Model for Dissociative H_2 Chemisorption on Transition Metals

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Earlier calculations have shown that hydrogen atoms can be strongly adsorbed on nickel and on copper surfaces although the character of the chemisorption bond is different. In the case of nickel both $3d$ and $4s$ electrons are involved, whereas for copper the bond is formed exclusively by $4s$ electrons. On the basis of this information a model is worked out for dissociative chemisorption of H_2 molecules, which is experimentally found to occur on nickel but not on copper. In this model the activity of $3d$ and $4s$ electrons is studied separately. The $3d$ electrons cause an unactivated dissociative chemisorption of H_2; the $4s$ electrons alone do not chemisorb an H_2 molecule unless a high activation-energy barrier is surmounted.

INTRODUCTION

It is well established experimentally[1] that some transition metals, for instance nickel and platinum, can dissociatively adsorb H_2 molecules even at very low temperatures. This dissociative chemisorption, which is very important for the catalytic activity of transition metals in many reactions,[2] requires practically no activation energy. It is also known[1] that copper, which is very similar to nickel except that it has a completely filled d band, does not chemisorb H_2 molecules dissociatively at room temperature. An explanation which ascribes the activity of nickel to the partial filling of the d band therefore becomes very plausible. Much work still has to be done, however, to give this hypothesis a more quantitative basis. Moreover, it must also be explained why predissociated hydrogen is adsorbed by copper almost as strongly as by nickel.[3,4]

Some time ago we proposed a model for dissociative chemisorption of H_2 on a nickel surface.[5] We assumed that the two hydrogen atoms interact mainly with two nickel atoms. The unpaired d electrons of nickel were represented by a single effective electron in a spherical orbital on each nickel atom. The argument justifying a spherical distribution was that in the bulk of the metal the splitting between d orbitals is very small compared to the energies involved in chemisorption. The interaction energy between the four atoms was calculated by a perturbation method which takes exchange as well as van der Waals forces into account.[6,7] This model indicated the possibility of unactivated H_2 dissociation which was mainly caused by the pair and three-body exchange interactions calculated in first-order perturbation theory.

Since then, we have obtained more information about the chemisorption bond by molecular-orbital calculations for hydrogen *atoms* adsorbed on clusters of nickel or copper atoms.[8] We have found

that, if a hydrogen atom is adsorbed on top of a nickel atom in a cluster, the main interaction takes place with the $3d_{z^2}$ and the $4s$ orbitals of this nickel atom. This conclusion applies to chemisorption on the different surfaces: (100), (110), and (111), although, of course, the interaction is influenced by the neighboring nickel atoms. (On each surface, the $3d_{z^2}$ orbital has to be understood as the d_{z^2} orbital of which the axis points perpendicularly out of the surface.) It is the chemisorption interaction itself, therefore, rather than the bulk structure which determines the nature of the d orbitals that are mainly involved. The covalent bonding of the hydrogen atom with the $4s$ orbital is comparable in strength with the bond involving $3d_{z^2}$. For copper we have found that the $3d$ orbitals do not take part in the bonding of the hydrogen atom, but that the increased bonding to the $4s$ orbital on the underlying copper atom causes the adsorption energy of a hydrogen atom to be of the same magnitude as for nickel.

This molecular-orbital (MO) model cannot be used to study dissociative chemisorption of H_2 molecules, since this requires interaction energies over a wide range of interatomic distances up to different dissociation limits. It is well known that the conventional MO method is not suitable for this purpose (except in special cases, such as interactions between closed-shell systems). Therefore, we used the information obtained from the MO calculation to improve our original model for dissociative chemisorption of H_2.

