. Furthermore, we have used the data at the optimum K coverage (maximum sticking probability).[13] This should correspond most closely to an optimized commercial catalyst.

Finally, the ground-state energies can be deduced from calorimetry or from thermal desorption experiments.[10,14] For atomically chemisorbed N we do not use the chemisorption energy quoted by Ertl[1] directly to deduce E_{N^a}, but rather reanalyze the thermal desorption data using the same equations [steps (1a) and (1b)] as used in the rate calculations to determine an improved value. Since the sticking coefficient for N_2 is very low, the preexponential factor for thermal desorption of N_2 from dissociated nitrogen is very different from the values usually used in obtaining binding energies from thermal desorption experiments. This results in a value for the N chemisorption energy (-161 kJ/mole), which is somewhat different from the one quoted by Ertl (-213 kJ/mole). We find it a strong point of our method that we use the same machinery for calculating desorption rates and the rate of ammonia synthesis.

The value[14] of E_{N^a} together with the sticking coefficient[13] δ are the parameters on which the results depend most sensitively. E_{N^a} determines the nitrogen coverage and since atomic nitrogen is by far the most abundant species on the surface, it strongly influences the coverage of free sites in Eq. (3). δ determines the rate constant k_2 in Eq. (3) directly through Eq. (6).

Given the equilibrium constants and sticking coefficient we can calculate the NH_3-synthesis rate per Fe surface area from Eq. (5). To get the NH_3 production from a catalytic reactor we must then know the active Fe surface area of the catalyst, and the rate must be integrated through the reactor changing the gas composition along the way as N_2 and H_2 are consumed and NH_3 produced. The total Fe area of the commercial catalyst is taken from CO chemisorption experiments assuming that each CO molecule titrates two Fe atoms.[15]

The results are summarized in Fig. 1. We compare the calculated NH_3 production to experiments in a plug-flow reactor with a commercial Topsøe KMIR catalyst.[5,16] It is seen that for a broad range of conditions, the agreement between the calculated and experimental results is very good. While we do not want to stress the absolute agreement in Fig. 1 too much in view of the approximations behind Eq. (5) and the uncertainties in the experimentally determined input to the calculation, the present results strongly suggest that the reaction mechanism (1) with step (1b) as rate limiting includes the essential features for the high-pressure ammonia-synthesis reaction. They also support the view of Ertl of the active part of an ammonia catalyst. Finally, and perhaps most importantly, they indicate that the fundamental understanding of chem-
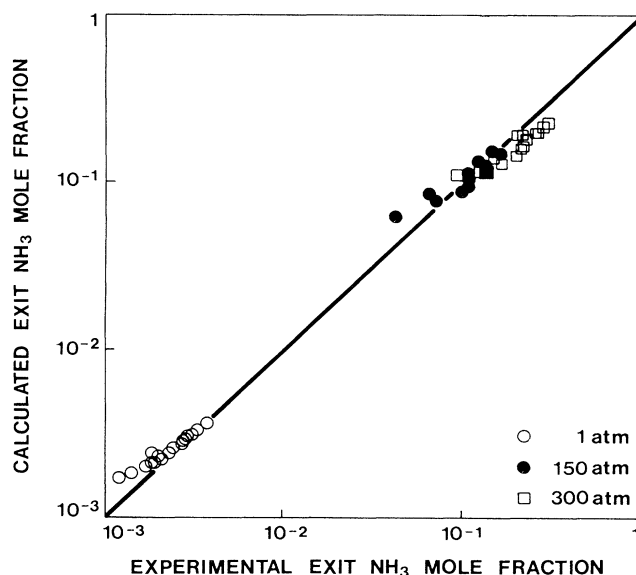

FIG. 1. Comparison of calculated and measured NH_3 mole fraction out of a catalytic reactor containing K-promoted Fe catalyst. In the experiments the commercial Topsøe KMIR catalyst is used. The data set include a broad range of external conditions: Inlet H_2 to N_2 ratios between 0.5 and 6, temperatures between 375 and 500 °C, pressures between 1 and 300 atm, and gas flows varying over a decade. The deviations between experimental and calculated NH_3 concentration at the reactor exit correspond to an error in the calculated rate constant by up to a factor of approximately 2.

isorption obtained in surface-physics experiments under well-controlled conditions at low pressures can be directly applicable to technical catalysts under working conditions. It is thus possible to bridge the "pressure gap."

