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Long and short range effect of alkali promoters on metal surfaces: K on Rh(111)

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Photoemission of physisorbed noble gases has been used to investigate the variation of the surface potential on a potassium-promoted rhodium (111) surface. The results confirm that the predominant effect of potassium is to lower the potential on nearest neighbour sites by 1–1.5 eV, but indicate also that the potential on next nearest neighbour sites is still 0.4–1 eV lower than on unpromoted rhodium, depending on the potassium coverage. Theoretical calculations show that the latter values are in qualitative agreement with the cumulative effect of potassium/rhodium dipoles which form an ordered array on the surface.

Keywords: Alkali; potassium; promoter; rhodium; surface potential; UPS

1. Introduction

Potassium is a common promoter for transition metal catalysts. Examples are its use in the iron catalysts for the ammonia synthesis [1] and the Fischer–Tropsch synthesis [2], where potassium promotes the dissociation of nitrogen and carbon monoxide, respectively. Fundamental knowledge on the effect of alkali atoms on transition metals comes from single crystal studies and from theoretical calculations [3–6].

Alkali adsorption on metals leads to a strong decrease of the macroscopic work function [6–10]. At low coverages (below 15% potassium atoms per Rh surface atoms), alkali is atomically dispersed on the surface. The work function decrease is explained by charge transfer from the alkali to the substrate, leading to positively charged potassium atoms on the surface. This results in a local modification of the electrostatic potential on the surface around the alkali atoms. Theoretical studies of potassium adsorption on jellium by Nørskov [4] and Holloway et al. [5] revealed

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that the influence of potassium on the surface has a predominantly local character. Such studies, however, deal with the effect of a single atom on an otherwise empty surface. In this paper we address the cumulative effect of potassium atoms on the electrostatic potential of a rhodium (111) surface.

Photoemission of adsorbed xenon has been used to probe the local surface potential of potassium on ruthenium [9,10]. In this letter we apply photoemission of adsorbed Xe, Kr and Ar, to obtain insight in the variation of the electrostatic surface potential around an adsorbed potassium atom and to estimate the range which is influenced by the adsorbed potassium.

The measurement of the local surface potential with photoemission of adsorbed Xe (PAX) is based on the experimental observation that the ionization potential of adsorbed Xe, i.e. the binding energy of the Xe 5p electrons with respect to the vacuum level, E_B^{vac}, is practically independent of the metal [9–11]. In UPS, however, one measures the Xe 5p binding energy with respect to the Fermi level, E_B^{Fermi}. For a homogeneous surface the two binding energies differ by the work function. Since the Xe atom only "sees" its own adsorption site, it feels the work function at the adsorption site about 2 Å in front of the surface and we can write

$$E_B^{Vac} = E_B^{Fermi} + \varphi_{loc}, \tag{1}$$

where the subscript "loc" reflects that the work function is measured locally. This local work function can have different values at different positions on the surface [11]. Its variation equals the difference in electrostatic surface potential. In fact, the local work function is a quantity that is defined along the trajectory of an escaping electron. Consequently, the local work function can have different values within atomic distances and an adsorbed atom or molecule can sense a varying work function on its adsorption site. Therefore, the local work function we measure with adsorbed xenon is an averaged value over the whole atom. For a constant or linearly varying local work function over the atom, this average equals the local work function at the centre of the noble gas atom. By using smaller probe atoms such as Kr and Ar we can vary the distance between potassium and noble gas atom. Provided the interpretation in terms of expression (1) is permitted, and this is a point we will check by adsorption of Kr and Ar on Rh(111), we can thus obtain information about the variation of the electrostatic potential around a potassium atom on a rhodium surface.

In this letter we show that the cumulative effect of well dispersed potassium atoms with coverages in the range of 2.5–5% (K atoms per Rh surface atoms) is that gases adsorbed on rhodium sites adjacent to potassium sense an electrostatic potential that is between 1 and 2 eV lower than on clean rhodium. The potential on sites further away from the potassium is still between 0.4 to 1 eV lower than on pure rhodium depending on the potassium coverage.

