First-principles study of the origin of alkali promotion of reactivity of metal surfaces.

Sergey Stolbov, Talat S. Rahman

Department of Physics, Cardwell Hall,
Kansas State University, Manhattan, KS 66506

Alkali metals are known as efficient promoters in heterogeneous catalysis but the nature of this phenomenon is as yet not understood. Our first principles calculations reveal a huge increase and delocalization of the isoelectronic reactivity index of Cu and Pd surfaces on alkali adsorption. We trace this phenomenon to an unusual feature in the surface potential formed by the adsorbate and propose it as a driving force for the "promotion effect". Our results also provide clues to some of the unusual optical properties of quantum wells formed when alkali adsorb on Cu surfaces.

Adsorption of alkali metals on transition or noble metal surfaces dramatically changes properties of the latter making these systems the subject of extensive studies in areas extending from fundamental physics to chemical engineering. First, alkalis work as efficient promoters in heterogeneous catalysis, as their small amount adsorbed on a catalyst surface substantially enhances the latter's reactivity. The global character of the promotion effect of alkali metal is also impressive. The enhancement of reactivity under alkali adsorption has been reported for such varied catalysts as noble metals (Ag, Cu), transition metals with varying number of valence d-electrons (Fe, Co, Ni, Pt, Pd, Ta, Rh, Ru) and, oxides like FeO\(^{1,2,3}\). The effect extends to various types of reactions, such as dissociation of O\(_2\), NO, N\(_2\) and CH\(_4\), oxidation of CO, and methanol synthesis\(^{1,2,3}\). Comprehending the nature of the change produced by alkali adsorption is thus essential for facilitating the design of new and efficient catalysts. In addition to the effect on surface reactivity, the formation of quantum wells has been observed on Na and Cs adsorption on Cu(111)\(^{5,6,7}\). For the Cs/Cu(111) system, extremely long-lived excited states have also been reported\(^{8,9}\). An understanding of these phenomena is important because of their impact on processes such as vibrational excitations, surface scattering, and photochemical reactions. The quantum-well states may well modify surface reactivity which brings us back to issues in catalysis.
Since catalytic processes are driven by the modification of chemical bonds and electronic charge transfer, understanding of their enhancement naturally entails examination of the electronic structure of catalyst surfaces. An important clue from experimental finding is that alkali adsorption on metal surface causes a significant reduction of its work function, as reported for Na and Cs adsorbed on Ru(0001), K on Pt(111), K on Rh(100), and Na on Cu(110). To explain the correlation between the promotion and reduction of the work function, it has been suggested that by bringing the Fermi level \((E_F)\) closer to the vacuum energy, alkali metals facilitate charge transfer between the reactant and the catalyst surface, thereby enhancing reactivity. There are also assumptions that alkali promote reactivity through depopulation of surface states and that reduction of work function upon alkali adsorption causes "some long-range perturbation" to the electronic structure, which strongly affects surface reactivity. Another approach focuses on the electrostatic interaction between the reactants and the adsorbed alkalis. In a more recent development, the proposed rationale is that the adsorbed alkalis deplete the electric field caused by the surface barrier, leading to a reduced interaction of the reactant dipole moments with this field and subsequent enhancement of their reactivity. There are thus indications that alkalis promote surface reactivity either through change in the surface potential itself, or through modification of the electronic states around the surface induced by that change in the potential. While these intuitive arguments have been very helpful in focusing the discussion on the subject, they have stopped short of establishing the microscopic mechanisms responsible for reactivity enhancement.

There are also other models of surface reactivity that, to our knowledge, have not yet been applied to the issue of alkali adsorption problem. Some of them correlate surface reactivity to the local densities of electronic states (LDOS) of surface atoms, more specifically, to LDOS at the Fermi-level \(N(E_F)\) or to the energy of the center of the local \(d\)-band. Others originate from the theory of chemical reactivity of molecules that characterizes the reactivity by the local softness function \(s(r)\) which is a measure of the electronic response to the change in the number of electrons in the system. In the context of metal surfaces \(s(r)\) can be regarded as the electronic response to \(N(E_F)\). Related to \(s(r)\), but more easily tractable from first principles calculations, is the isoelectronic reactivity index...
written as

\[ w^N(r) = \frac{1}{k^2 T_{el}} \left[ \frac{\partial \rho(r, T_{el})}{\partial T_{el}} \right]_{V(r), N} \approx \frac{\rho(r, T_{el}) - \rho(r, 0)}{(kT_{el})^2} \]  

