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Alkali Promotion of N₂ Dissociation over Ru(0001)

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Using self-consistent density functional calculations, we show that adsorbed Na and Cs lower the barrier for dissociation of N₂ on Ru(0001). Since N₂ dissociation is a crucial step in the ammonia synthesis reaction, we explain in this way the experimental observation that alkali metals promote the ammonia synthesis reaction over Ru catalysts. We also show that the origin of this effect is predominantly a direct electrostatic attraction between the adsorbed alkali atoms and the dissociating molecule. [S0031-9007(98)06016-5]

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Alkali metals are used extensively as promoters of catalytic reactions on metal surfaces. In the ammonia synthesis, for instance, where N₂ and H₂ are converted into NH₃, alkali promoters are used both in the traditional Fe-based catalyst [1] and in the Ru-based catalyst [2,3]. On Fe surfaces, adsorbed potassium is known to increase the rate of N₂ dissociation, which is the rate limiting step in the ammonia synthesis, by factors between 8 and 300 depending on the facet [4,5]. The effect on the ammonia synthesis rate of adding alkali promoters to Ru catalysts is as large [6]. Here, the effect has also been shown to depend strongly on the kind of alkali metal added, the trend being that the promotion increases with the atomic number of the alkali metal [6].

There has been a long debate about the origin of the large alkali promotion effect. Coadsorption of alkali metals and other atoms and molecules has been studied extensively on well-defined single crystal surfaces [7]. For N₂ dissociation on Fe(111), preadsorbed K has been shown to stabilize the adsorbed N₂ molecule and to lower the barrier for dissociation [4]. On Ru(0001), on the other hand, preadsorbed K decreases the stability of adsorbed N₂ [8]. On this surface, there is no direct measurement of the effect of alkali atoms on the dissociation, so it is not clear if the promotion of the ammonia synthesis is due to a lowering of the N₂ dissociation barrier as for Fe or due to some other effect. There have been several attempts to model the promotional effect of adsorbed alkali metals. One school of thought has focused on the alkali-induced changes in the density of metal states at the Fermi level [9], while others have focused on the electrostatic interaction between the adsorbed alkali atoms and the dissociating molecule [10]. A coherent picture of the relative importance of these effects has not been established yet [11].

In the present Letter, we use self-consistent density functional (DFT) calculations to investigate the effect of adsorbed alkali atoms on the adsorption and dissociation of N₂ on Ru(0001). We show that, while adsorbed alkali atoms destabilize molecularly adsorbed N₂ slightly, they lower the barrier for dissociation significantly. We also

show that the effect of Cs is considerably larger than that of Na and investigate the effect of the position of the dissociating molecule relative to the adsorbed Na or Cs. Using this large database, we can clearly show that the promoting effect is primarily of an electrostatic nature.

In Fig. 1, we summarize the main results of the calculation. The figure shows the calculated energy of the N₂/Ru(0001) system relative to molecular N₂ and the clean Ru(0001) surface as a function of the dissociation reaction coordinate. The latter is defined as the distance along the minimum energy path connecting the initial, molecularly adsorbed state and the final, dissociated state. Dissociation of N₂ on Ru(0001) is seen to be highly activated. This agrees with the extremely low sticking probability measured for this system [12] and the observation

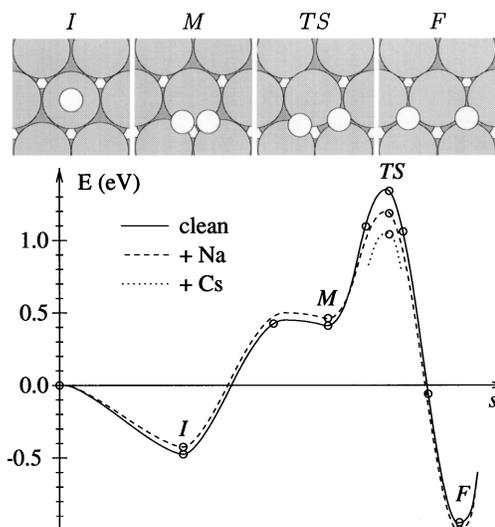


FIG. 1. Top: Snapshots of the minimum energy path for the N₂ dissociation reaction: initial state where the molecule is standing perpendicular to the surface (*I*), metastable state (*M*), transition state (*TS*), and final state (*F*). Bottom: The energy along the path (see text for details). The dashed line shows the energy along the same path in the presence of $\frac{1}{8}$ of a monolayer of Na (configuration *c* in Fig. 2). The effect of $\frac{1}{6}$ of a monolayer of Cs on the transition state is also shown (dotted line, configuration *e*).

in molecular beam scattering experiments that the sticking probability increases by 4 orders of magnitude by increasing the translational energy of the N_2 molecules above 1 eV [13]. The figure includes the effect of introducing $\frac{1}{8}$ of a monolayer of Na in the configuration *c* shown in Fig. 2. It is seen that the barrier for dissociation is lowered by 0.13 eV. The figure also shows that the lowering of the dissociation barrier is even larger (0.29 eV) when Cs is added to the surface instead of Na. The calculations therefore clearly describe the experimentally observed promoting effect of Na and Cs on the ammonia synthesis rate on Ru surfaces [6], and shows that it can be attributed to a lowering of the activation barrier for N_2 dissociation. At the same time, it shows that Na introduces a slight destabilization of the molecularly adsorbed state, in accordance with the experimental observations for the $K/N_2/Ru(0001)$ system [8].