2. Experimental

The UPS spectra were measured in an UHV-system with a base pressure of 10^{-10} Torr [12]. A Rh single crystal with a [111] oriented surface was mounted on a sample holder by two tungsten wires pressed into grooves on the side of the crystal. This allowed resistive heating of the sample up to 1300 K. The sample holder was connected by copper leads to a He-refrigerator that allowed cooling of the sample to 45 K, which is necessary for the adsorption of the noble gases. The temperature was measured by a NiCr–Ni thermocouple spotwelded to the back of the crystal. The cleaning procedure has been described elsewhere [8]. Potassium was evaporated from a commercial SAES-getter potassium source. To obtain a low potassium coverage, we deposited a few monolayers of potassium on the surface at ~ 50 K and annealed the sample at a certain high temperature (700–850 K), using a fixed heating rate (~ 2 K/s). As the resulting potassium coverage is very sensitive to the annealing temperature, this method allows an accurate and reproducible preparation of potassium-dosed surfaces with low coverages ($<5\%$). The potassium coverages studied here were prepared by annealing at 845, 755 and 710 K, which resulted in potassium coverages of 2.7, 4.1 and 5.0%.

Each K/Rh surface was exposed to Xe, Kr and Ar in small steps, until the first layer was fully saturated. Between the noble gas adsorption experiments, the surface was annealed at 600 K to remove the noble gas and contaminants such as CO and water. Since the potassium layers have been prepared by annealing at higher temperatures, they are not affected by this procedure. This is supported by the constant work function of the potassium covered surface just before each noble gas experiment. At low potassium coverages the work function is extremely sensitive to small coverage changes [6–8], and thus we can safely assume that the potassium coverage has not been affected by the short flash to 600 K.

3. Results and discussion

Fig. 1 shows typical UPS spectra of Xe, Kr and Ar physisorbed on clean and potassium covered Rh(111). The Xe 5p and Kr 4p signal are split into their $p_{3/2}$ and $p_{1/2}$ components, due to spin–orbit coupling. The spin–orbit splitting of the Ar 3p peak is too small to be resolved. We will first discuss the spectra of noble gases on clean rhodium and check whether expression (1) is also valid for the Kr and Ar UPS spectra.

The uniform signal of the noble gases adsorbed in the first layer on Rh(111) is characteristic for a homogeneous surface. The position of the Xe $5p_{1/2}$ signal at low Xe coverage (6.70 eV) and the macroscopic work function (5.60 eV) match the substrate-independent ionization energy of adsorbed Xe (12.3 ± 0.15 eV), that has been found on at least 25 other substrates, including transition metals, noble metals, Al, alkali metals (K, Cs), Si and oxides (ZnO and TiO_2) [11]. The Kr $4p_{1/2}$
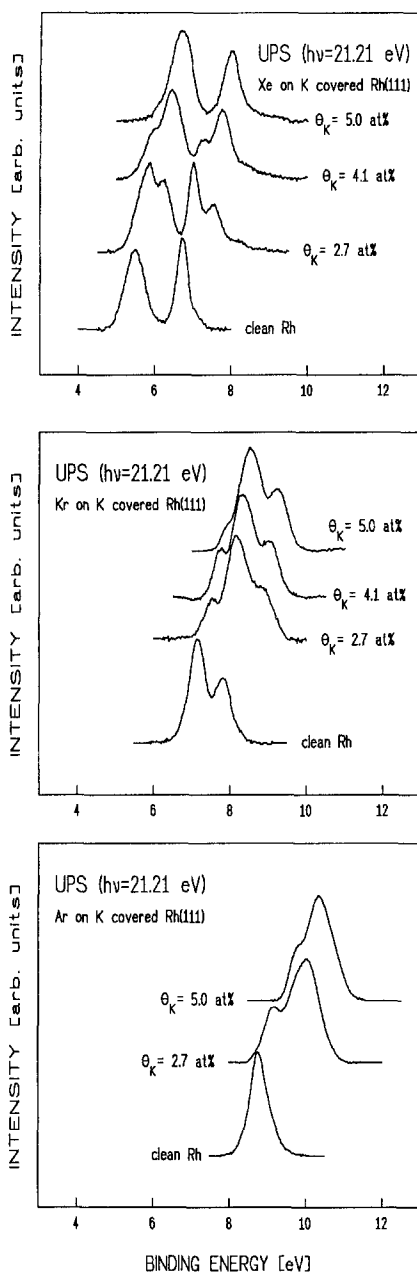
Fig. 1. Ultraviolet photoemission spectra (photon energy = 21.21 eV) of Xe (top), Kr (middle) and Ar (bottom) on clean and potassium covered Rh(111) at various potassium coverages. The position of the signals is indicative for the local work function at the noble gas adsorption site. The long range effect is seen in the shift to higher binding energy in the onset of the noble gas signal. The signals at higher binding energy correspond to the local work function at the adsorption site next to a potassium atom. The intensities of the spectra shown are normalized arbitrarily, so that comparison of the intensities is not permitted.