(1)

Here \( \rho \) is the electronic density, \( V(r) \) denotes an external potential, \( N \) is the number of electrons in the system, \( k \) is the Boltzmann’s constant and \( T_{el} \) is the electronic temperature. An increase in \( T_{el} \) from “0” to a finite value creates electron-hole pairs with the Fermi-Dirac distribution. These excitations cause an electronic density variation which is reflected in the last term of Eq. (1). If we treat the changes in \( T_{el} \) as a uniform perturbation, \( w^N(r) \) is then the electronic density response to such a perturbation. To establish the validity of \( w^N(r) \) as a measure of reactivity, it was shown\(^{20} \) that for Pd(100) the spatial distribution of \( w^N(r) \) allows rationalization of the preferred dissociation path for \( H_2 \) and the preferred chemisorption sites for \( H \) adatoms, in good agreement with the results of first principles calculations\(^{24} \).

In the present paper, we show for the first time that alkali adsorption leads to a giant increase and delocalization of \( w^N(r) \) towards the vacuum. We further show that this phenomenon is caused by an unusual feature in the surface potential formed by the adsorbates which we propose to be the driving force for the alkali "promotion effect”.

Our calculations are based on density functional theory in the local density approximation. To attest to the generality of the phenomenon, we present results for two prototype metal surfaces chosen because of their obvious differences in \( d \)-band fillings. To calculate the electronic structure, surface potential and \( w^N(r) \) of clean and adsorbate covered Pd(111) and Cu(111) we use the full-potential linearized augmented plane wave (FLAPW) method\(^{25} \) as embodied in the Wien2k code\(^{26} \). We mimic the surface system with a supercell consisting of 8 atomic layers of Cu or Pd and 11 Å thick vacuum. In the case of systems with adsorbates, we use a two-dimensional (2x2) unit cell consisting of four metal atoms per layer plus one alkali at the three-fold fcc hollow site on each side of the slab, corresponding to 0.25 monolayer coverage. A fragment of the surface with the adsorbate is shown in Fig. 1. Previous calculations have shown this to be the preferred adsorption site. Good convergence in the calculated total energy is obtained by sampling 25 k-point mesh in the two dimensional surface Brillouin zone and the basis cutoff at \( R K_{\text{max}} = 7 \). The exchange-correlation part of the potential is calculated in the local density approximation within the density functional theory\(^{27} \). The \( w^N(r) \) function is calculated for \( T_{el} = 0.01Ry. \)
Our calculations indicate that LDOS of the surface Pd atoms are practically not changed upon alkali adsorption. Within the FLAPW method LDOS represent electronic states located inside muffin-tin (MT) spheres. These are mostly $d$-states in the cases of Pd and Cu. We can thus conclude that the alkali adsorption does not affect the localized $d$-state of the metal surfaces. In contrast to the effect on the LDOS, the impact of K on the isoelectronic reactivity of the surfaces is found to be dramatic. Fig. 2 shows $w^N(r)$ plotted for Pd(111) and K$_{0.25}$/Pd(111) along the plane perpendicular to the surface. The projection of this plane is shown in Fig. 1. Adsorption of potassium induces a huge increase in $w^N(r)$ and its delocalization towards vacuum. Interestingly, the effect is present not only around the adsorbate atom, but also for the entire surface area. A similar and even larger effect is found for a 0.25 monolayer of Na on Cu(111). The effect can be illustrated more quantitatively in the one-dimensional plots of $w^N(r)$. The $w^N(r)$ for both systems, plotted along the surface normal passing fcc hollow site, which is maximally distant from the adsorbate atoms, is presented in Fig. 3. On the clean metal surface $w^N(r)$ decays rapidly, whereas, upon alkali adsorption, it is both enhanced and delocalized over 2 – 4 Å away from the surface. This remarkable behavior of $w^N(r)$ implies that alkali adsorption dramatically increases the density of low-energetic excited states in the vacuum region in the vicinity of the surface facilitating an increase in surface reactivity.