The results are based on self-consistent density functional calculations using the generalized gradient approximation to describe exchange and correlation effects [14]. We use norm conserving pseudopotentials and expand the pseudo-wave-functions in plane waves with a kinetic energy cutoff of 40 Ry [15]. For the Cs pseudopotential, we include $5p$ semicore states as valence states, and further use the nonlinear core correction scheme, proposed by Louie, Froyen, and Cohen [16]. A Fermi-Dirac function with $k_B T = 0.05$ eV is used to calculate occupation numbers and all energies are extrapolated to $T = 0$ K. The Ru(0001) surface is mimicked by a periodic array of two to six layer thick Ru slabs separated by ~ 9 Å of vacuum. Surface unit cells giving (2×2) , (2×3) , and (2×4) periodicity along the surface have been used, and the corresponding Brillouin zones have been sampled by 18, 12, and 8 k points, respectively.

The energy curves in Fig. 1 have been found in the following way. The starting point is a calculation of the minimum energy path and the energy along it for a six layer slab in a (2×2) unit cell. The minimum energy path has been determined by a self-consistent optimization involving all N_2 degrees of freedom as well as the Ru degrees of freedom in the uppermost two layers [17]. This is described in detail in Ref. [18]. This very elaborate calculation is only possible in the relatively small (2×2) unit cell. This cell is so small that interactions between dissociating molecules in adjacent cells cannot be excluded. The cell is also too small for studying the effect of small amounts of adsorbed alkali atoms. We have therefore extended the calculations to the larger (2×3) and (2×4) unit cells by restricting the slab thickness to two layers and by keeping the reaction path determined for the six layer calculation in the small unit cell. We have checked the quality of the two layer slab calculations by comparing to the six layer slab results in a (2×2) unit cell. The error in the absolute binding energies is very small, on the order of 0.1 eV. The path also changes only slightly as judged from the small forces on the N atoms in the two layer calculation. The

energy $E(s)$ along the reaction coordinate s for the clean Ru(0001) surface in Fig. 1 has then been constructed as

$$E(s) = D_6^{(2 \times 2)}(s) + [E_2^{(2 \times 3)}(s) - E_2^{(2 \times 2)}(s)], \quad (1)$$

where $E_n^{(k \times l)}$ is the N_2 -surface interaction energy for an n layer slab with a $(k \times l)$ unit cell. In the same way, the effect of adding, e.g., $\frac{1}{8}$ of a monolayer of Na is calculated as

$$E^{Na}(s) = E(s) + [E_2^{Na, (2 \times 4)}(s) - E_2^{(2 \times 4)}(s)], \quad (2)$$

where the superscript Na indicates that one Na has been added per unit cell. The geometry of the different unit cells used is shown in Fig. 2.

The Na and Cs atoms have been added in the threefold sites and the equilibrium heights above the Ru surface have been determined to be 2.4 and 3.3 Å, respectively. For the Cs/Ru(0001) system, where there is an experimental structure determination [19], the agreement with experiment is excellent. By varying the size of the unit cell, we can vary the coverage between $\frac{1}{8}$ for the (2×4) cell and $\frac{1}{4}$ for the (2×2) cell. The calculated changes in work function agree very well with experiment for both adsorbates as seen in Fig. 3.

Having established that the DFT calculations can describe the promoting effect of alkali adsorption on N_2 dissociation at least qualitatively, we now turn to the problem of the origin of the effect. We investigate this by looking at the effect of two different alkali atoms, Na and Cs, and the effect of coverage and geometrical arrangement of the alkali atoms relative to the dissociating molecule. To this end, we concentrate on the alkali-induced change ΔE_{TS} in the energy of the transition state, and we keep the geometry of this state fixed as we vary the position and kind of the surrounding alkali atoms. We will return to the role of alkali-induced changes in the reaction path later. The