binding energy of Kr on Rh(111) at low Kr coverage is 7.70 eV, which in combination with the Rh work function of 5.60 eV, corresponds to an ionization potential of 13.3 eV. This equals the E_B^{vac} value found for Kr adsorbed on the $Cu_3Pt(111)$ surface [13]. To the best of our knowledge, values of Kr adsorbed on other substrates are not available for angle integrated photoemission measurements. Similarly, the UPS Ar 3p binding energy of Ar on Rh(111) is 8.70 eV, resulting in an ionization potential of 14.3 eV. The same value has been found for Ar adsorbed on Ni(100) [14], while a value of 14.4 eV has been found for Ar on Ru(001) and on a monolayer of Cu on Ru(001) [15]. The good agreement between these E_B^{vac} values strongly suggests that the binding energies of Kr 4p and Ar 3p electrons with respect to the Fermi level, E_B^{Fermi}(Kr 4p) and E_B^{Fermi}(Ar 3p) as determined in UPS, can be interpreted in terms of expression (1), which has extensively been verified for adsorption of xenon on a large number of surfaces. Consequently, binding energy shifts reflect differences in local work functions (electrostatic potentials). This is the property we use to study the variation in electrostatic potential on potassium-promoted Rh(111) surfaces.

On the potassium covered surfaces, the Xe, Kr and Ar states on clean Rh(111) are replaced by two states, indicating that potassium induces a heterogeneous surface potential. The positions of the peaks reflect the local surface potential at the adsorption site of the noble gas atom. From a comparison of the spectra at different potassium coverages and from previous data [9,10,14], we assign the subspectrum at the lowest binding energy to the noble gas at bare Rh sites, and the one at higher binding energy to the adsorption sites on Rh adjacent to potassium atoms (which we denote as K/Rh sites).

The binding energies of the Xe and Ar spectra could straightforwardly be determined from the spectra. In the Kr UPS spectra we see at all potassium coverages an overlap of two Kr adsorption states. The binding energies of these two states have been obtained by fitting a combination of two experimental spectra of adsorbed Kr shifted on the binding energy scale to appropriate values to the Kr-UPS spectra in fig. 1.

Table 1 contains all binding energies, expressed with respect to the value of the respective noble gas signal on clean Rh(111). As can also be seen in fig. 1, all noble gas signals are shifted towards higher binding energy. This means, that on a potassium covered Rh surface *all adsorption sites available to the noble gas atoms, thus not only those immediately adjacent to K but also those further away, are affected by the coadsorbed potassium.*

The intensity ratio for Xe next to K and Xe on top of K indicates a five-fold coordination of Xe around K, as also has been reported for Xe on K covered Ru(001) [9]. For Kr and Ar we assume also a five-fold coordination. Based on the van der Waals radii of the noble gases (2.2 Å for Xe, 2.0 Å for Kr and 1.9 Å for Ar [16]), the ionic radius of potassium (1.33 Å [17]) and the five-fold coordination of the noble gases around potassium, we have estimated the distance between adsorbed potassium and a noble gas atom on the surface [18], see table 1.