For insights into the microscopic basis for these dramatic effects we have calculated the total self consistent potential for the surfaces under consideration. One-dimensional plots of the potentials in Fig. 4 testify to a reduction of the potential barrier at the surface which further manifest itself in the well-known decrease in the work functions for Pd(111) and Cu(111). What is indeed very intriguing and novel is that instead of an expected simple reduction of the barrier, alkali adsorbates also form a groove-like or plateau-like region of further reduced potential in the vicinity of the surfaces. Since this feature is energetically located around $E_F$, it leads to delocalization of the low energy electronic excitations. Bearing in mind that $w^N(r)$ characterizes the density of these excitations, we can conclude that the striking features in the surface potential are responsible for the characteristics found here for $w^N(r)$ which in turn is a measure of the surface reactivity. It is important to note that we find the increase in $w^N(r)$ for metals as varied as Cu with almost completely occupied $d$-band and low $N(E_F)$, and for Pd which has partially empty $d$-band and very high $N(E_F)$. It is thus reasonable to expect that the phenomenon is a general characteristic for most
metals. This is in agreement with the observation that alkalis promote reactions on metals with differing number of d-electrons, as mentioned earlier.

The novel features in the surface electronic structure found here, may also have other consequences. For instance, the delocalization of \( w^N(r) \) creates an unusual condition in which entire reactant molecule (like CO) may be "wrapped" with low-energy electronic excitations. Thus, the surface may affect the reactant not only through direct surface-reactant chemical bonds, but also through modification of the character of intra-molecule bonds caused by these excitations. Increasing the electronic response, they may also lead to vibrational softening. Since the excitations are substantially extended toward vacuum, they should affect the behavior of approaching reactant well before it forms a chemical bond with the surface atoms. The character of the reactant-surface interaction may thus be modified at the early stages of adsorption bringing about changes in the physisorption energetics. In the same spirit, the groove-like or plateau-like features of the potential revealed in our calculations create wide regions in the vicinity of the surface with almost zero electric field which may provide the rationale for the promotion mechanism proposed in Ref.\(^{17}\) (see above).

Our findings are also relevant to the unusually long-lived excited states observed for Cu(111) with adsorbed alkalis\(^7,8,28\) which have been proposed to be the result of the strong polarization of the anti-bonding adsorbate states away from the surface, thereby reducing the probability of transition between them and the quantum well surface states\(^9,28\). The potential well outside the surface found in our calculations could be the basis for this polarization. Interestingly, single-electron calculations overestimate lifetime of these excited states and good agreement between the calculated and observed lifetime is obtained only if a strong electron-electron interaction is assumed\(^7\). It has been suggested that this electron-electron interaction is the result of enhanced electronic screening outside of the surface. Since \( w^N(r) \) characterizes the electronic response (electronic susceptibility of the system), its high value and delocalization found in our work is evidence that the screening outside the surface is indeed strong.

In summary, our calculations reveal a giant increase and delocalization of the isoelectronic reactivity index of the metal surfaces upon alkali adsorption which we propose to be the driving force for the well-known alkali "promotion effect". We find that the phenomenon is accompanied by a groove-like or plateau-like feature in the surface potential formed on the alkali adsorption. Our findings also provide the rationale for the unusually long-lived
excited states observed for Cu(111) with adsorbed alkalis. The phenomenon is also expected
to be a general characteristic of alkali adsorption on metal surfaces, as exemplified in this
work through the application to two very different metal surfaces.

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I. FIGURE CAPTIONS

Fig. 1. (Color online) Top view of the $A_{0.25}/M(111)$ surface ($A=$Na, K; $M=$Cu,Pd). The large balls represent alkali atoms, small dark balls are for the first layer $M$ atoms and small grey balls are for the rest of the $M$ atoms. The dashed line represents the projection of the plane along which $w^N(r)$ is plotted in Fig. 3.

Fig. 2. (Color online) Plot of $w^N(r)$ for clean Pd(111) (left panel) and for K$_{0.25}$/Pd(111) (right panel) along the plane perpendicular to the surface. Pd1 mark the positions of the topmost Pd atoms and K that of potassium atoms. The white area corresponds to $w^N(r) = 0$.

Fig. 3. Plot of $w^N(r)$ along the surface normal. The upper panel shows $w^N(r)$ for Pd(111) (dashed line) and K$_{0.25}$/Pd(111) (solid line). The lower panel shows $w^N(r)$ for Cu(111) (dashed line) and Na$_{0.25}$/Cu(111) (solid line).

Fig. 4. The self consistent total potential plotted along the surface normal. The upper panel displays the potential for Pd(111) (dashed line) and K$_{0.25}$/Pd(111) (solid line). The lower panel provides the same for Cu(111) (dashed line) and Na$_{0.25}$/Cu(111) (solid line). Arrows indicate the heights of the alkali atoms.
Fig. 3. Stolbov, PRL
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