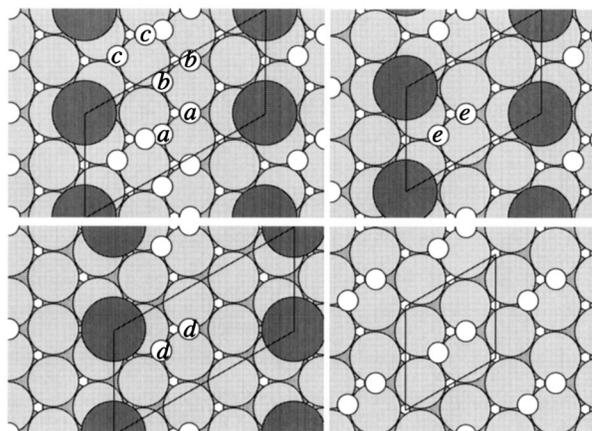


FIG. 2. Transition states for N_2 dissociation in different configurations. Top left: Na covered surface in a (2×2) unit cell. Bottom left: Same as above except that Na is in a hcp site. Top right: Na covered surface in a (2×3) unit cell. Bottom right: (2×2) unit cell on a clean Ru surface. *a-a*, *b-b*, *c-c*, *d-d*, and *e-e* indicate the position of the transition state N-N molecule.

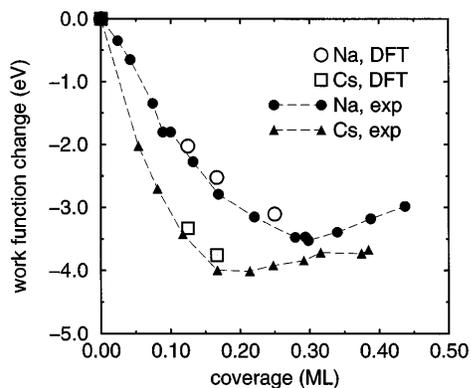


FIG. 3. Work function change induced by Na and Cs adsorption on Ru(0001) as a function of coverage. The open symbols are calculated results (circles and squares, respectively), and the filled symbols show experimental data from Ref. [20]. The work function for the clean surface is calculated to be 5.2 eV; the experimental value is 5.1 eV [21].

different geometries tested are illustrated in Fig. 2, and in Fig. 4 we show ΔE_{TS} for the different configurations. As discussed above, the effect of Cs is considerably stronger than of Na, and it can be seen that $|\Delta E_{\text{TS}}|$ increases as the alkali atoms get closer to the transition state complex (configurations *c* and *d* are lower in energy than *a* and *b* because they are closer to the alkalis, cf. Fig. 2).

In Fig. 4, we have plotted ΔE_{TS} as a function of the quantity

$$\Delta E_{\text{dip}} = -\mathcal{E}\mu, \quad (3)$$

which is the electrostatic interaction between a dipole with electric dipole moment μ and an electric field \mathcal{E} . For μ in Eq. (3), we have simply taken the calculated dipole moment of the transition state complex in the absence of the alkali:

$$\mu = \int d\vec{r} \Delta\rho_{\text{TS}}(\vec{r})z, \quad (4)$$

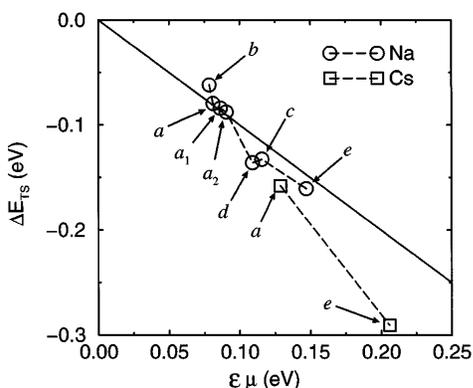


FIG. 4. Interaction energy between alkali atoms and N_2 in the transition state for dissociation as a function of $\mathcal{E}\mu$. The alkali atoms are Na (circles) and Cs (squares). The configurations *a*₁ and *a*₂ correspond to an *a* configuration, with the height of the Na atom increased from the equilibrium height by 0.1 and 0.2 Å, respectively (see Fig. 2).

where $\Delta\rho_{\text{TS}} = \rho_{\text{TS}}^{\text{N}_2/\text{Ru}} - \rho^{\text{Ru}}$ with the ρ 's including electronic and ionic charge density contributions. The value we find is $\mu = -0.13 \text{ eÅ}$. The electric field \mathcal{E} we determine from the alkali-induced electrostatic potential $\Delta\phi_{\text{alkali}} = \phi_{\text{alkali}/\text{Ru}} - \phi_{\text{Ru}}$ plotted along a line perpendicular to the surface through the center of mass of the adsorbate complex (see Fig. 5). We use the maximum field outside the surface as a measure of \mathcal{E} rather than attempting to find the local field at the height of the adsorbate. For the present purposes, this can be taken as an empirical choice, but a more detailed analysis of the electrostatic interaction between adsorbates shows that the screening of the field in the adsorbate region should not be included, and the field just outside the surface is a reasonable measure of the nonscreened field [10,22].