Table 1
Binding energy shifts in the UPS spectra of Ar, Kr and Xe adsorbed on K-promoted RH(111) with respect to adsorption on clean Rh(111), and distances to K, based on van der Waals radii of Ar, Kr and Xe, the ionic radius of K and a five-fold coordination of the adsorbed noble gases around potassium

Adsorption site	Distance to K (Å)	Binding energy shift relative to adsorption on clean Rh(111) (eV)		
		$\theta_K = 2.7$ at%	$\theta_K = 4.1$ at%	$\theta_K = 5.0$ at%
Ar/K/Rh	3.23	1.44	a	1.66
Kr/K/Rh	3.40	1.13	1.33	1.57
Xe/K/Rh	3.74	0.87	1.15	1.31
Ar/Rh	⩾5.90 [b]	0.43	a	1.04
Kr/Rh	⩾6.23 [b]	0.42	0.72	1.00
Xe/Rh	⩾6.83 [b]	0.35	0.61	–

[a] Not measured.
[b] Minimal distance from a Rh site to the nearest potassium.

Fig. 2 shows the binding energy shifts as a function of the estimated distance between the adsorption site and the nearest potassium, along the line between two K atoms. We note that for the K/Rh sites the distance between the noble gas and neighbouring potassium atom is quite accurate. The distances between noble gas atoms that are further away may vary. As the binding energy shifts vary only weakly with distance at distances larger than one Xe atom diameter (as can also be inferred from the absence of peak broadening effects for these adsorption states), this is of no consequence for the general picture that emerges from fig. 1.

If we interpret the binding energy shifts in terms of a change in the electrostatic surface potential, fig. 2 implies that the potential changes rapidly in the immediate vicinity of the potassium atom, whereas it becomes more or less constant at distances greater than about 5 Å. However, its value is significantly lower than on clean Rh(111) and depends on the potassium coverage. We find a lowering of the local work function of about 0.4 eV for 2.7 at% K and of about 1.0 eV for 5 at% K on the surface. As the potential varies hardly with distance in this range, we may take these values directly as the decrease in local work function of these sites.

The short range effect of potassium is in qualitative agreement with the potential calculated by Holloway et al. [5] for a single potassium atom on a jellium surface. However, our results suggest a stronger decrease of the local work function. This is in agreement with a cumulative electrostatic effect of all potassium atoms. The difference between their calculated values and our measured values arises mainly from the cumulative contribution of all potassium atoms at a given surface site.

Our interpretation presupposes that potassium is exclusively on the surface, and not dissolved in the outer layers. We think that the existence of subsurface potassium on Rh(111) (as suggested by a referee of this paper) can be excluded for
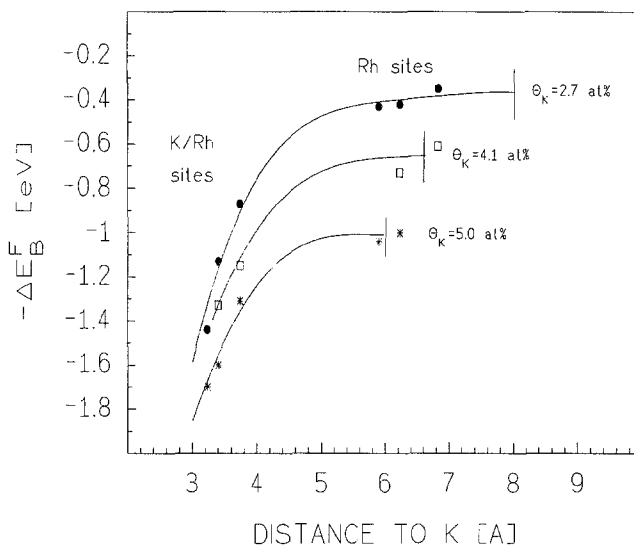
Fig. 2. Binding energy shifts of the noble gas signals with respect to clean Rh(111) as a function of the distance of the adsorption site to the nearest potassium atom. These curves reflect the variation of the local work function around an adsorbed potassium atom. Note the strong and distance dependent local work function at short distances and the constant local work function, which is lower than that of clean Rh(111) at larger distances from potassium. The lowering at larger distances depends on the potassium coverage. The averaged distances between the potassium atoms are 16.1, 13.2 and 12.0 Å for coverages of 2.7, 4.1 and 5.0% respectively. Solid lines are drawn as a guide to the eye.