DESCRIPTION OF THE MODEL

The MO calculations for hydrogen atoms on clusters of approximately 10 metal atoms showed that the main interaction takes place between a hydrogen atom and the underlying metal atom. Initially, it is justifiable, therefore, to include only two metal atoms in our model for dissociative H_2 chemisorption. On these metal atoms we place an electron either in a $3d_{z^2}$ or in a $4s$ orbital (see Fig. 1). The
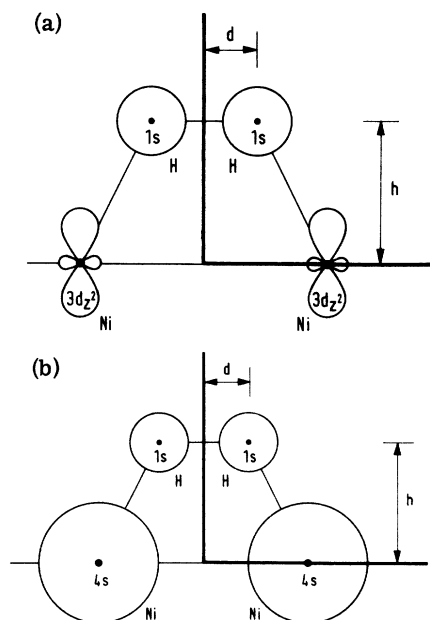
FIG. 1. Models for H_2 adsorption on a nickel surface. The model in Fig. 1(b) is also calculated with copper parameters.

interaction energy with two hydrogen atoms which contain an electron in a $1s$ orbital is calculated in first-order-exchange perturbation theory[6]:

$$\Delta E = \langle \phi_0 | \alpha \upsilon | \phi_0 \rangle / \langle \phi_0 | \alpha | \phi_0 \rangle .$$

The unperturbed wave function ϕ_0 is a product of four atomic orbitals, the two $3d_{z^2}$ orbitals or the $4s$ orbitals on the metal atoms and the two $1s$ orbitals on hydrogen. The radial parts of these orbitals are approximated by linear combinations of simple Gaussian functions. The exponents and coefficients are obtained from atomic SCF calculations for nickel and copper[9,10] and by a fit to the exact $1s$ orbital for hydrogen[11] (see Table I). The operator υ consists of the interatomic interaction terms in the total four-electron Hamiltonian. α is an operator which takes antisymmetry of the total wave function into account as well as the fact that this wave function should be a singlet eigenfunction of the total-spin operator. We can construct two such singlet wave functions and, actually, a 2×2 secular problem had to be solved in order to compute the energy of the lowest singlet state.[12]

If the unperturbed Hamiltonian $H_0 = H - \upsilon$ would have the products of atomic wave functions as its exact eigenfunctions, the first-order interaction energy would equal the interaction energy calculated by the valence-bond method. The metal orbitals are not eigenfunctions of their respective parts in H_0, however, and, therefore, both the perturbation method and the valence-bond method yield an approximation to the exact interaction energy. The second-

order energy is omitted as it showed no essential contribution to the process of dissociative chemisorption.[5] The first-order interaction energy is calculated as a function of h, the height of the H_2 molecule above the Ni atoms, and d, half the distance between the hydrogen atoms (see Fig. 1). In the case of nickel, we used both $3d_{z^2}$ and $4s$ orbitals and a Ni-Ni distance of $4.73a_0$ (the nearest-neighbor distance of the metal), for copper we only used $4s$ orbitals (since the $3d$ orbitals do not cause adsorption bonding of hydrogen atoms) and a Cu-Cu distance of $4.82a_0$.

RESULTS AND DISCUSSION

The results are shown in the contour maps of Figs. 2(a) and 2(b), where curves of equal interaction energy are plotted as a function of h and d. The interaction energy of H_2 with the copper $4s$ electrons is not shown as it is very similar to the one with nickel $4s$ electrons, which is drawn in Fig. 2(b).

At large distance h from the surface, the hydrogen atoms attract each other to form a stable molecule (equilibrium distance $2d = 1.65a_0$, binding energy 72 kcal/mole, the valence-bond results). The maps clearly show what happens if this hydrogen molecule approaches the "metal surface." The $3d_{z^2}$ electrons of the two nickel atoms in the "surface" [Fig. 2(a)] attract the molecule and, on coming closer to the metal atoms, it will be dissociated. This process of adsorption and dissociation requires no activation energy. The two separated hydrogen atoms will be strongly bound to the nickel atoms. The $4s$ electrons of nickel [Fig. 2(b)] or copper cause very different behavior. The hydrogen molecule is repelled and can only be chemisorbed and dissociated if an activation barrier of approximately 50 kcal/mole for nickel or 45 kcal/mole for copper can be surmounted. The hydrogen atoms are then bound.

An analysis of these results shows that the three- and four-atom contributions to the interaction

TABLE I. Atomic orbital data.