The present results are in disagreement with the conclusion of a recent publication by Bowker, Parker, and Waugh[17] that it should be necessary to include a substantially larger activation barrier for N_2 dissociation than obtained by Ertl et al. at low pressures in order to get a reasonable NH_3 production under high-pressure conditions. The disagreement may be due to the difference in approach in calculating the rates: They calculate forwards and backwards rates for all the reaction steps (1) and do not calculate the individual equilibrium constants from experimental data. Furthermore, they use the original value of the N chemisorption energy determined with a normal preexponential factor for thermal desorption. Finally, they assume the concentrations to be constant through the reactor bed (a backmix reactor). This is a poor approximation for the type of reactor (plugflow) used in the experiments.[5]

Given the reaction mechanism (1) the main approximation made in the derivation of the rate expression

Eq. (5) is the neglect of adsorbate-adsorbate interactions (apart from the short-range repulsion defining the maximum coverage). This is a serious approximation and one cannot *a priori* expect to get results of the quality presented here for other systems. We suspect that one reason why interactions between intermediates are apparently of no consequence in the ammonia synthesis may be that the "active sites" are dominated by the interactions with the potassium promoter. Another important factor is that for usual ammonia-synthesis conditions we find that N^a is by far the most abundant surface species covering more than 75% of the surface. Since the N^a coverage varies little with the external conditions, the interactions with adsorbed nitrogen are fairly constant. This would explain why calculations based on the clean Fe surface data of Ertl *et al.* also compare well (although not as well as in Fig. 1) with experimental results on K-free Fe catalysts.[16]

In summary, a kinetic model for the NH_3 synthesis is obtained by application of a generalization of Fowler and Guggenheim's treatment of adsorption to the reaction scheme proposed by Ertl.[1] As input we use the available UHV studies of N_2, H_2, and NH_3 adsorption on Fe single-crystal surfaces with and without the presence of chemisorbed K. Our method contains no adjustable parameters and correctly predicts the NH_3 synthesis rate for an iron-based industrial NH_3 catalyst at 1–300 atm and 375–500 °C. The result establishes an important link between basic science and technology. More specifically, it shows that our understanding of well-defined chemisorption systems can be transferred to the more complex systems where heterogeneous catalysis takes place. Together with the increased understanding of the surface and adsorbate parameters determining the interactions[2] it also opens new prospects in catalyst research and for the design of new catalysts.

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[11]Vibrational frequencies for the motion perpendicular to the surface for adsorbed H, N, and NH_3 are taken from A. M. Baró and W. Erley, Surf. Sci. **112**, L759 (1981); M. Grunze, M. Golze, W. Hirschwald, H.-J. Freund, H. Pulm, V. Seip, M. C. Tsai, G. Ertl, and J. Küppers, Phys. Rev. Lett. **53**, 850 (1984); and W. Erley and H. Ibach, Surf. Sci. **119**, L357 (1982). Parallel frequencies are estimated assuming an activation barrier for surface diffusion of 0.5 eV. None of these values affect the results in any critical way. All intramolecular frequencies are too high to contribute to Z_{vib} at the temperatures of interest.

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[13]The apparent activation energy of σ is $E_a + (E_{N_2^a} + \Delta E_{N_2^a}) - (E_{N_2} + \Delta E_{N_2}) + \frac{1}{2}kT = -12.1$ kJ/mole at 430 K, where $\Delta E_{N_2} \simeq \Delta E_{N_2^a} \simeq \frac{5}{2}kT$ represents the energy stored in the mechanical degrees of freedom at the temperature in question. The absolute value used for the sticking coefficient is $\sigma = 3.9 \times 10^{-5}$ at 430 K.

[14]The ground-state energies $E_{H^a} = -47.5$ kJ/mole and $E_{(NH_3)^a} = -106$ kJ/mole are deduced from Ref. 1. Following Ertl (Ref. 1), $E_{(NH)^a}$ and $E_{(NH_2)^a}$ are given values between E_{N^a} and $E_{(NH_3)^a}$. The exact position of these has no consequences for the calculated rate. $E_{N^a} = -91.5$ kJ/mole is determined from the results of Ref. 1 as discussed in the text.

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