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PRIORITY COMMUNICATION

The Brønsted–Evans–Polanyi Relation and the Volcano Plot for Ammonia Synthesis over Transition Metal Catalysts

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Using density functional calculations we show that there is an essentially linear relationship between the activation energy for N_2 dissociation and the binding energy of atomic nitrogen on a range of transition metal surfaces. This relation, known as the Brønsted–Evans–Polanyi relation, is further shown to depend on the structure of the active site. The consequences of the Brønsted–Evans–Polanyi relation in terms of the kinetics of the ammonia synthesis process under industrial conditions are discussed, and it is shown that the relation leads to a volcano-type dependence of the catalytic activity on the nitrogen heat of adsorption. The results show that density functional calculations can predict the relative catalytic activity of different transition metals. © 2001 Academic Press

Key Words: **N_2 dissociation; DFT calculations; kinetic; transition metals.**

I. INTRODUCTION

The Brønsted–Evans–Polanyi relation (1, 2) is an empirical rule stating that there is a linear relationship between the activation energy and the reaction energy for an elementary reaction. It is applied in many areas of chemistry and biochemistry, including heterogeneous catalysis, where it is often used to rationalize observed variations in catalytic activity from one catalyst to the next or to estimate activation barriers (3). There is little quantitative evidence behind the Brønsted–Evans–Polanyi relation in heterogeneous catalysis, because it is hard to measure both activation energies and reaction energies (or rates and equilibrium constants) reliably for elementary reactions on a surface of a catalyst. We show here that quantum chemical methods based on density functional theory (DFT) can be used to quantify the relation and to understand why it works.

We focus on the ammonia synthesis reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$. It is known that, over the industrial catalysts based on Fe or Ru, N_2 dissociation is the rate-limiting step (4–6). It is further known that adsorbed N (or NH) is the most abundant species on the surface during the reaction under industrially relevant conditions (7–11). For this reaction the Brønsted–Evans–Polanyi relation therefore does not only provide a method for estimating activation barriers from adsorption energies. It governs the reactivity completely, because it determines the relation between the rate of the slowest step and the amount of free sites on the surface. We show in the following that, given the calculated Brønsted–Evans–Polanyi relation and a microkinetic model for the ammonia synthesis, we can calculate the catalytic activity as a function of nitrogen binding strength. We find a volcano curve with Fe and Ru near the maximum, closely resembling what is found experimentally (12).

II. CALCULATIONAL DETAILS

We have applied our plane wave DFT method with a nonlocal description of exchange and correlation effects to the calculation of the activation barrier (E_a) for N_2 dissociation and the adsorption energy (ΔE) for dissociative N_2 adsorption over a range of transition metals.

We have used three- or four-layer slabs and a 2×2 (close-packed surfaces, $c(6 \times 2)$ for Pd(111)) or 2×4 (steps, (2×1) for Pd(211)) unit cell to model the surfaces. The wave functions are expanded in plane waves (up to 25 Ry), and the Brillouin zone is sampled by 18 k-points for the hcp surfaces, 16 k-points for the flat bcc surfaces, and 8 k-points for stepped bcc surfaces. The RPBE exchange correlation functional is applied (13), and Vanderbilt ultrasoft pseudopotentials (14) are used to describe the core electrons. The programs employed (DACAPO) are publicly available at http://www.fysik.dtu.dk/CAMPOS.

Two or more of the top layers are completely relaxed for the flat and stepped surfaces of Fe(110), Ru(0001), and Pd, while the surface atoms are kept fixed for the remaining

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calculations. This makes no difference for the relation between the activation energy and adsorption energy, since we find that the two vary similarly when relaxations are included (see later). The N atoms are completely relaxed in all the calculations of the dissociative N_2 adsorption energy (ΔE). The transition states are identified by calculating the energy for various lengths of the N_2 bond, while the remaining degrees of freedom are completely relaxed.