Atomic orbital	Exponents (a_0^{-2})	Contraction coefficients	Refs
Ni $3d$	6.731	0.40164	9
	1.353	0.78272	
Ni $4s$	0.1174	0.40986	
	0.05894	0.53552	10
	0.02428	0.09184	
Cu $4s$	0.1269	0.41618	
	0.06575	0.53280	10
	0.02122	0.09329	
H $1s$	0.1514	0.64767	
	0.6813	0.40789	11
	4.500	0.07048	

energy are of essential importance: The sum of pair-interaction energies would cause a different picture [Fig. 3(a) and 3(b)]. In the case of nickel $3d_{z^2}$ orbitals, the hydrogen molecule would be adsorbed, but a small activation barrier for dissociation would remain. This barrier is erased by the three- and four-atom contributions. With the 4s orbitals the effect of these contributions is even more important. The pair interactions alone would
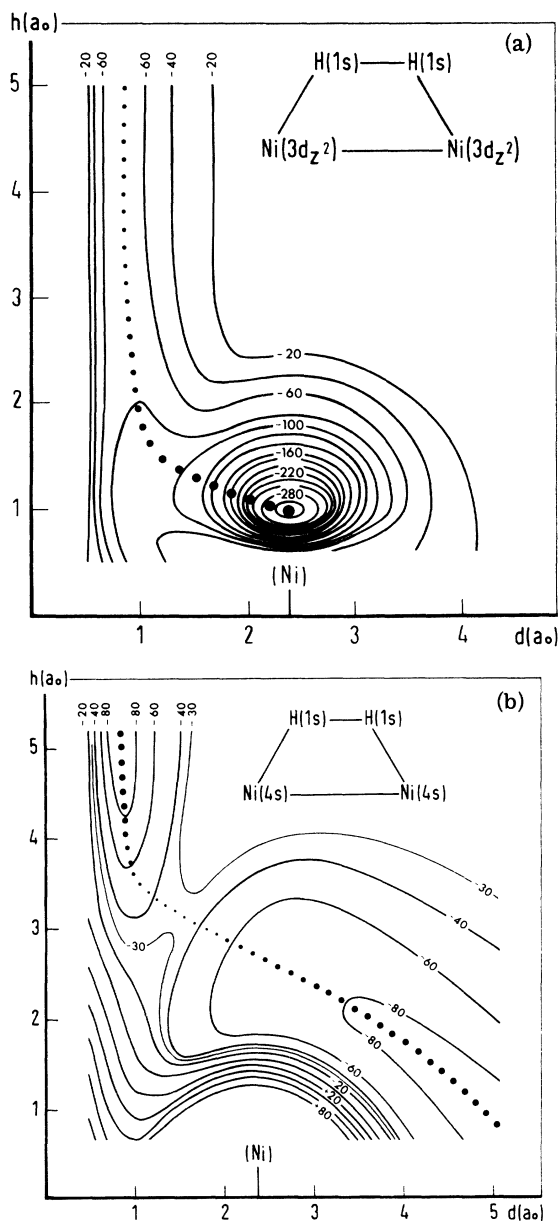