the following reasons: The strong work function decrease at low potassium coverages indicates that the positively charged potassium atoms are on the surface. Subsurface potassium ions are not expected to result in a work function decrease. Second, the radius of the potassium ions (1.33 Å) is about the same as the radius of the Rh atoms (1.34 Å), which rules out the existence of an interstitial subsurface potassium species, as known, e.g., for oxygen and carbon. As far as we know, alloys of Rh and potassium do not exist. Thus, the possibility that the modification of the potential at the bare Rh sites is caused by subsurface potassium can be excluded. We attribute the long range effect of potassium, i.e. the lowering of the potential at larger distances, also to the cumulative electrostatic effect of all $K^{\delta+}$ atoms on the surface.

The cumulative effect of $K^{\delta+}$ atoms on a surface can theoretically be simulated by an hexagonally ordered network of dipoles, as we will explain in detail elsewhere [18]. Fig. 3 shows that if we choose the dipole strength equal to 10 D, and place the noble gas probe atoms at 2.5 Å above the symmetry plane of the dipoles, the change in potential closely matches the measured binding energy shifts in the UPS spectra of the adsorbed noble gases. Fig. 4 shows a three-dimensional representation of the (electron) potential induced by the hexagonally ordered network of dipoles. The catalytic significance of this picture is, that it represents the differences
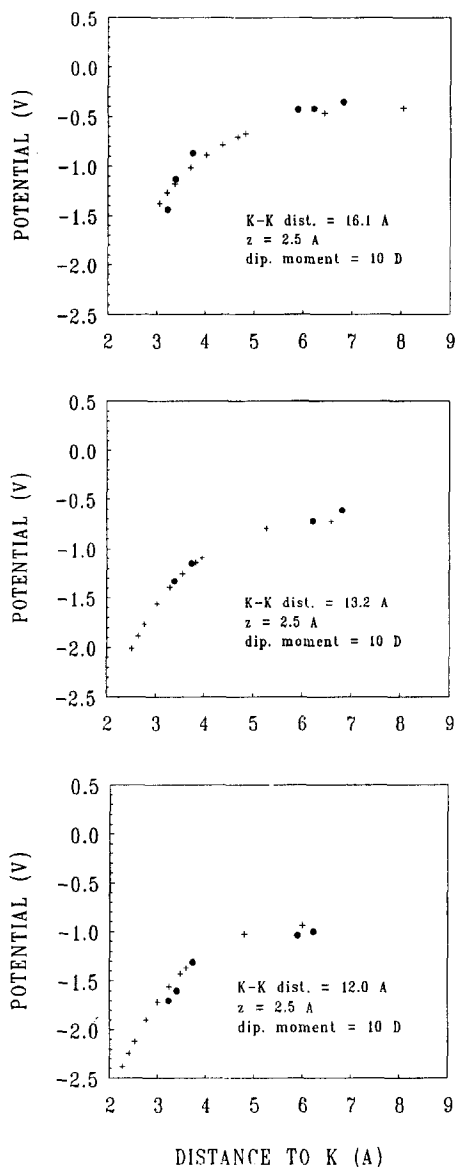
Fig. 3. Comparison of calculated electrostatic potentials (for a test electron) (+) in a network of hexa-gonally ordered dipoles (10 D) at 2.5 Å above their mirror plane with the measured local work function decreases (●). The lateral distance between the dipoles has been varied from 16.1 Å (top) to 13.2 Å (centre) and 12.0 Å (bottom), corresponding to potassium coverages of 2.7, 4.1 and 5.0% respectively. The potassium coverage dependence of the calculated potentials, reflecting the cumulative effect of the dipoles, agrees well with the measured binding energy shifts in the UPS spectra of the adsorbed noble gases.
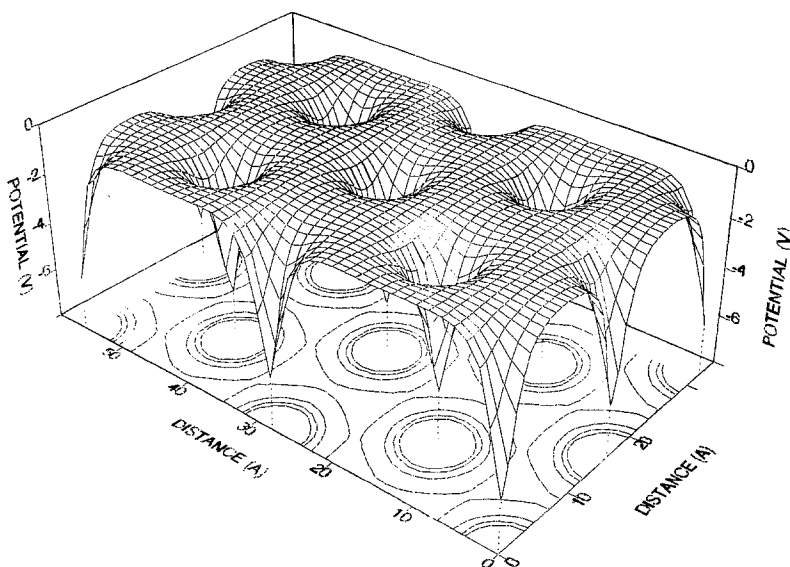
Fig. 4. Map of the calculated electrostatic potential (for a test electron) at 2.5 Å above the symmetry plane in a hexagonally ordered network of dipoles with a dipole–dipole distance of 16.1 Å and a dipole moment of 10 D (see also fig. 3 top). The dipoles are positioned at the minima. Note that the potential is lowered at every position on the surface. In the bottom plane the equipotential lines for −1.05, −0.84, −0.63 and −0.42 V are indicated. They are circular at short distance from a potassium atom indicating that at these sites the potential is largely dominated by the nearest potassium atom. The equipotential line for −0.42 V has hexagonal symmetry due to the influence of the dipoles further away.