III. THE BRØNSTED–EVANS–POLANYI RELATION

Consider first dissociation and adsorption of N_2 on the most closely packed surface of the different metals. We find an essentially linear relationship like that in the Brønsted–Evans–Polanyi relation over a broad range of adsorption energies and barriers (Fig. 1). The slope we find in the activation barrier vs adsorption energy plot is 0.9.

The calculations show why the Brønsted–Evans–Polanyi relation is obeyed in this case. The transition state we find for N_2 dissociation on all the surfaces is so stretched (see inset in Fig. 1) that the direct interaction between two N atoms is quite weak—the transition state is final state-like.

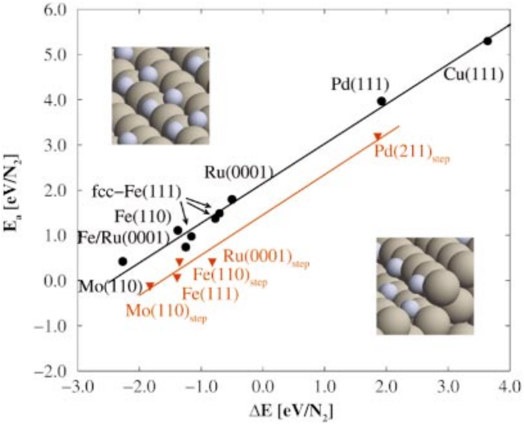

FIG. 1. Calculated activation energies (transition state potential energies) for N_2 dissociation on a number of different metals plotted as a function of the calculated N_2 dissociative chemisorption potential energy. All energies are relative to gas-phase N_2. Results for close-packed surfaces (fcc(111), hcp(0001), and bcc(110)) as well as for stepped surfaces are included and show the same trends, but group along two different straight lines. Results for the very open Fe(111)($\alpha \rightarrow \alpha'$) surface naturally falls on the "step line" since this surface has the same kind of reactive five-atom sites as the steps (15). Results for fcc Fe are also included for different lattice constants showing the effect of strain on the reactivity (nearest-neighbor distance from 2.40 to 2.60). Fe/Ru(0001) refers to a pseudomorphic overlayer of Fe on Ru(0001). The insets show the calculated geometry of the transition state for dissociation on the Ru(0001) surface, both on a flat and on a stepped surface. The geometry of the N_2 molecules indicates the size of the unit cell used in the calculations.

If we consider more open surfaces and steps as the active site, then a new Brønsted–Evans–Polanyi relation emerges (Fig. 1). This adds two new angles to the general description. First, it is clear that the Brønsted–Evans–Polanyi relation is not restricted to a single active site. Second, we get a clear view of two other concepts commonly used in heterogeneous catalysis. The two lines separate electronic and geometrical effects. For a fixed geometry the difference in electronic structure of the transition metals gives rise to the variations along each of the Brønsted–Evans–Polanyi lines. The difference between the two lines is a manifestation of the geometrical effect, in the present case the requirement for dissociation sites with at least five metal atoms in a non-planar geometry (16).

IV. THE VOLCANO CURVE

The results shown in Fig. 1 can be used to estimate the relative ammonia synthesis rates over different transition metals. In order to do this we have combined the Brønsted–Evans–Polanyi relation for the most active sites (the lower curve of Fig. 1) with a microkinetic model for ammonia synthesis, where N_2 dissociation is taken to be the rate-determining step and all other elementary reaction steps are assumed to be in equilibrium (7).

As a reference point we use the parameters of the kinetic model which is known to describe ammonia synthesis over nonpromoted ruthenium (10) very well. These parameters are in good agreement with results from the DFT calculations with respect to the values of the N_2 dissociation barrier, the adsorption energy, and the fact that only a small fraction of the surface sites on a real catalyst will have the proper geometry for being active. In order to find a synthesis rate for metals where the adsorption energy of N_2 and the dissociation barrier are different from those on ruthenium, we keep all other parameters of the model constant except the adsorption energy of NH*, which is taken to change like the adsorption energy of N*. The adsorption energy of hydrogen also changes from one transition metal to the next, but our calculations show thatthis variation is an order of magnitude smaller than the variation in adsorption energy of nitrogen, and we can therefore neglect it here.