FIG. 2. Total interaction energy (in kcal/mole) from the models of figs. 1(a) and 1(b). The dotted line shows the most favorable "reaction path" followed by the H₂ molecule. The size of the dots is a measure for the value of the interaction energy.
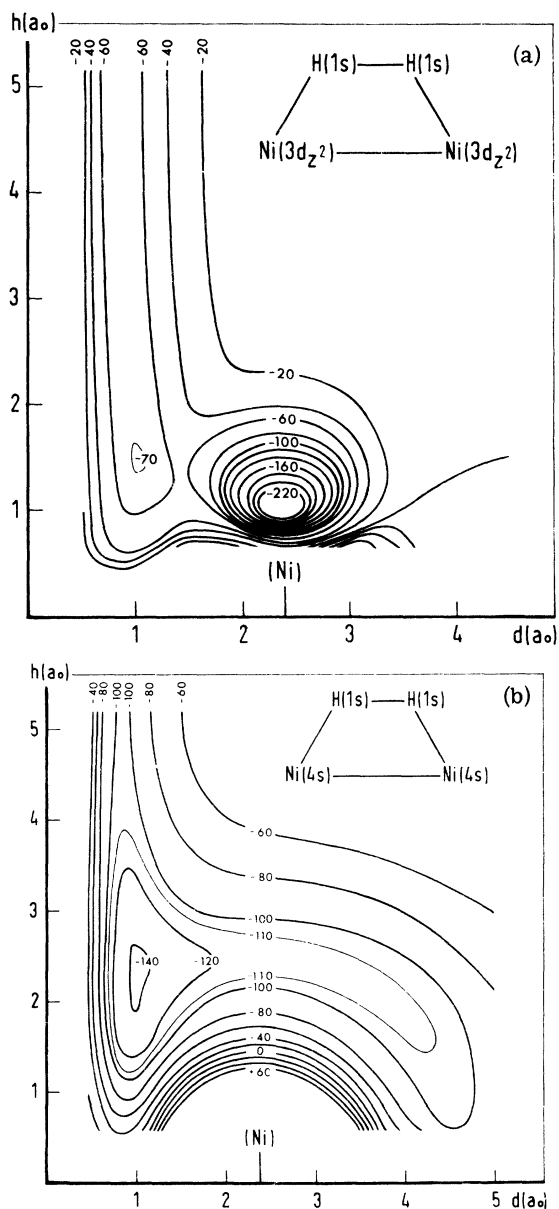

FIG. 3. Pair interaction energy (in kcal/mole) from the models of Figs. 1(a) and 1(b).

cause an H₂ molecule to be attracted instead of repelled.

This conclusion about the importance of at least three-center contributions, which is in agreement with the results from our earlier model,[5] prevents the use of simple pair potentials of the Lennard-Jones or other types. It requires an approach in which all exchange effects (also three- and four-electron interatomic permutations) are included. The present model is one of the simplest possibilities to perform this.

One additional remark about the model must be

made. If one considers the interaction energy with nickel $3d_{z^2}$ electrons only, one finds that the hydrogen atoms could come very close to the nickel atoms. This is not caused by the approximate form of the $3d_{z^2}$ orbitals; a fit of their radial parts with three Gaussians instead of two yielded practically the same result. Neither is it owing to our use of perturbation theory with atomic functions that are not exact eigenfunctions of the unperturbed Hamiltonian. When we approximated the interaction energy using the valence-bond method we found a similar result. The reason for this effect is probably that the interactions with the $4s$ electrons, the other $3d$ electrons and the core electrons must still be included. These interactions are very likely to be repulsive if a hydrogen atom comes close to the nickel atom.

Summarizing, the present model allows the following conclusions. For nickel, where MO calculations have shown a strong adsorption bond between a hydrogen atom and the $3d_{z^2}$ and $4s$ electrons of the underlying nickel atom, we find that the effect of the $3d_{z^2}$ orbitals could enable an H_2 molecule to become dissociatively chemisorbed without an activation energy. For copper, where only the $4s$ orbitals take part in the covalent chemisorption bond with a hydrogen atom, the chemisorption and dissociation of an H_2 molecule would require an activation energy of approximately 45 kcal/mole. For these results the three- and four-center interactions are important. Presently, we try to extend the model in order to calculate the combined effect of $3d_{z^2}$ and $4s$ electrons for nickel and, moreover, to include the effect of the other electrons as well.

[1]D. A. Cadenhead and N. J. Wagner, J. Catal. **21**, 312 (1971), and references therein.

[2]J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, J. Catal. **24**, 283 (1972).

[3]J. Pritchard and F. C. Tompkins, Trans. Faraday Soc. **56**, 540 (1960).

[4]S. J. Holden and D. R. Rossington, J. Catal. **4**, 403 (1965).

[5]A. van der Avoird, Surf. Sci. **18**, 159 (1969).

[6]A. van der Avoird, J. Chem. Phys. **47**, 3649 (1967).

[7]A. van der Avoird, Chem. Phys. Lett. **1**, 429 (1967).

[8]D. J. M. Fassaert, H. Verbeek, and A. van der Avoird, Surf. Sci. **29**, 501 (1972).

[9]G. A. van der Velde (private communication).

[10]H. Basch, C. J. Hornback, and J. W. Moskowitz, J. Chem. Phys. **51**, 1311 (1969).

[11]S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[12]A. van der Avoird, thesis (Eindhoven, 1968) (unpublished).