in the effective work functions that a molecule experiences upon adsorption at different positions on the surface.

4. Conclusions

Photoemission spectra of adsorbed noble gases of different size (Xe, Kr and Ar) have been used to probe local electrostatic potentials of potassium-promoted Rh(111) surfaces at different sites. The shift of the noble gas signals in the photoemission spectrum due to potassium adsorption is taken as a direct measure for the potassium-induced local work function change at the adsorption site. For the noble gas atoms at the neighbouring sites of potassium these shifts are different for the three gases used. We interpret this as a strong variation of the local work function within a radius of 4 Å around an adsorbed $K^{\delta+}$ atom. In contrast, the shifts corresponding to the adsorption sites further away (5.5–8 Å) are significant and independent of the noble gas, indicating that the local work function here does not depend on the distance, and is considerably lower than on clean Rh. In addition,

this lowering depends on the potassium coverage, indicating a cumulative effect of the potassium atoms.

We conclude that adsorbed potassium on Rh(111) results in a dominant lowering of the local work function on adsorption sites adjacent to a potassium atom and a smaller, but still significant lowering of the local work function on the rhodium sites further away. The latter effect amounts to a local work function that is 0.4 eV lower than on rhodium for a potassium loading of 2.7% to 1.0 eV for 5% potassium coverage and is caused by a cumulative effect of all potassium atoms on the surface.

A full report of these measurements will be presented elsewhere [18].

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