The result is a volcano curve describing the ammonia synthesis rate as a function of the adsorption energy as shown in Fig. 2. This curve indicates that iron and ruthenium are among the best choices of catalyst, which is in remarkably good agreement with the experimental findings (12). When we increase the ammonia concentration in the gas phase, we find that the maximum in catalytic activity moves toward smaller N binding energies, reflecting the larger poisoning of the surface by adsorbed N and NH under such conditions. This is also in agreement with detailed experimental evidence showing the ammonia order is less negative for Ru than for Fe catalysts (17).

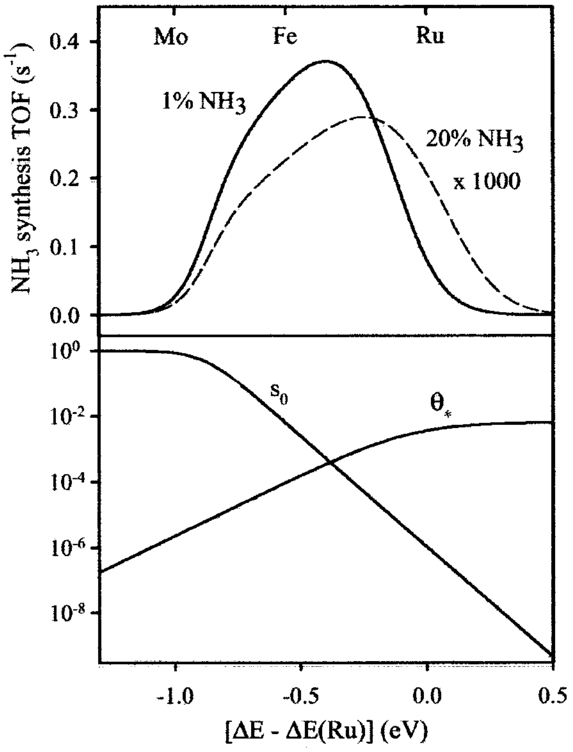

FIG. 2. Ammonia synthesis rate as a function of the N_2 dissociative chemisorption energy of nitrogen relative to that on ruthenium. The rates are given as turnover frequencies (TOF), which were calculated by combining the lower Brønsted–Evans–Polanyi relation in Fig. 1 with the microkinetic model for ammonia synthesis described in the text. The TOFs are obtained at 673 K and 100 bar in a stoichiometric $H_2 : N_2$ gas mixture containing 1% or 20% (dashed) of NH_3. Below we show the N_2 sticking probability, S_0, and the coverage of free sites, θ_*, on the surface for each value of the adsorption energy. These results refer to the case where there is 1% conversion. It can be seen how the maximum in activity is a compromise between a high sticking probability (low barrier for N_2 dissociation) and a large number of free sites (low N and NH coverage) where reaction can occur.

V. CONCLUSIONS

We have shown that density functional theory (DFT) calculations can be a powerful tool in describing chemical processes in heterogeneous catalysis. On the basis of such calculations we have shown that there is an essentially linear relationship between the activation energy for N_2 dissociation and the nitrogen chemisorption energy for a broad range of transition metals. This confirms that the Brønsted–Evans–Polanyi relation is valid also for systems of interest in heterogeneous catalysis.

The calculations illustrate both the variations in chemical activity from one transition metal to the next and the effect of geometry. The latter is found to be independent of the metal, and to be crucially important for the catalytic activity.

Finally, we have used the calculated variations in activation barriers and adsorption energies in conjunction with a well-established microkinetic model for the ammonia synthesis to show that the *variation* in the synthesis rate under industrial conditions can be calculated from first principles. The results show that, even though the accuracy of DFT calculations is not at present sufficient to predict absolute chemical reaction rates, it is good enough to predict the overall variations in rates from one system to the next.

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