It is clear from Fig. 4 that there is a very good correlation between ΔE_{TS} and ΔE_{dip} . At higher values of ΔE_{dip} , there is a tendency that ΔE_{TS} varies even more strongly than ΔE_{dip} . This is what one would expect: For small fields the interaction is proportional to the field, while for larger fields polarization effects introduce an attractive term which is second order in the field strength [10]. The correlation in Fig. 4 strongly suggests that the direct electrostatic interaction between the adsorbed alkalis and the transition state complex dominates the promotion effect. We have also checked that there is no correlation between the alkali-induced change in adsorption energy and the change in the density of the states at the Fermi level. In fact, the latter changes extremely little as can be seen from the inset in Fig. 5.

We can also consider what determines the energy change for the adsorbed N_2 molecule and for the dissociated state. In the molecularly adsorbed state, the N_2 -induced dipole moment is extremely small (+0.01 eÅ for the six layer slab and -0.01 eÅ for the two layer slab). This is too little to give the effect seen in Fig. 1. For such small dipole moments, another effect, which we

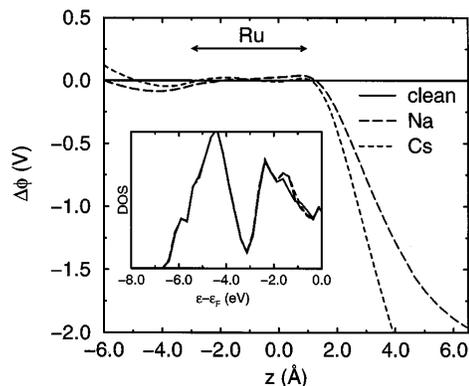


FIG. 5. Na- and Cs-induced electrostatic potential plotted along lines perpendicular to the surface through the fcc site farthest away from the alkali atoms (see Fig. 2, top left). The arrow shows the position of the slab (the Ru layers are at $z = 0.0$ and -2.2 Å). The inset shows the local density of states projected onto a Ru atom neighboring the dissociating molecule in configuration *c*.

scribe to a Pauli repulsion, dominates [22]. We note that, for molecular adsorbates with a larger dipole moment, the electrostatics still dominates. For CO adsorbed on Ru(0001), we calculate a much larger dipole moment of $-0.11 \text{ e}\text{\AA}$, and here the electrostatic interaction also describes the interaction with Na very well [22].

For the dissociated state, the dipole moment is $-0.10 \text{ e}\text{\AA}$. This is smaller than for the transition state, and the effect of Na adsorption [-0.07 eV (see Fig. 1)] is correspondingly smaller. Again the interaction is dominated by electrostatics. According to our calculations, the alkali promotion thus provides a means of lowering the energy barrier while changing the stability of the reactants and the products considerably less. Alkali promotion of N_2 therefore does not follow the Brønsted-Polanyi relations [23], where the lowering of a reaction barrier is a fraction of the lowering of the potential energy of either the reactant or the product.

DFT calculations for H_2 dissociation on Pd(100) have shown that a (2×2) overlayer of K and S increases the barrier [11,24]. It is concluded that no single contribution to the interaction energy can explain this behavior. Our results are simpler to interpret for three reasons: (i) The N_2 transition state has a much larger dipole moment, (ii) Na and Cs do not induce any changes in the d bands of the surrounding Ru atoms, and (iii) the unit cells used are larger (the adsorbates are not forced to be very close to each other). Point (i) means that the electrostatic interaction is stronger, and points (ii) and (iii) ensure that, at the same time, the direct or indirect interaction is weaker. We saw above that the dipole moment of molecularly adsorbed N_2 is much smaller than for N_2 in the transition state. For molecular N_2 , reason (i) is therefore less dominant, and the simple electrostatic picture of the alkali- N_2 interaction does not hold. In general, there are thus several interaction mechanisms in coadsorption, but, for the interaction of adsorbed alkali atoms with the transition and final states of dissociating N_2 on Ru, the electrostatics dominates.

The variation of the field along the surface gives rise to forces acting on the transition state complex due to the alkali atoms. These forces will tend to change the minimum energy path so that in the presence of the alkali atoms the path and the transition state geometry will not be completely the same as the one determined from the clean surface calculation. The change in the transition state energy $|\Delta E_{\text{TS}}|$ considered above is therefore a lower bound on the change in the true activation barrier. We have estimated the effect of including relaxation of the transition state from the alkali-induced forces on the transition state complex and the calculated curvature of the potential energy surface around the transition state on the clean surface. For the worst case, the correction amounts to 30 meV .

We conclude that DFT calculations are able to describe in some detail the promotional effect of alkali adsorbates on the dissociation of N_2 and thus the promotion of

ammonia synthesis on Ru catalyst surfaces. We also conclude that the main component of this effect is an electrostatic interaction between the adsorbed alkalis and the transition state complex.

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